



## Communication

# Electronic and magnetic properties of graphene quantum dots with two charged vacancies

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## ABSTRACT

Electronic and magnetic properties of a system of two charged vacancies in hexagonal shaped graphene quantum dots are investigated using a mean-field Hubbard model as a function of the Coulomb potential strength  $\beta$  of the charge impurities and the distance  $R$  between them. For  $\beta = 0$ , the magnetic properties of the vacancies are dictated by Lieb's rules where the opposite (same) sublattice vacancies are coupled antiferromagnetically (ferromagnetically) and exhibit Fermi oscillations. Here, we demonstrate the emergence of a non-magnetic regime within the subcritical region: as the Coulomb potential strength is increased to  $\beta \sim 0.1$ , before reaching the frustrated atomic collapse regime, the magnetization is strongly suppressed and the ground state total spin projection is given by  $S_z = 0$  both for opposite and same sublattice vacancy configurations. When long-range electron–electron interactions are included within extended mean-field Hubbard model, the critical value for the frustrated collapse increases from  $\beta_{cf} \sim 0.28$  to  $\beta_{cf} \sim 0.36$  for  $R < 27\text{\AA}$ .

## 1. Introduction

Recent advances at the atomic scale control of graphene through vacancies [1–4], charged impurities [5,6] and adatoms [7–11] open up possibilities for tailoring graphene's electronic and magnetic properties [12–17] for future spintronic and computing applications, as well as for investigating relativistic quantum effects such as atomic collapse [6,18–23]. While pure graphene is not expected to be magnetic, breaking of the sublattice symmetry of the honeycomb lattice through atomic defects is expected to exhibit local magnetization as predicted by theoretical calculations [12,24–29]. This local magnetization was recently observed experimentally using scanning tunneling microscopy (STM) around hydrogen adatoms [30] and single atomic vacancies [4].

On the other hand, Mao et al. [31] have shown that carbon vacancies in graphene can host a stable positive effective charge  $Z$  which can be gradually increased by applying STM voltage pulses. This tunability of the coupling constant  $\beta = Z\alpha_g$ , where  $\alpha_g = 2.2/\kappa$  is the effective fine-structure constant and  $\kappa$  is the dielectric constant, allows the observation of the system to undergo a transition from subcritical to supercritical regime where the 1S-like state dives into Dirac continuum, forming quasi-bound states and mimicking the atomic collapse expected to occur in ultra-heavy nuclei [32–37] with  $Z \sim 172$  [38] which do not exist in nature. Theoretically predicted by

Pereira et al. [39], the atomic collapse in graphene was first successfully observed through clusters of charged calcium dimers [6]. On the other hand, when two or more impurities with identical charges are present a frustrated supercritical regime occurs at a distance dependent critical value  $\beta_{cf}$  which is lower than the critical value  $\beta_c = 0.5$  for a single charge impurity [23,40,41].

An open question that we address in this work is, how do charged vacancies magnetically couple to each other as a function of  $\beta$ . For  $\beta = 0$ , a theorem due to Lieb for bipartite Hubbard systems predicts [42] that the local magnetic moments formed around the vacancies should couple to each other ferromagnetically or antiferromagnetically over large distances depending on whether they lie on the same or opposite sublattices. Moreover, as the system is reminiscent of Ruderman–Kittel–Kasuya–Yoshida (RKKY) model, one expects to observe oscillations of magnetic coupling if the vacancies are along the zigzag directions as opposed to a smooth decrease along the armchair directions [43]. On the other hand, as  $\beta$  is increased, Lieb's theorem does not apply anymore, the local magnetization around vacancies is suppressed and one expects the magnetic coupling between the two local moments to be severely distorted.

In this work, we consider a finite size graphene quantum dot (GQD) [43–50] with hexagonal armchair edges to investigate the magnetic coupling properties between the charged vacancies. The armchair

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edges make the system free of additional edge state effects. Moreover, the critical  $\beta$  value for which the 1S state crosses the Dirac point is known to be independent of the size of the quantum dot both within effective mass approximation and mean-field Hubbard models [51,52]. Thus, the hexagonal GQD system provides us with a practical way to understand bulk properties as well. Here, we perform mean-field Hubbard calculations to show that the magnetization of the vacancies is strongly suppressed for  $\beta > 0.1$  which is in the subcritical regime, i.e., lower than the frustrated critical value  $\beta_{cf} \sim 0.28$  for the range of  $R$  studied here. As a result, the ground state total spin projection of the double vacancy system reduces to  $S_z = 0$  for both opposite (AB) and same (AA) sublattice configurations. When we include long-range electron–electron interactions within extended MFH approximation,  $\beta_{cf}$  is renormalized from 0.28 to 0.36 by suppression of overscreening [24,53,54]. We also investigated the effect of second nearest neighbor hopping  $t_{nm}$ . For  $t_{nm} = 0.2$  eV, we found that Lieb’s predictions for magnetization of same sublattice vacancy system is violated even for  $\beta = 0$ .

## 2. Model and method

We use a one-band mean-field Hubbard (MFH) model where the single electrons states are written as a linear combination of  $p_z$  orbitals on every carbon atom since the sigma orbitals are considered to be mainly responsible for mechanical stability of graphene. Including long range interactions, the extended mean-field Hubbard Hamiltonian can be written as

$$\begin{aligned}
 H_{MFH} = & \sum_{ij\sigma} t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) \\
 & + U \sum_{i\sigma} \langle (n_{i\bar{\sigma}}) - \frac{1}{2} \rangle n_{i\sigma} \\
 & + \sum_{ij} V_{ij} \langle (n_j) - 1 \rangle n_i \\
 & + \sum_{i\sigma} V_C(\mathbf{r}_i) c_{i\sigma}^\dagger c_{i\sigma}
 \end{aligned} \quad (1)$$

where the first term represents the tight-binding Hamiltonian and  $t_{ij}$ ’s are the hopping parameters given by  $t_{nn} = -2.8$  eV for nearest neighbors and  $t_{nmn} = -0.1$  eV for next nearest-neighbors [14]. Additionally, in this work we considered  $t_{nmn} = 0$  eV and  $t_{nmn} = -0.2$  eV to investigate the stability of Lieb’s theorem against  $t_{nmn}$ . The  $c_{i\sigma}^\dagger$  and  $c_{i\sigma}$  are creation and annihilation operators for an electron at the  $i$ th orbital with spin  $\sigma$ , respectively. Expectation value of electron densities are represented by  $\langle n_{i\sigma} \rangle$ . The second term represents on-site Coulomb interactions. We take on-site interaction parameter as  $U = 16.522/\kappa$  eV, with effective dielectric constant  $\kappa = 6$  to take into account screening effects due to substrate [55]. The third term stands for long-range Coulomb interaction. Interaction parameters  $V_{ij} = 8.64/\kappa$  and  $V_{ij} = 5.33/\kappa$  for the first and next nearest neighbors respectively, numerically calculated using Slater  $p_z$  orbitals [56]. Beyond second nearest neighbors, interactions are calculated assuming point charges. Finally, the last term represents the Coulomb potential due to vacancy charges located at  $\mathbf{R}_1$  and  $\mathbf{R}_2$ , expressed as

$$V_C(\mathbf{r}_i) = -\hbar v_F \beta \left( \frac{1}{|\mathbf{r}_i - \mathbf{R}_1|} + \frac{1}{|\mathbf{r}_i - \mathbf{R}_2|} \right) \quad (2)$$

where  $v_F = 3at/2$  ( $\sim 10^6$  m/s) is the Fermi velocity. The dimensionless Coulomb potential strength  $\beta$  can be tuned as discussed above. In this work, we assume that the charged impurities cause ideal vacancies in the honeycomb lattice where relaxation and bond reconstruction effects are neglected.

The hexagonal armchair quantum dot system that we consider in this work consists of 5512 atoms for MFH calculations and up to 10806 atoms for TB calculations. A critical step in the numerical calculations is the initial guess state used for the self-consistent diagonalization of the MFH Hamiltonian. We have used various initial guess spin states to ensure to the convergence to lowest possible ground states consistent with the two competing total spin projections  $S_z = 1$  (ferromagnetic coupling) and  $S_z = 0$  (antiferromagnetic coupling).

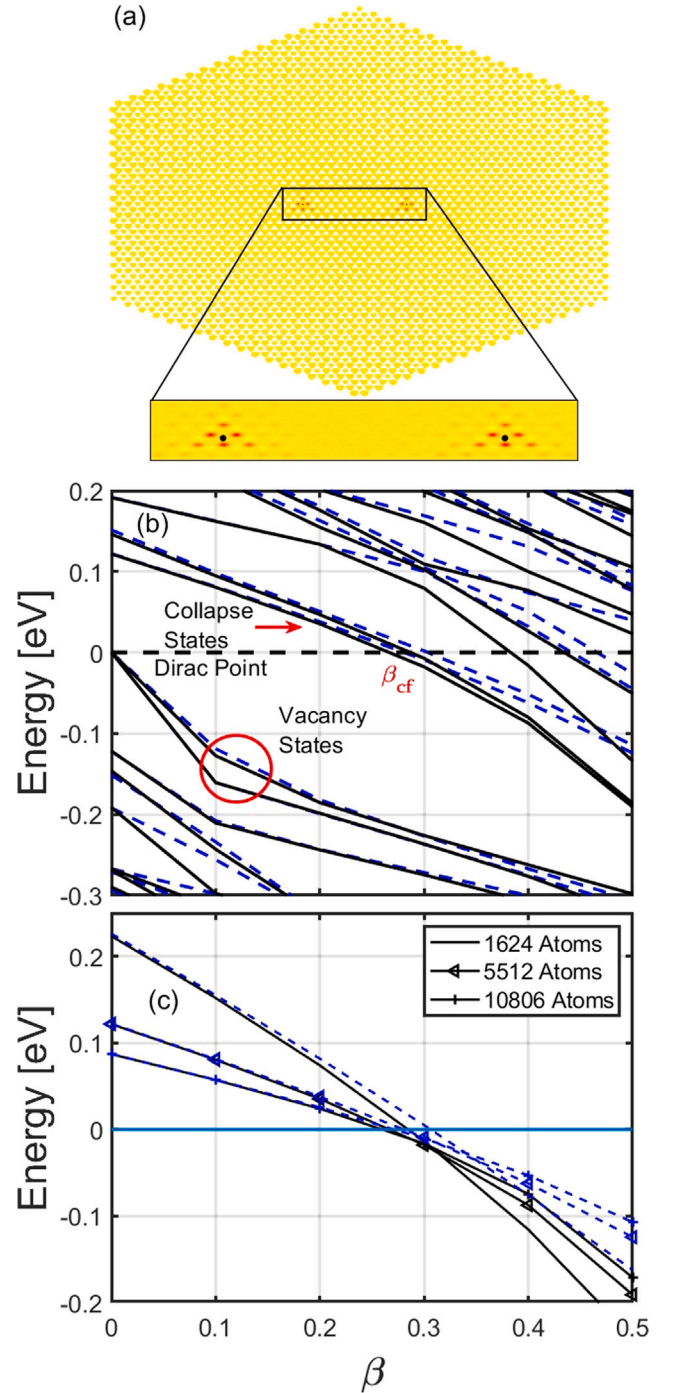


Fig. 1. (Color online) (a) Cross section image of electron density for a hexagonal armchair GQD, 5512 atoms, with two vacancies for AA case. Inter-vacancy distance is set to  $R = 11b$  where  $b$  is second nearest-neighbor distance. Black dots represent vacancy positions. (b) TB energy spectrum versus  $\beta$  and (c) GQD size comparison for  $R/b = 3$  (black-solid lines) and  $R/b = 9$  (blue-dashed lines).

## 3. Results and discussion

### 3.1. Tight-binding results

As mentioned above, we consider AA and AB configurations for vacancies located along the zigzag direction and separated by a distance  $R$ , as shown in Fig. 1a for the AA configuration. The midpoint between

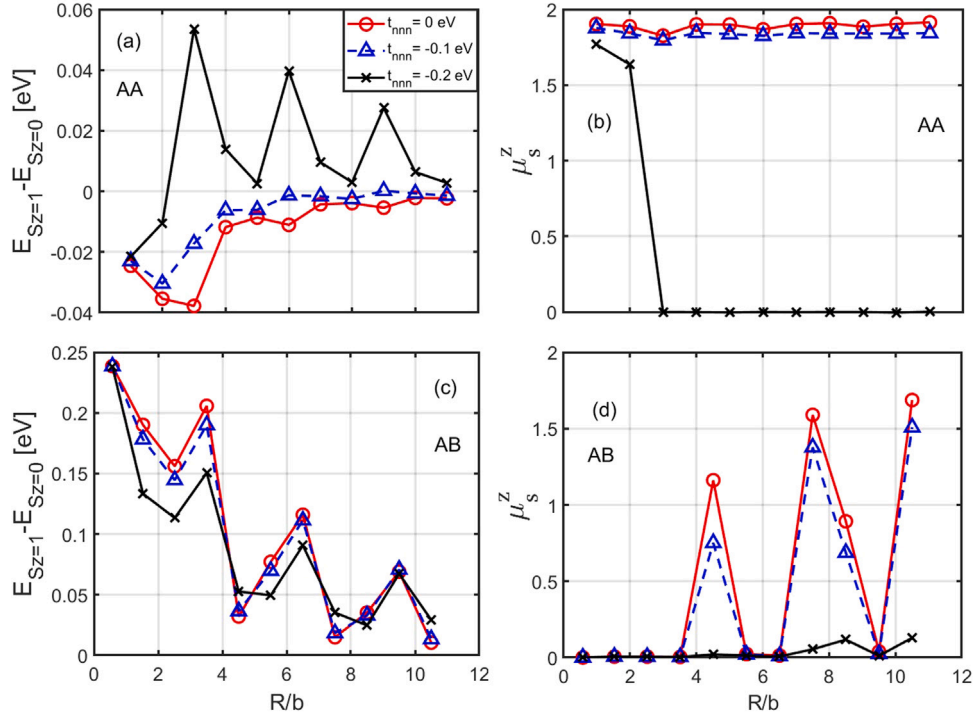


Fig. 2. (a, c) Ground state energy differences  $E_{S_z=1} - E_{S_z=0}$  for AA and AB cases and  $\beta = 0$ , (b, d) corresponding staggered magnetisms versus  $R/b$ . Results are obtained using MFH method for hexagonal armchair GQD with 5512 atoms for different second nearest neighbor hopping parameters  $t_{nnn}$ .

the vacancies is chosen to be the center of the dot to minimize edge effects. Fig. 1b shows a typical tight-binding (TB) energy spectrum as a function of  $\beta$  in the vicinity of the Dirac point, obtained for the AA configuration with  $R/b = 3$  (solid lines) and  $R/b = 9$  (dashed lines) where  $b = 2.46 \text{ \AA}$  is the second nearest neighbor distance. As expected, there are two sets of vacancy states and collapse states corresponds to the bonding and anti-bonding states [40,41] of two charged vacancies. Collapsing states cross the Dirac level at the critical value  $\beta_{cf} \sim 0.28$  indicating the lower limit for the frustrated supercritical regime before the system enters the molecular collapse regime at  $\beta_c = 0.5$  [23,40,41]. The lower value of  $\beta_{cf} = 0.28$  for the double impurity system is expected since the Coulomb potential due to each impurity feed each other, accelerating the collapse. This effect is expected to vanish for large distances  $R$ . For the range of  $R$  values studies in this work,  $\beta_{cf}$  is nearly constant. More importantly,  $\beta_{cf}$  is also found to be largely independent of finite size effects for dots larger than few thousands atoms, consistent with single charged impurity results [51] as seen in Fig. 1c, provided  $R$  is smaller than the dot diameter. We also note that, increasing  $\beta$  lifts the degeneracy of the vacancy states initially. The energy gap between the vacancy states increases up to  $\beta \sim 0.1$  but, starts decreasing again as  $\beta$  is increased further, pointing to a decoupling of bonding and anti-bonding vacancy states at large  $\beta$  values. This observation have important consequences for the understanding of mean-field Hubbard results discussed below.

### 3.2. Mean-field Hubbard results for bare vacancies

In order to understand magnetic properties, we first focus on  $\beta = 0$  and examine the stability of magnetic coupling between the vacancies. Fig. 2a and 2c show the spin gap  $E_{S_z=1} - E_{S_z=0}$  as a function of distance  $R$  for AA and AB configurations respectively, obtained using MFH (without long range interactions  $V_{ij}$ ) for different second nearest neighbor hopping parameters  $t_{nnn}$ . For  $t_{nnn} = 0$ , ferromagnetic ( $S_z = 1$ ) ground state for AA configuration and antiferromagnetic ( $S_z = 0$ )

ground state for AB configuration are obtained as expected. Moreover, the observed distance dependent oscillations are reminiscent of RKKY model for graphene along zigzag direction [43,57], assuming  $E_{S_z=1} - E_{S_z=0}$  is proportional to the effective magnetic coupling parameter  $J$  in the RKKY model. Here, however, the spins are localized on three atoms neighboring each vacancy unlike in the RKKY model. We have also investigated (not shown) the behavior of  $E_{S_z=1} - E_{S_z=0}$  as a function of distance along the armchair direction and found a smooth decrease without oscillations, again consistent with RKKY results. On the other hand, Fig. 2a shows that the magnetic coupling between the bare vacancies is strongly affected by  $t_{nnn}$ . For  $t_{nnn} = -0.1$  eV, the value usually accepted for graphene systems, the oscillations lose their characteristic period of  $3a$ , where  $a = 2.46 \text{ \AA}$  is the lattice constant of graphene. Moreover, for  $t_{nnn} = -0.2$  eV, the ground state total spin projection becomes  $S_z = 0$ , and the staggered magnetization defined as  $(-1)^x(n_{i\downarrow} - n_{i\uparrow})/2$  where  $x$  is even for A and odd for B sublattice sites, is completely suppressed as shown in Fig. 2b. The losing of staggered magnetization is also observed for the AB configuration as shown in Fig. 2d. These results shown that magnetic properties of the double vacancy system are sensitive to  $t_{nnn}$ . In the remaining of this work,  $t_{nnn}$  will be set to zero.

### 3.3. Mean-field Hubbard results for charged vacancies

We now investigate the effect of the Coulomb coupling strength  $\beta$ . Fig. 3a and 3c show  $E_{S_z=1} - E_{S_z=0}$  as a function of  $R/b$  for different values of  $\beta$ , for the AA and AB configurations respectively obtained using MFH calculations excluding long-range electron-electron interactions. Even at low values of  $\beta = 0.1$ ,  $S_z = 0$  becomes the ground state for AA configurations, and staggered magnetization is quenched (see Fig. 3b). A similar quenching of staggered magnetization is also observed for the AB configuration. As  $\beta$  is increased further, spin gaps gradually approach zero for both AA and AB configurations.

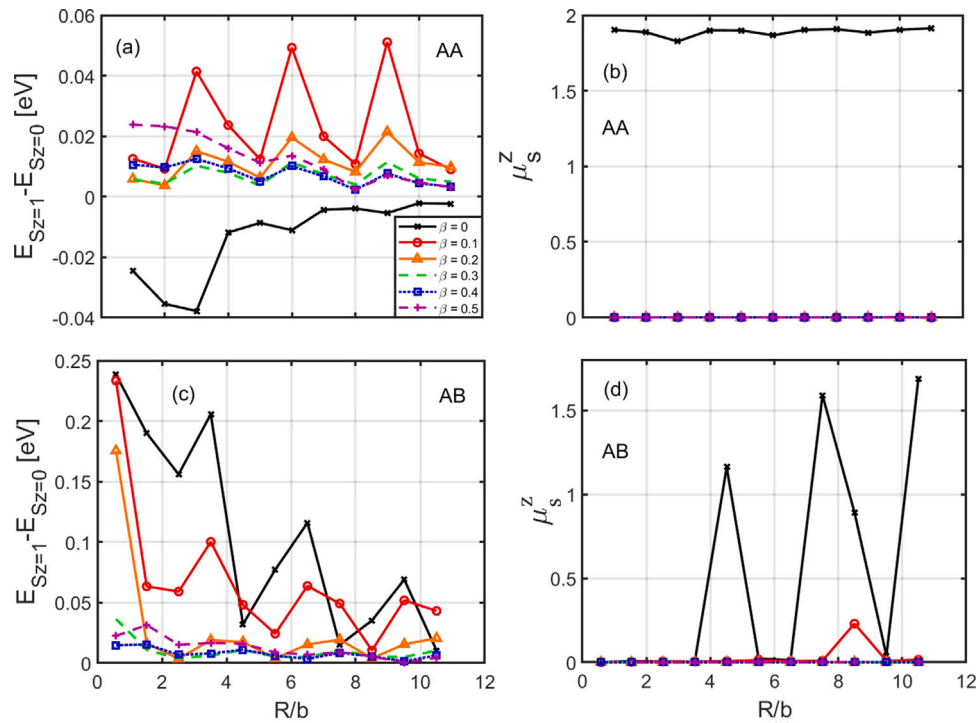


Fig. 3. (a, c) Ground state energy differences  $E_{S_z=1} - E_{S_z=0}$  and (b, d) corresponding staggered magnetisms versus  $R/b$  for different  $\beta$  values obtained using MFH method for hexagonal armchair GQD with 5512 atoms.

In order to understand the behavior of the spin gap shown in Fig. 3 further, we plot the tight-binding energy differences between the two vacancy states as a function of  $R/b$  for different  $\beta$  values as shown in Fig. 4. Clearly, the tight-binding energy gaps show qualitatively similar features compared to the spin gaps shown in Fig. 3a and c, except for the AA configuration at  $\beta = 0$ . Indeed the vacancy states are degenerate in this latter case and the spin gap is dominated by electron–electron interactions, leading to an effective ferromagnetic interaction. In other cases, the degeneracy is lifted and the spin gaps are mainly dictated by tight-binding kinetic energies.

### 3.4. Extended mean-field Hubbard method calculations

We now investigate the effects of long-range electron–electron interaction terms  $V_{ij}$ . Since charged impurities causes the charge distribution to be inhomogeneous, long-range electron interactions can be expected to play an important role. Fig. 5 shows the spin gaps  $E_{S_z=1} - E_{S_z=0}$  and energy spectra for spin up electrons obtained using the extended mean-field Hubbard model. Although Fig. 5a, c are qualitatively similar to Fig. 3a, c, we see that it takes larger values of  $\beta$  to cause any change in the ground states for both AA and AB configurations. In particular, for AA configuration at  $\beta = 0.1$ ,  $S_z = 1$  remains the ground state for several  $R$  values, unlike in Fig. 3a. This is due to the screening of charged impurities by electron–electron interactions. Also,  $\beta_{c,f}$  value is increased to 0.36, consistent with single charged vacancy results where  $\beta_c$  is increased from 0.5 to 0.7 [51].

## 4. Summary

To conclude, we have investigated the electronic and magnetic properties of a system of two charged vacancies in hexagonal graphene quantum dots using mean-field Hubbard approach. We focused on two properties: (i) stability magnetic of phases of the two impurity

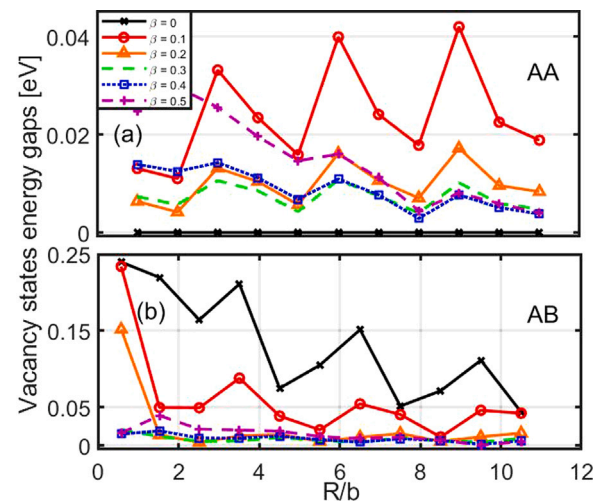


Fig. 4. TB vacancy states gap for (a) AA and (b) AB cases along zigzag direction versus  $R/b$  for different  $\beta$  values.

system and (ii) critical value of the Coulomb potential strength for the frustrated collapse  $\beta_{c,f}$ . We found that the magnetic properties are sensitive to next nearest neighbor hopping parameter  $t_{nnn}$  and  $\beta$ . In particular, if  $\beta$  approaches 0.2, staggered magnetization is strongly suppressed pointing to a non-magnetic regime within the subcritical region of molecular collapse. On the other hand,  $\beta_{c,f}$  is found to be nearly constant for quantum dots sizes containing more than few thousands of atoms. Finally, long range electron–electron interactions cause an increase up to 28% of  $\beta_{c,f}$  as a result of smearing out the electron density near the Coulomb impurities.

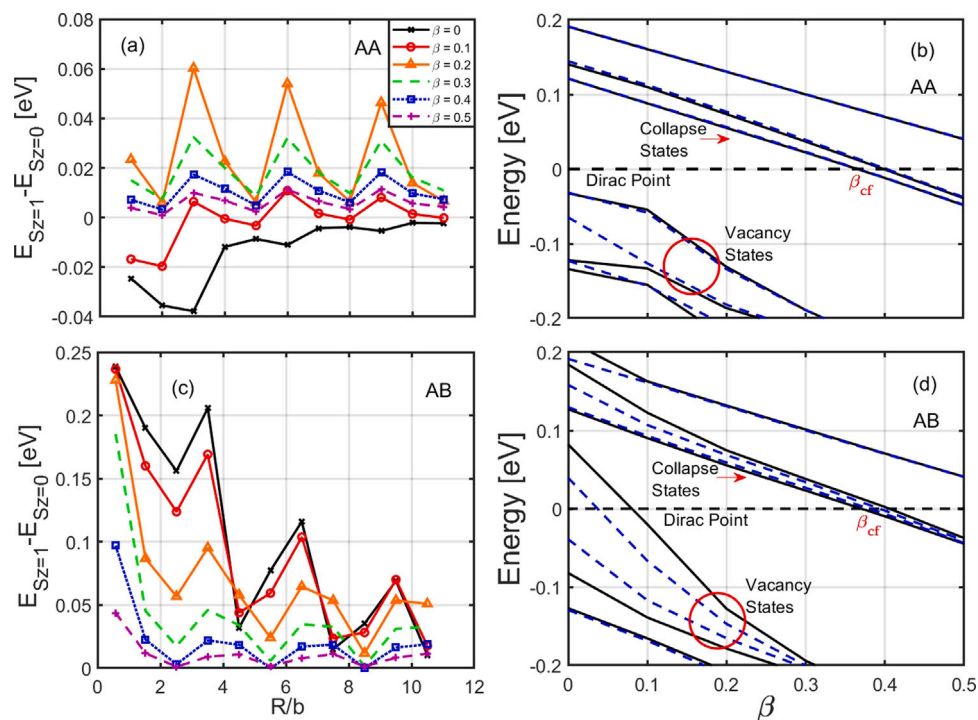


Fig. 5. (Color online) (a, c) Ground state energy differences  $E_{S_z=1} - E_{S_z=0}$  versus  $R/b$  for different  $\beta$  values, and (b, d) energy spectra versus  $\beta$  for  $R/b = 3$  (black-solid lines) and  $R/b = 9$  (blue-dashed lines). Results are obtained using extended MFH method for GQD's with 5512 atoms.

### CRedit authorship contribution statement

**E. Bulut Kul:** Conceptualization, Methodology, Software, Visualization, Writing - review & editing, Writing - original draft, Formal analysis, Investigation. **M. Polat:** Writing - review & editing, Validation. **A.D. Güçlü:** Supervision, Project administration, Conceptualization, Validation, Writing - review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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