Comment on "Imaging the atomic orbitals of carbon atomic chains with field-emission electron microscopy"

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The observation of a stable doublet pattern in the field-emission electron microscopy of a linear atomic chain requires a stable mechanism breaking the axial symmetry, which is not identified correctly by Mikhailovskij *et al.* [Phys. Rev. B **80**, 165404 (2009)]. Using microscopic calculations, we attribute the observed pattern to the symmetry breaking produced by the ligand where the chain is attached, plus carbon π-bonding alternation.

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Very recent field-emission electron microscopy (FEEM) experiments[1] show compelling evidence of emission from individual molecular orbitals (MO) of free-standing carbon atomic chains. The data are consistent with alternatively a single spot or a doublet of spots, which the authors identify as emission from s-type or p-type MO respectively. s/p labeling refers to the angular momentum of these electronic states around the chain axis, usually denoted by σ/π in the quantum-chemistry literature. An electronic wave function of the axially symmetric chain depends on the azimuthal angle φ around the chain axis as $\exp(\pm in\varphi)$, with $n=0$, 1 for s, p states respectively, see Eq. (5) of Ref. 1.

Contrary of the arguments of Ref. 1, $n=1$ does *not* imply the existence of angular nodes. If $\exp(\pm i\varphi)$ was indeed the angular dependency, FEEM would display an axially symmetric (possibly ring-shaped) pattern. Of course, a perturbation could localize the electron in the azimuthal angle, by inducing a splitting between the $\cos(\varphi-\varphi_0)$ and $\sin(\varphi-\varphi_0)$ components of the p state, which do in turn display nodes. However, any sort of fluctuating perturbation, such as those associated to the thermal oscillation of the free-standing chain, would produce a rapidly fluctuating phase φ_0, with the eventual result of an axially symmetric pattern. A stable doublet could arise in FEEM only due to a symmetry-breaking perturbation that *locks the node at a fixed* φ_0. This perturbation needs to be sufficiently large and stable to overcome the tendency of thermal vibrations and quantum kinetic energy to wash out all localization effects.

What can induce such a symmetry-breaking perturbation in a several-atom-long free-standing chain? The answer is: the anchored end of the chain. Whenever this end binds an sp^2 hybridized atom of the carbon tip, the chain acquires a partial cumulenic character.[2] All bonds are double, and the memory of the orientation of the sp^2 termination propagates along the chain through an alternating orientation of π bonds.[3] We illustrate this point by carrying out standard calculations within the density-functional theory in the local-density approximation (DFT-LDA) with a plane-waves package[4,5] using default ultrasoft pseudopotentials, and wave function/charge cutoffs of 15/120 Hartree. We relax the atomic positions until the largest residual force is less than 10^{-4} Hartree/a_0 (8 pN). For a eight-atom chain, Fig. 1(a) shows the highest-occupied molecular orbital (HOMO), made of the four π bonds oriented normally to the sp^2 plane.[8] As a result, emission from the terminal atom is dominated by this asymmetric π orbital, and displays a clear nodal plane which is parallel/antiparallel to the sp^2 plane, depending on the chain being composed by an even/odd number of atoms.

Alternatively, the anchored end, rather than sp^2, could have sp^3 hybridization [e.g., a generic atom in the "bulk" of a graphene fragment or fullerene or nanotube cap, represented by a simple H atom in Fig. 1(b)]. Such a ligand would induce a polyyinic-type electronic structure of the chain. As a result, a highly dimerized configuration, with alternating single/triple bonds and an essentially unbroken axial symmetry is realized. However, even in this case, eventually the HOMO is a π bonding orbital. The main difference is that as the cylindrical symmetry is unbroken, a cylindrically symmetric "doughnut-shaped" orbital is generated, precisely of the type described by Eq. (5) of Ref. 1. Such a state vanishes *along the molecular axis*, as can be seen in Fig. 1(b), but, due to thermal vibrations of the chain, it is unlikely that its FEEM pattern could distinguish it from that of a singlet σ-type orbital.[9] Indeed higher currents in excess of 100 pA can induce switching from one type of FEEM pattern to the other, most likely by exciting a jump of the chain attaching point, not unlike those observed in recent experiments[6,7] under the beam of an electron microscope.

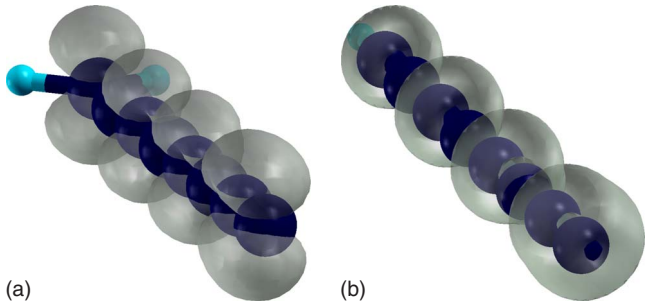

FIG. 1. (Color online) The HOMO (gray transparent level surface surrounds the region where $|\psi_{\mathrm{HOMO}}|^2 > 0.004\ a_0^{-3}$) of a linear chain of carbon atoms (dark balls) attached to (a) two ligands or (b) one ligand (hydrogen, clear balls).

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[8] The remaining three π bonds point horizontally, in the sp^2 plane.
[9] For increasing chain length, the dangling-bond terminal σ orbital remains energetically below the HOMO level, with an increasing separation from the HOMO, in the 100–400 meV range.