Research team devises better method for mapping orbitals of molecules

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(PhysOrg.com) -- A team of physicists comprised of members from IBM Research in Switzerland and the University of Liverpool in the U.K. have figured out a way to improve on results obtained using a Scanning Tunneling Microscope (STM) that allows for the orbitals of single molecules to be mapped. They have published a paper on *Physical Review Letters* describing their procedure.

Molecular orbitals represent regions in a molecule where an electron is likely to be found; they are derived using mathematical formulas and are represented by cloudlike drawings with multiple nodes that are supposed to represent where electrons can go and are meant to demonstrate how molecules can share those electrons in chemical interactions or bonding.

Since it was first invented in 1981, using the STM has generally been the best method available for creating images of individual atoms and their electronic properties. The STM is basically a piece of equipment with a metal appendage that has a tip width of just a few atoms. The tip is moved back and forth in the air very close to a sample being studied. Voltage is then applied allowing electrons to move between the tip and the sample. Doing so allows for measuring of the density of electrons on the surface of the material being studied which is then used to build the models.

Unfortunately however, traditional STM has not been able to map orbitals of single molecules. This is because the density of electrons on the surface of an object, don't give up the mathematical orbital nor does

it have a fine enough resolution. Also there is the problem of having to place the sample on a metal surface which can hide what is going on with the molecules that comprise the sample.

In the new approach the team solved the easiest part of the problem by coating the surface that the sample lays on with salt. Next, to improve resolution, they stuck a single carbon monoxide molecule on the end of the tip; this because carbon monoxide molecules have the property of having its outermost lobes paired close, with one positive the other negative phased. Such an arrangement makes the tip more sensitive to the sample material placed below it.

Using this method the researchers were able to map the structure of the nodes of the molecular orbitals which allowed them to create images based on the places that held electrons.

More information: High-Resolution Molecular Orbital Imaging Using a p-Wave STM Tip, *Phys. Rev. Lett.* 107, 086101 (2011) DOI:10.1103/PhysRevLett.107.086101

Abstract
Individual pentacene and naphthalocyanine molecules adsorbed on a bilayer of NaCl grown on Cu(111) were investigated by means of scanning tunneling microscopy using CO-functionalized tips. The images of the frontier molecular orbitals show an increased lateral resolution compared with those of the bare tip and reflect the modulus squared of the lateral gradient of the wave functions. The contrast is explained by tunneling through the p-wave orbitals of the CO molecule. Comparison with calculations using a Tersoff-Hamann approach, including s- and p-wave tip states, demonstrates the significant contribution of p-wave tip states.

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