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# Bandgaps of atomically precise graphene nanoribbons and Occam's razor†

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Rationalization of the “bulk” ( $\Delta E_{ac}$ ) or “zigzag-end” ( $\Delta E_{zz}$ ) energy gaps of atomically precise armchair graphene nanoribbons (AGNRs), which are directly related to fundamental applications in nanoelectronics, could be challenging and largely controversial with respect to their magnitude, origin, substrate influence ( $\Delta E_{sb}$ ), and spin-polarization, among others. Hereby a simple self-consistent and “economical” interpretation is presented, in full accordance with Occam's simplicity principle, which is highly successful (within less than 1%) in predicting all energy gaps of the 5-, 7-, and 9-AGNRs, in contrast to other complicated and/or contradicting prevailing views in the literature for  $\Delta E_{ac}$ ,  $\Delta E_{zz}$ , and  $\Delta E_{sb}$ . The present approach is based on “appropriate” DFT (TDDFT) calculations, general symmetry principles, and plausibility arguments. The excellent agreement with experiments and the new insight gained is achieved by invoking the approximate equivalence of Coulomb correlation energy with the staggered sublattice potential. Breaking established stereotypes, we suggest that the measured STS gaps are virtually independent of the substrate, essentially equal to their free-standing values, and that the “true” lowest energy state is a closed singlet with no conventional magnetism. The primary source of discrepancies is the finite length of AGNRs together with inversion/reflection symmetry conflict and the resulting topological end/edge states. Such states invariably mix with other “bulk” states making their unambiguous detection/distinction difficult. This can be further tested by eliminating end-states (and  $\Delta E_{zz}$ ), by eliminating “empty” zigzag rings.

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## 1. Introduction

Edge or end states in graphene nanoribbons (GNRs), and in particular armchair GNRs (AGNRs), have attracted much interest recently,<sup>1–8</sup> due to their anticipated magnetic properties,<sup>9,10</sup> although their presence in finite nanographenes (NGRs) was predicted a long time ago.<sup>11</sup> However, the significance and importance of end states for AGNRs was recognized only recently,<sup>1–8</sup> after the pioneering bottom-up synthesis of atomically precise AGNRs of finite lengths  $L$  with short zigzag ends, and their characterization by scanning tunnelling microscopy (STM) and spectroscopy (STS).<sup>3–16</sup> Clearly no end states appear in the common infinite AGNRs fabricated *via* the usual top-bottom techniques, which are theoretically described by periodic boundary conditions at their two ends.<sup>1</sup> The new developments have brought to the forefront new concepts and properties such as the “bulk band gaps”  $\Delta E_{ac}$  (or  $\Delta_{ac}$ )<sup>1,6</sup> *i.e.*, the energy gaps between delocalized states, and the energy separation of the zigzag-end-localized “end-states”, denoted here by ( $\Delta E_{zz}$ ) (or  $\Delta_{zz}$ )<sup>6–8</sup>, thus

increasing both the quantity and quality of the key properties to be rationalized, understood, or interrelated at the atomic scale. At the same time, despite the increased complexity, such advances have also allowed the study of the  $L$ -dependence of key-quantities such as the bandgaps<sup>4–7</sup> (both,  $\Delta E_{ac}$  and  $\Delta E_{zz}$ ), conductivity, aromaticity,<sup>1,3,4</sup> and even Raman spectra.<sup>17</sup> The  $L$ -dependence studies<sup>4,5</sup> revealed that the changes in such properties *versus* length are not always gradual (or smooth). The presence of a metal-insulator-like phase transition at a critical length  $L_c$  was advocated by two different recent studies, Lawrence *et al.*<sup>8</sup> and Zdetsis *et al.*,<sup>4</sup> almost simultaneously. However, these two studies have offered different assessments and interpretations on the nature of the transition and magnetism, as well as the value of  $L_c$ .<sup>4,8</sup> This is not something new or unusual in a rapidly grown pioneering field like this,<sup>1</sup> and this is not the only existing “discrepancy”. Other conflicting (or conflicting-looking) results (experimental and theoretical) include the magnitude and nature of the bandgaps,<sup>1,6,7,12,13</sup> the existence and nature of magnetism in the edge states,<sup>1,3–7</sup> and the magnitude of the substrate's influence on these properties.<sup>1,5–7</sup> For example, the magnitude of the bandgap for the 5-AGNRs has been measured by (at least) three different groups<sup>8,12,13</sup> to be 0.85 eV,<sup>8</sup> 2.8 eV,<sup>12</sup> and 0.1 eV<sup>13</sup> respectively, while the theoretical values vary from 0.1 eV<sup>1</sup> to 1.7 eV.<sup>14</sup> For the 7-AGNRs the measured values of  $\Delta E_{zz}$  vary

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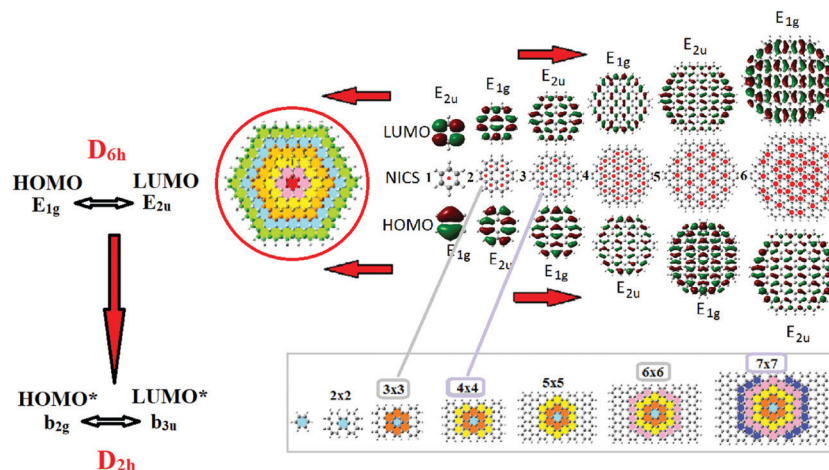


Fig. 2 The shell model and the “main sequence of PAHs (shown up to  $n = 6$ ), illustrating the aromaticity patterns (with red dots at the centers of the aromatic or “full” rings), and the structure and symmetry of the HOMO and LUMO orbitals (top). The bottom part illustrates the analogy with corresponding rectangular NGRs or AGNRs with an equal number of armchair and zigzag rings (see the text).

“spin” densities ( $b$ ). Such spin densities, in Fig. 1(b–d), which are generated self consistently (through the DFT convergence process) are in fact pseudospin densities. The open singlet reflects the sublattice symmetry (with different types of atoms at the two ends) with an equal number of up and down (pseudo) spins, or A and B sublattice points. This results in a balanced (nearly zero spin distribution in the middle). The triplet state on the other hand has also a region of zero spin in the middle, exactly where the sublattice imbalance occurs. In contrast to the band description (in  $k$ -space), in the real-space (“molecular”) calculations the sublattice degree of freedom does not enter in the spatial Hamiltonian and can only be introduced as (pseudo)spin. Then, due to the better account of Coulomb interaction, open shell states (triplet or singlet) appear energetically lower than the closed singlet state. This is because the additional degree of freedom of “pseudospin”, introduced to take care of the sublattice topology (and the staggered potential), facilitates the optimization of Coulomb interaction by keeping away each of the other electrons of different spin (for which Pauli repulsion is not operative), but of identical pseudospins. Moreover, as was illustrated in Section 2.1 (and Fig. 2), based on the shell model,<sup>2,3</sup> the unoccupied states of the “previous” (shell number smaller by 1) PAH are the occupied ones of the current PAH. In AGNRs this is responsible for the interplay between odd and even parity HOMOs as the width of AGNRs is growing ( $3n$  AGNRs have an odd HOMO and even LUMO, whereas  $3n + 1$  AGNRs are characterized by an even HOMO and odd LUMO).<sup>2,3</sup> This is also responsible for the well-known  $3n$ ,  $3n \pm 1$  width rule for AGNRs.<sup>3</sup> Note that the (pseudo)spin densities invariably reflect the sublattice (pseudospin) structure within the frustrated molecular ( $D_{2h}$ ) symmetry<sup>3</sup> in the first case, or the sublattice symmetry ( $C_{2v}$ ) in the latter, where opposite end sites have opposite spins. It should be emphasized at this point that for wider AGNRs (where  $n > 1$  in the above rule for width<sup>3</sup>), higher spin states are required<sup>3</sup> to lower the total energy (within the molecular  $D_{2h}$  symmetry group). Such larger (pseudo)spin-polarized states optimize better the

sublattice distribution (within the  $D_{2h}$  molecular group),<sup>3</sup> whereas the open-shell singlets lie higher in energy and revert to the closed singlet state. This illustrates emphatically that the open-singlet state is not the true ground (lowest energy) state of AGNRs (and, consequently, no conventional magnetism is truly present). Nevertheless, the open singlet state is still a very useful and efficient concept for the description of end-states. It should be emphasized that in both cases of Fig. 1, when correlation is introduced even at the MP2 level, the energetical ordering is reversed and the lowest energy structure is a closed singlet.<sup>4</sup> In addition, the MP2 correlated “spin” density of the triplet, as we can see in Fig. 1(c), is rather correcting the HF failure (having the opposite sign) than reflecting the full sublattice structure. Note also in Fig. 1(c and d) that the triplet state is slightly lower than the open singlet, and that the energy difference of the open shell singlet and triplet states (which are practically isoenergetic) from the closed singlet is about 0.95 eV. This should be a good estimate of the “missing” Coulomb energy in this case and based on the (approximate) electron–hole symmetry, the expected (HOMO–LUMO) separation of the open singlet (or the triplet) should be about twice as large ( $\sim 2$  eV). Indeed, the calculated open-singlet HOMO–LUMO gap for the 9-AGNRs (or  $4x$ ) is 2.2 eV, and so is  $\Delta E_{zz}$  (*vide infra*). Even more important is the fact that the corresponding value for the  $3 \times 6$  or  $(7, 12)$  AGNR is also about 0.93 eV, suggesting an open-singlet gap of about 1.9 which is in excellent agreement with both the measured value<sup>6</sup> of  $\Delta E_{zz}$  (1.90 eV), and the calculated open singlet gap. It is important to observe also that the open-singlet value “ $\Delta E_{zz}$ ” = 1.2 eV for the 5-AGNRs and the 1.9 eV open singlet gap for the 7-AGNRs are practically equal to the correlation improved GW-LDA bandgap differences,<sup>14</sup> which is highly suggestive for the essential correctness of our claim. Thus, within the one-electron approximation we have established the correct basis for discussion and analysis of both  $\Delta E_{zz}$  and  $\Delta E_{ac}$ .  $\Delta E_{zz}$  is identified as the open-singlet HOMO–LUMO gap, whereas  $\Delta E_{ac}$  can be identified as the difference  $|(HOMO-1)-(LUMO+1)|$ , with the understanding that both HOMO and LUMO are end-states. Nevertheless,

















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