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ERRATUM

Erratum to: Conformation-dependent conductance through a molecular break junction

Bartłomiej M. Szyja · Huu Chuong Nguyen · Daniel Kosov · Nikos L. Doltsinis

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Figures 5 and 6 in the original article http://dx.doi.org/10.1007/s00894-013-1794-z were incorrect. Figure 5 did not show the energies of the five highest occupied and the two lowest unoccupied molecular orbitals, as claimed, but rather the orbitals LUMO+2 to LUMO+8, due to an erroneous assignment of the Fermi level. Analogously, Fig. 6 showed LUMO+5 to LUMO+7 instead of HOMO–1 to LUMO. This also slightly affects the discussion of these figures on page 5 (last two paragraphs in column 1 and first paragraph in column 2). However, the main conclusions of the paper remain unchanged. Here we present the corrected Figs. 5 and 6 together with a revised discussion.

Results and discussion

The evolution of a selection of Kohn-Sham orbitals in the vicinity of the Fermi level is shown in Fig. 5. The question is whether it is possible to rationalise the variations in the conductance in terms of orbital energies. We observe that the LUMO energy (red line) slightly decreases, while the HOMO energy (black line) remains roughly constant during the pulling process up to the rupture point D. Consequently, the HOMO–LUMO gap narrows, which should contribute to an increase in conductance, as it is inversely proportional to the HOMO–LUMO gap [1]. This effect should be enhanced by the fact that the LUMO+1 energy decreases and the orbital energies of HOMO–4 to HOMO–1 slightly increase (see Fig. 5). However, the opposite is actually observed; the conductance *decreases*, on the whole, as the wire is stretched (see Fig. 3). Despite this overall trend, there are local peaks in conductance that do coincide with a near degeneracy of the HOMO and LUMO levels.

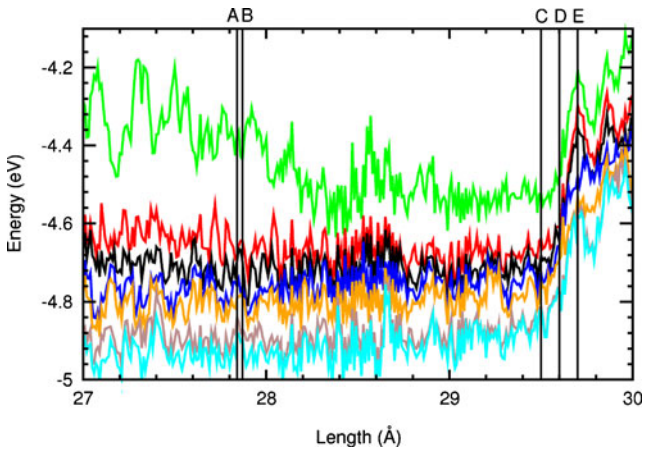

Fig. 5 Kohn-Sham orbital energies for the five highest occupied and two lowest uncoccupied molecular orbitals. The electronic structure at points A–E is analysed in more detail in Fig. 6

The online version of the original article can be found at http://dx.doi.org/10.1007/s00894-013-1794-z.

B. M. Szyja (✉) · H. C. Nguyen · N. L. Doltsinis
Institute for Solid State Theory,
Department of Physics, University of Münster,
Wilhelm-Klemm Str. 10,
48149 Münster, Germany
e-mail: b.szyja@uni-muenster.de

D. Kosov
School of Engineering and Physical Science,
James Cook University, Townsville, Australia

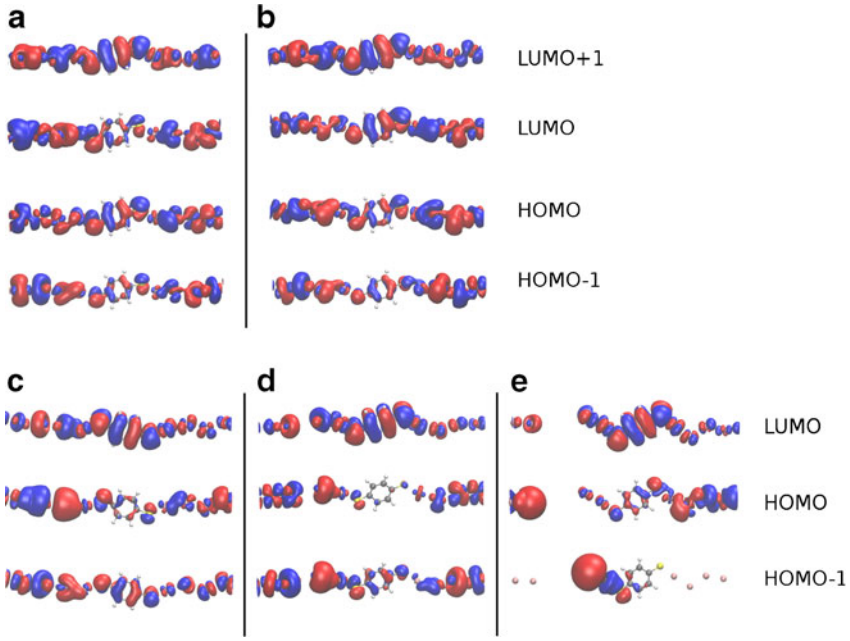

Fig. 6 Isosurface representation of selected Kohn-Sham orbitals at geometries A–E as defined in Fig. 5

The above analysis confirms that orbital energies alone are insufficient to explain variations in the conductance. The other important factor is the shape of the MOs near the Fermi level [1–3]. Figure 6a, b depicts the HOMO–1, HOMO, LUMO, and LUMO+1 for the high conductance geometry A ($z = 27.84$ Å, $G = 1.88\ G_0$) and the neighbouring low conductance geometry B ($z = 27.87$ Å, $G = 0.16\ G_0$). Despite the hugely different conductance values, the differences in the orbital shapes are rather subtle. Most notably, for the HOMO of B the BDT molecule appears to be drained of electron density. In fact, it appears that the HOMO and LUMO levels have crossed over going from A to B.

Figure 6c–e shows the HOMO–1, HOMO, and LUMO orbitals at a point just before (C), during (D), and after (E) bond rupture. Our motivation for analysing the electronic structure at those points was to see whether, for instance, the population of a particular antibonding orbital is responsible for triggering bond dissociation. As is apparent from Fig. 6, the HOMO–1, HOMO, and LUMO are all antibonding along the rupturing bond (between the second and third Au atom from the left). Compared to points A and B, there is significantly less charge density on the gold chain, which might contribute to the dissociation. A visual comparison of the LUMO at point C and the LUMO+1 at B suggests that these two levels have crossed over in between. At point D, the HOMO has hardly any electron density at the BDT molecule, rationalising the corresponding low conductance value.

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