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Electron-electron interactions on the edge states of graphene: A many-body configuration interaction study

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We have studied zigzag and armchair graphene nanoribbons (GNRs), described by the Hubbard Hamiltonian using quantum many-body configuration interaction methods. Due to finite termination, we find that the bipartite nature of the graphene lattice gets destroyed at the edges, making the ground state of the zigzag GNRs a high spin state, whereas the ground state of the armchair GNRs remains a singlet. Our calculations of charge and spin densities suggest that, although the electron density prefers to accumulate on the edges (instead of spin polarization), the up and down spins prefer to mix throughout the GNR lattice. While the many-body charge gap results in insulating behavior for both kinds of GNRs, the conduction upon application of electric field is still possible through the edge channels because of their high electron density. Analysis of optical states suggest differences in quantum efficiency of luminescence for zigzag and armchair GNRs, which can be probed by simple experiments.

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Nanomaterials of carbon of different dimensionalities have been a subject of interest over the past few decades due to their potential applications in various nanoscale electronic devices.[1–3] Compared to fullerenes and carbon nanotubes, which are effectively zero and one dimensional in nature, the two-dimensional flat monolayer of carbon atoms packed into a honeycomb lattice, i.e., graphene, has started gaining prominence very recently owing to the recent progress in experimental techniques.[4–7] Because of its sophisticated low-dimensional electronic properties and huge application possibility, it has attracted a big scientific army to explore it in various aspects.[8–11]

The size and geometry of the nanoscale carbon systems govern their electronic properties. Recent progress in experiments allows to make finite size graphene layers, termed as graphene nanoribbons (GNRs), with varying widths either by mechanically cutting exfoliated graphenes[4–6] and patterning by electron beam lithography[12] or by controlling the epitaxial growth of graphenes.[13,14] Different possibilities of geometrical termination of the graphene layer give rise to two different edge geometries, namely, zigzag and armchair edges, differing largely in their electronic properties. These different edge geometries have been modeled by imposing different boundary conditions on Schrödinger's equation within the tight-binding limit[15–18] or on the Dirac equation for two-dimensional massless fermions with an effective speed of light[19–22] in previous studies. These have also been extensively studied using density functional theory.[23,24] However, the proper many-body description of the GNR is still lacking. To obtain new inroads in the rich physics of a one atom thick finite graphene material, we use configuration interaction (CI) method based on many-electron theory with proper inclusion of electron interaction term which plays a crucial role in low-dimensional systems.

Our CI approach with correlation parameters in Hamiltonian obtained semiempirically can directly connect to the real description of the system under investigation. We study both the zigzag and armchair edges with a fixed width and vary their size by translating it in one direction up to a large limit to reduce finite size effects. Since the full many-body CI calculation is not possible for a very large system, we map the whole system into a complete active space (CAS) which captures the low-energy states accurately. We have also considered the singles CI (SCI) which shows the same qualitative features as obtained from CAS-CI.

We employ the Hubbard Hamiltonian for the GNRs,

$$H=\sum_i \epsilon_i a^{\dagger}{}_i a_i+\sum_{\langle i,j\rangle,\sigma} t_{ij}(a^{\dagger}_{i,\sigma}a_{j,\sigma}+\text{H.c.})+U\sum_i n_{i\uparrow}n_{i\downarrow}, \quad (1)$$

with standard notations. The nearest neighbor hopping integral t_{ij} is considered to be 2.4 eV which is standard for the C-C bond. We consider U as the difference between the first ionization energy and the electron affinity for carbon, which comes out to be ~9.66 eV. Due to finite termination of the GNRs, the chemical nature of the edge atoms changes abruptly because of the unsatisfied valence of carbon atoms. As a result, the lattice deviates from its bipartite nature at the edges. So, to differentiate these edge atoms from the bulk, we model our system by putting nonzero negative on-site energy ϵ_{edge} at the edge atoms to mimic hydrogen passivation and $\epsilon_i=0$ for the bulk. Although the on-site energies at edges are expected to be modified compared to the bulk as a difference between the electronegativities of carbon and hydrogen,[18] they have been neglected in most of the studies so far. Moreover, the scanning tunneling microscopy images of graphite shows bright stripes along the edges, suggesting more electron density on the edge atoms compared to the bulk.[25] This observation motivates us to simulate the GNRs with negative on-site energies at the edge carbon atoms to create a potential well which can trap the electrons on the edges. We compare and contrast our model with the bipartite lattice model, where all the lattice points are assigned $\epsilon_i=0$ both at the tight binding (TB) and at the CI level of calculations.

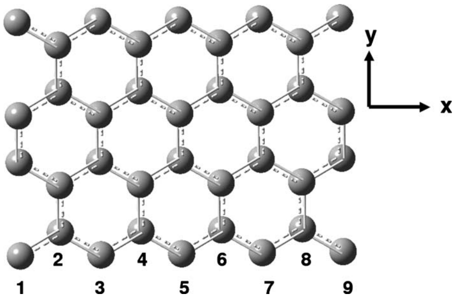

FIG. 1. The unit cell of GNR. The translations along the x and y axes give the zigzag and armchair edge GNRs. The number of atoms at the zigzag terminal of an armchair GNR is represented by the integers.

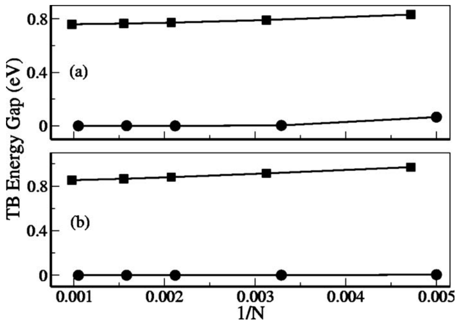

FIG. 2. The lowest gap in tight-binding calculations as a function of inverse system size $(1/N)$ for both zigzag (circle) and armchair (square) GNRs with ϵ_{edge} equal to (a) -2.0 and (b) 0.

Figure 1 displays the GNRs under investigation. The translations along the x axis and y axis produce zigzag and armchair GNRs of different sizes, respectively. We consider the armchair GNRs with $3p$ number of atoms constituting the two zigzag terminals, where p (=3 in our case) is an integer. In Fig. 2, we plot the TB $(U=0)$ gap for both types of GNRs with and without consideration of edge hydrogen passivation energies, with inverse system size. The calculated TB gap reproduces the well established previous observations of zigzag being metallic and armchair $(3p)$ being semiconducting GNRs.[15–21,23,24,26] However, inclusion of electron correlations is expected to open up a gap, reducing the kinetic stabilization.

Based on the TB wave functions, we perform the CI calculations over the electron correlations within many-body formalism. The z component of total spin (S_z^{tot}) is used as a quantum number together with the N number of electrons. We vary S_z^{tot} from zero to higher values for half-filled systems. In CAS-CI, we consider all possible configurations within a small energy window (the active space) and obtain the CI matrix of order 4900. We have verified our results with 63 504 states in certain cases. We have also considered SCI calculations by varying the number of occupied and unoccupied single particle levels. However, since the CAS-CI includes all the configurations within a certain energy cutoff, the resulting low-energy states are more size consistent than those from the SCI and unless otherwise stated, all the results reported below are obtained using the CAS-CI approach. For any kind of energy cutoff with $S_z^{tot}=0$, we find that the diagonals of the CI matrix appears in the order of $\frac{NU}{4}$ after correction for the levels beyond the cutoff.

Our many-body calculations for half-filled GNRs with different choices of ϵ_{edge} value and with varying S_z states lead to results that have been anticipated[23,27] but not observed until now: The ground state of the zigzag GNR is always a high spin state, whereas it remains in a singlet state for the armchair GNRs. In Table I, the numbers enclosed in parentheses for various size GNRs are the total ground state spins. This observation remains consistent for all nonzero negative ϵ_{edge} values. However, for $\epsilon_{edge}=0$, both the GNRs show singlet ground state, which is expected when the lattice is bipartite with the same number of atoms in the two sublattices.[28] These observations are consistent with the gradual increase of the system size for a fixed width. To correlate the experimental observation,[25] we calculate the charge density over all the atoms for both zigzag and armchair GNRs with $N=104$, with $\epsilon_{edge}=0$ and -2.0 (Fig. 3). The $\epsilon_{edge}=0$ value shows almost the same electron densities on all the atoms, whereas nonzero ϵ_{edge} leads to fairly large charge densities on the edge atoms (maxima in Fig. 3) for both types of GNRs, as can be seen from Fig. 3. This is the result of unsatisfied coordination of the edge atoms, passivated by hydrogen. Interestingly, the charge accumulation at the zigzag edges is more than that at the armchair edges. Note that the minima in the charge density plots correspond

TABLE I. The ground state energies $[E(S_z^{tot})]$ per atom for two different system sizes (N) for both zigzag and armchair GNRs at half filling with different ϵ_{edge} (eV) values. Since all total spin states (S^{tot}) have projection into $S_z^{tot} \leqslant S^{tot}$, the ground state spin is determined by the highest S_z^{tot} value with ground state energy.

Zigzag			Armchair		
	$E(S_z^{tot})$			$E(S_z^{tot})$	
ϵ_{edge}	$N=304$	$N=952$	ϵ_{edge}	$N=320$	$N=1022$
−0.2	−1.1951(4)	−1.1913(4)	−0.2	−1.2508(0)	−1.2576(0)
−0.5	−1.2750(4)	−1.2672(4)	−0.5	−1.3247(0)	−1.3272(0)
−1.0	−1.4046(4)	−1.3914(4)	−1.0	−1.4492(0)	−1.4446(0)
−2.0	−1.6580(4)	−1.6313(4)	−2.0	−1.6982(0)	−1.6830(0)

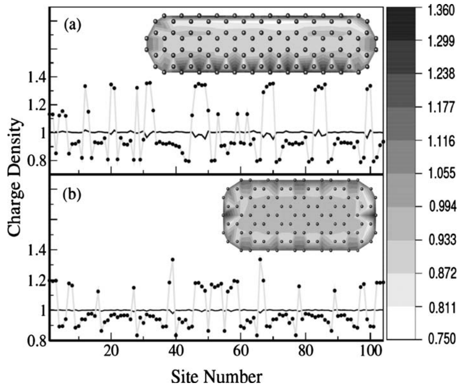

FIG. 3. Charge density on each and every site for both (a) zigzag and (b) armchair GNRs with $\epsilon_{edge}=-2.0$ (gray lines with circles) and 0 (solid lines without any symbol) on the edge atoms of the system with $N=104$. Insets present the contour plot of the charge density for the corresponding systems with $\epsilon_{edge}=-2.0$.

to the atoms directly connected to the edge atoms. This reduction in charge densities on the left and right neighbors of edge atoms gives kinetic stability to the extra electrons accumulated at the edge atoms.

To understand the nature of the spin at the edges, we calculate the spin density over all the atoms, which suggests that both zigzag and armchair GNRs do not prefer any dominant spin at the edges as well as on the bulk atoms for both zero and nonzero ϵ_{edge} values. Instead, a proper many-body consideration shows that the GNRs prefer to have a mixture of both up and down spin densities at the edges. This observation clearly contradicts previous density functional studies which predict the dominance of up spins and down spins on either edges of zigzag GNRs.[23,24] Those studies conclude this observation as the property of bipartite lattice with two different sublattice points. However, the presence of passivating hydrogen atoms on the edges would destroy the bipartite nature of the lattice which, however, have been completely ignored. Moreover, the one-electron definition of the exchange correlations in density functional theory studies cannot capture the dominant electron-electron interactions in GNRs. The more realistic many-body calculations infer that, although the electrons have the tendency to accumulate at the edges, a net spin polarization of the edges is highly improbable.

Now, to investigate the possibility of electron conduction in the different GNRs, we calculate the charge gap. The many-body charge excitation gap is defined as the difference between the energies required to add (μ_+) and remove (μ_-) electrons from the ground state,[29]

$$\Delta_{charge}=\mu_+-\mu_-, \tag{2}$$

where $\mu_+=E(N+1)-E(N)$ and $\mu_-=E(N)-E(N-1)$. $E(N)$, $E(N+1)$, and $E(N-1)$ are the energies of the half-filled system and the systems with one extra and one less electron, respectively. The charge gap results from our calculations show Mott insulating behavior for both zigzag and armchair GNRs even for very large system sizes with more than 1000 atoms, as observed in earlier many-body study.[27] This result is expected since the kinetic stabilization is suppressed by strong electron correlations, which is unexpected within one-electron theories. For a half-filled system, with large electron densities at the edges, the conduction, however, is still possible through edge channels.

TABLE II. The square of the transition dipole moment (μ^2) for transitions from the ground state to the few optically allowed excited states with the corresponding excitation gaps for the system with $N=104$ in both zigzag and armchair GNRs with $\epsilon_{edge}=-2.0$

Zigzag		Armchair	
Gap (eV)	μ^2	Gap (eV)	μ^2
0.016	2.801	0.906	3.770
0.071	0.440	0.969	0.001
0.073	3.069	1.060	3.027
0.115	0.168	1.136	0.002

Motivated by the difference in the spin multiplicities of the ground and low-lying excited states between the zigzag and armchair GNRs, we study their optical properties. We have calculated the transverse and longitudinal transition dipole moments μ_T and μ_L, respectively, for the excitations from the ground state to the optically allowed excited states and present $\mu^2=\mu_T^2+\mu_L^2$ for $N=104$ in Table II. As can be seen from Table II, the energy levels in zigzag GNRs are more closely spaced than those in the armchair GNRs. Similar to the ground state, the first few excited states of zigzag GNRs are also of higher spin states. However, due to nonzero ϵ_{edge}, the high spin ground states are not degenerate with different S_z^{tot} components. With nonzero gap values, these low-energy excitations show large absorption cross sections. Moreover, the optically allowed emissions from the excited states are expected to show very high quantum efficiency (QE) in the luminescence spectroscopy, since according to Kasha's rule,[30] the spin allowed optical emission can occur from the high spin excited state to the high spin ground state. In the case of armchair GNRs, however, the singlet ground state is followed by a few high spin excited states. This dipole forbidden excited states below the allowed optical excitation originate from the strong electron-electron interactions.[31,32] Thus, it is expected that the optically excited state in armchair GNRs would decay to the low-energy dipole forbidden states through magnon emission, thereby preventing the radiative transition considerably. As a result, the armchair GNRs are expected to show very low QE in luminescence spectroscopy. These results are all consistent with the gradual increase of system size with fixed width. Thus, from our study on optical properties, we are able to propose a simple experimental technique of measuring luminescence to differentiate the zigzag and armchair GNRs.

While our discussions so far are based on the short range Hubbard Hamiltonian, it is known that the one-dimensional conjugated carbon systems are best described by long range Coulomb interactions.[32] For the graphene class of systems, however, even the on-site Hubbard correlations have hardly been considered.[15–24,26] There are also suggestions that the Hubbard repulsion can at best be 3–4 eV in graphene,[33] three times smaller in magnitude than what is considered for the conventional conjugated polyemers.[32] Interestingly, we have verified that all our observations described earlier are consistent even with $U=3$ eV. However, to test whether longer range interactions exist in such systems, we have investigated these GNRs with long-range Coulombic interactions using Pariser-Parr-Pople Hamiltonian within two decay profile schemes originally given by Ohno and by Nishimoto and Mataga.[34] Our results indicate that for both these potential profiles, the ground state has large contribution from either high-energy singles configuration (in the case of SCI) or configurations with two- or three-electron excitations within the energy window for the CAS-CI calculations. Contributions from these configurations, in fact, raise the energy of the state with finite magnetic moment. This, hence, results in both zigzag and armchair GNRs having a singlet ground state, while the lowest excitations become magnetic.

In summary, the quantum many-body configuration interaction method captures the low-energy properties of the nanoscale systems such as graphene and our development of the CI method allows us to handle fairly large systems which can effectively be considered as infinite lattice. Within the Hubbard model, the ground state of the zigzag GNRs is a nonzero spin state, while for armchair GNRs, it remains a singlet. Though the hydrogen passivation of the edge atoms leads to higher charge density at the edges, the electronic correlations mix the up spin and down spin throughout the GNR lattices instead of making the edges spin polarized. We propose that the zigzag GNRs can be differentiated from armchair GNRs from the higher quantum efficiency of luminescence originating from their magnetic ground and low-lying excited states. It would also give an indication of the importance of the long range Coulomb interactions in these class of systems. Our findings on GNRs suggest rich low-energy physics and provoke further studies within the many-body limit for these class of low-dimensional systems.

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