

# CHCRUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

# Correlated electronic properties of some graphene nanoribbons: A DMRG study

V. M. L. Durga Prasad Goli, Suryoday Prodhan, Sumit Mazumdar, and S. Ramasesha Phys. Rev. B **94**, 035139 — Published 18 July 2016 DOI: 10.1103/PhysRevB.94.035139

#### Correlated Electronic Properties of Some Graphene Nanoribbons: A DMRG Study

V. M. L. Durga Prasad Goli,<sup>1, \*</sup> Suryoday Prodhan,<sup>1, †</sup> Sumit Mazumdar,<sup>2, 3, ‡</sup> and S. Ramasesha<sup>1, §</sup>

<sup>1</sup>Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India.

<sup>2</sup>Department of Physics, University of Arizona, Tucson, Arizona 85721, USA.

<sup>3</sup>College of Optical Sciences, University of Arizona, Tucson, Arizona 85721, USA.

The significant electron-electron interactions that characterize the  $\pi$ -electrons of graphene nanoribbons (GNRs) necessitate going beyond one-electron tight-binding description. Existing theories of electron-electron interactions in GNRs take into account one electron-one hole interactions accurately but miss higher order effects. We report highly accurate density matrix renormalization group (DMRG) calculations of the ground state electronic structure, the relative energies of the lowest one-photon versus two-photon excitations and the charge gaps in three narrow graphene nanoribbons (GNRs) within the correlated Pariser-Parr-Pople model for  $\pi$ -conjugated systems. We have employed the symmetrized DMRG method to investigate the zigzag nanoribbon 3-ZGNR and two armchair nanoribbons 6-AGNR and 5-AGNR, respectively. We predict bulk magnetization of the ground state of 3-ZGNR, and a large spin gap in 6-AGNR in their respective thermodynamic limits. Nonzero charge gaps and semiconducting behavior, with moderate to large exciting binding energies are found for all three nanoribbons, in contradiction to the prediction of tight-binding theory. The lowest two-photon gap in 3-ZGNR vanishes in the thermodynamic limit, while this gap is smaller than the one-photon gap in 5-AGNR. However, in 6-AGNR the one-photon gap is smaller than the two-photon gap and it is predicted to be fluorescent.

#### I. INTRODUCTION

Carbon has come to the fore in the last few decades for many exciting electronic and magnetic properties with the discovery of buckyball in the eighties to carbon nanotubes in the nineties to graphene and graphene nanoribbons in the last  $decade^{1-3}$ . In all these systems, we can assume that the carbon atom is in  $sp^2$  hybridization and hence, these systems belong to the class of  $\pi$ -conjugated carbon systems. In recent years, graphene nanoribbons (GNRs) have attracted considerable attention because of their exotic electronic properties and plausible applications in nanoelectronics<sup>4–8</sup>. GNRs with different widths can be made using various techniques like mechanical cutting of exfoliated graphenes or by patterning epitaxially grown graphenes<sup>9-14</sup>. GNRs are quasi onedimensional forms of graphene, which exhibit exciting electronic properties because of the confinement of electrons in low dimension $^{4,15-18}$ . These electronic properties also depend crucially on the geometry of the edges of the ribbons. The GNRs are classified into two types based on the edge structures, namely, zigzag and armchair GNRs (ZGNRs and AGNRs respectively). Within the one-band tight-binding theory, ZGNRs are predicted to be metallic with zero bandgap, while AGNRs can be both semiconducting or metallic, depending upon their width<sup>15–17,19</sup>; AGNRs with 3p+2 (with integer p) dimer bonds between nearest neighbor carbon atoms across the ribbon width are metallic and others are semiconducting $^{17}$ .



FIG. 1. Molecular structures of (a) zigzag 3-ZGNR, (b) armchair 6-AGNR and (c) armchair 5-AGNR. The unit cell for each nanoribbon is indicated by the square brackets.

The quasi one-dimensional character of the GNRs leads to confinement and enhanced electron repulsion between the  $\pi$ -electrons. Thus extended screening lengths and long range electron-electron interactions are expected in the semiconducting GNRs, and even in the metallic GNRs which are better described as zero gap semiconductors  $^{16,17}$ . Electron-electron interactions in GNRs and single-walled carbon nanotubes have been considered in the past within the time-dependent density functional approach 20-22 as well as the GW approximation accompanied by Bethe-Salpeter corrections  $2^{23-25}$ . These approaches take into account one electron-one hole (1e-1h) interactions, are equivalent to the singles configuration interaction approximation of quantum  $chemistry^{26-28}$ , and have successfully predicted the excitonic character of the lowest optical absorption in the semiconductors. Our goal here, however, is to probe the consequences of the strong four-fermion two electron-two hole (2e-2h) interactions. As in previous  $work^{26-28}$ , we

<sup>\*</sup> Electronic mail:durgaprasad.vml@gmail.com; VMLDPG and SP have contributed equally to this work.

<sup>&</sup>lt;sup>†</sup> Electronic mail: suryodayp@sscu.iisc.ernet.in

<sup>&</sup>lt;sup>‡</sup> Electronic mail: sumit@physics.arizona.edu

<sup>&</sup>lt;sup>§</sup> Electronic mail: ramasesh@sscu.iisc.ernet.in

probe the consequences of realistic electron-electron interactions on the optical and charge gaps in three narrow GNRs. the ZGNR with three carbon-carbon bonds across its width (3-ZGNR) and AGNRs with 6 and 5 carbon-carbon bonds across their widths (6-AGNR and 5-AGNR), respectively (see Fig. 1). Beyond this, however, we also probe their ground state magnetic character and the spin gap. We further determine the relative energy orderings of the lowest one-versus two-photon states in all three nanoribbons. In the past, the experimental demonstration that the lowest two-photon state occurs below the optical one-photon state in linear polyenes $^{29}$ , in contradiction to the predictions of tight-binding and Hartree-Fock theories<sup>29</sup>, provided the most convincing demonstration of the strong electron correlations in these systems. More recently, similar experimental results have also been obtained from nonlinear optical measurements of graphene nanofragments<sup>30</sup>. Accurate computational investigation of the relative energy orderings of one- and two-photon states also requires going beyond existing

tendency to structural distortions. For conjugated carbon systems, the Pariser-Parr-Pople (PPP) model, which assumes  $\sigma - \pi$  separability and incorporates long-range electron-electron repulsions<sup>31</sup>, is known to reproduce ground and excited state properties very well<sup>32–35</sup>. It has also been demonstrated that the symmetrized DMRG method can provide highly accurate descriptions of ground and low-lying excited states within the PPP model<sup>36,37</sup>. We report here symmetrized DMRG calculations on the three GNRs of **Fig. 1**.

techniques. Finally, we compute nearest neighbor bond

orders (nearest neighbor charge-transfers) to examine the

We briefly mention here existing related works about edge-magnetism in zigzag nanoribbons which was speculated quite early in the literature and has been studied rather extensively. Fujita et al. have studied both armchair and zigzag graphene ribbons with tight-binding approximation and reported the presence of a flat band and localized edge states near the Fermi level for zigzag nanoribbons, resulting in high density of states near the Fermi level<sup>15</sup>. In armchair nanoribbons, these almost flat bands (which are a consequence of the topology of the  $\pi$ -conjugation) are absent. In the correlated picture, these almost flat bands result in magnetic states whose spins are arranged ferromagnetically at the edges<sup>15</sup>. Opposite edges of the ribbon will have opposite alignment of spins making the ribbon non-magnetic in the thermodynamic limit. Even in a general nanoribbon which cannot be classified either as perfectly armchair or perfectly zigzag, a few sequentially placed zigzag sites can result in significant density of states at the Fermi level resulting edge ferromagnetism<sup>16</sup>. Sasaki and coworkers studied graphene in the continuous model using Weyl equation with a special gauge field resulting from the local deformation in the  $\pi$ -backbone and confirmed presence of localized states at zigzag edges<sup>38</sup>. Consequences of the presence of these edge states in quantum Hall effect in graphene have also been studied within localized<sup>39</sup>

2

and continuum pictures<sup>40</sup>. Wakabayashi et al. studied electronic and magnetic properties of GNRs in the presence of a magnetic field in the tight-binding approximation and proposed that zigzag nanoribbons will show diamagnetic behavior at high temperature and paramagnetic behavior at low temperature<sup>41</sup>. Louie et al. have also showed that the edge-magnetic nature of ZGNRs can induce half-metallicity in the presence of transverse electric field across the ribbon width, resulting in a spin current<sup>42</sup>. The edge magnetism in zigzag nanoribbon has also been studied using mean-field Hubbard model by Jung and coworkers<sup>43</sup>, employing quantum Monte Carlo technique by Golor et al.<sup>44</sup> and by renormalization technique by Hikihara et al.<sup>45</sup> and experimentally at room temperature by Magda and coworkers<sup>46</sup>. Instead of the presence of ferromagnetically aligned spins at the edges, all the above studies predicted singlet ground state in ZGNR in absence of an external field; however, a few density functional studies predicted a ferromagnetic ground state in ZGNR on doping<sup>47</sup>. Dutta et al. have studied low-energy properties of both zigzag and armchair GNRs within the Hubbard model using quantum many-body configuration interaction method and predicted that the ground state of zigzag GNRs is a high-spin state while for armchair GNRs the ground state is a singlet<sup>48</sup>. Spin density calculations at the edges of zigzag nanoribbons show presence of both up and down spin at a given edge instead of predominance of a specific spin as predicted by tight-binding and density functional theories. This study indicates that the picture can be significantly different in the presence of long-range electronic correlation.

There are also extensive studies of electronic properties such as band gaps, quasiparticle energies in GNRs. Ezawa has studied bandgaps in a range of nanoribbons in the Hückel picture and predicted the width dependence of the bandgaps in these systems<sup>17</sup>. He has also found that incorporation of edge effects by changing the transfer term or site energies of the edge sites has little effect on the band structure. Brey and Fertig studied electronic structure of zigzag and armchair nanoribbons using massless Dirac equation and their results are in agreement with the tight-binding results, except for narrow nanoribbons<sup>19</sup>. They proposed that the continuum analysis of graphene can quantitatively predict the properties of these nanoribbons. Louie et al. have computed the band gaps for zigzag and armchair GNRs employing the first-principle approach within local (spin) density approximation<sup>49</sup> and GW approximation with manybody Green's function technique<sup>25</sup> and proposed analytical expressions for band gaps as a function of GNR widths. They argued all GNRs to be semiconducting, contradicting earlier tight-binding predictions. Recently, spin and charge gaps of the armchair polyacene have been studied within the PPP model<sup>50</sup>. It has been shown that the ground state of armchair polyacene is a singlet and the system is an insulator in the ground state.

This paper is organized as follows. In section II, we introduce the model Hamiltonian and briefly describe the

DMRG scheme which we have employed in our study. In section III, we present and discuss our results for the three GNRs. In the final section, we present a comparison of these three GNRs and summarize our results.

#### II. THEORETICAL MODEL, THE DMRG SCHEME FOR GNRS AND SYMMETRY SUBSPACES

#### A. PPP Hamiltonian and parameters

The PPP Hamiltonian is written as,

$$H = \sum_{\langle i,j \rangle,\sigma} t_{ij} (a_{i\sigma}^{\dagger} a_{j\sigma} + a_{j\sigma}^{\dagger} a_{i\sigma}) + \frac{1}{2} \sum_{i} U_{i} n_{i} (n_{i} - 1) + \sum_{i > j} V_{ij} (n_{i} - 1) (n_{j} - 1)$$
(1)

where  $\langle i, j \rangle$  are the bonded pair of atoms and  $t_{ij}$  is the corresponding hopping or transfer integral,  $a_{i\sigma}^{\dagger}(a_{i\sigma})$ is the creation (annihilation) operator at site i with spin  $\sigma$  and  $n_i$  is the number operator. U is the Hubbard onsite repulsion and  $V_{ij}$  are the intersite electron-electron repulsion between carbon atoms i and j.  $V_{ij}$  are obtained from the Ohno parametrization<sup>51</sup>,

$$V_{ij} = 14.397 \left[ \left( \frac{14.397}{U_i} \right)^2 + r_{ij}^2 \right]^{-\frac{1}{2}}$$
(2)

which is arrived at by interpolating between U at  $r_{ij} = 0$ and  $e^2/r_{ij}$  for  $r_{ij} \to \infty$ . In Eq. 2 the distances are in Å while the energies are in  $eV^{52}$ . We have taken the nearest neighbor distance between the carbon atoms as 1.42 Å and we fixed parameters  $t_{ij} = -2.40 \ eV$  and  $U = 11.26 \ eV$  as in many of the previous studies involving carbon-based conjugated systems<sup>34,36,37</sup>; the U value chosen<sup>53</sup> is the sum of ionization energy and electron affinity of carbon and gives the energy change in the process  $CC \to C^+C^-$ .

#### B. The DMRG scheme

We are interested in the properties of the three GNRs of **Fig. 1** in the thermodynamic limit, which is reached from finite size scaling. Exact studies of the model Hamiltonian is confined, at best, to about 18 carbon sites and hence cannot be employed for extrapolation to the thermodynamic limit. Restricted configuration interaction approaches are not size consistent and cannot be employed with finite size scaling. Quantum Monte Carlo approach is also not suitable since we have long-range interactions in the model. For semiconducting narrow nanoribbons, the DMRG method will be the method of choice as the area law of entanglement entropy holds and for the same DMRG cut-off similar accuracy is retained independent of the length of the nanoribbons<sup>54,55</sup>. In case of metallic nanoribbons, gapless low-lying excitations are present and the area law of entanglement entropy will not hold. This leads to increasing errors with increasing system sizes in the DMRG method if we employ a fixed cut-off in the number of block states  $(M_1)$  for all system sizes. However, for finite systems in correlated models, there is always a finite gap in the excitation spectrum and by keeping a large number of block states, we can deduce correct excitation energies. While our calculations will not reproduce all behavior of metals, we believe that the particular properties we are investigating can be obtained from extrapolations of these excitation energies. It has also been shown that for models with diagonal interactions in the real space such as the PPP model, the entanglement entropy is similar to those in the Hubbard and the Heisenberg models in one-dimension  $^{56}$ . Taken together, the above justify the use of the DMRG approach for PPP calculations of GNRs.

The DMRG method, discovered by White in 1992 divides a system block into two sub-blocks  $^{54,55,58,59}$ , generally referred to as the left sub-block (L) and the right sub-block (R), while the wavefunction of the total system block is described in the direct product space of these two sub-block basis states. In the DMRG method, the Fock spaces of the two sub-blocks are approximated and it has been found that the best approximations of the sub-block Fock spaces can be obtained by retaining a small number of reduced density matrix eigenvectors corresponding to the highest reduced density matrix eigenvalues. Reduced density matrix of a chosen sub-block is obtained by treating the other block as an environment block and tracing the density over the states of the environment block. The reduced density matrix for a sub-block of size l, so obtained, is diagonalized and  $M_l$  eigenvectors with the highest reduced density matrix eigenvalues are stored as column vectors of a  $M_{l-1}d_{\sigma} \times M_l$  matrix where  $M_{l-1}$ is the number of density matrix eigenstates retained at l-1-th iteration and  $d_{\sigma}$  is the dimension of the Fock space of the new site added to the sub-block at the l-th iteration. The Hamiltonian of the sub-blocks are renormalized using this  $M_{l-1}d_{\sigma} \times M_l$  matrix and the matrices of site operators are also transformed to this new basis. All terms in the PPP Hamiltonian including the long-range correlation terms can be expressed using these renormalized site operators and the matrix elements of the system Hamiltonian can be obtained by taking appropriate direct products. The next step in the DMRG algorithm involves expanding the system block by adding a few sites (usually two) to the previous system block. The Hamiltonian matrix is constructed in the direct product basis of the retained block states of the two sub-blocks and Fock states of the newly added sites. From the Hamiltonian matrix, desired eigenstates are obtained and the process of constructing the reduced density matrix, truncating the Fock



FIG. 2. (a) Construction of 3-ZGNR of 16 sites in the infinite DMRG method starting from a small system (4 sites). The number of bonds between the new and the old sites at the intermediate system sizes are kept close to that in the final system for higher accuracy. At every step of the algorithm two new sites are added, one to the left sub-block (L) and other to the right sub-block (R). The sites in L are denoted by unprimed numbers while those in R are denoted by primed numbers. The newly added sites are shown by filled square ( $\blacksquare$ ) while old sites are denoted by filled circles ( $\bullet$ ). Solid lines are bonds within a sub-block. The broken lines denote the bonds between • and  $\blacksquare$ . Bonds between the two sub-blocks as well as the bond between  $\blacksquare$  are denoted by hatched lines. (b) Scheme for sweeping in finite DMRG method for 16-site (2N=16) 3-ZGNR. In the forward sweep, the left block size increases from N - 1 to 2 sites; in the reverse sweep, the opposite happens. During finite DMRG sweepings, the total system size remains constant. The corresponding figures for 6-AGNR and 5-AGNR are shown in Figs. 1, 2 and 3 in the supplementary material<sup>57</sup>.

TABLE I. Exact versus DMRG ground state energies (in eV) of 3-ZGNR, 6-AGNR and 5-AGNR within the non-interacting model (U= $V_{ij}=0$ ). The DMRG cut-off in the number of block states is 500.

System type and size	Ground state energy							
	Exact calculation	DMRG method						
3-ZGNR and 40 sites	-137.841	-137.738						
6-AGNR and 40 sites	-139.503	-139.312						
5-AGNR and 40 sites	-137.859	-137.813						

space of the augmented system and expanding the system by adding two additional sites and again solving for the desired eigenstate is repeated until we achieve the targeted system size. The dimension of the Hamiltonian matrix is independent of the system size as the number of block states retained to span the Fock space of the sub-blocks is fixed, independent of the physical size of the sub-block. The method described above is known as the infinite DMRG method.

In order to obtain the behavior in the thermodynamic limit using only the infinite DMRG method, we would need to retain a rather large number of block states  $(M_l)$ and go to much larger system sizes which is beyond our current computational capability. Instead, we have carried out finite DMRG calculations on systems of moderate sizes to obtain energy gaps with high accuracy and rely on finite size scaling to obtain the physical properties in the thermodynamic limit.

The finite DMRG algorithm was introduced by White to improve the accuracy of finite system calculations. In the infinite DMRG method, the density matrix of a psite sub block is built from the eigenstates of a 2p site system block. This leads to errors in the target system of 2N sites (N >> p). In order to correct this error, the psite density matrices are iteratively constructed from the eigenstates of the 2N site target system block, until convergence is achieved. This procedure is termed 'sweeping' where iteratively the size of one of the sub-blocks increases at the expense of the other, while the total system block size remains unchanged. At the final step of one full sweep, sizes of the two sub-blocks become equal and same as in the infinite DMRG step. The finite DMRG procedure for molecular systems is nontrivial but essential as the energies improve considerably following the sweeping. We have employed the finite DMRG algorithm with a block state cut-off  $(M_l)$  of 500 and finite DMRG iteration of two sweeps to compare the DMRG method results with the exact calculation results for all the three nanoribbons within the non-interacting model (Table I). The ground state energies compare well with the exact nearest neighbor tight-binding energies in all cases with a cut-off in the number of block states  $M_l = 500$ . For the interacting models, we expect the DMRG method to be more accurate for the same cut-off as interacting



FIG. 3. (Color online) Calculated lowest one-photon (optical) gaps ((a), (c) and (e)) and lowest two-photon gaps ((b), (d) and (f)) in short 3-ZGNR (left panel), 6-AGNR (middle panel) and 5-AGNR (right panel), plotted against the number of unit cells for different cut-off values of block states ( $M_l$ ). The symbols denote the following: black open circle- onephoton gap with  $M_l = \sim 750$ ; red open square- one-photon gap with  $M_l = \sim 900$ ; blue open triangle- one-photon gap with  $M_l = \sim 1000$ . Corresponding filled symbols denote two-photon gaps.

systems are less entangled. The method of constructing the GNRs in the infinite DMRG procedure as well as the method of finite sweeps are shown in Fig. 2 and Figs. 1, 2 and 3 in the Supplementary Material<sup>57</sup>.

### C. Symmetry subspaces and one versus two-photon excitations

The GNRs of interest possess  $C_2$  symmetry along the axis perpendicular to the plane of the molecule, which we utilize in our computations as well as characterization of eigenstates. Eigenstates are labeled A or B depending upon whether they are of even or odd parity with respect to  $C_2$  operation. The PPP Hamiltonian conserves total spin S, but total spin conservation is difficult within the DMRG scheme with large cut-off in the block states. We exploit partial spin symmetry by performing our calculations for the  $S_z = 0$  sector in which the Hamiltonian has spin inversion symmetry, corresponding to invariance of the Hamiltonian when all spins of the system are reversed. This symmetry bifurcates the  $S_z = 0$  space into a subspace with even total spin, i.e.,  $S = 0, 2, 4, \cdots$  (hereafter designated as 'e') and another with odd total spin,  $S = 1, 3, 5, \cdots$  (designated as 'o'). Finally, the exactly half-filled band that we are investigating also exhibits charge-conjugation symmetry (CCS); eigenstates are labeled even or odd (hereafter '+' or '-') depending upon



FIG. 4. Ground state energy in eV per unit cell vs 1/N for (a) 3-ZGNR, (b) 6-AGNR and (c) 5-AGNR within the PPP model. Here N is the number of unit cells as depicted in **Fig. 1**.

the eigenvalue  $\pm 1$  reached when operated by the CCS operator<sup>60,61</sup>. The identity, the three symmetry operators and their products form an Abelian group of eight elements. Hence, the  $S_z = 0$  sector gets subdivided into 8 subspaces.

In general, the ground state is even with respect to all symmetry operations and lies in the  ${}^{e}A^{+}$  subspace. Optical one-photon states are reached by one application of the current operator j on the ground state

$$\hat{j} = (i/\hbar) \sum_{\langle i,j \rangle,\sigma} t_{ij} (a^{\dagger}_{i\sigma} a_{j\sigma} - a^{\dagger}_{j\sigma} a_{i\sigma})$$
(3)

which clearly changes the parity under  $C_2$  symmetry while conserving  $S_z$ . It can also be shown that the application of the  $\hat{j}$  changes  $CCS^{60}$ . Two-photon states are reached by one application of  $\hat{j}$  on the optical state (or two applications of the operator on the ground state), thus indicating that they also lie in  ${}^eA^+$  subspace. In the  $S_z = 1$  sector, spin inversion symmetry cannot be implemented and the lowest S = 1 state is in the  $B^+$  space. Using the symmetrized DMRG method  ${}^{62}$  with a modified algorithm ${}^{63}$ , all of these symmetries have been exploited in our calculations.

In each symmetry subspace, we have calculated a few low-lying energy states of the Hamiltonian using Davidson's algorithm for symmetric sparse matrices. At each step of the DMRG algorithm, block states are computed from the average reduced density matrix obtained from these eigenstates instead of the reduced density matrix of a single state. The average reduced density matrix is defined by  $\rho = \sum_k \omega_k \rho_k$  where  $\rho_k$  are the reduced density matrices corresponding to eigenstates  $|k\rangle$  and  $\omega_k$ are the weights of the corresponding eigenstates<sup>58</sup>. We



FIG. 5. (Color online) Spin gaps (see text) in eV versus the inverse of the number of unit cells for (a) 3-ZGNR (b) 6-AGNR and (c) 5-AGNR within the PPP model. Insets:  $(\Delta_2 - \Delta_1)$  [black solid triangle up] and  $(\Delta_3 - \Delta_2)$  [red solid triangle down], also versus the inverse of the number of unit cells.

have taken  $\omega_k = 1/N_k$ , where  $N_k$  is the number of lowlying eigenstates computed in the symmetry subspace. In what follows we define all energy gaps with respect to the ground state energy (thus the lowest one and two-photon gaps are the energy differences between the corresponding eigenstates and the ground state).

In order to arrive at the desired cut-off in block states  $M_l$  for our calculations, we have calculated lowest twophoton gaps and lowest optical gaps with different cutoffs for small systems of 3-ZGNR, 6-AGNR and 5-AGNR (**Fig. 3**). We note that  $M_l \simeq 750$  is adequate for comparisons with experiments in all three GNRs.

#### III. RESULTS AND DISCUSSION

We have used the unsymmetrized DMRG technique to calculate the ground state energies of these nanoribbons within the PPP model (**Fig. 4**). The excellent linear fit of the energies as a function of system size shows that the procedure is stable and accurate.

#### A. Spin gaps

As mentioned above, it is difficult to exploit total S invariance in the DMRG scheme. We have therefore computed the lowest energy states in the different  $S_z$  sectors; the total S are determined from the calculated energy gaps  $\Delta_k = E_0(S_z = k) - E_0(S_z = 0)$ , where  $E_0(S_z = k)$ is the lowest energy in the  $S_z = k$  sector. In the absence of external magnetic field, the different z-components of

TABLE II. Different  $\Delta_k$  values in eV calculated for 3-ZGNR with 5 unit cells, for different number of retained block states. The change in the energy gaps for the different cut-off values are not significant.

Block states cut-off	$\Delta_1$	$\Delta_2$	$\Delta_3$
700	0.290	1.608	4.174
750	0.292	1.610	4.177
800	0.293	1.612	4.180

a given total S are degenerate; thus  $\Delta_1 = 0$  implies that the ground state lies in the total spin S = 1 subspace. This is true for arbitrary  $\Delta_p$ , and hence in general for  $\Delta_1 = \Delta_2 = \cdots = \Delta_p = 0$  and  $\Delta_{p+1} > 0$ , the ground state has spin S = p.

We have shown the dependence of the computed energy gaps  $(\Delta_k)$  on the DMRG cut-off for a moderate-sized 3-ZGNR system in Table. II. We find that keeping ~ 750 block states is sufficient for getting accurate gaps. Among all GNRs in this study, the energy gaps are smallest in 3-ZGNR; hence, we expect the same cut-off to be adequate for AGNRs also.

In Fig. 5(a) we have plotted spin gaps  $\Delta_k$  as a function of the inverse of the number of unit cells (N) for 3-ZGNR. For N < 14, we find  $\Delta_1 > 0$ , indicating that the ground state is a singlet. For  $N \ge 14$ ,  $S_z = 1$  and  $S_z = 0$ states are degenerate (within the DMRG accuracy) which implies that the ground state has S = 1.  $\Delta_2 > 0$  in this region, but becomes smaller as N is further increased. It appears that S=2 will become the spin of the ground state for larger N values. Similarly, the gap between  $S_z =$ 3 and  $S_z = 0$  states also decreases with increasing N. The inset to Fig. 5(a) shows the behavior of  $\Delta_3 - \Delta_2$  and  $\Delta_2 - \Delta_1$ , both of which rapidly approach 0 at large N. From these trends in the the spin gaps, we predict that the ground state of this system is ferromagnetic in the thermodynamic limit.

The spin gaps  $\Delta_k$  for 6-AGNR are shown in **Fig. 5(b)**.  $\Delta_1$  now exhibits weak size dependence and continues to be nonzero even in the thermodynamic limit. The extrapolated  $\Delta_1$  in the thermodynamic limit is 1.43 eV which is actually larger than the non-interacting tight-binding bandgap of 1.19 eV. This implies that the ground state of this system is a singlet. Indeed  $\Delta_1$  is larger than that in polyacene which has a spin gap of ~0.5 eV in the thermodynamic limit<sup>37</sup>. The spin gaps  $\Delta_2$  and  $\Delta_3$  are also large and weakly size-dependent, as are the differences between the spin gaps  $\Delta_2 - \Delta_1$  and  $\Delta_3 - \Delta_2$ , plotted in the inset of **Fig. 5(b)**. In general E(S) > E(S') for S > S'here, where E(S) is the lowest energy in the total spin S subspace, and the corresponding energy differences are large.

For 5-AGNR, the spin gaps between different  $S_z$  sectors and  $S_z = 0$  are shown in Fig. 5(c). The extrapolated ( $\Delta_1$ ) in the thermodynamic limit is 0.15 eV, in-



FIG. 6. A few energy levels near the Fermi level for (a) 3-ZGNR (b) 6-AGNR and (c) 5-AGNR within the tight-binding model are plotted as a function of number of unit cells. The hopping energy considered is 2.40 eV. The symbol index is same for all the three panels and are as follows: HOMO energy level (solid circle); HOMO-1 energy level (solid square); HOMO-2 energy level (solid triangle up); LUMO energy level (open circle); LUMO+1 energy level (open square) and LUMO+2 energy level (open triangle up).

dicating that the ground state is spin singlet. From the N-dependent behavior of  $\Delta_2$  and  $\Delta_3$  (see in particular the inset) it is conceivable that the energy spectrum above  $\Delta_1$  may be gapless.

It is instructive to see what is to be expected for the spin gaps in the non-interacting limit. The energy levels of the frontier molecular orbitals of the three GNRs are shown in Fig. 6. We see that in 3-ZGNR, the energy gap between frontier orbitals approach zero rapidly implying that switching on exchange interaction will lead to a high spin ground state. In 6-AGNR, the gap between bonding and antibonding frontier orbitals is finite for all system sizes. Introduction of electron-electron interaction will therefore not change the spin of the ground state and the ground state will always be a singlet. In 5-AGNR, the gap between the bonding and antibonding frontier orbitals progressively decreases but remain finite for large system sizes. The small band gap implies a small spin gap in the interacting picture.

In summary, the effects of electron-electron interactions on the three GNRs we have studied are very different and could not have been anticipated from their tightbinding electronic structures. The ferromagnetic ground state in 3-ZGNR is different from the edge-state ferromagnetism found earlier in wider ZGNRs<sup>15,42,49</sup>. More interestingly, while within tight-binding theory 5-ZGNR is metallic and is hence expected to be without a spin gap, we find a small but nonzero spin gap here, although the spectrum of spin excitations above the lowest gap may be gapless. As we show in section III(C), this system



FIG. 7. (Color online) Lowest optical and two-photon gaps in 3-ZGNR versus the inverse of number of unit cells. As the ground state spin value changes on increasing the number of monomer units, lowest optical gaps and lowest two-photon gaps in both S = 0 and S = 1 sectors are plotted. Symbols represent the following: lowest optical gap in singlet space ( $\Delta$ ); lowest two-photon gap in singlet space ( $\Box$ ); lowest optical gap in triplet space ( $\blacktriangle$ ); lowest two-photon gap in triplet space ( $\blacksquare$ ). Inset: Magnified plot of the lowest optical gaps and its extrapolation in 3-ZGNR systems, 11-16 monomer units.

also has a nonzero exciton binding energy for nonzero electron-electron interactions. In 6-AGNR, which is a band semiconductor, both charge and spin gaps are expected within the tight-binding model. Our calculated results indicate that electron-electron interactions further enhance the spin gap here. We discuss these effects further in section section III(B).

## B. Excited state ordering of one- versus two-photon states

As already mentioned in section II(C), the occurrence of the lowest two-photon states below the lowest optical one-photon states in linear polyenes<sup>64,65</sup> was the strongest evidence for higher order Coulomb interaction effects beyond 1e-1h interactions. It is therefore of interest to determine the excited state ordering in these narrow GNRs we are probing; this is particularly so because should the present systems become available experimentally, the corresponding two-photon states can be reached by a variety of nonlinear spectroscopic techniques, and our theoretical predictions tested.

We have obtained the low-lying one- and two-photon excited states for all three GNRs within the PPP model. We have done calculations starting from 2 units up to a maximum of 16 units of 3-ZGNR, from 2 units up to a maximum of 8 units of 6-AGNR and from 1 unit up to 9 units of 5-AGNR, which correspond to about 100 carbon atoms in the largest systems studied. For extrapolation of different energy gaps in all three nanoribbons, we have



FIG. 8. (Color online) Lowest one-photon (optical) ( $\Delta$ ) and two-photon ( $\Box$ ) gaps in (a) 6-AGNR and (b) 5-AGNR, versus the inverse of the number of unit cells. The ground state remains in both the cases in S = 0 space. The extrapolated one-photon and two-photon gaps are also indicated in the figures.

considered the largest system sizes, specifically, from N = 10 to N = 16 for 3-ZGNR, from N = 5 to N = 8 in 6-AGNR and from N = 4 to N = 9 in 5-AGNR (N is number of unit cells).

In 3-ZGNR, the lowest two-photon state occurs above the lowest optical state for system sizes up to three units, but this energy ordering is reversed in larger systems (**Fig.** 7) Similar size-dependence has also been observed in linear polyenes and is expected from theoretical considerations<sup>29</sup>. As pointed out above, the ground state of 3-ZGNR changes beyond a certain size. We have therefore plotted in Fig. 7 the lowest optical and twophoton gaps for both S = 0 and S = 1 ground states. In Fig. 7 inset, the data points are shown on an expanded scale and appear to be scattered. However, the calculated standard deviation<sup>66</sup> for the linear fit is small  $(0.036 \ eV)$ . The extrapolated value of the optical gap in thermodynamic limit is found to be 2.25 eV, irrespective of the ground state spin, which is in contradiction to the prediction of a metallic state for this nanoribbon within one-electron theory (see also section I). Note that for system sizes where the ground state is a triplet, the singlet optical gap increases with system size. This is an artifact that is irrelevant for the real system with a magnetic ground state. As shown in the figure as well as in the inset, the triplet and singlet optical gaps lie on the same continuous curve if the data from the artificially large singlet gaps are ignored. However, the two-photon gaps in both singlet and triplet spaces extrapolate to zero in the thermodynamic limit. In linear polyenes, the lowest twophoton state is known to be a quantum-entangled state of two triplets with overall spin angular momentum of zero. The zero gap two-photon state in the present case is to be anticipated, should the same theoretical description as a triplet-triplet state persist here.



FIG. 9. Extrapolation of the charge gaps against the inverse of the number of unit cells, for (a) 3-ZGNR, (b) 6-AGNR and (c) 5-AGNR, respectively.

In 6-AGNR, the lowest optical state always remains below the lowest two-photon state for all system sizes. The extrapolated one- and two-photon gaps at the thermodynamic limit are quite distinct (Fig 8a). The extrapolated value of the optical gap is 2.45 eV while that of the two-photon gap is 2.72 eV. The standard deviations of the linear fits of the optical gaps and the two-photon gaps are 0.032 eV and 0.026 eV respectively. The larger twophoton gap here is a reflection of the predominantly band semiconductor character of 6-AGNR, therefore the oneelectron contribution to the optical gap must be larger than the many-electron contribution. The relative energy locations of the optical and two-photon states in 6-AGNR suggest that these systems will be fluorescent. In the case of 5-AGNR, on the other hand, the optical state always remains above the lowest two-photon state, although the lowest two-photon gap does not vanish in the thermodynamic limit (**Fig 8b**) but saturates at a value of 0.60 eV. The optical gap in 5-AGNR extrapolates to 1.33 eV at the thermodynamic limit. Optical gap larger than the two-photon gap in 5-AGNR is a consequence of the former being dominated by Coulomb as opposed to band contribution.

#### C. Charge gap

We have calculated the charge gaps in these nanoribbons to explore the conducting nature in the thermodynamic limit, in the presence of long-range interactions (**Fig. 9**). The charge gap of a system with N unit cells,  $\Delta_c(N)$  is defined as the energy required to create a well separated electron-hole pair from the ground state of the system:  $\Delta_c(N) = E^+(N) + E^-(N) - 2E^0(N)$ , where  $E^+(N)$  and  $E^-(N)$  are the ground state energies of the cation and anion respectively and  $E^0(N)$  is the ground state energy of the neutral system. In the thermodynamic limit, the charge gaps of 3-ZGNR, 6-AGNR and 5-AGNR extrapolate to 3.09 eV, 3.58 eV and 2.46 eV



FIG. 10. Bond indices for the interior bonds of (a) 3-ZGNR, (b) 6-AGNR and (c) 5-AGNR.

respectively. Interestingly, the exciton binding energy  $(E_{xb})$  of the optical state  $(E_{1ph})$  which is measured as  $E_{xb} = E_{cg} - E_{1ph}$  is quite small in all the three GNRs compared to other known organic conjugated systems. The exciton binding energies are 0.84 eV in 3-ZGNR, 1.13 eV in 6-AGNR and 1.13 eV in 5-AGNR. Hence, these conjugated systems can have importance in molecular photovoltaics as the electron-hole pair can be relatively easily disassociated.

#### D. Bond order

We have calculated bond orders for the ground state and a few low-lying excited states of the largest systems we studied. The bond order  $(p_{ij})$  for the  $\langle i, j \rangle$  bond in a given state  $|R\rangle$  is defined as  $(-\frac{1}{2})\sum_{\sigma}\langle R|(a_{i\sigma}^{\dagger}a_{j\sigma}+$ h.c.  $|R\rangle$ , and their deviation from an average value shows the tendency for the bond to distort. If the bond order is more (less) than the average, we expect the bond to shorten (lengthen) at equilibrium geometry. The numbering of bonds in the interior units of 3-ZGNR, 6-AGNR and 5-AGNR are shown in Fig. 10. The bond orders towards the ends of the ribbons are normally different from the bond orders in the interior because of edge effects. In Table III, the bond orders of the interior unit of 3-ZGNR are given. In 3-ZGNR series, we have given bond orders for two different system sizes; one with 13 monomer units, which has a singlet ground state and another one with 16 monomer units with triplet ground state. In both systems, the bond order difference between edge bonds in the ground state are small, implying almost uniform geometry of the edges. The rung bond orders are slightly smaller than the edge bonds, implying longer rung bonds than edge bonds at equilibrium geometry. The ground state, optical state and the lowest spin state all have similar geometries. The bond orders in the singlet and triplet two-photon states are similar away from middle of the ribbon. However, in the middle of the ribbon, the triplet two-photon state has marked single and double bond character in the top and bottom edge bonds (bonds 1, 2, 10, 11).

The bond orders in 6-AGNR systems show somewhat different behavior. In the ground state, bonds on the ring and on the exterior of the edge (bond 13) show tendency

				0							
State	1	2	3	4	5	6	7	8	9	10	11
Ground state	0.54	0.56	0.47	0.47	0.52	0.52	0.52	0.47	0.47	0.56	0.54
	0.56	0.54	0.47	0.47	0.52	0.53	0.52	0.47	0.47	0.54	0.56
Optical state	0.54	0.57	0.46	0.46	0.54	0.50	0.54	0.46	0.46	0.57	0.54
	0.56	0.54	0.46	0.46	0.51	0.54	0.51	0.46	0.46	0.54	0.56
Two-photon state	0.52	0.58	0.48	0.47	0.50	0.54	0.50	0.47	0.48	0.58	0.52
	0.54	0.56	0.47	0.47	0.51	0.52	0.51	0.47	0.47	0.56	0.55
Spin state	0.56	0.53	0.47	0.47	0.52	0.53	0.52	0.47	0.47	0.53	0.57
	0.54	0.55	0.47	0.47	0.53	0.52	0.53	0.47	0.47	0.55	0.54

TABLE III. Bond orders of an interior unit of 3-ZGNR. Bond orders in systems with  $\leq 13$  monomer units are given in the first row while that for systems with > 13 monomer units are given in the second row.

TABLE IV. Bond orders of an interior unit of 6-AGNR.

State	1	2	3	4	5	6	7	8	9	10	11	12	13
Ground state	0.58	0.59	0.37	0.57	0.56	0.44	0.45	0.51	0.57	0.56	0.58	0.58	0.66
Optical state	0.49	0.50	0.48	0.53	0.50	0.48	0.50	0.51	0.53	0.50	0.49	0.50	0.72
Two-photon state	0.57	0.57	0.38	0.54	0.54	0.47	0.47	0.50	0.55	0.54	0.56	0.58	0.65
Triplet state	0.48	0.48	0.50	0.52	0.48	0.48	0.51	0.51	0.52	0.48	0.47	0.48	0.73

TABLE V. Bond orders of an interior unit of 5-AGNR.

State	1	2	3	4	5	6	7	8	9	10	11	12	13
Ground state	0.60	0.39	0.60	0.63	0.51	0.51	0.52	0.51	0.51	0.61	0.39	0.60	0.63
Optical state	0.57	0.42	0.57	0.67	0.51	0.51	0.51	0.51	0.52	0.57	0.42	0.57	0.67
Two-photon state	0.50	0.48	0.51	0.72	0.52	0.52	0.49	0.52	0.52	0.51	0.48	0.50	0.71
Triplet state	0.52	0.47	0.51	0.72	0.52	0.52	0.50	0.52	0.52	0.52	0.47	0.51	0.72

to contract, while bond 3 on the edge which is on the interior shows a tendency to expand. There appears to be a period (short-short-short-long) on one edge and out of phase by two bonds on the opposite edge. In the twophoton state, the bond orders remain almost the same as those in the ground state. In the one-photon state, there is considerable deviation in the bond orders in the central region of the nanoribbon, but the effect decreases towards the ends. However in the triplet state it appears that this distortion is much more pronounced. Thus, the equilibrium geometries of the excited states are quite different from that in the ground state and we may expect larger Stokes shifts in the spectra of 6-AGNR compared to 3-ZGNR.

The bond orders on the edges of 5-AGNR are similar to those in the 6-AGNR. Except for the bonds which have rather large and small bond order values, all other bonds have nearly equal bond orders. So the distortion is expected more on the edges than in the interior. In all excited states, the interior bonds remain almost unperturbed. The edge bond structure in the central region of the nanoribbon shifts from short-long-short-short modulation to long-long-long-short modulation, while being unchanged towards the ends of the nanoribbon. The extent of distortion in the central region is highest in the two-photon and triplet states as compared to one-photon state.

#### IV. CONCLUSION

We have studied correlated electronic properties of 3-ZGNR, 6-AGNR and 5-AGNR within the PPP Hamiltonian with long range Coulomb interactions. In all three cases the ground state, as well as excited state behavior are qualitatively different from the predictions of tightbinding theory, as summarized below.

We find 3-ZGNR to be a magnetic semiconductor with a Mott-Hubbard optical gap and a substantive exciton binding energy. The lowest two-photon state is gapless. The semiconducting behavior of 3-ZGNR is not entirely unanticipated, as similar Mott-Hubbard semiconducting behavior was previously predicted from correlated-electron calculations<sup>67,68</sup> and also experimentally demonstrated<sup>69</sup> in narrow single-walled carbon nanotubes which would be metallic within one-electron theory. As with 3-ZGNR, 5-AGNR is expected to exhibit metallic behavior within tight-binding theory, but is also found to be a Mott-Hubbard semiconductor here, with now however a singlet ground state with small spin gap. The two-photon

state is again below the optical gap. 5-AGNR thus resembles an idealized trans-polyacetylene strand, where bonddimerization leads to a spin gap, and where the occurrence of the two-photon state below the one-photon optical gap is believed to be a signature of greater Mott-Hubbard contribution to the optical gap than the contribution due to the Peierls bond-dimerization<sup>35</sup>. In 6-AGNR, the one-electron optical gap is enhanced by Coulomb interactions, there occurs a large spin gap and the two-photon state occurs above the optical gap. The overall behavior is reminiscent now of the conjugated polymers polyparaphenylene and poly-paraphenylenevinylene, where the optical gap is dominated by the one-electron gap expected in systems with unit cells containing an even number of carbon  $atoms^{33}$ . The three GNRs we have studied thus span the full range of behavior expected in quasi-one dimensional correlated-electron systems. Conversely, the apparent similarities between these narrow GNRs and conjugated polymers reflect the deep and fun-

- <sup>1</sup> R. Saito, G. Dresselhaus, and M. S. Dresselhaus, eds., *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
- <sup>2</sup> M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, and H. A. Goldberg, eds., *Graphite Fibers and Filaments* (Springer-Verlag, Berlin, 1988).
- <sup>3</sup> A. K. Geim and K. S. Novoselov, Nature Materials 6, 183 (2007).
- <sup>4</sup> A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. 81, 109 (2009).
- <sup>5</sup> M. J. Allena, V. C. Tung, and R. B. Kaner, Chem. Rev. **110**, 132 (2010).
- <sup>6</sup> S. Das Sarma, S. Adam, E. H. Hwang, and E. Rossi, Rev. Mod. Phys. 83, 407 (2011).
- <sup>7</sup> F. Schwierz, Nature Nanotechnology **5**, 487 (2010).
- <sup>8</sup> J. E. Morris and K. Iniewski, eds., Graphene, Carbon Nanotubes, and Nanostructures: Techniques and Applications (CRC Press, Florida, 2013).
- <sup>9</sup> C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science **312**, 1191 (2006).
- <sup>10</sup> Z. Chen, Y.-M. Lin, M. J. Rooks, and P. Avouris, Physica E 40, 228 (2007).
- <sup>11</sup> M. Y. Han, B. Özyilmaz, Y. Zhang, and P. Kim, Phys. Rev. Lett. **98**, 206805 (2007).
- <sup>12</sup> L. Tapasztó, G. Dobrik, P. Lambin, and L. P. Biró, Nature Nanotechnology 3, 397 (2008).
- <sup>13</sup> S. S. Datta, D. R. Strachan, S. M. Khamis, and A. T. C. Johnson, Nano Lett. 8, 1912 (2008).
- <sup>14</sup> X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, Science **319**, 1229 (2008).
- <sup>15</sup> M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. **65**, 1920 (1996).
- <sup>16</sup> K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B 54, 17954 (1996).
- <sup>17</sup> M. Ezawa, Phys. Rev. B **73**, 045432 (2006).
- <sup>18</sup> K. Wakabayashi and S. Dutta, Solid State Commun. **152**, 1420 (2012).

damental universality that exists among low-dimensional correlated-electron systems. Experimental tests of our theoretical predictions will provide fresh insight on the role of electron-electron interactions in carbon nanostructures. It is also of interest to determine how these features evolve upon controlled increase in the widths of GNRs. This is a topic of future research.

#### ACKNOWLEDGMENTS

We acknowledge Indo-US Science and Technology Forum for financial assistance through a Joint Center, that made this collaboration possible. SR thanks DST for providing additional financial assistance. SM acknowledges partial support from National Science Foundation grant DMR-1151475 and the UA-REN Faculty Exploratory Research Grant. SP acknowledges CSIR India for senior research fellowship.

- <sup>19</sup> L. Brey and H. A. Fertig, Phys. Rev. B **73**, 235411 (2006).
- <sup>20</sup> A. G. Marinopoulos, L. Reining, A. Rubio, and N. Vast, Phys. Rev. Lett. **91**, 046402 (2003); A. G. Marinopoulos, L. Wirtz, A. Marini, V. Olevano, A. Rubio, and L. Reining, Appl. Phys. A **78**, 1157 (2004).
- <sup>21</sup> H. Tachikawa, Y. Nagoya, and H. Kawabata, J. Chem. Theory Comput. 5, 21012107 (2009).
- <sup>22</sup> B. F. Habenicht and O. V. Prezhdo, J. Phys. Chem. C 113, 14067 (2009).
- <sup>23</sup> C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004).
- <sup>24</sup> R. B. Capaz, C. D. Spataru, P. Tangney, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **94**, 036801 (2005).
- <sup>25</sup> L. Yang, C.-H. Park, Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **99**, 186801 (2007).
- <sup>26</sup> H. Zhao and S. Mazumdar, Phys. Rev. Lett. **93**, 157402 (2004).
- <sup>27</sup> Z. Wang, H. Zhao, and S. Mazumdar, Phys. Rev. B 74, 195406 (2006).
- <sup>28</sup> Z. Wang, H. Zhao, and S. Mazumdar, Phys. Rev. B 76, 115431 (2007).
- <sup>29</sup> B. S. Hudson, B. E. Kohler, and K. Schulten, *Excited States*, edited by E. C. Lim, Vol. 6 (Academic Press, New York, 1982) p. 1.
- <sup>30</sup> K. Aryanpour, A. Roberts, A. Sandhu, R. Rathore, A. Shukla, and S. Mazumdar, J. Phys. Chem. C **118**, 3331 (2014).
- <sup>31</sup> R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466 (1953);
   J. A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
- <sup>32</sup> P. Tavan and K. Schulten, J. Chem. Phys. **70**, 5407 (1979);
   **70**, 5414 (1979); **85**, 6602 (1986); Phys. Rev. B **36**, 4337 (1987).
- <sup>33</sup> Z. G. Soos, S. Ramasesha, and D. S. Galvao, Phys. Rev. Lett. **71**, 1609 (1993).
- <sup>34</sup> Z. G. Soos and S. Ramasesha, Phys. Rev. B **29**, 5410 (1984).
- <sup>35</sup> D. Baeriswyl, D. K. Campbell, and S. Mazumdar, *Conjugated Conducting Polymers*, edited by H. Kiess, Springer Series in Solid-State Sciences, Vol. 102 (Springer, Berlin, 1997).

1992).

- <sup>36</sup> C. Raghu, Y. Anusooya Pati, and S. Ramasesha, Phys. Rev. B **65**, 155204 (2002); M. Kumar and S. Ramasesha, **81**, 035115 (2010); S. Thomas, Y. A. Pati, and S. Ramasesha, J. Phys. Chem. A **117**, 78047809 (2013); S. Mukhopadhyay and S. Ramasesha, J. Chem. Phys. **131**, 074111 (2009).
- <sup>37</sup> C. Raghu, Y. Anusooya Pati, and S. Ramasesha, Phys. Rev. B 66, 035116 (2002).
- <sup>38</sup> K. Sasaki, S. Murakami, and R. Saito, J. Phys. Soc. Jpn 75, 074713 (2006).
- <sup>39</sup> A. H. Castro Neto, F. Guinea, and N. M. R. Peres, Phys. Rev. B **73**, 205408 (2006).
- <sup>40</sup> D. A. Abanin, P. A. Lee, and L. S. Levitov, Phys. Rev. Lett. **96**, 176803 (2006).
- <sup>41</sup> K. Wakabayashi, M. Fujita, H. Ajiki, and M. Sigrist, Phys. Rev. B 59, 8271 (1999).
- <sup>42</sup> Y.-W. Son, M. L. Cohen, and S. G. Louie, Nature 444, 347 (2006).
- <sup>43</sup> J. Jung and A. H. MacDonald, Phys. Rev. B **79**, 235433 (2009).
- <sup>44</sup> M. Golor, T. C. Lang, and S. Wessel, Phys. Rev. B 87, 155441 (2013).
- <sup>45</sup> T. Hikihara, X. Hu, H.-H. Lin, and C.-Y. Mou, Phys. Rev. B 68, 035432 (2003).
- <sup>46</sup> G. Z. Magda, X. Jin, I. Hagymási, P. Vancsó, Z. Osváth, P. Nemes-Incze, C. Hwang, L. P. Biró, and L. Tapasztó, Nature **514**, 608 (2014).
- <sup>47</sup> S. Okada and A. Oshiyama, Phys. Rev. Lett. **87**, 146803 (2001); S. Dutta and S. K. Pati, J. Phys. Chem. B **112**, 1333 (2008).
- <sup>48</sup> S. Dutta, S. Lakshmi, and S. K. Pati, Phys. Rev. B 77, 073412 (2008).
- <sup>49</sup> Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006).
- <sup>50</sup> M. Das, J. Chem. Phys. **140**, 124317 (2014).
- <sup>51</sup> K. Ohno, Theor. Chim. Acta 2, 219 (1964); G. Klopman, J. Am. Chem. Soc. 86, 4550 (1964).
- <sup>52</sup> A. Race, W. Barford, and R. J. Bursill, Phys. Rev. B 64,

035208 (2001); 67, 245202 (2003).

- <sup>53</sup> L. Salem, The Molecular Orbital Theory of Conjugated Systems (W. A. Benjamin, Inc., Massachusetts, 1966) p. 420.
- <sup>54</sup> U. Schollwöck, Rev. Mod. Phys. **77**, 259 (2005).
- <sup>55</sup> K. A. Hallberg, Adv. Phys. **55**, 477 (2006).
- <sup>56</sup> S. Sahoo, V. M. L. D. P. Goli, S. Ramasesha, and D. Sen, J. Phys.:Condens. Matter **24**, 115601 (2012).
- <sup>57</sup> See Supplemental Material for the method of constructing the AGNRs in the infinite DMRG procedure as well as the block building scheme of finite sweeps for 6-AGNR and 5-AGNR.
- <sup>58</sup> S. R. White, Phys. Rev. Lett. **69**, 2863 (1992); Phys. Rev. B **48**, 10345 (1993).
- <sup>59</sup> S. Ramasesha, S. K. Pati, Z. Shuai, and J. L. Brédas, Adv. Quantum Chem. **38**, 121 (2000).
- <sup>60</sup> R. Pariser, J. Chem. Phys. **24**, 250 (1956).
- <sup>61</sup> J. Cizek, J. Paldus, and I. Hubac, Int. J. Quantum Chem. 8, 951 (1974).
- <sup>62</sup> S. Ramasesha, S. K. Pati, H. R. Krishnamurthy, Z. Shuai, and J. L. Brédas, Phys. Rev. B **54**, 7598 (1996).
- <sup>63</sup> S. Prodhan, S. Mazumdar, and S. Ramasesha, "Efficient symmetrized dmrg algorithm for low-lying excited states of conjugated carbon systems: Application to coronene, ovalene and 1,12-benzoperylene," arXiv:1601.00053 [chemph].
- <sup>64</sup> B. S. Hudson and B. E. Kohler, Chem. Phys. Lett. **14**, 299 (1972).
- <sup>65</sup> K. Schulten and M. Karplus, Chem. Phys. Lett. **14**, 305 (1972).
- <sup>66</sup> S. C. Chapra and R. P. Canale, Numerical Methods for Engineers, 6th ed. (McGraw Hill Education (India) Private Limited, New Delhi, 2012) chapter 17.
- <sup>67</sup> Y. A. Krotov, D.-H. Lee, and S. G. Louie, Phys. Rev. Lett. 78, 4245 (1997).
- <sup>68</sup> L. Balents and M. P. A. Fisher, Phys. Rev. B **55**, R11973 (1997).
- <sup>69</sup> V. V. Deshpande, B. Chandra, R. Caldwell, D. S. Novikov, J. Hone, and M. Bockrath, Science **323**, 106 (2009).