Graphene quantum dot with a hydrogenic impurity

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Abstract. We investigate the electronic energy levels of a circular graphene quantum dot with a hydrogenic impurity placed at the center of the dot. We have adopted a variational scheme in such a way that the trial wave functions take into account the carrier confinement due to the dot geometry as well as the effect of the magnetic field. We found that the presence of impurity strongly modifies the electronic spectrum of the graphene quantum dot. We also calculated the critical value of the impurity strength as a function of dot radius.

1. Introduction
Since the discovery of graphene [1, 2] impurity related effects in graphene have been extensively reported in the graphene literature [3–19]. The study of impurity states in graphene quantum dots (GQDs) is itself important, since it is expected that these effects will be more pronounced in such structures due to the reduction of the dimensionality. Since experiments with adatoms in monolayer graphene clearly address the long range impurities [13], which are responsible for limiting the mobility of graphene [15], Coulomb like hydrogenic impurities are of particular interest in the relevant literature [7–10, 15]. Moreover, the strength of Coulomb interaction, which is proportional to dimensionless quantity \( Z (Z \alpha) \) defined by the valency of impurity \( Z \) and \( \alpha = e^2/\varepsilon v_F \), introduces a new kind of quantum electrodynamics regime (QED), which is strictly different from the usual perturbative one. Here, \( \varepsilon \) is the dielectric constant, and \( v_F \) is the Fermi velocity for massless Dirac fermions which is of order of \( 10^6 ms^{-1} \). Since \( \alpha \) is of order of unity for conventional SiO₂ substrate [7, 8], such a new regime needs nonperturbative methods to investigate long range impurity related effects.

On the one hand, due to their controllable sizes and shapes, GQDs are the center of both experimental and theoretical interest in graphene physics [20–63]. On the other hand, the formation of spin qubits in GQDs [46] with controllable valley splitting is another active research area in the field. The crucial requirement for this formation is to lift the valley degeneracy of the pristine graphene. It is shown that this is achievable in GQDs.

Since it is also possible to control where the adsorbate can be placed in graphene, controlling the impurity related effects are not only important for graphene, but also for graphene based nanostructures such as GQDs.

The continuum model of confined states of Dirac electrons in GQDs provides a simple physical insight into understanding the bound states in such structures. It is shown that [59, 60], it presents results in full agreement with those found from tight binding calculations (TBCs) for bound QD states in which their radii are much larger than the carbon-carbon distance. Even for small radii the agreement between continuum description and TBC is always reasonable for...
low-lying bound states with high values of the angular momentum. This establishes the use of continuum approach to study the confinement effects.

With these motivations, in the present work, we study the combined effects of quantum confinement due to GQD and hydrogenic donor impurity located at the center of the GQD. To do this, we take a circular confinement potential in order to model the GQD, and place the hydrogenic impurity at the center of dot. The calculation is performed within the framework of a variational approach based on using exact solutions of Dirac-Weyl equation in the absence of quantum dot potential as trial wave functions.

2. Theory

The Hamiltonian of a system consisting of an electron (hole) bound to a donor (acceptor) ion inside a parabolic graphene quantum dot, in the presence of a magnetic field perpendicular to GQD plane, is given by

$$\mathcal{H} = v_F \mathbf{\alpha} \cdot (\mathbf{p} + e^{-}\mathbf{A}) + \beta \Delta_0 \nu^2 - \frac{Z e^2}{cr}$$

where \(\mathbf{A}\) is the vector potential chosen at symmetrical gauge, i.e., \(\mathbf{A} = B_0 (-y, x, 0)/2\), \(\Delta_0 = U_0/2R_0^2\) wherein \(U_0\) and \(R_0\) are the strength and the radius of GQD, respectively. In Eq.(1), \(\mathbf{\alpha}\) and \(\beta\) are Dirac matrices, and the Fermi velocity \(v_F = (3a/2) J_0\) is given in terms of \(J_0\) and \(a\), which are the resonance integral between nearest neighbour carbon atoms, and is of order of 2.7 eV, and the equilibrium bond length of the graphene, respectively. The solution of Eq.(1) in the absence of both GQD potential and the impurity is well established in Ref. 17. In order to study the combined effects of these two, we use the exact wave functions in their absence as trial wave functions corresponding to the Dirac-Weyl equation \(\mathcal{H}\Psi_n = E_n \Psi_n\) in which four-component spinors are given by

$$\Psi_n^{K}(x, \varphi) = R_n(x) e^{im\varphi} e^{-x^2/2} \begin{pmatrix} L^0_0 \\ 0 \\ 0 \\ L^K \end{pmatrix}$$

$$\Psi_n^{K'}(x, \varphi) = R_n(x) e^{im\varphi} e^{-x^2/2} \begin{pmatrix} 0 \\ L^0_0 \\ L^{K'} \\ 0 \end{pmatrix}$$

with \(R_n(x) = [\nu!/2\pi(\nu + |m|)!]^{1/2} \gamma_0^{m|x|}\). In Eq.(2) we have defined \(L^0, L^K\) and \(L^{K'}\) in terms of Laguerre polynomials as \(L^0_\nu(x) = L^{|m|}_\nu(x^2)\),

$$L^K = \frac{ix e^{i\varphi}}{\sqrt{n}} \begin{cases} L^{|m|+1}_\nu(x^2) & m \geq 0 \\ -\frac{n}{2x} L^{|m|-1}_\nu(x^2) & m < 0 \end{cases}$$

$$L^{K'} = \frac{ix e^{-i\varphi}}{\sqrt{n}} \begin{cases} -\frac{n}{2x} L^{|m|-1}_\nu(x^2) & m \geq 0 \\ L^{|m|+1}_\nu(x^2) & m < 0 \end{cases}$$

respectively. The corresponding eigenvalues are given by \(E_n = \lambda \epsilon_n\) wherein \(\epsilon_n = \hbar v_F\sqrt{2n}/\ell_B\), \(\lambda\) is the chirality index and takes \(-1\) and \(+1\) values, which correspond to valence and conduction bands of graphene, respectively. \(\ell_B = (\hbar c/eB)^{1/2}\) is the magnetic confinement length, and \(n = \nu + (|m| + m + \tau + 1)/2\) where \(\tau\) is considered as a pseudospin index whose \(-1\) and \(+1\) values specifies the two valleys, i.e., \(K\) and \(K'\), respectively. In the following, we will restrict
ourselves to only conduction band. Extension of the results to the other band is straightforward. In Eq. (3), \( x = \gamma_0 \rho \) is a dimensionless, and \( \gamma_0 \) is the inverse of characteristic length of the system. On the one hand, without spatial parabolic confinement, \( \gamma_0 \) is proportional to inverse of magnetic confinement length \( \ell_B \), i.e., \( \gamma_0 = \gamma = 1/\sqrt{2} \ell_B \). On the other hand, in the presence of spatial confinement, graphene system described by the Hamiltonian Eq.(1) suggest a natural unit of length \( R = (\hbar v_F R_0^2 / U_0)^{1/3} \) which characterises the size of a scalar parabolic quantum dot in graphene [20, 21]. Therefore, we use the ansatz of Ref. 21 to characterize the system by only one parameter, i.e., we write \( \gamma_0^I = \gamma^2 + R^{-2} \) and take \( \gamma \) to be a variational parameter, so as to reduce to \( 1/\sqrt{2} \ell_B \) in the limit \( R \to \infty \). Therefore, the variational eigenenergies of GQD is given by

\[
E_n = \int d^2r \Psi_n^* \left[ \alpha \cdot \left( -i \nabla + \frac{e}{\hbar c} A \right) + \beta \Delta_0 \nu^2 - \frac{Ze^2}{\epsilon r} \right] \Psi_n. \tag{4}
\]

Inserting Eqs. (2) and (3) into Eq.(4) we get a general expression for the variational energy as

\[
\mathcal{E}_n = \left( \sqrt{n} - \frac{Z}{2} M_n^m \right) \gamma_0 + \frac{\sqrt{n}}{2 \ell_B} \frac{\gamma 1}{\gamma_0} + \frac{1}{4 \gamma_0^2} \frac{1}{\gamma_0^2} \mathcal{M}_n^{II} \tag{5}
\]

In Eq.(5), the energy and all lengths are expressed in units of \( J_0 \) and \( a \), respectively. The integrals \( \mathcal{M}_m^I \) and \( \mathcal{M}_m^{II} \) in Eq.(5) are defined in terms of Laguerre polynomials as

\[
\mathcal{M}_m^I = F_n + \frac{1}{n} \mathcal{G}_n \tag{6}
\]

with

\[
\mathcal{F}_n = \frac{\nu^I}{(\nu + |m|)!} \int_0^\infty dr e^{-r|m|+\frac{1}{2}} \left| L_\nu^m (r) \right|^2
\]

\[
\mathcal{G}_n = \frac{\nu^I}{(\nu + |m|)!} \int_0^\infty dr e^{-r|m|+\frac{1}{2}} \left| \mathcal{H}_\nu^{m} (r) \right|^2
\]

and

\[
\mathcal{M}_m^{II} = F_n - \frac{1}{n} \mathcal{G}_n
\]

with

\[
F_n = \frac{\nu^I}{(\nu + |m|)!} \int_0^\infty dr e^{-r|m|+\frac{1}{2}} \left| L_\nu^m (r) \right|^2
\]

\[
G_n = \frac{\nu^I}{(\nu + |m|)!} \int_0^\infty dr e^{-r|m|+\frac{1}{2}} \left| \mathcal{H}_\nu^{m} (r) \right|^2
\]

where

\[
\mathcal{H}_\nu^{m} (r) = \begin{cases} 
\frac{r^2}{2} L_{\nu+\alpha}^{m+1} (r), & \alpha = \begin{cases} 0 & m \geq 0 & \tau = +1 \\
-1 & m < 0 & \tau = -1 \end{cases} \\
\frac{r^{\alpha+1}}{2} L_{\nu+\alpha}^{m-1} (r), & \alpha = \begin{cases} 0 & m \geq 0 & \tau = -1 \\
+1 & m < 0 & \tau = +1 \end{cases}
\end{cases}
\]

respectively. \( \mathcal{M}_m^{II} \) can be integrated analytically to yield \( F_n = 2\nu + |m| + 1 \) and \( G_n = 2n - m \), respectively. Thus, we have exactly \( \mathcal{M}_m^{II} = -\tau \). For each \( n \) values, \( \mathcal{M}_0^I \) can also be integrated.
analytically [64] so that, for instance, it yields $M_0^n = \Gamma(|m| + 1/2)/\Gamma(|m| + 1)$ for $n = 0$. Here, $\Gamma(x)$ is the Gamma function. To get an approximate analytical expression for the energy given by Eq.(5), we investigate some of its limiting cases. In the absence of impurity, since its minimization with respect to $\gamma$ gives $\gamma = 1/p^2\ell_B$, as $R$ goes to infinity. By replacing this value back into the relevant variational energy, one gets $\tilde{E}_n = p^2 n/\ell_B$, which are the well-known Landau levels for massless graphene. Consequently, substituting this value back into Eq.(5) as a first approximation yields

$$\tilde{E}_0 = \frac{Z \Gamma(|m| + 1/2)}{2l_0 \Gamma(|m| + 1)} - \frac{p^2}{4R^3} \tau \bar{l}^2_0 \tag{7}$$

where $1/l_0^2 = 1/2\ell_B^2 + 1/R^2$ defines the effective confinement length. Eq.(7) may give an idea about the effect of hydrogenic donor impurity onto the energy spectrum of a parabolic GQD as well as the critical value of the impurity strength. In the absence of impurity and magnetic field, Eq.(7) works well, as reported in Ref. 65, for the graphene devices fabricated by Ponomarenko et al [66], wherein the GQDs have a gap value of 0.010 – 0.5eV for the GQDs with diameter of $D = 40 – 1.0nm$. Eq.(7) predicts their corresponding values as 0.014 – 0.57eV. Even in the high magnetic field case it yields the well-known relativistic LLs, which are also confirmed experimentally [67]. From Eq. (7), we estimate the critical value of $\bar{Z}$ as

$$Z_{\text{crt}} = \frac{l_0^2 \Gamma(|m| + 1)}{2R^3 \Gamma(|m| + 1/2)}$$

This reduces to $\bar{Z}_{\text{crt}} = 1/2\sqrt{\pi}$ in the absence of magnetic field.

![Figure 1](image.png)

**Figure 1.** The magnetic field dependence of parabolic quantum dot energy spectra in the presence of hydrogenic donor impurity. While the bold gray lines (represented by labels [n]) correspond to the unperturbed LLs (in the limit $R \to \infty$), the dashed (straight) curves represents $K$($K'$) valleys. For all curves, from the bottom to the top, $m = 0, -1, -2$ and $-3$ levels are depicted by gray, red, green and blue colors.
Figure 2. (Color online) (a) The lowest-lying energy eigenvalues of GQD as a function of effective dot radius $R = (\hbar v_F R_0^3 / U_0)^{1/3}$ at a constant magnetic field and impurity strength, i.e., $B = 5$ T and $Z = 0.15$, respectively. (b) The effective dot strength $U = U_0 / R_o^2$ dependence of the same levels with $m = 0$.

FIG. 1 shows the ground- and the first excited-state energies of parabolic GQD as a function of $\sqrt{B}$ both in the presence (thin dashed ($K'$) and thin straight ($K$) lines) and absence (bold dashed ($K'$) and bold straight ($K$) lines) of hydrogenic donor impurity. We also included for comparison the first two LLs of the gapless graphene (thick straight gray lines). It is clearly seen that the impurity energy levels in GQD goes up to well known LLs with increasing $B$ for a constant $U_0$. To understand the effect of confinement on impurity energy levels itself, for a fixed impurity strength, we plot the lowest-lying energies as a function of dot radius in FIG. 2. In both figure, to see better the valley splitting for the associated levels, space arising from this splitting is coloured by grey. It is seen that, since the narrower dot creates stronger confinement the magnitude of valley splitting, $K(K')$ becomes larger as the confinement becomes stronger. We found that, the magnitude of the valley degeneracy, with decreasing the strength of GQD, first drop slowly and then approach to its value in the gapless graphene, that is, zero. This is more clearly seen from the FIG. 2(b). However, introduction of donor impurity causes these levels to shift down to lower energies, and leads enhancement in the size of the valley splitting for constant $U$. On the other hand, inclusion of such a long range donor hydrogenic impurity leads to decrease in valley splitting.

In FIG. 3, the associated energy levels are plotted as functions of impurity strength $\bar{Z}$. 
3. Conclusion
In conclusion, we have investigated the effect of a hydrogenic donor impurity on the energy levels of a parabolic GQD. For this purpose, we use a variational scheme based on the choice of trial wave functions taking into account carrier confinement together with the effect of the magnetic field. On the basis of our results, we have found that the magnitude of valley splitting is strongly dependent on the impurity strength and the strength of the magnetic field, and concluded that the size of valley splitting can easily be controlled by the valency of the impurity. We hope that the presented results may be useful to gain insight how to control some electronic properties of GQDs with impurities.

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