

Visualizing orbitals and bonds

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Seeing is believing! There are many things which we are skeptical about, especially when we cannot experience them with our five senses. Orbitals and bonds are definitely in that category. It was not long ago that the advancement in science which allowed one to see and move atoms earned for its discoverers the Nobel prize in Physics. Now another barrier in visualization has been scaled. One that allows us to virtually see orbitals in atoms where electrons are housed! Zuo *et al.*¹ at the Arizona State University have studied the electron density distribution in cuprite, Cu₂O and unraveled the shape of the d_{z^2} orbital on copper. Excess electron density has been located in the regions away from the O–Cu–O axis, between the tetrahedral arrays of copper ions, making them stick to one another!

Electron density associated with bonds is a small fraction of the total electron density in a molecule. In the case of molecules with only first row elements, the electron density associated with bonds can be distinguished with the help of careful X-ray diffraction studies². However, in transition metal oxides, the difficulty in locating the bonding electrons in the presence of core electrons is like looking for a needle in a haystack. The researchers solved the problem using Convergent-Beam Electron Diffraction³ (CBED) – a new technique they had recently developed. CBED gave low-order diffraction data from a small region in the crystal where there was no imperfections. Diffraction from this region allows one to use 'perfect-crystal theory of dynamical diffraction'. This data was then combined

with X-ray diffraction data to get structure factors for the higher-order reflections. Equipped with this data, they were able to determine the charge density map of the crystal in real space very accurately. A theoretical electron density map was generated assuming a spherical charge density around the Cu⁺ ion and the O²⁻ ion. A difference map between the theoretical and experimental electron densities provided some amazing pictures.

Before we delve into the pictures they have obtained, let us take a moment to understand the structure of Cu₂O. The cuprite structure stands out and is a unique lattice. Among the oxides, Ag₂O and Pb₂O are those that adopt a similar structure. The metal ions form a face centered cubic lattice. The oxide ions are found at positions 0.25, 0.25, 0.25, and

0.75, 0.75, 0.75 of the unit cell. This results in a tetrahedral coordination of copper ions around each oxygen and a linear coordination geometry for each copper (see Figure 1). What is strange is that each copper ion finds itself in the neighbourhood of 12 copper ions at a distance of 3.02 Å. Since copper is present in the +1 oxidation state – it has a filled shell of electrons ($3s^2$, $3p^6$, and $3d^{10}$) – these close contacts should be purely repulsive, very much like the interaction of two helium atoms in close proximity. Only worse since electrostatic factors are also unfavourable. However, in several molecular complexes much shorter Cu(I)–Cu(I) distances have been observed engendering controversial explanations for the last twenty years!⁴ The results of Zuo *et al.* appear to have shed some light on the matter. Let us see how.

As mentioned earlier, if the two ions have spherical electron density around them, and **only** electrostatic interactions are present, the difference map should have revealed no regions of electron density depletion or accumulation. Instead, Zuo *et al.*¹ found a region of electron density depletion at each copper along the O–Cu–O axis (see Figure 2) exactly in the shape of the d_{z^2} orbital found in chemistry text books! Generation of a hole in this axis is favourable and encourages better electrostatic interaction between the positively charged copper and negatively charged oxide ions, leading to stabilization of the lattice.

The question of where the electron density from copper has been transferred to and why, needs to be addressed. To answer these questions we return to the controversy regarding copper–copper bonding in cluster complexes. Merz and Hoffman⁵ had suggested on the basis of EHT calculations and symmetry arguments that there are two ways by which repulsive interaction between copper(I) centers are mitigated. One is the escape of electron density into ligand orbitals having the right symmetry. A second possibility is mixing of the copper 3d orbitals with empty 4s or 4p orbitals which would release some electron density from the filled shell and allow for ‘soft’ bonding between the metal centers. Cuprite adopts the second option. Due to symmetry around the copper ion, mixing of the 4s and the $3d_{z^2}$ orbitals occurs. A linear combination of the $3d_{z^2}$ and 4s orbitals

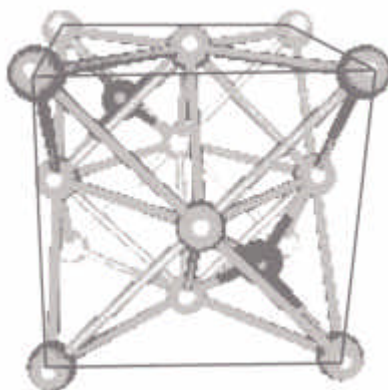


Figure 1. Perspective view of the unit cell of cuprite: blue balls are copper ions at the corners and centers of the faces of a cube; red balls are oxide ions. Two faces of the unit cell are marked.

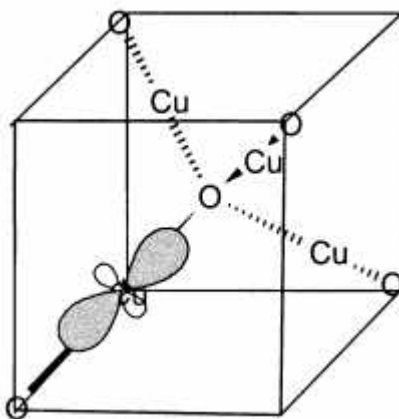


Figure 2. Only one d_{z^2} orbital is shown for clarity. Tetrahedrally coordinated oxygen is shown at the center of a cube. Each copper(I) ion is coordinated to two oxide ions.

results in reduced electron density along the z axis. Excess electron density would be in the other combination pushing the electron density into a region of space between the copper ions. What is amazing is that Zuo *et al.*¹ have located these regions of excess electron density in the tetrahedral voids between the copper ions revealing significant bonding interactions between the copper centers! In fact, they have calculated the electron density shared between copper ions to be as high as 0.22 electrons! It is surprising that they do not find any distortion of the electron cloud around oxide ions. Presumably the more symmetrical tetrahedral arrangement of copper ions around oxygen has masked the distortions of the oxide ion electron density.

Zuo's experiment is definitely a great technological achievement. However, it is the choice of system to study that was significant. The symmetry around copper is such that only one of the d orbitals mixed with a higher lying 4s orbital. This allowed a clear picture of the d orbital to emerge. Secondly, it solved a long standing puzzle about the stability of cuprite lattice where Cu^+ centers were in close proximity to other Cu^+ centers. It confirmed the weak bonding between copper ions through d + s mixing. Interestingly, the other possibility mentioned by Merz and Hoffman⁵, was recently verified by Bera and coworkers⁶ who synthesized a series of complexes where the ligands controlled the Cu–Cu distances. Through *ab initio* calculations, on model systems, they confirmed the role of bridging ligands in affecting Cu–Cu distances and explained the anomalous variations in trinuclear copper clusters.

Can Zuo's experiment now be carried out on more complex molecular systems? One area where physicists and chemists want help is with the electronic structure of superconductors. In this case there are CuO_2 planes. Theory predicts that the holes are located on the oxygen. At temperatures below T_c , will they be able to see the holes? Time will tell. Seeing orbitals and bonds definitely makes one salute those who dared to postulate them without being able to see!

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