

## All India Coordinated Project on Taxonomy (AICOPTAX)

In the background of declining taxonomic expertise in our country, the Ministry of Environment & Forests, Government of India organized a two-day National Workshop at Jaipur in February 1997. This workshop was attended by the top taxonomic experts of the country. The meeting identified the critical gap areas in which taxonomic expertise in the country was either nil or fast dwindling. One of the recommendations of the workshop was to develop an All India co-ordinated project for capacity building in taxonomy. Thereafter, the Ministry set up a Technical Group to develop the All India project and after interministerial consultations, the project has been approved.

The project envisages establishment of centres for research in identified priority gap areas (e.g. virus, bacteria, microlepidoptera, etc.) in the field of taxonomy, education and training (fellowships, scholarships, chairs, career awards, etc.) and strengthening of BSI

and ZSI as the coordinating units. The modalities of implementing the All India project, and prioritizing activities under the project have been decided after detailed consultations with experts.

Nine centres for research and two centres for training and coordinators for these centres have been identified in the first phase. Subject areas identified for establishing centres for research include animal viruses, bacteria and archaea, fungi, lichens and bryophytes, palms, grasses and bamboos, helminthes and nematodes, insects: microlepidoptera and mollusca. The centres for training include one each for plant biosystematics and animal biosystematics.

The coordinators for the centres together with the collaborators are required to undertake: survey, collection, identification and preservation; maintain collections and taxonomic data banks; develop identification manuals; and train college teachers and students and local communities in parataxonomy.

An interactive brainstorming session with the identified coordinators and some collaborators was held on 3 June 1999.

A high level steering committee consisting of H. Y. Mohan Ram, C. J. Saldanha and M. S. Jairajpuri, and representatives from UGC, CSIR, ICAR, DBT, DST, ICMR, ICFRE, Planning Commission, Directors of BSI and ZSI, and some experts has been constituted to oversee the implementation of the project. The first meeting of the steering committee was held on 22 July 1999. The committee after evaluating the proposals received from the centres has recommended the quantum of assistance to be released. The committee has also recommended 14 scholarships at the M Sc level in various identified priority areas in the centres for research.

**G. V. Sarat Babu**, Ministry of Environment & Forests, Paryavaran Bhavan, CGO Complex, Lodhi Road, New Delhi 110 003, India.

## RESEARCH NEWS

### Visualizing orbitals and bonds

*A. G. Samuelson*

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.*<sup>1</sup> at the Arizona State University have studied the electron density distribution in cuprite,  $\text{Cu}_2\text{O}$  and unraveled the shape of the  $d_{xz}$  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 studies<sup>2</sup>. 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 Diffraction<sup>3</sup> (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  $\text{Cu}^+$  ion and the  $\text{O}^{2-}$  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  $\text{Cu}_2\text{O}$ . The cuprite structure stands out and is a unique lattice. Among the oxides,  $\text{Ag}_2\text{O}$  and  $\text{Pb}_2\text{O}$  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!<sup>4</sup> 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.*<sup>1</sup> 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 Hoffman<sup>5</sup> 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 results in reduced electron

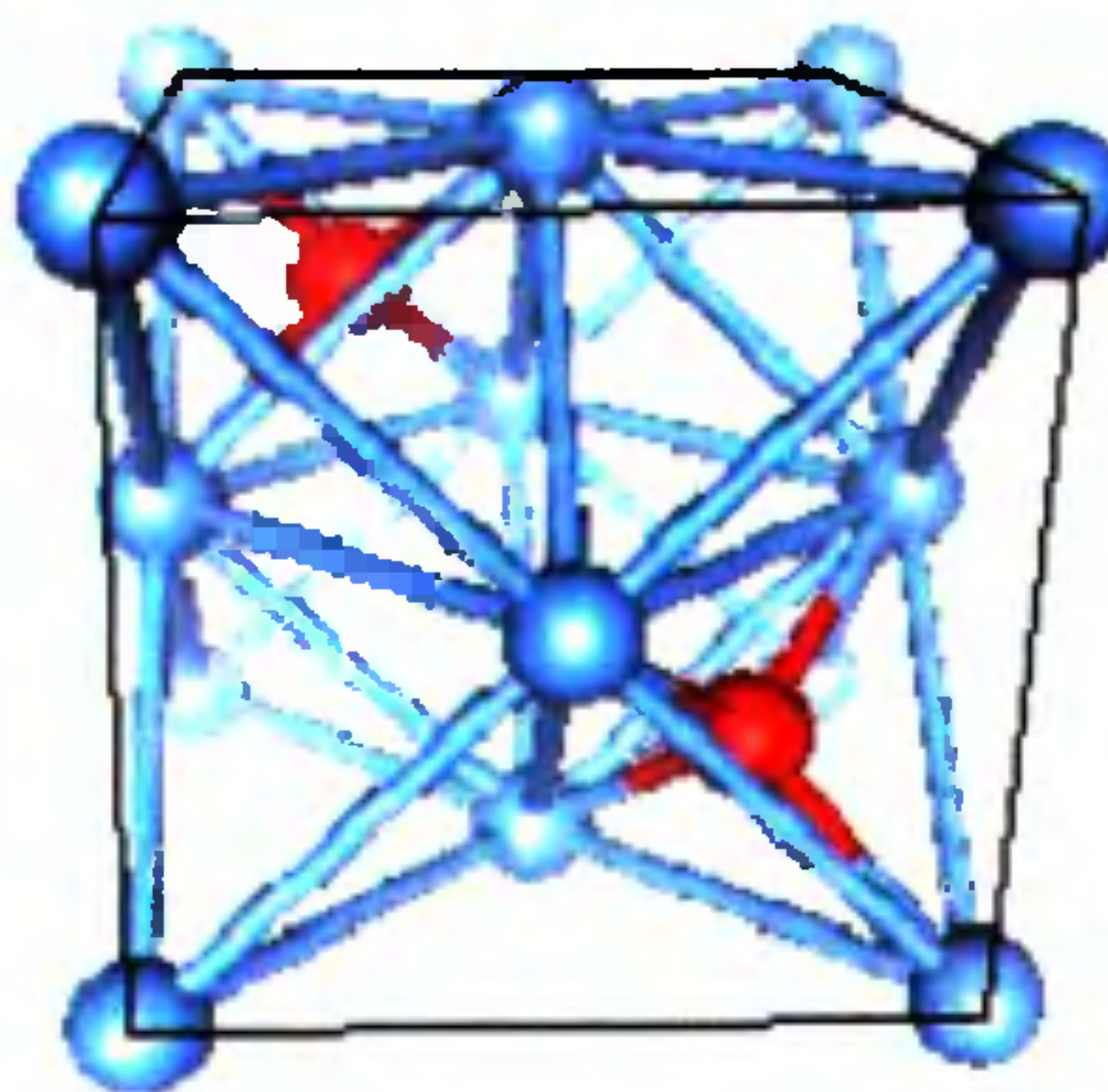


Figure 1. Perspective view of the unit cell of cuprite: blue balls are copper ions at the corners and centers of the faces of a cube; red balls are oxide ions. Two faces of the unit cell are marked.

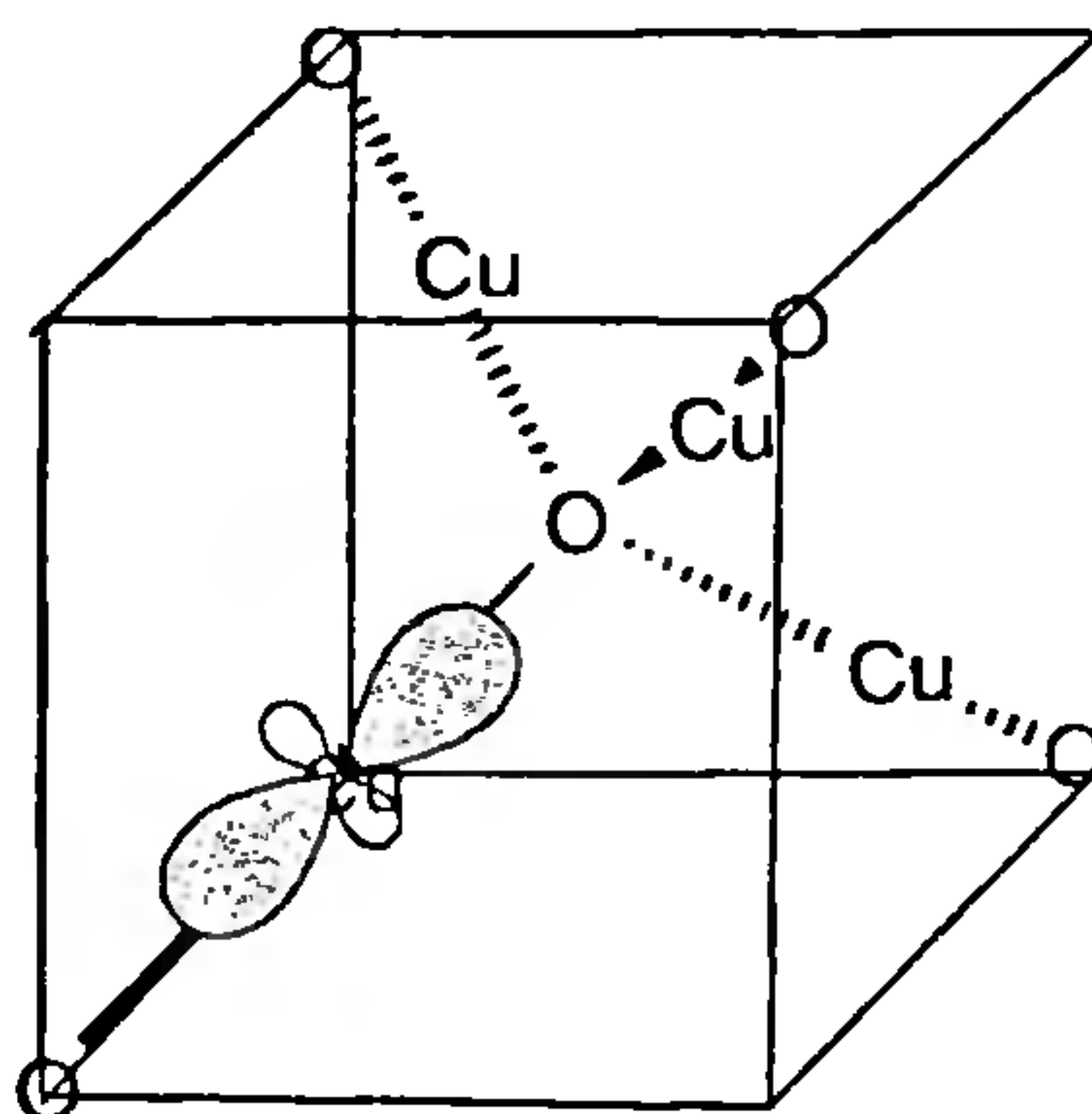


Figure 2. Only one  $d_{z^2}$  orbital is shown for clarity. Tetrahedrally coordinated oxygen is shown at the center of a cube. Each copper(I) ion is coordinated to two oxide ions.

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.*<sup>1</sup> 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  $\text{Cu}^+$  centers were in close proximity to other  $\text{Cu}^+$  centers. It confirmed the weak bonding between copper ions through d + s mixing. Interestingly, the other possibility mentioned by Merz and Hoffman<sup>5</sup>, was recently verified by Bera and coworkers<sup>6</sup> 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  $\text{CuO}_2$  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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ACKNOWLEDGEMENTS. I thank Prof. K. L. Sebastian for helpful discussions and Prof. R. Hoffmann for helpful comments.

A. G. Samuelson is in the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India.