Effect of carrier doping and external electric field on the optical properties of graphene quantum dots

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Abstract. In this paper, we demonstrate that the optical properties of finite-sized graphene quantum dots can be effectively controlled by doping it with different types of charge carriers (electron/hole). In addition, the role played by a suitably directed external electric field on the optical absorption of charge-doped graphene quantum dots have also been elucidated. The computations have been performed on diamond-shaped graphene quantum dot (DQD) within the framework of the Pariser-Parr-Pople (PPP) model Hamiltonian, which takes into account long-range Coulomb interactions. Our results reveal that the energy band-gap increases when the DQD is doped with holes while it decreases on doping it with electrons. Further, the optical absorption spectra of DQD exhibits red/blue-shift on doping with electrons/holes. Our computations also indicate that the application of external transverse electric field results in a substantial blue-shift of the optical spectrum for charge-doped DQD. However, it is observed that the influence of charge-doping is more prominent in tuning the optical properties of finite-sized graphene quantum dots as compared to externally applied electric field. Thus, tailoring the optical properties of finite-sized graphene quantum dots by manipulative doping with charge carriers and suitably aligned external electric field can greatly enhance its potential application in designing nano-photonic devices.

1. Introduction

The excellent thermal, mechanical and electrical properties of graphene, due to its unique band structure, has rendered it as an ideal material platform for designing numerous nano-electronic devices [1-4]. However, a major drawback of pure graphene is its zero band-gap which limits its applications in the field of optoelectronics. This deficiency can be overcome by reducing the dimensionality of graphene to one-dimensional graphene nano-ribbons (GNRs) and further to zero-dimensional graphene quantum dots, thereby, leading to creation of finite band-gap [5]. The finite band-gap of graphene quantum dots can be altered by tuning their shape, size, edge character and doping with hetero-atoms [6-11]. In addition, recent studies have indicated that the application of suitably directed external electric field can significantly manipulate the band-gap, magnetic and optical properties of graphene nano-fragments [12-17].

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A recent first-principles study by Wang et. al. [18], have focused on the effect of electric field on charge-doped graphene tri-layers. However, the finite-size and nonlocal effects which become dominant in quantum confined graphene nano-fragments are absent for extended graphene and hence, the response of charge-doped graphene nano-structures to externally applied electric field is expected to be significantly different. This has motivated us to perform detailed investigation of the role played by charge doping and suitably aligned external electric field on the optical properties of DQD. The manuscript is organized as follows. In Sec. 2, we briefly provide the details of the computational methodology while the results and discussions are given in Sec. 3. This is followed by conclusions in Sec. 4.

2. Computational Methodology
The symmetric hydrogen-saturated diamond-shaped graphene quantum dot considered in this work consists of 16 carbon atoms (figure 1) and will be henceforth referred as DQD-16. The quantum dot considered here is in the x-y plane, with the longer diagonal of the DQD along the y-axis and the shorter diagonal along the x-axis. The bond-lengths and bond-angles between the carbon atoms have been set as 1.4 Å and 120°, respectively.

Figure 1. Diamond-shaped graphene quantum dot consisting of 16 carbon atoms (DQD-16). The black spheres indicate the position of the carbon atoms. The y-axis is along the longer diagonal while the x-axis is along the shorter diagonal of DQD-16.

The computations have been performed within the framework of the effective π-electron Pariser-Parr-Pople (PPP) model Hamiltonian [19-20] given by

$$H = - \sum_{i,j,\sigma} t_{ij}\left(c_{i\sigma}^{+}c_{j\sigma} + c_{j\sigma}^{+}c_{i\sigma}\right) + U \sum_{i} n_{i\uparrow}n_{i\downarrow} + \sum_{i<j} V_{ij}\left(n_{i}-1\right)\left(n_{j}-1\right) \qquad (1)$$

where, $c_{i\sigma}^{+}$ ($c_{i\sigma}$) represents creation (annihilation) operator for a π-orbital of spin σ, localized on the ith carbon atom, and the matrix elements t_{ij} indicates the nearest neighbours one-electron hopping terms. The value of t_0 has been kept fixed at 2.4 eV, consistent with our earlier studies on conjugated polymers [21], polycyclic aromatic hydrocarbons [22] and graphene nano-fragments [11, 17]. The electron-electron repulsion terms are represented by the second and third terms in equation (1), with the parameters U and V_{ij} denoting the on-site and long-range Coulomb interactions respectively, while $n_i = \sum_{\sigma} c_{i\sigma}^{+} c_{i\sigma}$ denotes the total number of electrons having spin σ on i^{th} carbon atom. The coulomb interaction in our Hamiltonian is parametrized as per the Ohno relationship [23] given by

$$V_{ij} = \frac{U}{\kappa_{ij}\left(1+0.6117\,R_{ij}^{2}\right)^{1/2}} \qquad (2)$$

where, the dielectric constant simulating the screening effects is denoted by κ_{ij}, while the distance (in Å) between the ith and j^{th} carbon atoms is represented by R_{ij}. In our computations, we have considered "screened parameters" with U = 8.0 eV and κ_{ij} = 2.0 (i ≠ j) as employed in several of our earlier works [11, 17, 24-31]. In this work, the computations were done at the restricted Hartree-Fock (RHF) level employing a code developed by our group [31]. The electro-absorption (EA) spectra has been computed for the application of external electric field along y-axis (transverse direction) of DQD-16.

3. Results and Discussion
In this section, we first present the results of the impact of charge doping on the optical properties of DQD-16. This is followed by the effect of externally applied transverse electric field in tuning the optical properties of neutral and charge-doped DQD-16.

3.1. Effect of charge doping on the optical properties of DQD-16
The energy band-gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO) for single electron-doped (Q = -1) DQD-16, single hole-doped (Q = 1) DQD-16 and neutral (Q = 0) DQD-16 is given in Table 1.

Table 1. HOMO-LUMO band-gap of neutral, electron-doped and hole-doped DQD-16.

System	HOMO-LUMO band-gap (eV)
Neutral DQD-16	3.91
Electron-doped DQD-16	3.37
Hole-doped DQD-16	3.98

It is observed that in case of electron-doped DQD-16, the HOMO-LUMO band-gap is lesser than that of neutral-charged DQD-16. This behaviour is in contrast to the increasing trend exhibited by hole-doped DQD-16. This implies that the energy band-gap can be effectively manipulated by suitable doping of graphene quantum dots with charge carriers. In addition, the difference between the HOMO-LUMO band-gap of neutral-charged DQD-16 and electron-doped DQD-16 is more as compared to that between hole-doped DQD-16 and neutral-charged DQD-16. Hence, it is evident that the extent of change in band-gap depends strongly on the type of charge doped in the DQD.

Figure 2 represents the linear absorption spectra for neutral (solid line), single electron-doped (dashed line) and single hole-doped (dotted line) DQD-16. The following salient features are observed on analyzing the absorption spectra.
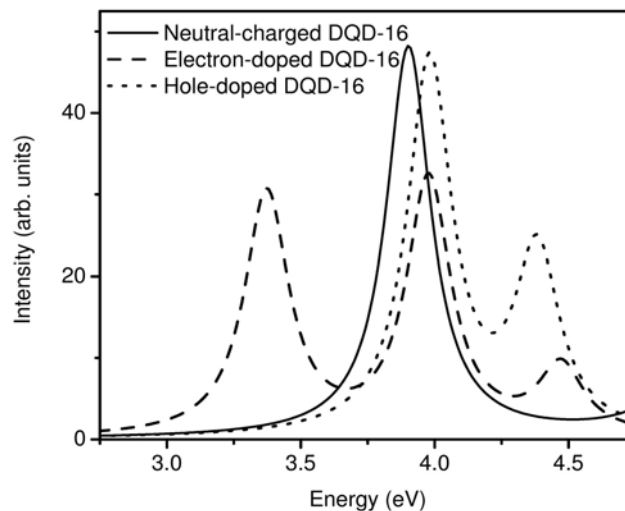

Figure 2. Linear absorption spectra for neutral (solid line), electron-doped (dashed line) and hole-doped (dotted line) DQD-16.

1. The absorption spectrum is blue-shifted when the graphene quantum dot is doped with holes, while the spectrum is red-shifted for the case of electron-doping. The extent of red-shift in the absorption spectrum for electron-doped DQD-16 is much more than the corresponding blue-shift for hole-doped DQD-16. Thus, the optical properties of graphene quantum dots can be appropriately tuned by doping it with suitable charge carriers.

2. The first peak in the absorption spectra for neutral as well as charge-doped DQDs is due to excitation of a single electron from the HOMO (H) orbital to the LUMO (L) orbital and hence corresponds to the optical band-gap. This peak is y-polarized for neutral and single hole-doped DQD-16, while it is x-polarized for single electron-doped DQD-16. Hence, the polarization as well as the position of the first peak signifying the optical band-gap exhibits a strong dependence on the type of charge carriers.

3. The intensity profile of the linear absorption spectrum for electron-doped and hole-doped DQD-16 differs significantly from its neutral-charged counterpart. The y-polarized first peak is the most intense peak for neutral and single hole-doped DQD-16 while the y-polarized second peak is the most intense peak for single electron-doped DQD-16. The intensity of this peak for hole-doped DQD-16 is much greater than its electron-doped counterpart. However, the difference in their energies is marginal. This indicates that the energy as well as the polarization of the most intense peak is not much affected by the type of charge carriers. This is in contrast to the behaviour exhibited by the first peak of the absorption spectrum.

4. The most intense peak for neutral and single hole-doped DQD-16 is due to an electron excitation from H$\rightarrow$ L orbital while for electron-doped DQD-16, it is due to excitation of an electron from H$\rightarrow$ L+2 orbital. Hence, the microscopic nature of the most significant peak of the absorption spectrum for electron-doped DQD-16 is different from the hole-doped and neutral-charged DQD-16.

5. The optical spectra corresponding to up and down spins of the carbon atoms are degenerate for neutral DQD-16, while the degeneracy is lifted for charge-doped quantum dot.

Thus, the linear absorption spectrum exhibits a conspicuous dependence on the type of charge-doping. This property empowers us to manipulate the optical properties of graphene quantum dots by doping it with suitable charge carriers.

3.2. Effect of externally applied transverse electric field on the optical properties of neutral and charge-doped DQD-16

Figures 3, 4 and 5 represent the influence of externally applied transverse electric field (E_y) on the optical properties of neutral (Q = 0), single hole-doped (Q = 1) and single electron-doped (Q = -1) DQD-16, respectively. The solid line and dashed line represent the electro-absorption spectrum at E_y = 0 V/Å and E_y = 0.15 V/Å, respectively.
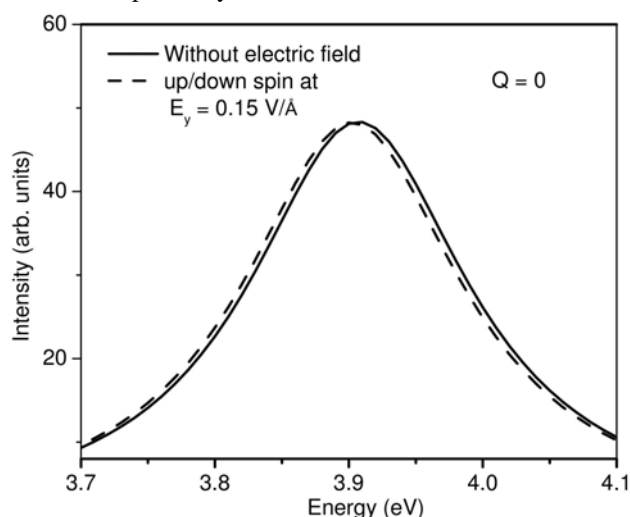

Figure 3. Calculated EA spectrum (dashed line) broadened with uniform line-width of 0.1 eV at E_y = 0.15 V/Å for up/down spin carbon atoms of neutral (Q = 0) DQD-16. The solid line represents the linear absorption spectrum in the absence of electric field.

The important characteristics of the spectra are summarized below.

1. The EA spectrum of neutral DQD-16 exhibits a marginal red-shift with the application of increasing transverse electric field. However, the EA spectrum of hole-doped as well as electron-doped DQD-16 is blue-shifted with increasing strength of transverse electric field (E_y). The extent of blue-shift for charge-doped DQD-16 is much more as compared to the red-shift exhibited by its neutral counterpart. Hence, the role played by electric field in manipulating the optical properties is more conspicuous in charge-doped DQDs as compared to neutral DQD.
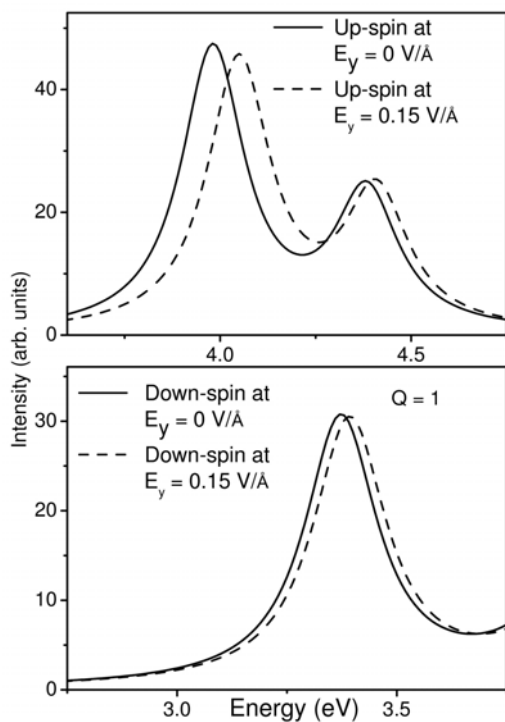

Figure 4. Calculated electro-absorption spectrum (dashed line) broadened with uniform line-width of 0.1 eV at E_y = 0.15 V/Å for up and down spin carbon atoms of hole-doped (Q = 1) DQD-16. The solid line represents the electro-absorption spectrum in the absence of electric field.
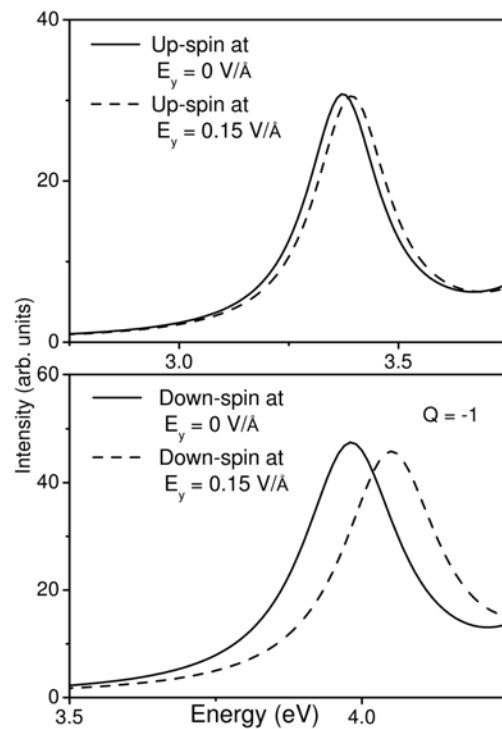
Figure 5. Calculated electro-absorption spectrum (dashed line) broadened with uniform line-width of 0.1 eV at E_y = 0.15 V/Å for up and down spin carbon atoms of electron-doped (Q = -1) DQD-16. The solid line represents the electro-absorption spectrum in the absence of electric field.

2. In hole-doped DQD-16, the extent of blue-shift of the EA spectrum for up-spin carbon atoms on application of transverse electric field is more as compared to the corresponding blue-shift observed for its down-spin carbon atoms. However, this trend is reversed for the case of electron-doped DQD-16.

3. The magnitude of blue-shift of the EA spectrum for up-spin carbon atoms for hole-doped DQD-16 is equal to the magnitude of blue-shift for down-spin carbon atoms for electron-doped DQD-16. A similar behaviour in the extent of blue-shift of the EA spectrum is also exhibited by the down-spin carbon atoms of hole-doped DQD-16 and the up-spin carbon atoms of its electron-doped counterpart.

This remarkable property of selectively tuning the spin-dependent optical properties of charge-doped graphene quantum dots by the application of electric field can effectively be used in the

field of spintronics. Thus, the band-gap as well as optical properties of graphene quantum dots can be selectively tuned by the application of an external transverse electric field.

A comparison between the impact of charge-doping and application of transverse external electric field on band-gap and optical absorption spectrum of DQD-16 reveals that charge-doping has a more pronounced effect on these properties than the application of transverse electric field. This implies that charge-doping is a more effective means of engineering the optical properties of graphene nano-structures.

4. Conclusion

In this work, we have performed detailed investigations of the effects of charge-doping and externally applied transverse electric field separately on the optical properties of DQD-16. Our results have indicated that the energy band-gap increases when the diamond-shaped graphene quantum dot is doped with holes while it decreases on doping it with electrons. Further, the optical absorption spectrum of DQD-16 undergoes blue/red-shift on doping it with hole/electron. However, the extent of red-shift is greater than the corresponding blue-shift indicating that electron-doping has a more pronounced effect on the optical properties of DQD-16. It is also observed that the energy/intensity of the most intense peak exhibit minimal/significant dependence on the nature of charge carriers. Further, our computations reveal that the application of transverse electric field results in a red/blue-shift of the optical spectrum for neutral/charge-doped DQD-16. However, the substantial blue-shift of the EA spectrum (in comparison to the marginal red-shift) implies that electric field plays a significant role in tuning the optical properties of charge-doped DQD-16. In addition, our studies have illustrated that the influence of charge-doping is dominant over the application of transverse electric field in manipulating the optical properties of finite-sized graphene quantum dots. Hence, we expect that our analysis will guide experimentalists in designing nano-photonic devices with tunable band-gaps.

5. References

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