Pauli Principle

- The complete wave function for a system of electrons in a multielectron atom depends upon orbital (spatial) and spin contributions; i.e., $\psi = \psi_{\mathrm{orb}}\psi_{\mathrm{spin}} = \psi(n,l,m_l)\psi(m_s)$.

- All electrons are identical and indistinguishable, so interchanging positions or spins of any two must leave the system unchanged; e.g., $P \propto \psi^2 = (\pm\psi)^2$.

- This implies that on interchange either ψ retains its sign (symmetrical) or changes its sign (antisymmetrical).
  - Particles with unit spin (bosons; e.g., alpha particles, photons) are symmetrical on interchange ($\psi \rightarrow \psi$).
  - Particles with half-integer spins (fermions; e.g., protons, neutrons, neutrionos, electrons) are antisymmetrical on interchange ($\psi \rightarrow -\psi$).

  ☞ Only antisymmetrical wave functions are found to represent the the properties of electrons in multielectron systems.

☞ Pauli Principle for Electrons: When the roles of any two electrons are interchanged, the total wave function must change sign; i.e., it must be antisymmetric.

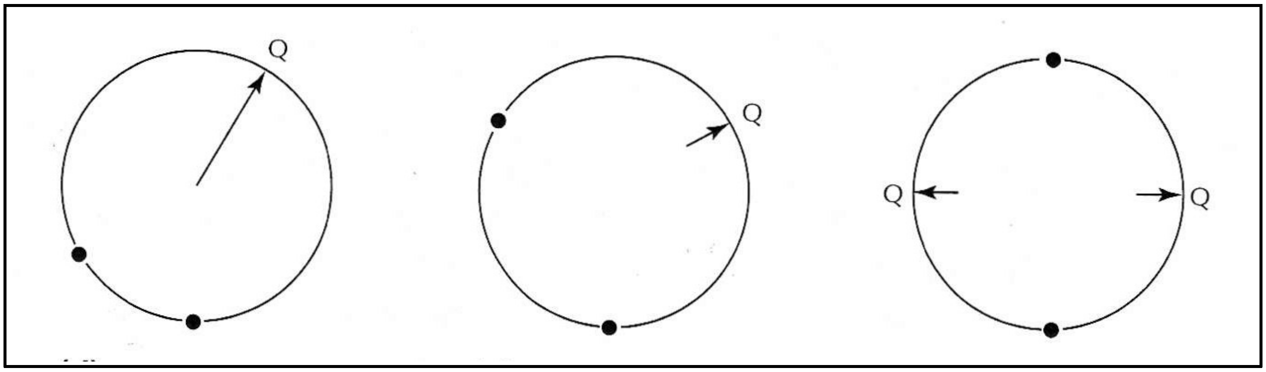
- This requirement (which has no theoretical proof) does not change the overall state of the system.

Pauli Exclusion Pinciple

- ☞ Corollary — Pauli Exclusion Principle: No two electrons with the same orbital (same n, l, m_l) may have the same spin states (i.e., one must be α, and one must be β).

- ☞ Corollary — No two electrons with the same spin can occupy the same point in space simultaneously.
  - If two electrons with the same spin occupied the same location, then interchanging their positions would not result in a sign change for the overall ψ.

- As shown by Lennard-Jones[1], same-spin electrons keep as far apart as possible, not because of their like charge, but because of the Pauli Principle. (Sometime called the "Pauli force", but not a real force.)
  - If two hypothetical uncharged particles with half-spin are confined to a ring, a third like particle will occupy a position opposite and equidistant from the first two.



- ☞ Electrons with the same spin in an atom or molecule keep as far away from each other as possible and have zero probability of being found at the same point in space.

---

[1] J. E. Lennard-Jones, *Adv. Sci.* **1954**, *11* (*54*), 136.

Pauli Principle and Coulombic Repulsions

- The Pauli Principle prohibits two electrons with the same spin from occupying the same point in space, but not two of opposite spin.

- Two electrons of opposite spin can occupy the same point in space, but unless compelled to do so by a force field Coulombic repulsions will generally prevent it.

- In a free atom the α set of electrons and the β set of electrons avoid interacting.

  > "There are two worlds that do not see each other in terms of the Pauli principle: the set of α electrons and the set of β electrons."[2]

- An α and β electron with the same spatial wave function, $\psi(n,l,m_l)$, are not occupying a single orbital with a certain orientation in space.

- Each electron in each set has its own wave function (its own orbital) with its own (not necessarily coincident) orientation.

---

[2] R. J. Gillespie & P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford, New York, 2001, p.66.

Electrons in a Free Atom

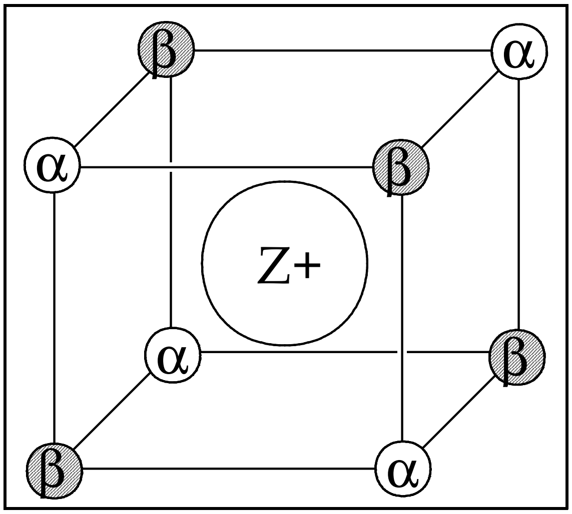
Consider the arrangement of electrons in space in a free atom with eight valence electrons (e.g., Ne, F^-, O^{2-}, N^{3-}).

Electrons in each set (4α and 4β) will have a tetrahedral average arrangement *relative to each other*, owing to the Pauli Principle.

Each tetrahedron has no orientation in space, so the overall electron density of each set is spherical.

Electrostatic repulsion keeps the tetrahedral α and β sets apart and reenforces the individual tetrahedra.

The most probable *relative* arrangements of the two spin sets has electrons occupying alternate corners of a cube.

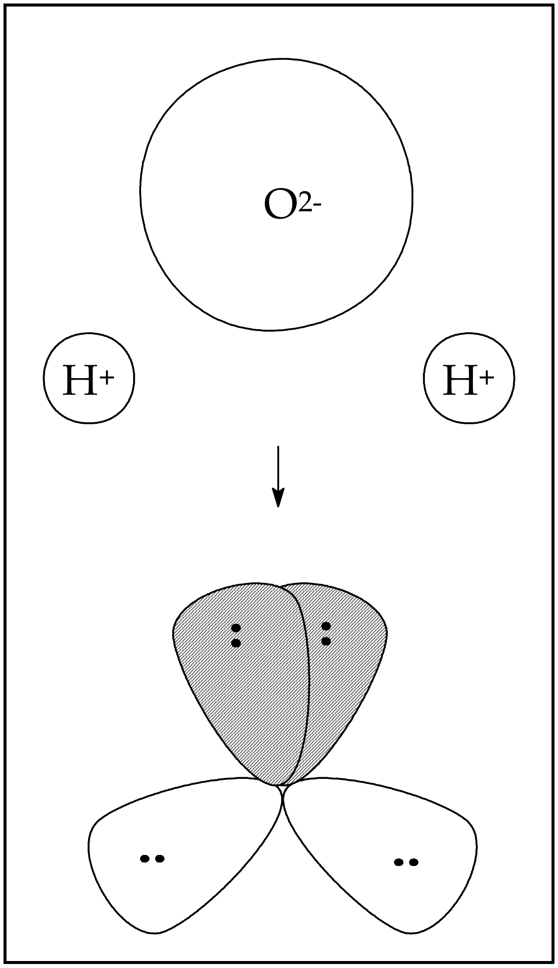


Because the cube has no specific orientation, the overall average electron density is spherical.

- ☞ There are no electron pairs in free atoms or ions!
- ☞ Electron pairing only occurs in molecules.

Electron Pairing in Molecules
H_2O

Electron pairing *can* occur in the central atom of a molecule *if* the pendant atoms attract the central atom electrons strongly enough to bring the α and β tetrahedra into approximate coincidence.



Four pairs (2 bond pairs and 2 lone pairs) are created by bringing the two tetrahedra together.

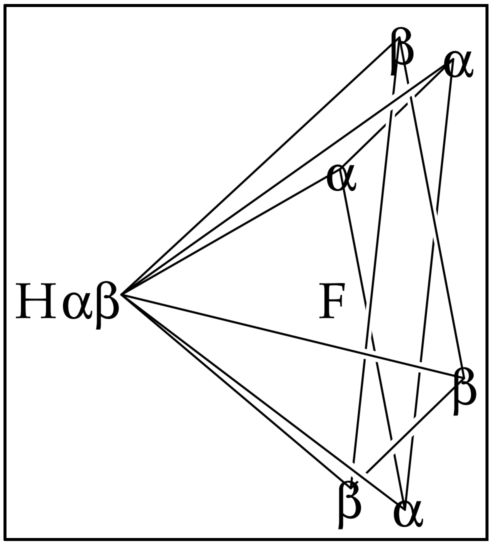
By the Pauli Principle, only α and β electrons can be brought into pairs.

Similar pair formation occurs in cases like NH_3 and CH_4.

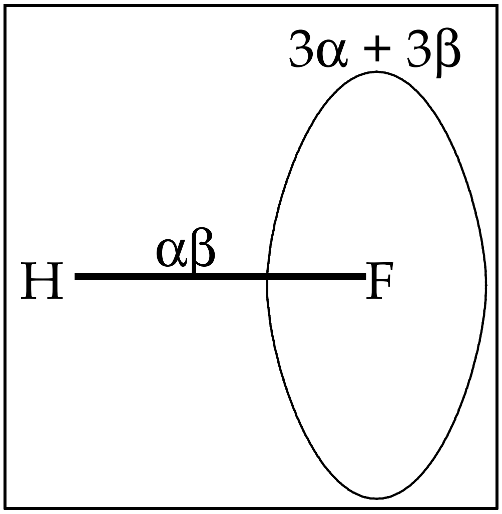
Linear Molecules

In a linear case like HF, only one α and one β electron are brought together to form a bond pair.

The α and β tetrahedra are free to rotate about the bond axis, so the remaining three electrons are not brought into coincidence.



They form a torus of electron density centered somewhat beyond the F^- nucleus.



☞ In linear molecules, non-bonding electrons are not brought together in pairs.

Electron Pairs in Molecules

If pendant atoms sufficiently polarize the electron density on a central atom, αβ pair formation may occur.

A region of space about a central atom occupied by one or more electron pairs defines a *domain* of electron density.

An electron domain constitutes a concentration of electron charge density in space.

For any number of electron domains about a central atom there is a preferred geometry, called the *domain geometry*, which can be deduced from a consideration of a points-on-a-sphere model.

Domains	Geometry	Domains	Geometry
2	linear	7	pentagonal bipyramid[3]
3	trigonal plane	8	square antiprism
4	tetrahedron	9	tricapped trigonal prism
5	trigonal bipyramid		
6	octahedron		

Recognition of the basic preferred geometry for a certain number of electron pairs grouped into domains of electron density forms the basis of the Valence Shell Electron Pair Repulsion Theory, also called the Electron Domain theory.

---

[3] Capped trigonal prism, capped octahedron, and pentagonal bipyramid have nearly the same energy, but all known examples appear to be pentagonal bipyramid.

Nyholm and Gillespies's
Valence Shell Electron Pair Repulsion Theory
(V.S.E.P.R. Theory)
or
Electron Domain Theory[4]
(E.D. Theory)

☞ Electrons in bonded atoms occupy spatially oriented orbitals in such a way as to minimize electron-electron repulsions arising from the Pauli principle and electrostatic (coulombic) forces.

- For every number of electron pairs about a central atom, each occupying a separate electron domain, there is a preferred arrangement that minimizes repulsions.

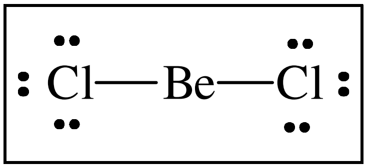
- The shape of a molecule is based on the preferred arrangement of electron pair domains.

---

[4] R. J. Gillespie. *J. Chem. Educ.* **1992,** *69*, 116.

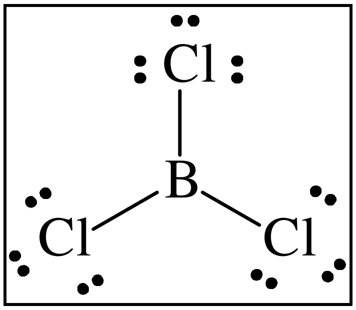
Basic Geometries for 2, 3, and 4 Electron Pairs

$BeCl_2$



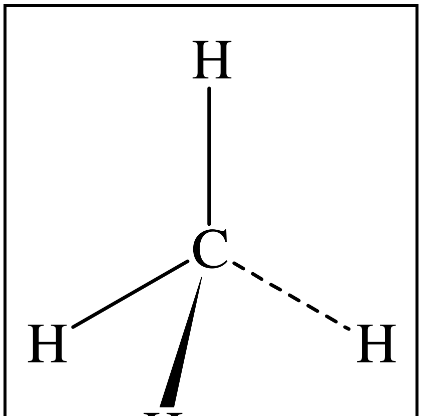
Two pairs minimize repulsions if oriented 180° from one another, giving a **linear** geometry.

BCl_3



Three pairs minimize repulsions if oriented 120° from one another, giving a **trigonal planar** geometry.

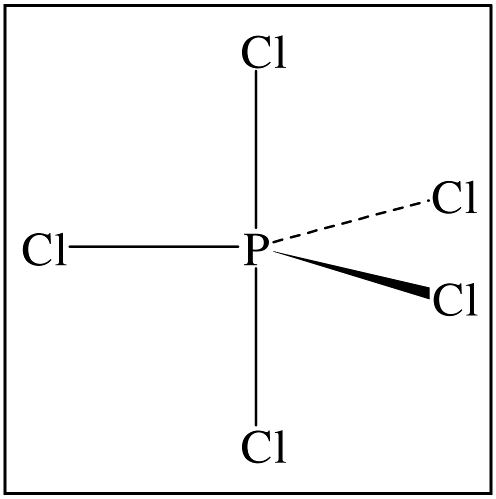
CH_4



Four pairs minimize repulsions if oriented 109.5° from one another, giving a **tetrahedral** geometry.

Basic Geometry for 5 Electron Pairs

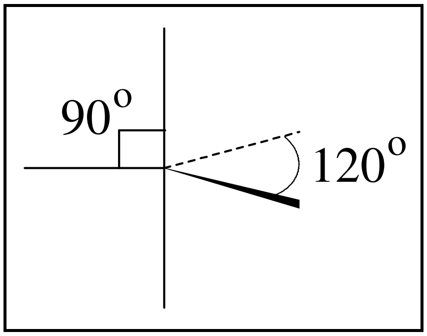
PCl_5



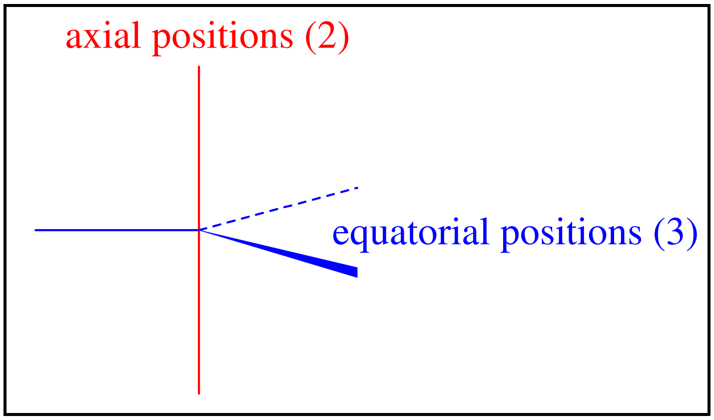
Five pairs minimize repulsions in a **trigonal bipyramidal** geometry.

Geometry of a Trigonal Bipyramid (*tbp*)

Two angles:



Two different kinds of positions:

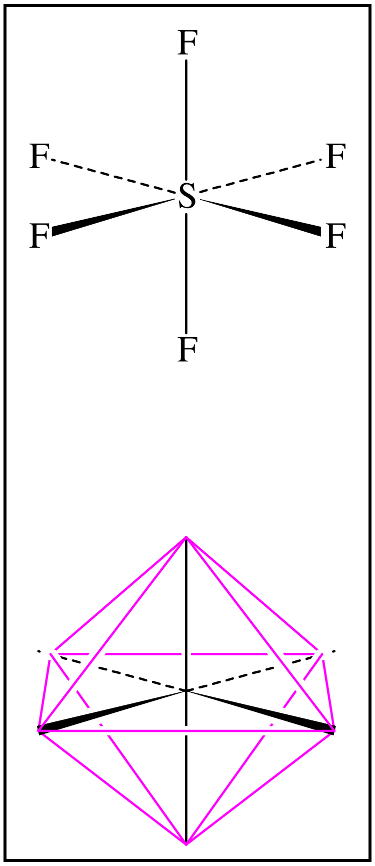


☞ The axial bonds are longer than the equatorial bonds.

- This difference in bond lengths is simply a consequence of geometry and cannot be explained by any orbital model.

Basic Geometry for 6 Electron Pairs

SF_6

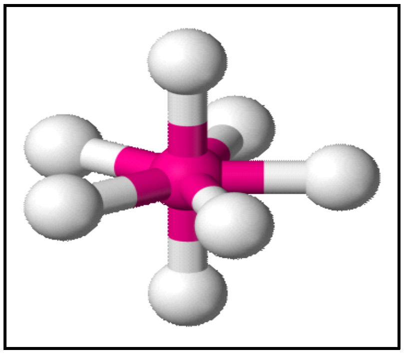


Six pairs minimize repulsions in an **octahedral** geometry.

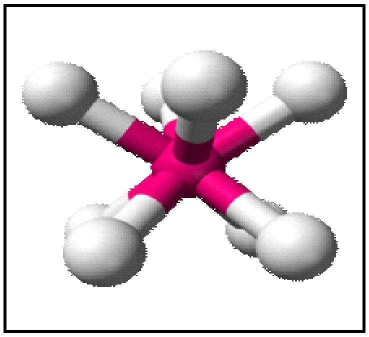
☞ All bond lengths are equivalent and form 90° or 180° angles to each other.

Shapes for CN7, CN8, CN9

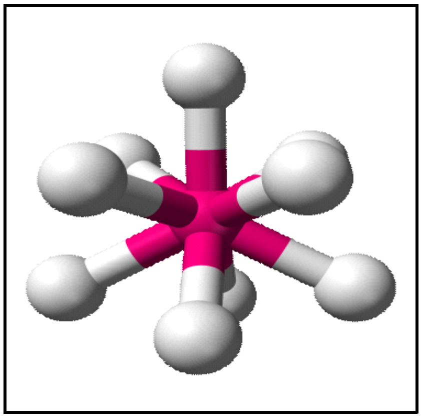
CN7: pentagonal bipyramid



CN8: square antiprism

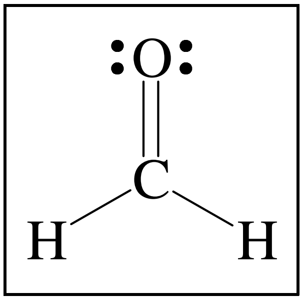


CN9: tricapped trigonal prism

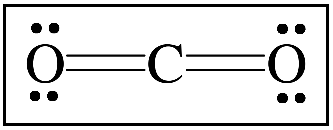


Double and Triple Bond Domains

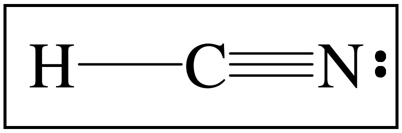
☞ Shape is determined by the number of *electron domains* (regions), not simply the number of electron pairs.



4 pairs in 3 regions
⇒ trigonal planar



4 pairs in 2 regions
⇒ linear

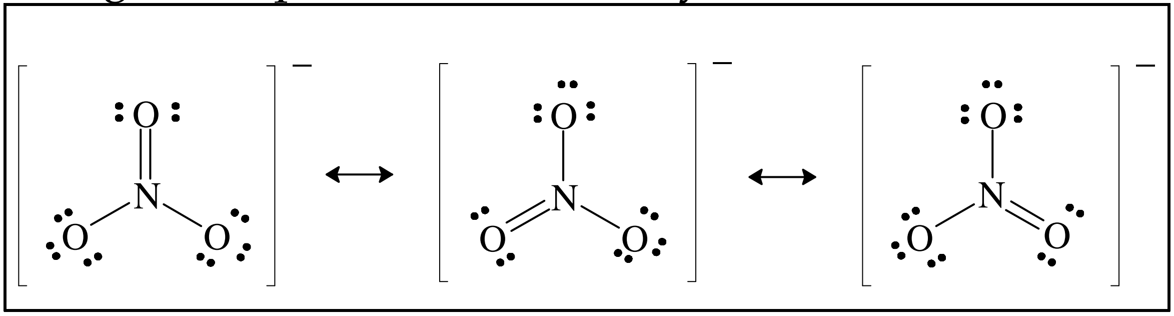


4 pairs in 2 regions
⇒ linear

Domains in Resonance Hybrid Molecules

☞ Molecules that in Lewis representation are resonance hybrids have domains that are defined by electron densities that are intermediate between single, double, or triple.

- Any individual resonance (canonical) form can be used to identify the number of domains and predict the gross shape, treating "multiple bonds" as if they were real.



4 pairs in 3 domains in any canonical form
⇒ trigonal planar

- All domains in NO_3^- are equivalent, being defined by 1⅓ electron pairs.

- All O–N–O bond angles in NO_3^- are 120°.

Molecules with Lone Pairs and Multiple Bonds

☞ Shape refers to the geometrical arrangement of the atoms relative to one another in a molecule, *not* to the idealized arrangement of electron domains.

- Molecules with non-bonding pairs on a central atom have shapes based on the arrangement of the electron domains, but bond angles may be altered by repulsions among lone pairs (l.p.) and bond pairs (b.p.), which diminish in strength in the order

  l.p.-l.p. > l.p.-b.p. > b.p.-b.p.

  (This is the original casting of VSEPR theory, but because Pauli repulsions are not real forces, it is preferable to understand this result on the basis of size and shape of electron pair domains.)

- Lone pairs have larger domains than bond pairs.

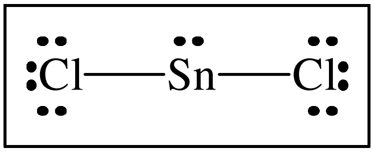
- Bonding domains decrease in size and occupy less space around a central atom with increasing electronegativity of the ligand and/or decreasing electronegativity of the central atom.

- Double-bond and triple-bond domains occupy increasingly greater space around a central atom, compared to single bonds.

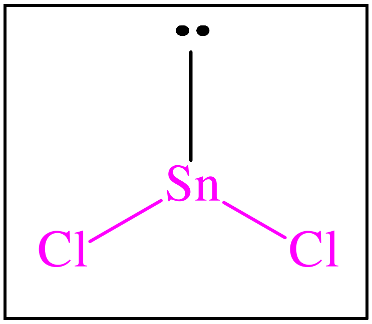
Three Electron Domains
AX_2E (2 b.p + 1 l.p.)

$SnCl_2$

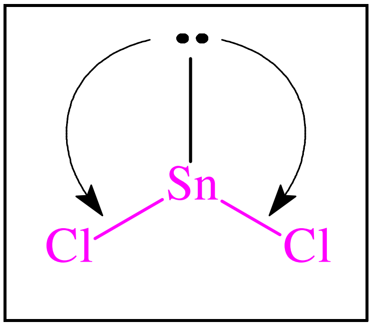
Lewis model:



Shape: **Bent**



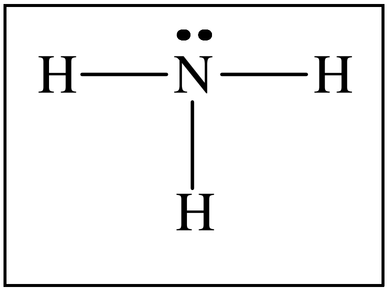
L.p.-b.p. repulsions cause the Cl-Sn-Cl angle to close to less than 120 ° (~95°).



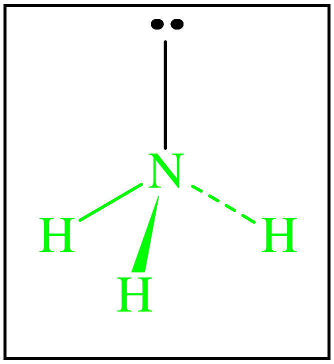
Four Electron Domains
AX_3E (3 b.p. + 1 l.p.)

NH_3

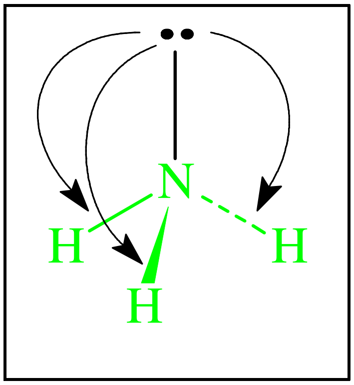
Lewis model:



Shape: **Trigonal pyramid**



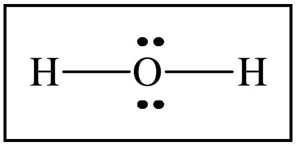
L.p.-b.p. repulsions cause the H-N-H angles to close to less than 109.5 ° (107.3 °).



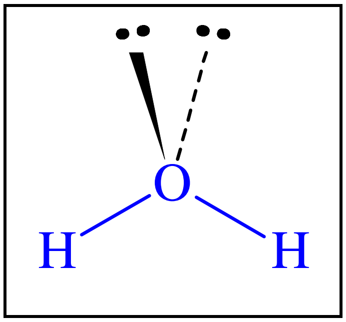
Four Electron Domains
AX_2E_2 (2 b.p. + 2 l.p.)

H_2O

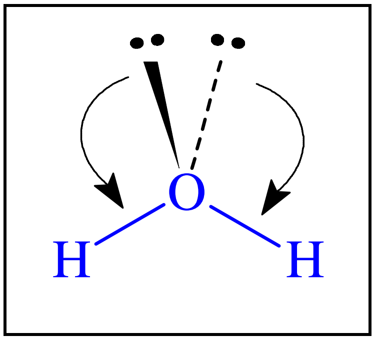
Lewis model:



Shape: **Bent**



L.p.-b.p. repulsions cause the H-O-H angle to close to less than 109.5 ° (104.5 °).

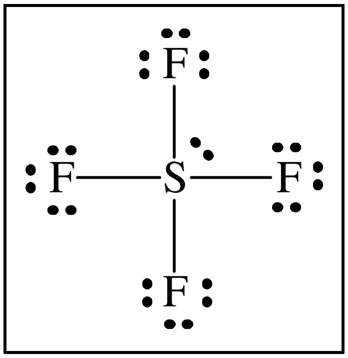


Five Electron Domains
AX$_4$E (4 b.p. + 1 l.p.)

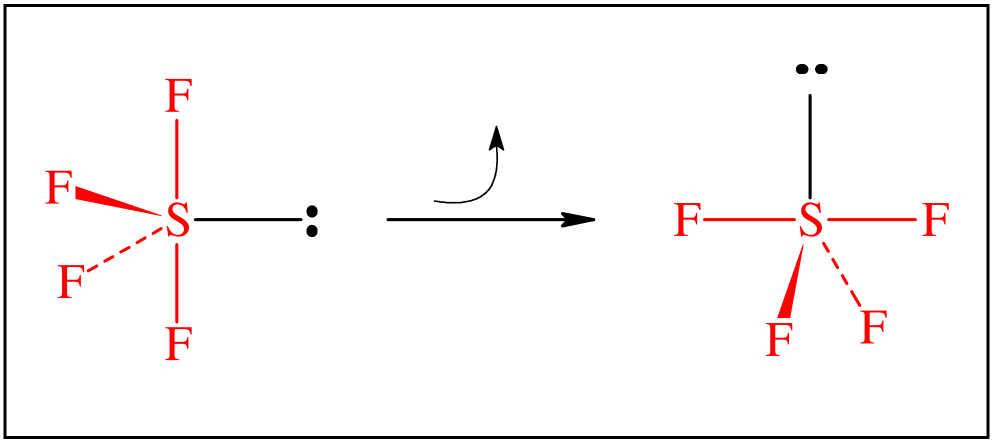
☞ Shapes of molecules based on a *tbp* geometry of electron domains (5 pairs) result from preferentially placing any lone pairs in equatorial positions.

SF$_4$

Lewis model:



Shape: **Irregular tetrahedron or disphenoid ("see-saw" shape)**



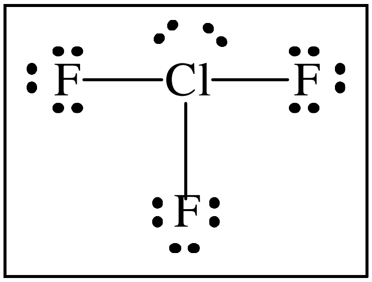
Note: Lone pair occupies an equatorial position of *tbp*.

L.p.-b.p. repulsions cause both F-S-F angles to close to less than 120° (101.6°) and 180° (167°) with bond lengths of 154.5 pm and 164.6 pm, respectively.

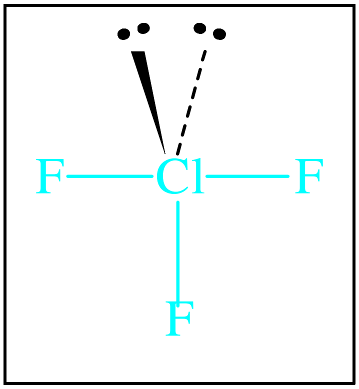
Five Electron Domains
AX_3E_2 (3 b.p. + 2 l.p.)

ClF_3

Lewis model:

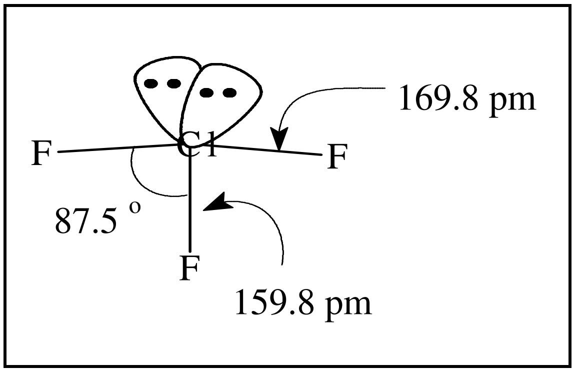


Shape: **T-shape**



Note: Lone pairs occupy equatorial positions of *tbp*.

L.p.-b.p. repulsions cause F-Cl-F angle to close to less than 90 ° (87.5°).

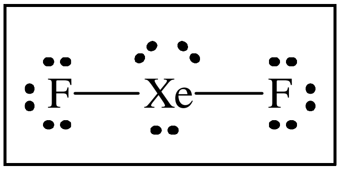


Five Electron Domains

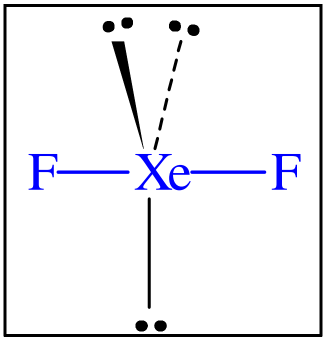
AX_2E_3 (2 b.p. + 3 l.p.)

XeF_2

Lewis model:



Shape: **Linear**



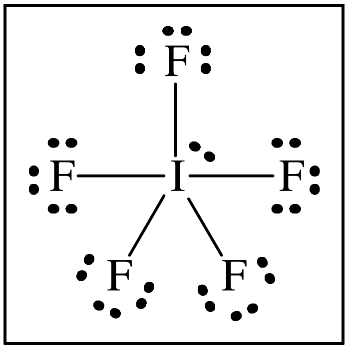
Note: Lone pairs occupy equatorial positions of *tbp*.

L.p.-b.p. repulsions *do not* cause angle distortions in this case, but rather enforce the linearity of the molecule. Bonds are equal length (197.7 pm).

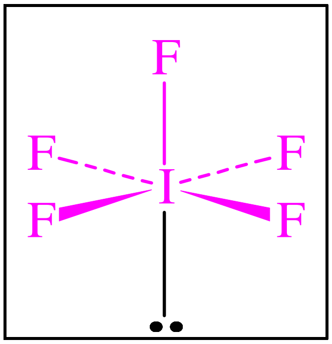
Six Electron Domains
AX_5E (5 b.p. + 1 l.p.)

IF_5

Lewis Model:



Shape: **Square Pyramid**

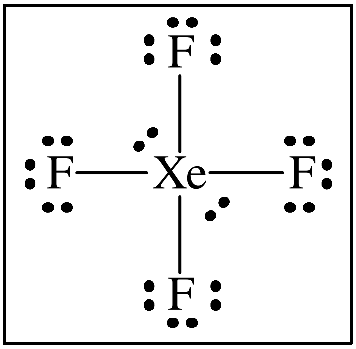


L.p.-b.p. repulsions cause the plane of the four basal F atoms to move slightly above the I atom, making the F-I-F angle between any basal F and the axial F less than 90° (81.5°). The four basal bonds are 186.9 pm, and the one axial bond is 184.4 pm.

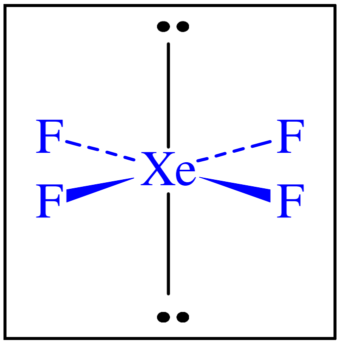
Six Electron Domains
AX_4E_2 (4 b.p. + 2 l.p.)

XeF_4

Lewis model:



Shape: **Square Planar**



Note: Lone pairs occupy opposite positions.

L.p.-b.p. repulsions *do not* cause angle distortions in this case, but rather enforce the planarity of the molecule. All bonds are equal (194 pm).

SHAPES OF AX_n MOLECULES BY V.S.E.P.R. THEORY

Electron Regions	Arrangement of Regions	Bond Domains[5]	Lone Pairs	Molecular Shape	Polar?[6]
2	linear	2	0	linear [AX_2]	No
3	trigonal planar	3	0	trigonal planar [AX_3]	No
		2	1	bent (<120°) [AX_2]	Yes
4	tetrahedral	4	0	tetrahedral [AX_4]	No
		3	1	trigonal pyramidal [AX_3]	Yes
		2	2	bent (<109.5°) [AX_2]	Yes
5	trigonal bipyramidal	5	0	trigonal bipyramidal [AX_5]	No
		4	1	irregular tetrahedron [AX_4]	Yes
		3	2	T-shaped [AX_3]	Yes
		2	3	linear [AX_2]	No
6	octahedral	6	0	octahedral [AX_6]	No
		5	1	square pyramid [AX_5]	Yes
		4	2	square planar [AX_4]	No

---

[5] A single, double, or triple bond constitutes one domain of electron density. Therefore, count bond domains around the central atom (i.e., the number of atom-pair linkages), not numbers of electron pairs. For this reason, the co-author of V.S.E.P.R. theory has renamed it the Electron Domain theory. [R. J. Gillespie. *J. Chem. Educ.* **1992,** *69*, 116.]

[6] Listed polarity is for *binary* compounds (AX_n) only. Composition of ternary (AX_nY_m) and higher compounds may result in polarity for a shape that might be nonpolar if the compound were binary.

VSEPR-Predicted Shapes for AX_n Molecules ($n = 2, 3, 4, 5, 6$)

Formula	Case	Shape	Example
AX_2	2 bonds + 0 lone pairs	linear	BeF_2
AX_2E	2 bonds + 1 lone pair	bent (<120°)	$SnCl_2$
AX_2E_2	2 bonds + 2 lone pairs	bent (<109.5°)	H_2O
AX_2E_3	2 bonds + 3 lone pairs	linear	XeF_2
AX_3	3 bonds + 0 lone pairs	trigonal planar	BF_3
AX_3E	3 bonds + 1 lone pair	trigonal pyramidal	NH_3
AX_3E_2	3 bonds + 2 lone pairs	T-shape	ClF_3
AX_4	4 bonds + 0 lone pairs	tetrahedral	CH_4
AX_4E	4 bonds + 1 lone pair	irregular tetrahedron	SF_4
AX_4E_2	4 bonds + 2 lone pairs	square planar	XeF_4
AX_5	5 bonds + 0 lone pairs	trigonal bipyramid (*tbp*)	PF_5
AX_5E	5 bonds + 1 lone pair	square pyramid	IF_5
AX_6	6 bonds + 0 lone pairs	octahedral	SF_6

Note: In this table, "bond" means a linkage between two atoms in a molecule. Thus a single-, double-, or triple-bond constitutes only one bond.

Effects of Lone Pairs on Bond Angle

In molecules with lone pairs, bond angles are smaller than the ideal values associated with a given number of equivalent pairs, and they decrease with number of lone pairs.[7]

- Smaller bond angles tend to be observed when the ligands are more electronegative than the central atom.

  NF_3 – 102.2° OF_2 – 103.1° PF_3 – 97.38° SF_2 – 98.2°

- Molecules with central N or O with less electronegative ligands tend to have *larger* bond angles, because the central atom valence electrons are not strongly polarized into pairs and ligand-ligand repulsions govern geometry.

  $N(CH_3)_3$ – 110.9° $(CH_3)_2O$ – 111.7° OCl_2 – 111.2°

- Hydrogen is less electronegative ($\chi_H = 2.2$) than N ($\chi_N = 3.1$) or O ($\chi_O = 3.5$), but NH_3 and H_2O have *smaller* bond angles, suggesting that the assumption of a constant electronegativity value of H is not valid.

  NH_3 – 107.2° H_2O – 104.5°

---

[7] R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, 2001, p. 95.

Bond Angle, Lone Pairs, and Central Atom Size

☞ The trend that bond angles “decrease with number of lone pairs” is not generally observed when comparing cases of different central atoms.

AX_3E	AX_2E_2	AX_3E	AX_2E_2
NF_3 102.2	OF_2 103.1	NCl_3 107.1	OCl_2 111.2
PF_3 97.8	SF_2 98.2	PCl_3 100.3	SCl_2 102.8
AsF_3 96.1	SeF_2 94	$AsCl_3$ 98.6	$SeCl_2$ 99.6
SbF_3 87.3	TeF_2 –	$SbCl_3$ 97.2	$TeCl_2$ 97.0

- Size of the central atom has a mitigating effect on the influence of number of lone pairs on bond angle.

☞ Bond angles tend to decrease with increasing central atom size.

Effect of Ligand Electronegativity

When a ligand is more electronegative than the central atom, it draws the bonding electron density away from the central atom so that the space occupied by the bonding domain in the valence shell of the central atom decreases with increasing difference in electronegativity between the ligand and the central atom.[8]

☞ Bond angles decrease with increasing electronegativity of the ligand or decreasing electronegativity of the central atom.

- Electronegativity decreases with increasing size for elements in the same group, so trends can be understood on the basis of either size or electronegativity.

AX_3E	AX_3E	AX_2E_2	AX_2E_2
NF_3 102.2	NCl_3 107.1	OF_2 103.1	OCl_2 111.2
PF_3 97.8	PCl_3 100.3	SF_2 98.2	SCl_2 102.8
AsF_3 96.1	$AsCl_3$ 98.6	SeF_2 94	$SeCl_2$ 99.6
SbF_3 87.3	$SbCl_3$ 97.2	TeF_2 –	$TeCl_2$ 97.0

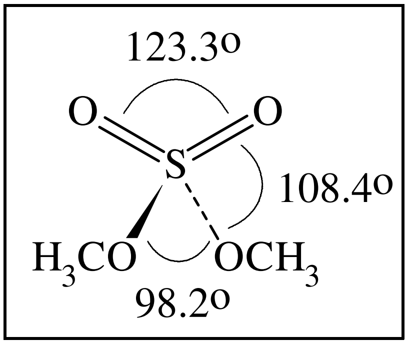
---

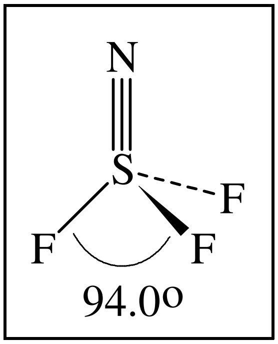
[8] Gillespie and Popelier, *ibid.*, pp. 98-99.

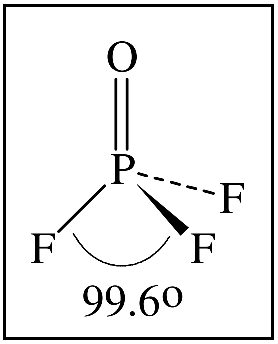
Molecular Geometry and Multiple Bonds

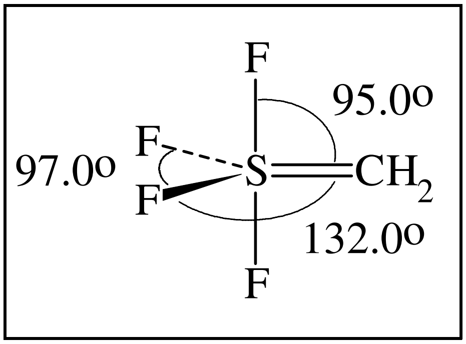
- A double or triple bond defines one electron domain for purposes of determining shape.

- Bond angles involving multiple bonds are larger in the order triple > double > single.









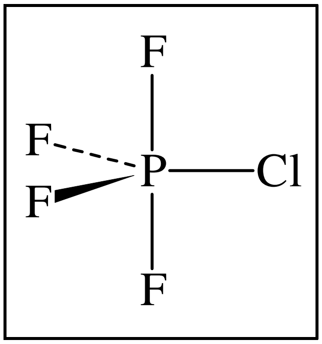
☞ Multiple bonds shown in these Lewis structures should not be taken too literally!

Special Consideration for *tbp* Domain Geometries

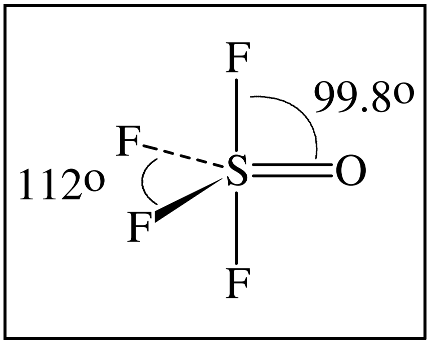
- Axial bonds are longer than equatorial bonds.

- Lone pairs in AX_4E, AX_3E_2, and AX_2E_3 cases occupy equatorial positions.

- With mixed ligands, less electronegative ligands occupy equatorial positions, and more electronegative ligands occupy axial positions.



- Multiple bonds always occupy the less crowded equatorial positions.

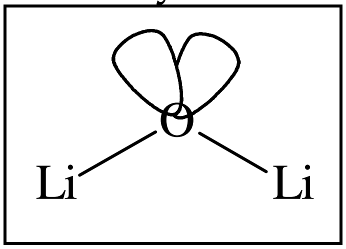


Limitations and Exceptions to VSEPR

- Large and/or low electronegativity ligands have larger bond angles.

$N(CH_3)_3$ – 110.9° $(CH_3)_2O$ – 111.7° OCl_2 – 111.2°

- Ligands that are not electronegative enough to polarize the central atom may not have expected VSEPR shape.



VSEPR prediction

Li——O——Li

ab initio prediction

- VSEPR largely ignores repulsive effects of ligands themselves.

- VSEPR cannot predict shapes of transition metal complexes, due to non-spherical cores of transition metals.

☞ Many of the shortcomings of VSEPR theory are overcome by the Ligand Close Packing (LCP) model.