

Molecular shape

The shapes of molecules:

- van't Hoff (1874): CH₄ tetrahedron
- Werner (1893): Pt(NH₃)₂Cl₂ planar
- Lewis (1915): Electron pairs and octets
- Sidgwick and Powell (1940): Foundations of *Valence Shell Electron Pair Repulsion* theory

Bonding pairs and lone pairs are of equal importance and these distribute themselves to minimize interelectron repulsion

Problems, for example, with the deviation from tetrahedral angles in H₂O and NH₃

Proc. R. Soc. London A 176 (1940) 153

Ram Seshadri <seshadri@mrl> Lone Pairs, 2008

BAKERIAN LECTURE

Stereochemical types and valency groups

By N. V. SIDGWICK, F.R.S. AND H. M. POWELL

(Delivered 27 June 1940—Received 27 June 1940)

The arrangements in space of the valencies of a polyvalent atom, while they are subject to small variations seldom exceeding 5 or 10°, tend to conform to quite a limited number of types. It is desirable to relate this grouping to some familiar property of the atom. The property here used is the size (in G. N. Lewis's sense) of the valency group of the central atom, and the number of shared electrons which it contains, together with that of the preceding (unshared) electronic group in the atom. The experimental results show the following relations.

I. When the valency group is less than 8 we have with a covalency of 2 a linear structure (as in Cl-Hg-Cl), and with one of 3 a plane with equal angles of 120° (as in BF₃).

II. With a complete octet the arrangement can be either tetrahedral or planar. When the covalency is less than 4 it is always derived from the tetrahedron, as in the triangular OH₃ and the pyramidal NH₃. The fully shared octet is always tetrahedral when the preceding group (*n*) is 2, 8, or 18. In the transitional elements where 8 < *n* < 18, it is tetrahedral if *n* is not much more than 8, and planar if it is not much less than 18; but the two series overlap.

III. When there are 10 valency electrons, at least 2 of them (the "inert pair") unshared, the structure with a divalent atom (as in M[I₂]) is linear: that of a 4-covalent atom is found in the thalious and plumbous salts to be planar, but in tellurium tetrachloride it may be a distorted tetrahedron.

IV. The peculiar 4-covalent duocet in M[ICl₄] is planar.

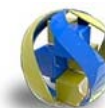
V. A covalency of 5 is always found to give a trigonal bipyramid.

VI. Covalency 6. Three structures are theoretically possible, a trigonal prism, a trigonal antiprism, and a regular octahedron. Experimentally the octahedron is always found, except in a few giant molecules such as those with a nickel-arsenide lattice. The regular octahedron has been found with practically every possible size of the preceding group, as well as with the "inert pair" of electrons.

VII. A covalency of 7 can have two different structures, one derived from the octahedron and the other from the trigonal prism.

VIII. Covalency 8. The only compound examined, K₄[Mo(CN)₈], has a dodecahedral arrangement of the 8 CN groups.

Nearly (but not quite) all the structures can be even more simply related to the size of the valency group by assuming that the mean positions of the electron pairs in this group are the same whether they are shared or not, the structure being linear for 4 electrons, plane symmetrical for 6, either tetrahedral or plane for 8, a trigonal bipyramid for 10, and an octahedron for 12.



VSEPR

- Gillespie and Nyholm (1957): “(1) that a lone pair repels electron pairs more than a bonding pair of electrons, (2) that a double bond repels other bonds more than a single bond; (3) . . .

The tendency of the electrons pairs in a valency shell to keep apart is mainly due to the exclusion principle.”

Problems: Fails for XeO_3

Quart. Rev. Chem. Soc. 11 (1957) 339

Ram Seshadri <seshadri@mrl> Lone Pairs, 2008

INORGANIC STEREOCHEMISTRY

By R. J. GILLESPIE, D.Sc., and R. S. NYHOLM, M.Sc., D.Sc.
(UNIVERSITY COLLEGE, LONDON, W.C.1)

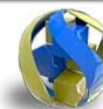
DURING the past few years there have been several developments in theoretical chemistry which have led to a much better understanding of the factors responsible for the shapes of inorganic molecules. These developments have also made it clear that some apparently different approaches to stereochemistry can be integrated and, indeed, shown to be complementary. This Review attempts to bring together these approaches and to apply them to elements over the whole of the Periodic Table. Perhaps the most important result emerging from this unification is the conclusion that the simple qualitative Sidgwick-Powell¹ theory of electron-pair repulsions is of great value in accounting for the stereochemistry of practically all inorganic compounds.

In early applications of the valence-bond method to stereochemistry only the σ -bond electrons were considered, the stereochemistry being inferred from the bonding orbitals they were presumed to occupy. Later, consideration in addition of non-bonding lone pairs generally gave a better approximation to the actual shape of molecule. Sidgwick and Powell¹ assumed that lone pairs of electrons and bonding pairs were of equal importance and that they arranged themselves symmetrically so as to minimize the repulsions between them. The ligand(or crystal)-field theory is concerned with the influence of the non-bonding electrons upon the arrangement of the ligands which are assumed to be negative ions or dipoles surrounding a central metal atom. Recently the influence of covalent binding has also been considered. These various theories are in fact closely related and an attempt has been made in this Review to integrate them. It appears that the simple theory of electron-pair repulsions receives considerable justification from quantum-mechanics and when refined to take into account differences between the repulsions between lone pairs and bonding pairs of electrons provides a very satisfactory theory of the stereochemistry of inorganic molecules.

A simple electrostatic theory

The Arrangement of Electron Pairs in Valency Shells.—Sidgwick and Powell¹ pointed out in 1940 that the arrangements in space of the covalencies of multivalent atoms are very simply related to the size of the valency shell of electrons. The pairs of electrons in a valency shell, irrespective of whether they are shared (*i.e.*, bonding) pairs or unshared (*i.e.*, non-bonding) pairs, are always arranged in the same way which depends *only* on their number. Thus two pairs are arranged linearly, three pairs

¹ Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, *A*, 176, 163.



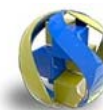
The solid state

- Hyde and Andersson, Inorganic Crystal Structures, Wiley (1988):

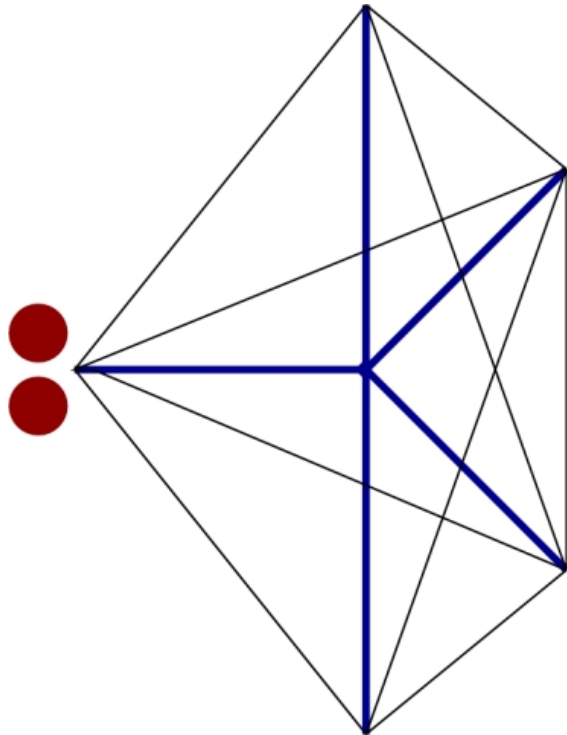
In many crystalline solids with cation-centered lone pairs, the lone pair occupies the same volume as an oxide or fluoride ion. However the cation-lone pair distance (in Å) is much shorter than the cation-anion distance:

	1+	2+	3+	4+	5+	6+
$3d^{10} 4s^2$	Ga 0.95	Ge 1.05	As 1.26	Se 1.22	Br 1.47	
$4d^{10} 5s^2$	In 0.86	Sn 0.95	Sb 1.06	Te 1.25	I 1.23	Xe 1.49
$5d^{10} 6s^2$	Tl 0.69	Pb 0.86	Bi 0.98	Po 1.06		

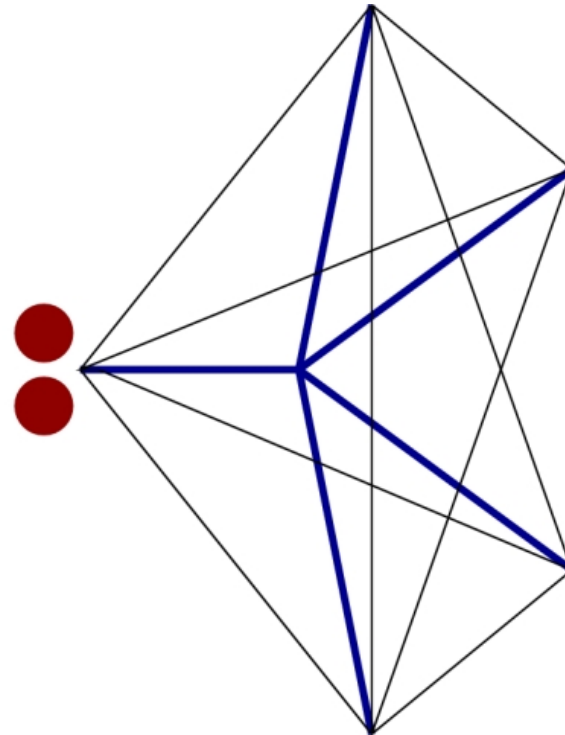
Polyhedra of anions and lone pairs must have off-centric cations.



Andersson & Galy vs. Gillespie & Nyholm



Traditional view



Modified/corrected



Why is this important ?

Cation-centered lone pairs (often with Pb^{2+} as the central cation, but also Sn^{2+} and Bi^{3+}) are tremendously important for applications requiring off-centered polyhedra and their associated dipoles:

- Ferroelectric and piezoelectric materials, actuators
- Multiferroic materials
- Non-linear optical materials
- Ionic conductors
- High-refractive index materials (lead crystal)
- Semiconductor/semimetal to insulator transitions
- Phosphors (?)



This talk

Density Functional calculations of the electronic structure of crystals, combined with special tools for visualization of lone pairs:

- What constitutes a lone pair ?
- When are lone pairs *stereochemically* active ?
- Lone pairs and inert pairs
- What is the cooperative behavior of lone pairs ?
- Can lone pairs be used to *design* polar polyhedra ?
- Can lone pairs be *frustrated* ?

DFT: Stuttgart TB-LMTO-ASA program [O. K. Andersen, O. Jepsen *etc.*]

Electron localization functions (ELFs): An orbital independent measure of electron localization based on the pair probability of electrons.

A. D. Becke and K. E. Edgecombe *J. Chem. Phys.* 92 (1990) 5397



The ELF

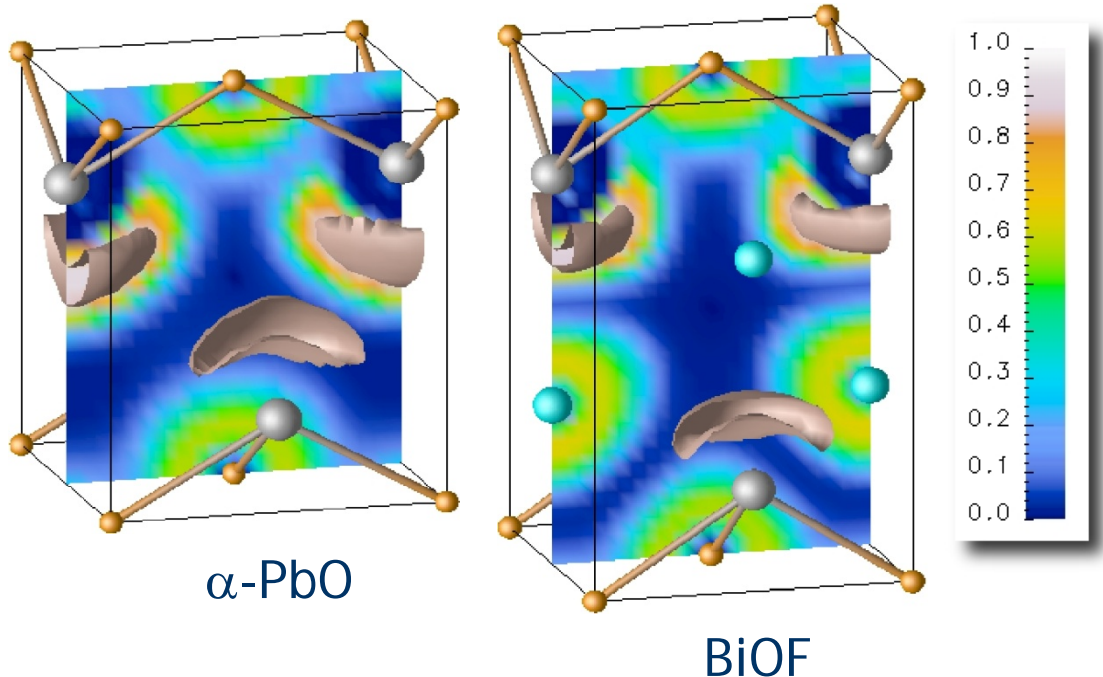
$$\text{ELF} = \frac{1}{1 + \left(\frac{D}{D_H}\right)^2} \in (0, 1)$$

with

$$D = \frac{1}{2} \sum_i |\nabla \phi_i|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}$$

and

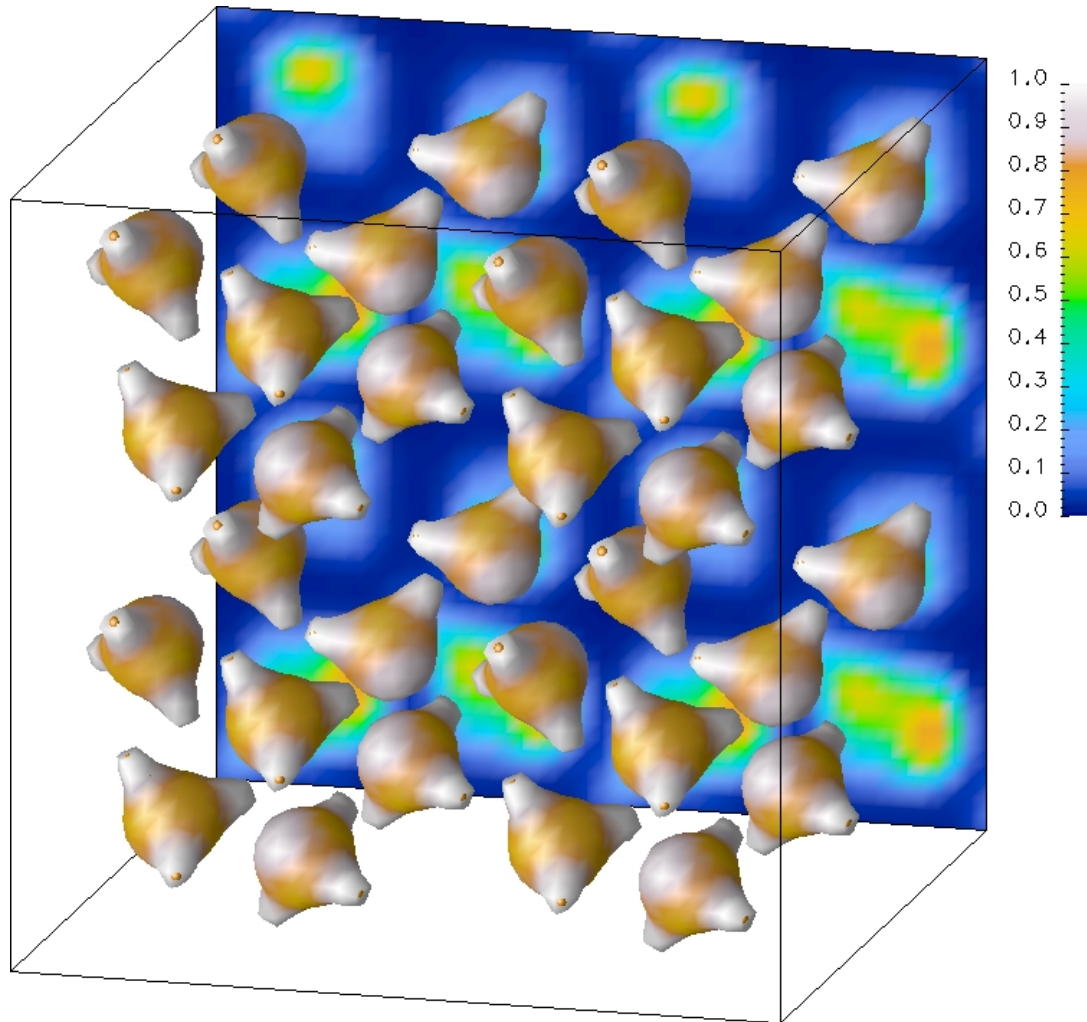
$$D_H = \frac{3}{10} (3\pi^2)^{5/3} \rho^{5/3}$$



B. Silvi and A. Savin, *Nature* **371** (1994) 683.

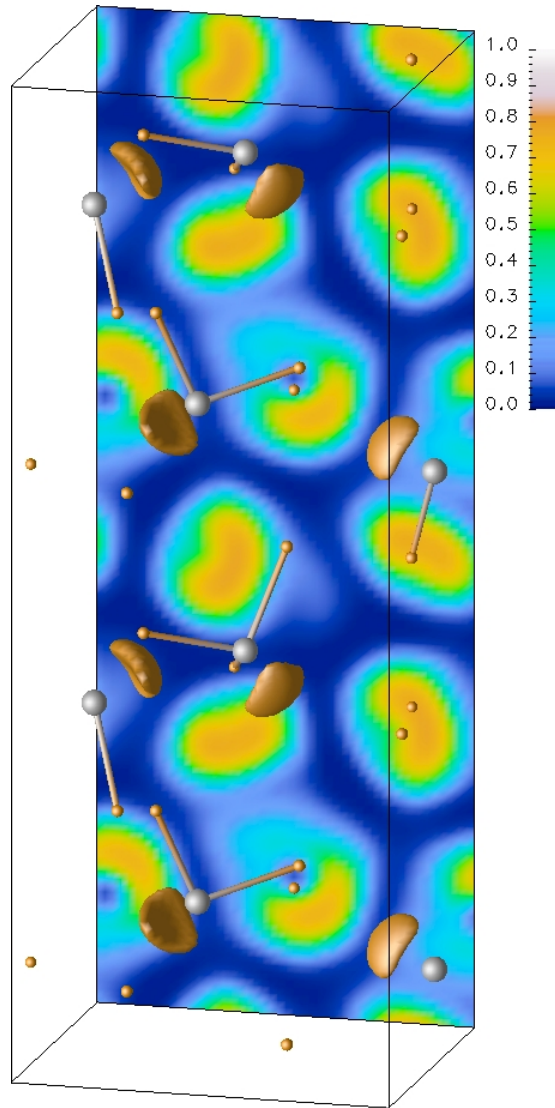
J.-M. Raulot, G. Baldinozzi, R. Seshadri, and P. Cortona, *Solid State Sciences* **4** (2002) 467; R. Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* **113** (2001) 487.





Electron density
decorated by the
ELF





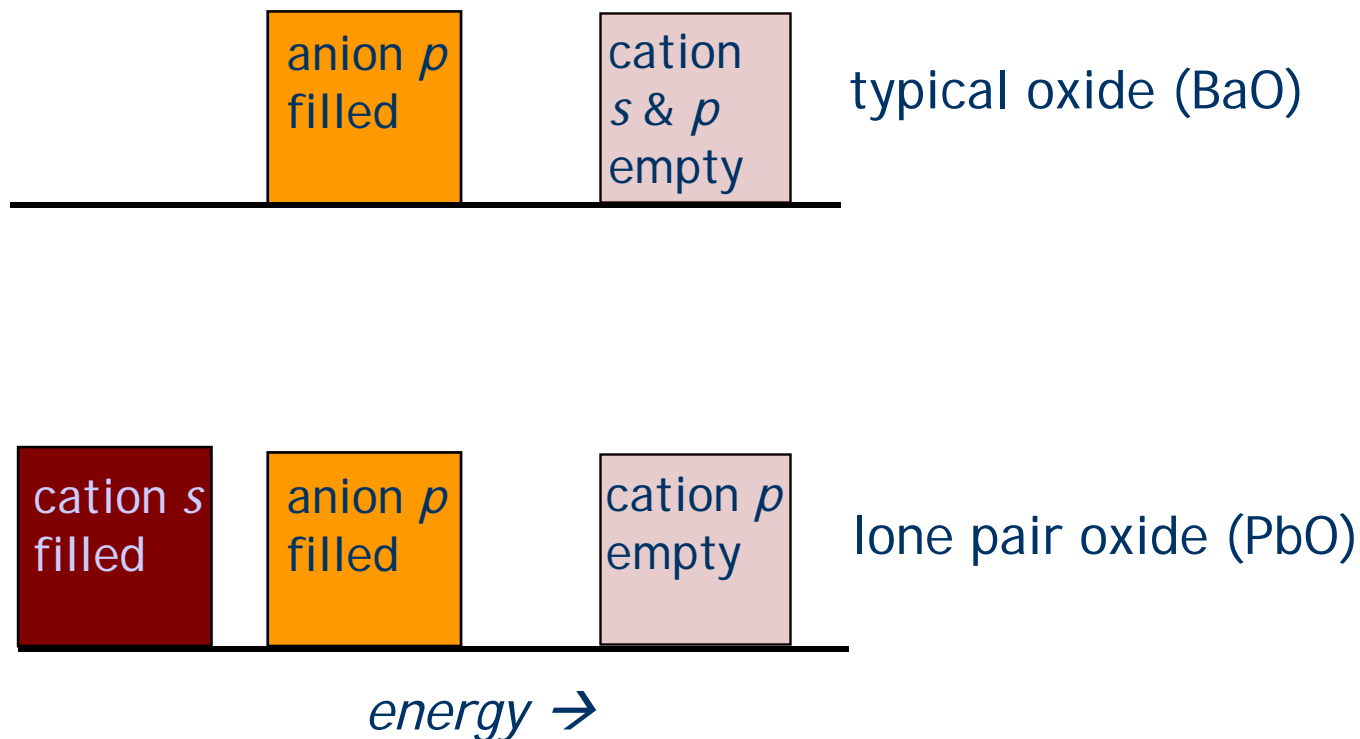
Three-coordinate Xe, is described by Sten Andersson as being Xe outside a trigonal prism.



What is the composition of the lone pair ?

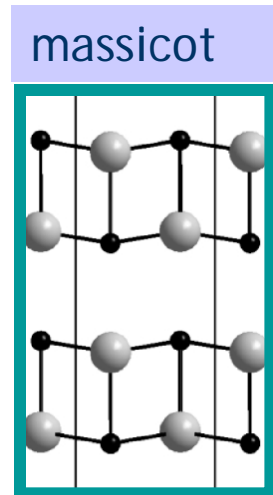
Orgel (1959): The lone pair cannot have purely s character when it is *stereochemically* active; it must admix with p .

Bersuker (1984): Filled anion p states must play a role.

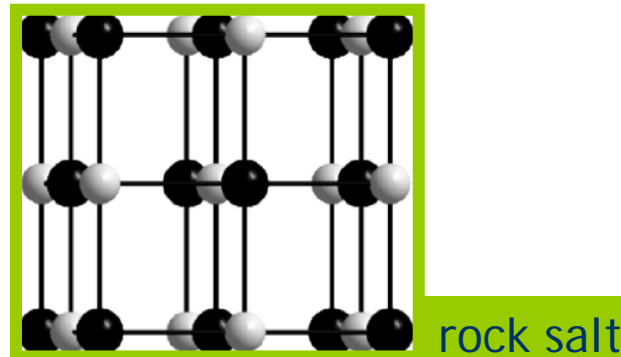
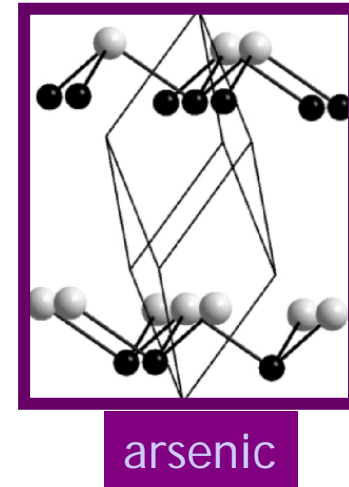


What is the composition of the lone pair ?

A lone pair sorted structural field (IV-VI semiconductors):



	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe



U. Waghmare, N. A. Spaldin, H. C. Kandpal, and R. Seshadri,
Phys. Rev. B. 67 (2003) 125111.

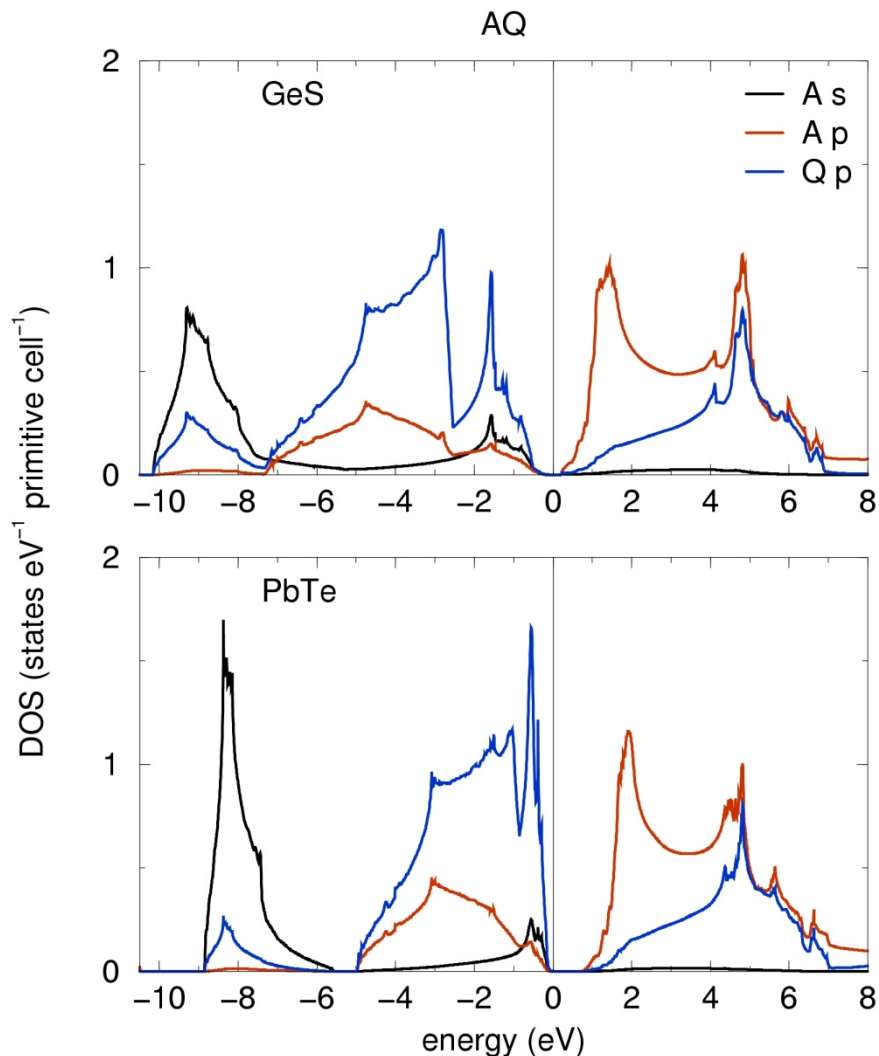
Ram Seshadri <seshadri@mrl> Lone Pairs, 2008



UC SANTA BARBARA
engineering and the sciences

What is the composition of the lone pair ?

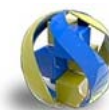
Electronic structure of cubic AQ



	S	Se	Te
Ge	GeS	GeSe	GeTe
Sn	SnS	SnSe	SnTe
Pb	PbS	PbSe	PbTe

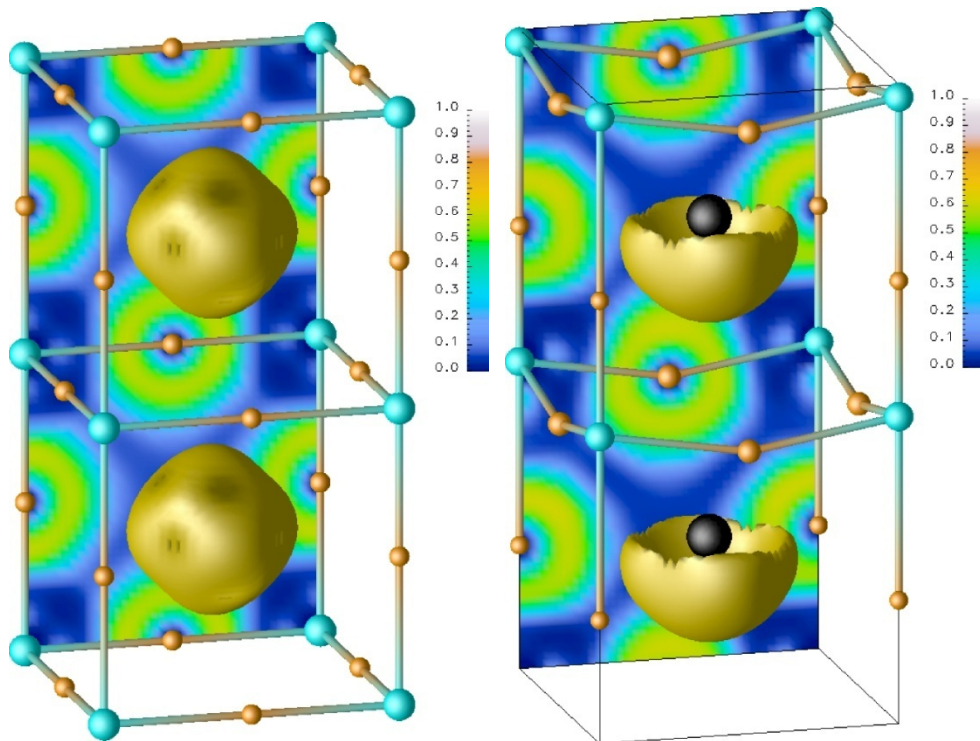
When the lone pair is stereochemically active (as in GeS), cation s states are broader and are better mixed with anion p states. The mixing is intermediated by empty cation p .

Cation s states are narrow and largely unmixed with anion p in cases when the lone pair is not stereochemically active (*Cf.* the inert pair effect).



Cooperative behavior

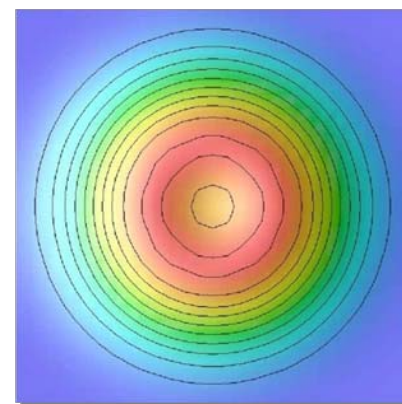
The expression of cooperative stereochemical activity of the lone pair plays an important role in the development of polar behavior.



PbTiO₃ above 766 K
Pm-3m

PbTiO₃ below 766 K
P4mm

Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* 113 (2001) 487.



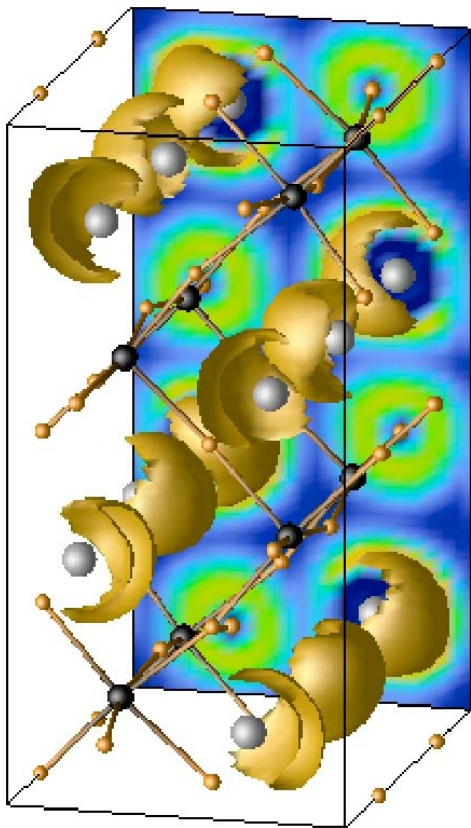
Even above the phase transition, the Pb²⁺ ion (in Pb₂NbYbO₆) is not really where it is supposed to be.

Baldinozzi, Raulot, Seshadri, *MRS Symp. Proc.* 718 (2002) D12.7.1.

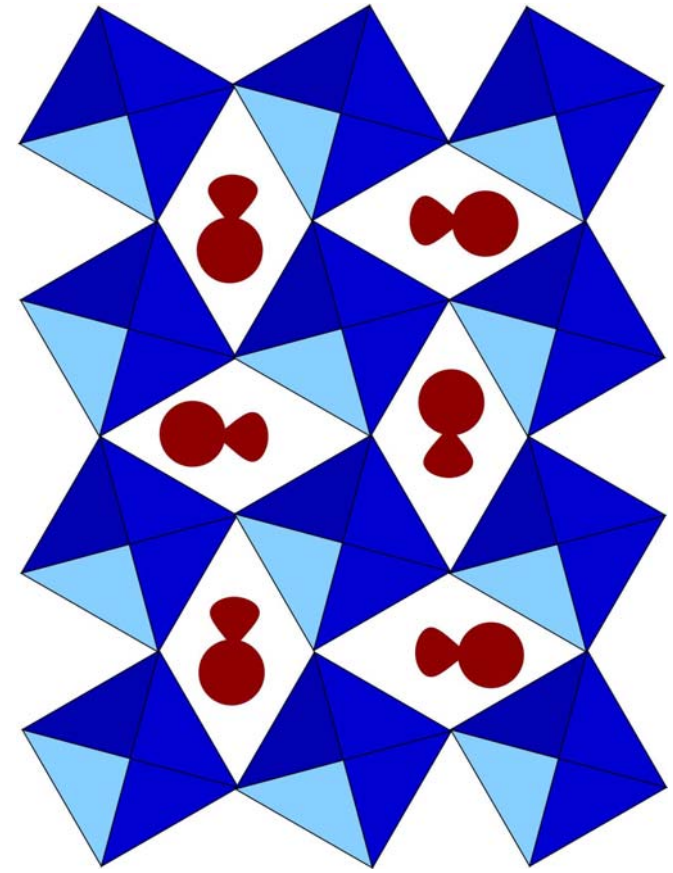


Lone pair cooperativity

Octahedral rotations coupled with lone pair activity make PbZrO_3 antiferrodistortive (antipolar).



PbZrO_3 below 503 K
Pbam



R. Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* 113 (2001) 487.

Lone pair cooperativity



Cubic paraelectric

↓ 445 K ↓

Orthorhombic antiferroelectric



Cubic paraelectric

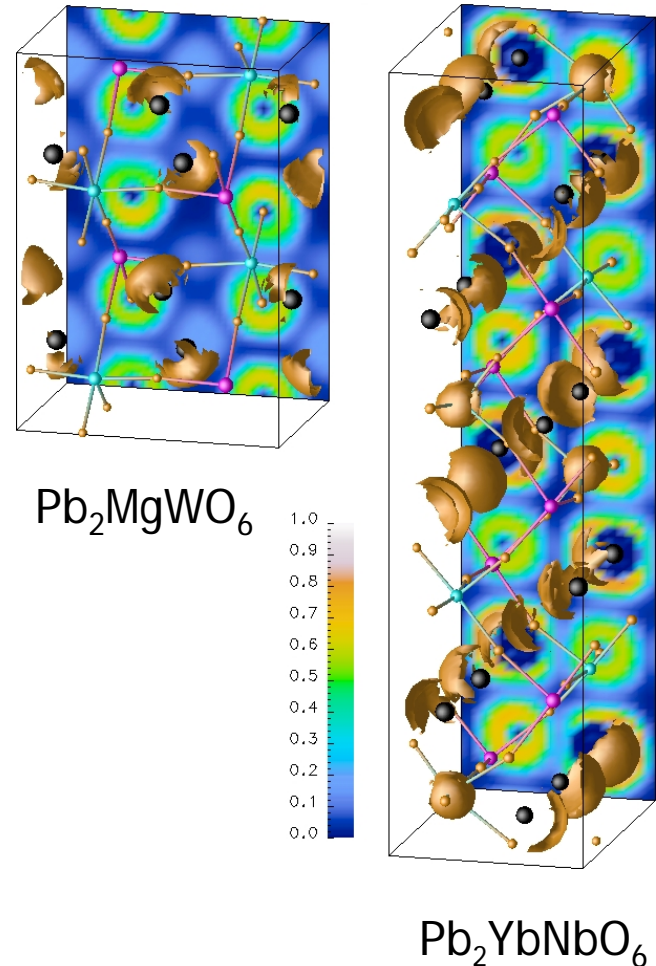
↓ 300 K ↓

Incommensurate antiferroelectric

↓ 230 K ↓

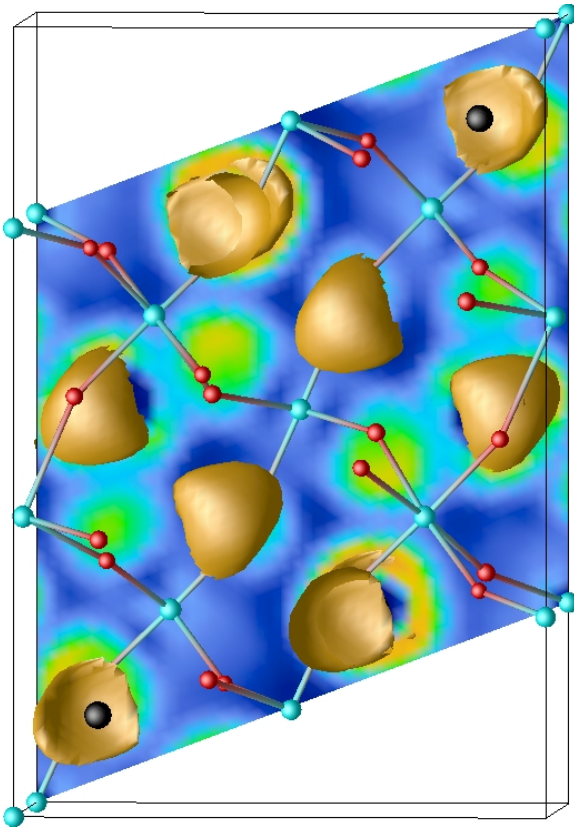
Ferroelectric

Lone pair & d^0 SOJT
distortions strongly coupled



Multiferroics

ABO_3 perovskites where A is lone pair active and is associated with ferroelectricity, while B is magnetic and associated with ferromagnetism
 $BiMnO_3$:

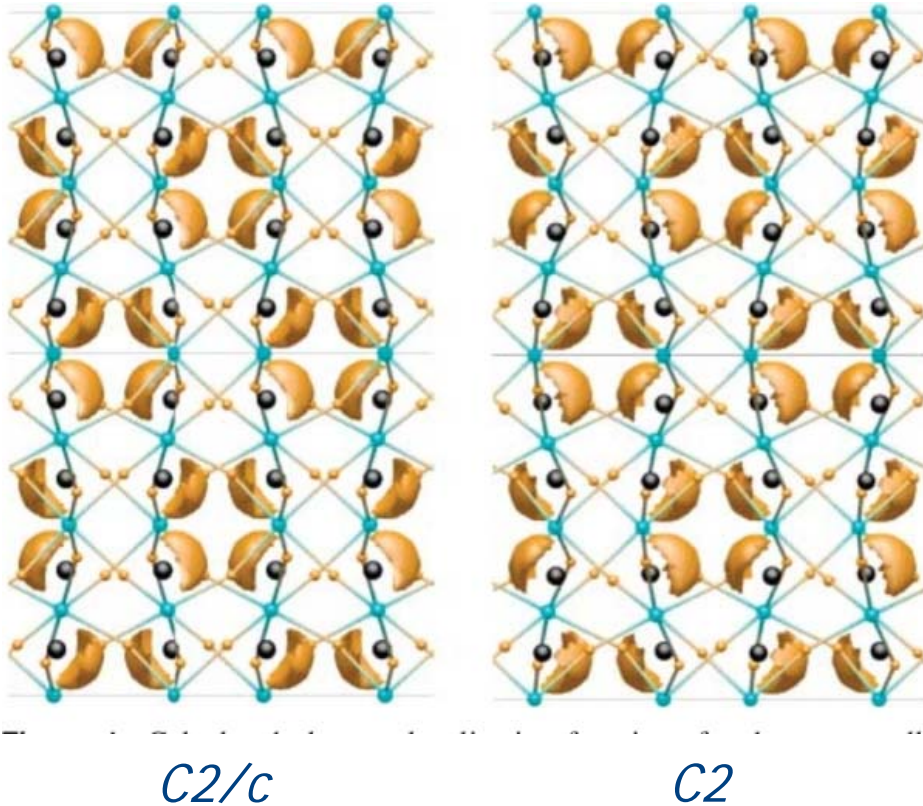


T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, *J. Solid State Chem.* 145 (1999) 639; R. Seshadri and N. A. Hill, *Chem. Mater.* 13 (2001) 2829.



Multiferroics

Structural relaxation (DFT-LDA and DFT-LDA+ U) indicates that the polar structure is actually not stable for BiMnO_3 .



P. Baettig, R. Seshadri and N. A. Spaldin, *J. Am. Chem. Soc.* **129** (2007) 9854-9855.



Lone pairs and d^0 ions

3586

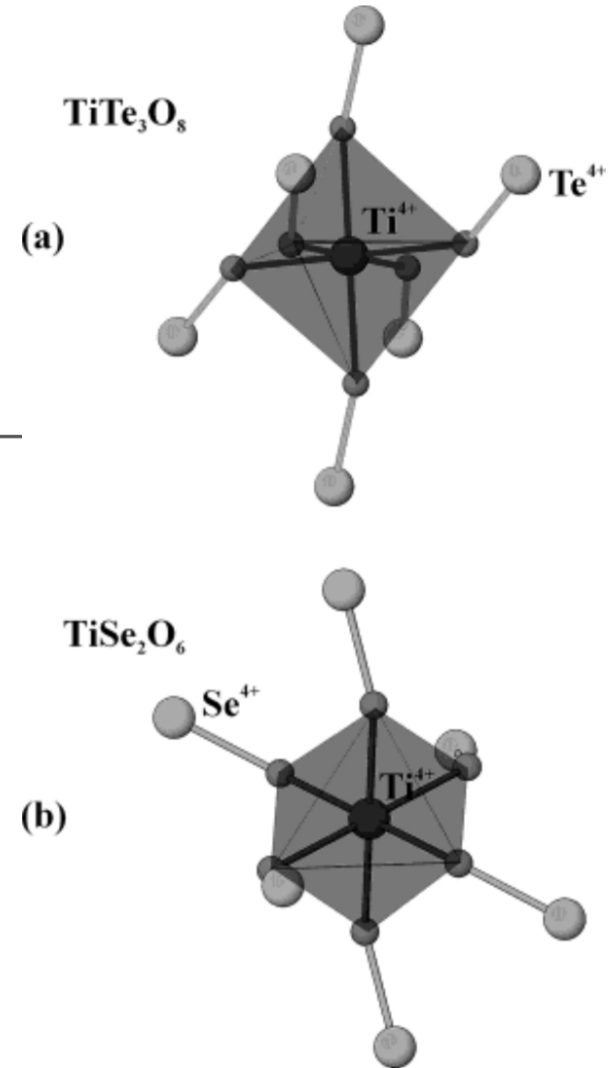
Chem. Mater. 2004, 16, 3586–3592

Reviews

Asymmetric Cation Coordination in Oxide Materials: Influence of Lone-Pair Cations on the Intra-octahedral Distortion in d^0 Transition Metals

P. Shiv Halasyamani

*Department of Chemistry and the Center for Materials Chemistry, University of Houston,
136 Fleming Building, Houston, Texas 77204-5003*



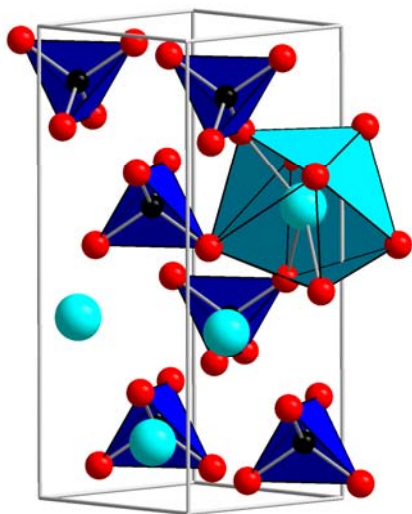
Lone Pairs: Constitution; Sn^{2+} vs. Pb^{2+} vs. Bi^{3+} in ternary systems

Interactions that drive lone pair activity in more complex (than binary) systems:

- What are the periodic trends in lone pair activity ?
- What is the cooperative/competitive nature of A—O—M networks ?

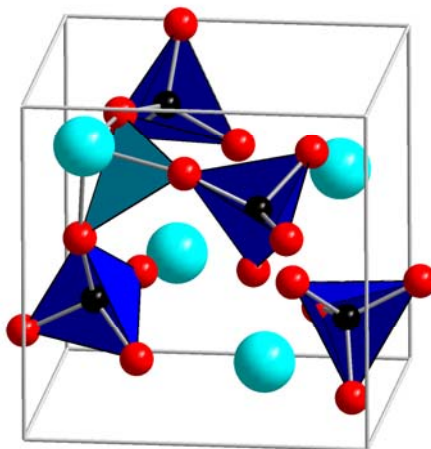
Experiments and calculations on ternary compounds: lone pair + d^0 + oxygen

Scheelite ($I4_1/a$) type



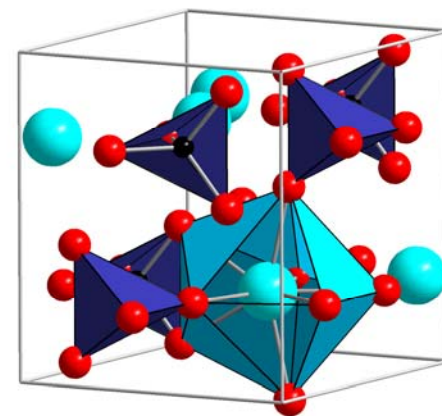
PbWO_4 (inactive)

$\beta\text{-SnWO}_4$ (P213)



SnWO_4 (active)

Zircon ($I4_1/amd$) type



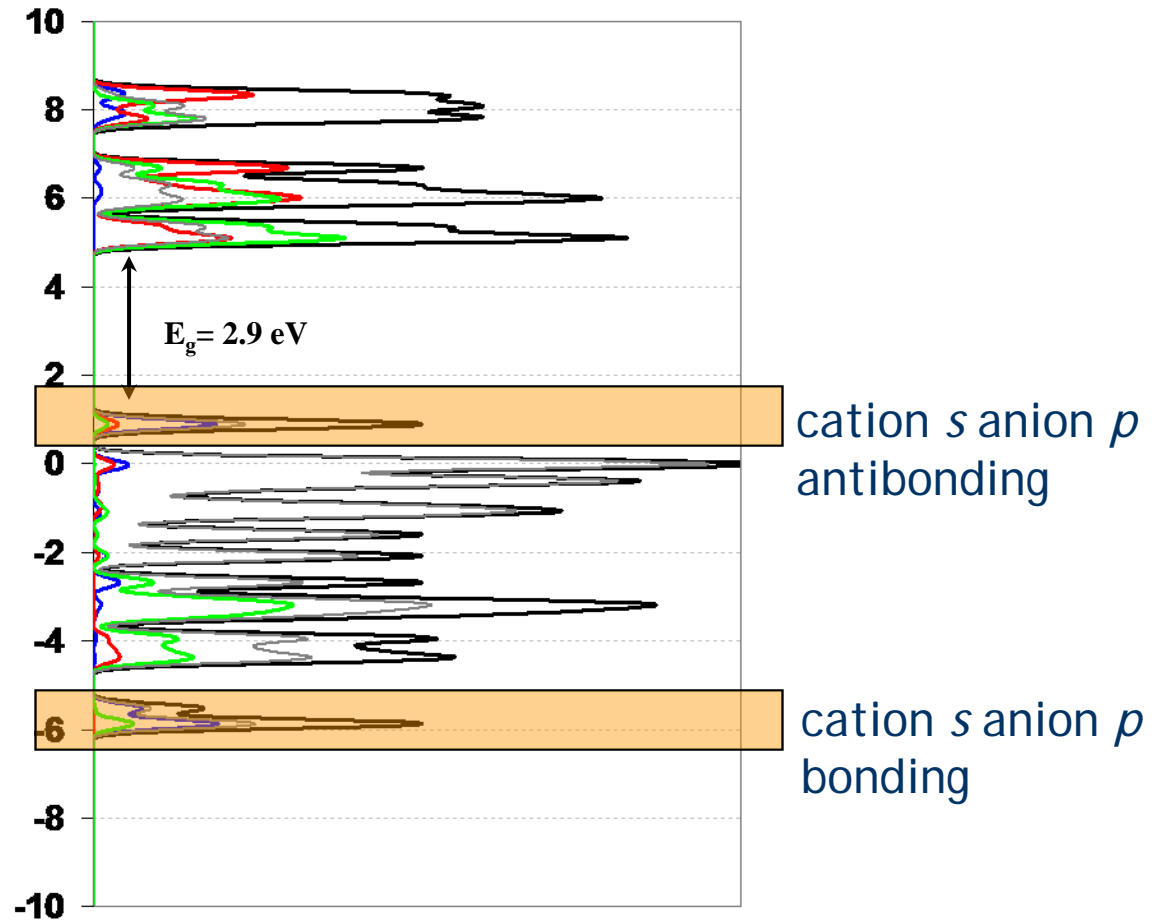
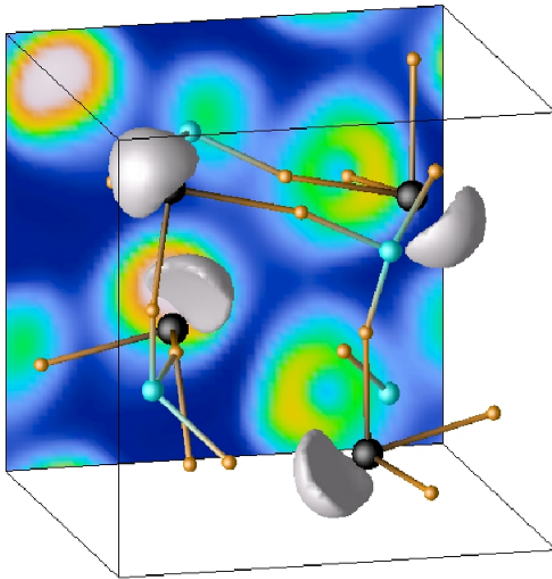
BiVO_4 (active)

Why are these structures so different ? $\beta\text{-SnWO}_4$ is quite unique.



Lone Pairs: Constitution; Sn^{2+} vs. Pb^{2+} vs. Bi^{3+} in ternary systems

$\beta\text{-SnWO}_4$



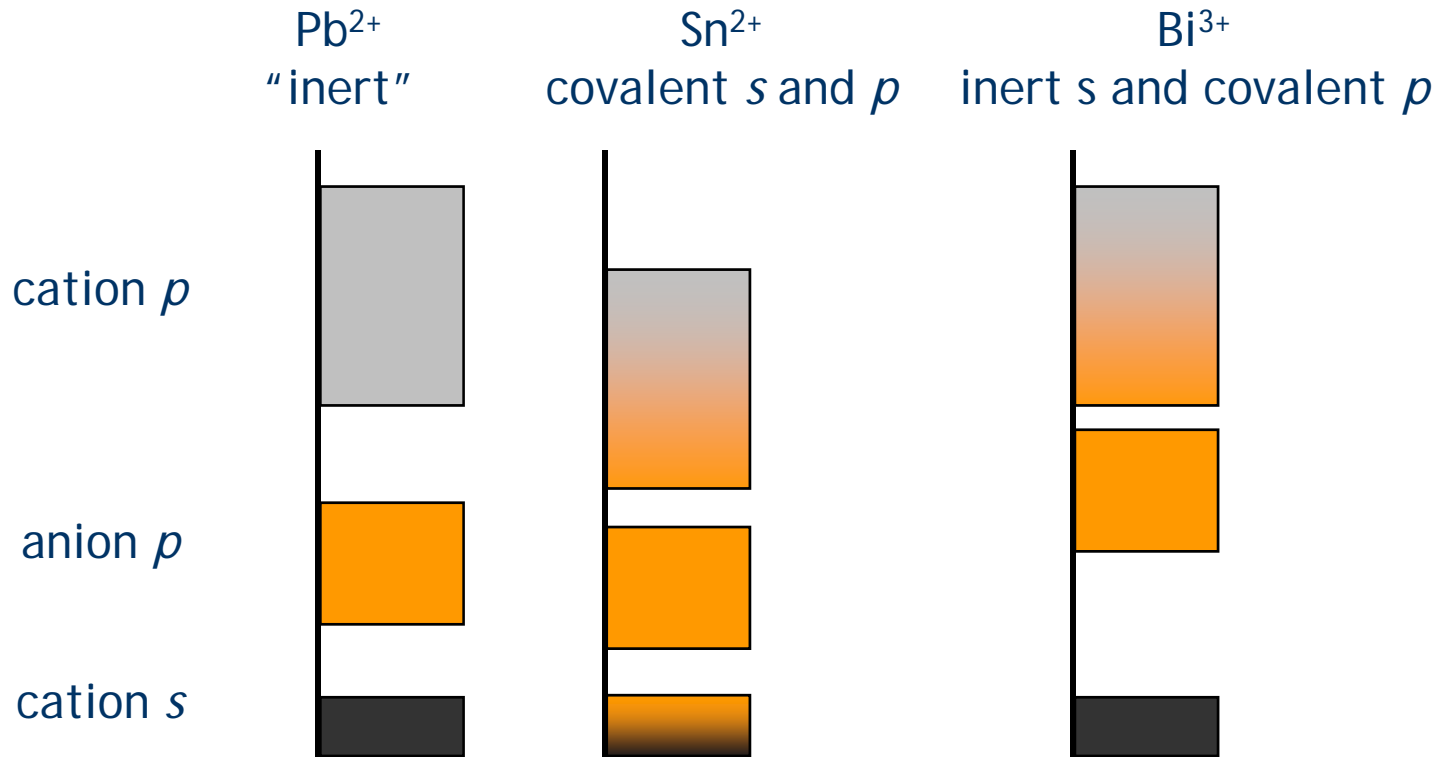
With Sn^{2+} there is hybridization and covalency between the Sn $6s$, Sn $6p$ and O $2p$ orbitals. This leads to a highly stereoactive, localized lone pair.

Pb^{2+} in PbWO_4 does not show these features \rightarrow no lone pair activity ("inert").



Lone Pairs: Constitution; Sn^{2+} vs. Pb^{2+} vs. Bi^{3+} in ternary systems

The differences arise because of energy levels are distinct (5s vs. 6s) and because of differences in charge: 2+ vs. 3+. In addition, how strongly oxygen bonds the second cation.



M. W. Stoltzfus, P. M. Woodward, R. Seshadri, J.-H. Klepeis, and B. Bursten, *Inorg. Chem.* 46 (2007) 3839.

