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.
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$_3$
The solid state


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:

<table>
<thead>
<tr>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
<th>6+</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3d^{10} 4s^{2}</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>0.95</td>
<td>Ge</td>
<td>1.05</td>
<td>As</td>
<td>1.26</td>
</tr>
<tr>
<td><strong>4d^{10} 5s^{2}</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>0.86</td>
<td>Sn</td>
<td>0.95</td>
<td>Sb</td>
<td>1.06</td>
</tr>
<tr>
<td><strong>5d^{10} 6s^{2}</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>0.69</td>
<td>Pb</td>
<td>0.86</td>
<td>Bi</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*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.

The ELF

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

with

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

and

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


NH₃

Electron density decorated by the ELF

Ram Seshadri <seshadri@mrl> Lone Pairs, 2008
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.

What is the composition of the lone pair?

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

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>Se</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>GeS</td>
<td>GeSe</td>
<td>GeTe</td>
</tr>
<tr>
<td>Sn</td>
<td>SnS</td>
<td>SnSe</td>
<td>SnTe</td>
</tr>
<tr>
<td>Pb</td>
<td>PbS</td>
<td>PbSe</td>
<td>PbTe</td>
</tr>
</tbody>
</table>

massicot


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What is the composition of the lone pair?

Electronic structure of cubic AQ

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 $p$ states.

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.

Even above the phase transition, the Pb$^{2+}$ ion (in Pb$_2$NbYbO$_6$) is not really where it is supposed to be.

Lone pair cooperativity

Octahedral rotations coupled with lone pair activity make PbZrO$_3$ antiferrodistortive (antipolar).

PbZrO$_3$ below 503 K

Pbam

Lone pair cooperativity

\[ \text{Pb}_2\text{MnWO}_6 \]
- Cubic paraelectric
  \[ \downarrow \text{445 K} \downarrow \]
- Orthorhombic antiferroelectric

\[ \text{Pb}_2\text{CoWO}_6 \]
- Cubic paraelectric
  \[ \downarrow \text{300 K} \downarrow \]
- Incommensurate antiferroelectric
  \[ \downarrow \text{230 K} \downarrow \]
- Ferroelectric

Lone pair & \( d^0 \) SOJT
distortions strongly coupled

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**Multiferroics**

$\text{ABO}_3$ perovskites where A is lone pair active and is associated with ferroelectricity, while B is magnetic and associated with ferromagnetism $\text{BiMnO}_3$:

Multiferroics

Structural relaxation (DFT-LDA and DFT-LDA+U) indicates that the polar structure is actually not stable for BiMnO$_3$.

Lone pairs and $d^0$ ions

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)

$\beta$-SnWO$_4$ (P213)
- SnWO$_4$ (active)

Zircon ($I4_1/amd$) type
- BiVO$_4$ (active)

Why are these structures so different? $\beta$-SnWO$_4$ is quite unique.
Lone Pairs: Constitution; Sn$^{2+}$ vs. Pb$^{2+}$ vs. Bi$^{3+}$ in ternary systems

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 no show these features → 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.

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