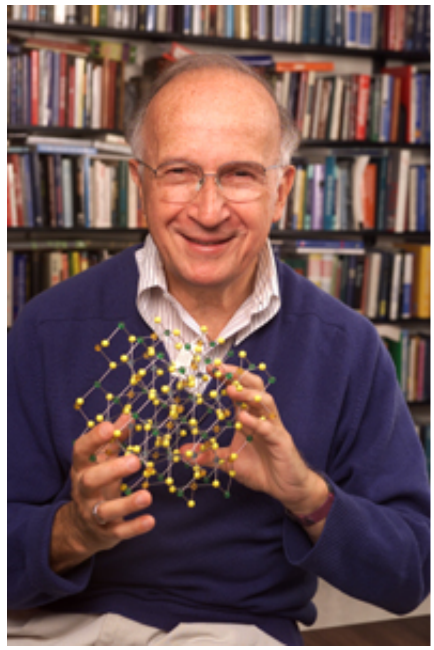
Cornell University
Chemistry and Chemical Biology

Faculty Research

Roald Hoffmann



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Educational Background:

PhD, Harvard University, 1962

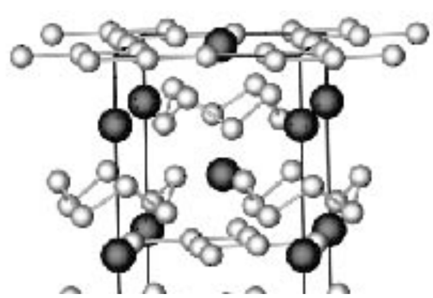
MA, Harvard University, 1960

BA, Columbia College, 1958

Awards:

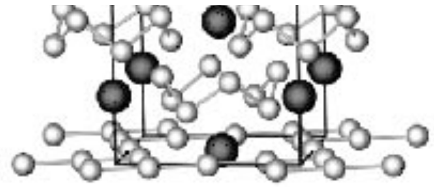
•Nobel Prize, 1981 (chemistry)
•American Chemical Society: Priestley Medal; Arthur C. Cope Award in Organic Chemistry; Inorganic Chemistry Award; Pimentel Award in Chemical Education; Award in Pure Chemistry
•Monsanto Award
•National Medal of Science
•National Academy of Sciences
•American Academy of Arts and Sciences Fellow
•American Philosophical Society Fellow
•Foreign Member, Royal Society

Research Description:



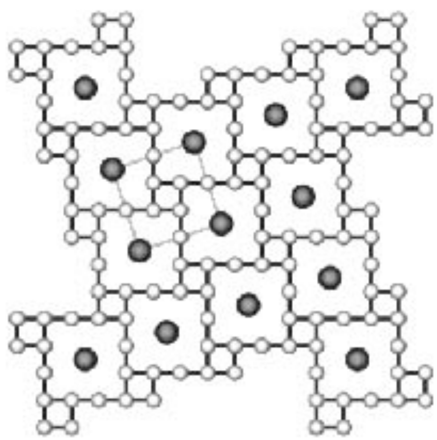
Our group looks at the electronic structure of molecules of any complexity, whether organic or inorganic, discrete molecular structures, or extended arrays in one, two, or three dimensions. We are interested in why they have the structures they do, how they might react, and whether they are stable or good conductors.

The answers lie in the electronic structure of the molecules. Thus we do molecular orbital calculations, often very simple



ones, seeking orbital explanations and relationships between the molecule at hand and any related systems.

The following study illustrates our approach: In a February 1995 issue of *Angewandte Chemie,* W. S. Sheldrick and M. Wachhold published a paper on the synthesis and structure of Cs_3Te_{22}. The beautiful structure of this molecule (fig. 1) displays unusual features. Discrete crown Te_8 entities (well known for sulfur and selenium, they had not been previously observed for tellurium) can be easily identified, as can infinite two-dimensional sheets that are formed by Te atoms and include one Cs atom per six telluriums. If one assumes the Te_8 rings to be neutral molecular entities and assigns the valence electrons of cesium fully to the only atoms left, the tellurium sheets, the compound may be described as $[Cs+]_3[Te_8]_2[Te_6 3-]$. The Te63- net is definitely rich in electrons.



The pattern of the $CsTe_6$ sheet (fig. 2), looking down the c-axis onto the sheet; the darker and larger spheres are Cs, the light ones (Te) is remarkable. This is a net of rare symmetry containing only fourfold and twofold rotation axes.

In this net, the Te atoms are bonded in unusual ways. One sees three coordinate T-shaped Te atoms (as in BrF_3) and linear two-coordinate Te (as in I_3- or XeF_2, not as in TeR_2). All these features-the unusual coordination geometries, the electron richness of the net, the net itself-were explained by postdoctoral fellow Norman Goldberg and graduate student Qiang Liu. They calculated the electronic structure of the material and figured out the bonding in a qualitative way, relating it to molecular models. We predict conductivity for the net and the existence of $CsTe_7$ and Cs_2Te_{15}. $CsTe_7$ has just been synthesized.

Selected Publications:

Hypervalent Bonding in One, Two and Three Dimensions: Extending the Zintl-Klemm Concept to Nonclassical Electron-Rich Networks. Garegin Papoian and Roald Hoffmann, *Angew. Chem.* **39,** 2408-2448 (2000).

A comparative theoretical study of the hydrogen, methyl and ethyl chemisorption on the Pt(111) surface. G. Papoian, J. Nørskov, and R. Hoffmann, *J.Am.Chem.Soc.* **122***(17),* 4129-4144 (2000).

Real and Hypothetical Intermediate-Valence Fluoride Ag^{2+}/Ag^{3+} and Ag^{2+}/Ag^{1+} Systems as Potential Superconductors. W. Grochala & R. Hoffmann, *Angew. Chem.,* **40***(15),* 2742-2781 (2001).

Deformation and Bonding in a Puckered Re-C Square Net. E. Merschrod, A. Courtney & R. Hoffmann, *Zeitschrift f. anorg. allgem. Chemie* **628***(12),* 2757-2763 (2002).

Sigmatropic Shiftamers: Fluxionality in Broken Ladderane Polymers. D. Tantillo & R. Hoffmann, *Angew. Chem. Int. Ed.,* **41***(6),* 1033-1036, (2002).

A full listing of publications can be found here.