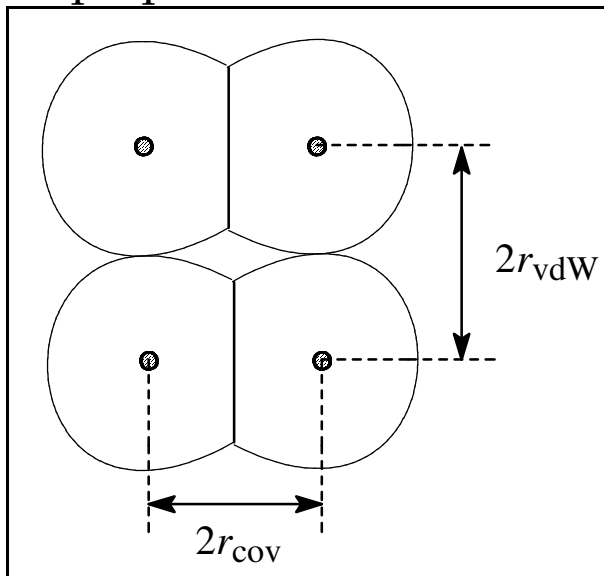


Ligand Close-Packing Model

- VSEPR is an *electronic* model for explaining molecular geometry.
- The Ligand Close-Packing (LCP) model is a *steric* model.
- ☞ The geometry of an AX_n molecule is that which allows the n ligands to approach as closely as possible to the central A atom, adopting a close-packed arrangement around A, thereby minimizing the energy of the molecule.

Atomic Dimensions in Molecules

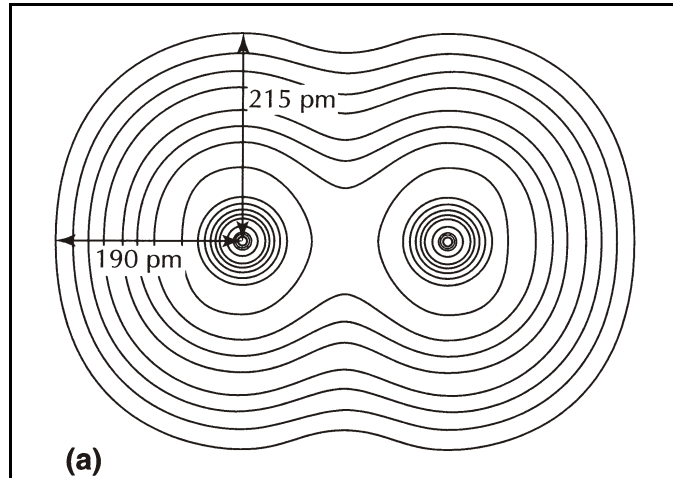
- To a first approximation, atoms in molecules have spherical shapes, truncated perpendicular to the bond line.



- ☞ The radius in a nonbonding direction is the van der Waals radius.
- The van der Waals radius is half the distance between identical nuclei on adjacent molecules at equilibrium.
- Definition of van der Waals radius assumes spherical shape except in bonding direction and essentially incompressible atoms.
- ☞ Atoms in molecules are not truly spherical and are not incompressible.
- Based on the electron density about an atom, there can be two or more van der Waals radii.

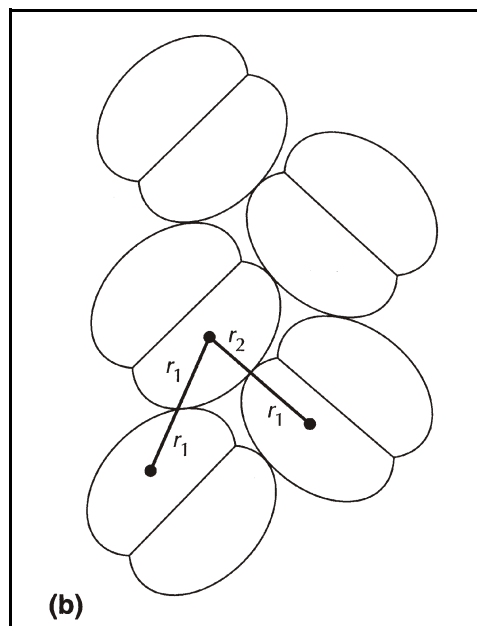
Electron Contour Map of Cl₂

- Non-spherical electron density results in a maximum ($r_1 = 215$ pm) and minimum ($r_2 = 190$ pm) value for the Cl van der Waals radius in free Cl₂.



Outer contour defined by $\rho = 0.001$ au.

- The non-spherical profile of Cl atoms in Cl₂ affects the packing of molecules in the solid state.



- ✓ Molecules are compressed together in the solid, making smaller van der Waals radii: $r_1 = 171$ pm, $r_2 = 157$ pm.

van der Waals Radii

- ☞ The concept of a constant, single van der Waals radius for an element is a gross simplification.
- Tabulated values are rarely accurate to better than ± 5 pm.
- For some elements values vary considerably from different sources (e.g., F, 150-160 pm; Cl, 170-190 pm).

Selected van der Waals Radii and Calculated Atomic Radii (pm)^a

Element	r_{vdW}	r_{atom}
H	120	134
C	170 ^b	173
N	150	162
O	140	154
F	135	147
Si	210 ^b	212
P	190	203
S	185	197
Cl	180	189

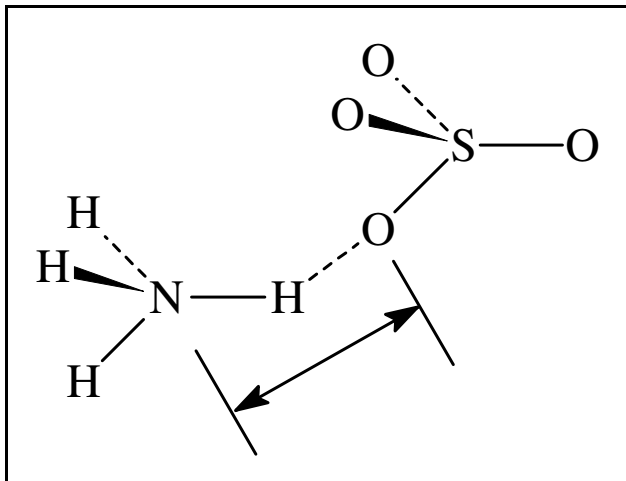
a. Values from Gillespie & Popelier, *ibid.*, p. 115, except as noted. Atomic radii calculated from electron densities for the isolated gas atom.

b. Values of A. J. Bondi, *J. Phys. Chem.* **1964**, 68, 441.

- ✓ Cl r_{vdW} value pertains to *bonded* Cl, which is larger than r_1 and r_2 for solid Cl_2 , owing to Cl's high electronegativity.

Use of van der Waals Radii

- ☞ Despite limitations, van der Waals radii are frequently used to suggest bonding interaction between atoms when the experimentally determined distance between them is substantially less than the sum of the van der Waals radii.
- Hydrogen bonding in solids is suggested when two electronegative atoms, one with covalently bonded H, approach closer than the sum of their van der Waals radii.

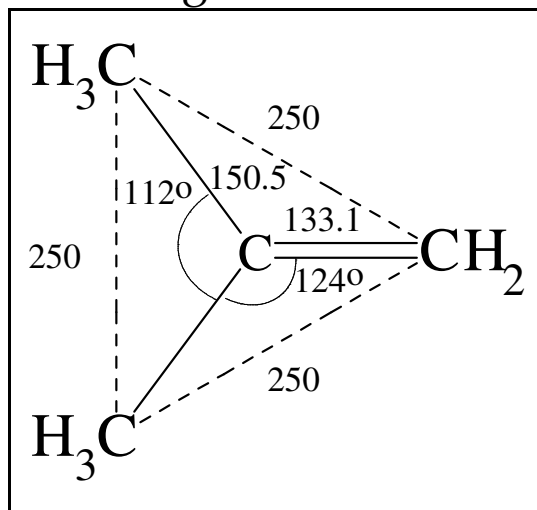


$$d_{\text{NO}} \ll r_{\text{N}} + r_{\text{O}} = 290 \text{ pm}$$

- H scatters x-rays too weakly to be located in most structure determinations.

Interactions of Geminal Ligands

- Repulsions between two ligands attached to the same atom (*geminal* ligands) can be important in determining bond lengths and angles.
- ✓ In 1960, Bartell and Bonham¹ showed that the three terminal carbons in 2-methylpropene form an equilateral triangle, despite differences in single and double bond lengths.



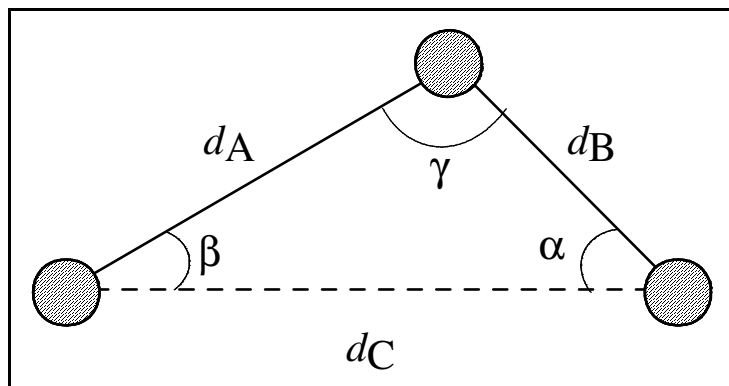
- Suggests that terminal carbons are close-packed about central carbon (steric effect).
- Shorter C-C distance (cf. $d = 154$ pm) due to closer approach possible in trigonal planar arrangement than tetrahedral.
- ✓ Bartell was able to determine radii to account for internuclear distances between substituents in ethenes and ketones.
- ✓ Work was extended by Glidewell², who called these *1,3 radii*.

¹L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **1960**, 32, 624.

²C. Glidewell, *Inorg. Chim. Acta* **1975** 12, 219; *Inorg. Chim. Acta* **1976** 20, 113.

Trigonometry of Three Bonded Atoms

- ☞ Two atoms bonded to a third atom in general define an obtuse triangle, whose inter-atomic distances and angles are given by the Law of Cosines.



$$d_C = \sqrt{d_A^2 + d_B^2 - 2d_A d_B \cos\gamma}$$

and

$$\gamma = \arccos\left(\frac{d_A^2 + d_B^2 - d_C^2}{2d_A d_B}\right)$$

- ☞ If $d_A = d_B$ (isosceles triangle),

$$d_C = \sqrt{2d_A^2(1 - \cos\gamma)} = 2d_A \sin(\gamma/2)$$

and

$$\gamma = \arccos\left(1 - \frac{d_C^2}{2d_A^2}\right) = 2\arcsin\left(\frac{d_C}{2d_A}\right)$$

- ☞ In either case, d_C is ideally the sum of the 1,3 radii of the two geminal atoms.

1,3 Radii, van der Waals Radii, and Atomic Radii

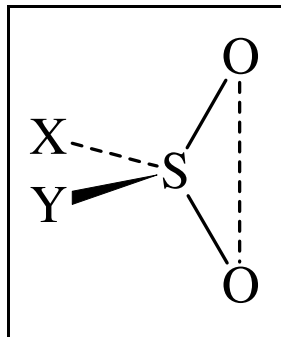
- ☞ Bartell and Glidewell's 1,3 radii are smaller than either van der Waals radii or isolated gas phase atomic radii, because bonding to a central atom draws the geminal atoms together against each other (i.e., compresses them).³

Element	r_{vdW}	r_{atom}	$r_{1,3}$
H	120	134	92
C	170	173	125
N	150	162	114
O	140	154	113
F	135	147	108
Si	210	212	155
P	190	203	145
S	185	197	145
Cl	180	189	144

³Data for 1,3 radii from Gillespie and Popelier, *ibid.*, p. 115.

Problems with the Bartell-Glidewell 1,3 Radii

- ☞ Distances between geminal atoms, particularly when bonded to elements other than C, often show poor agreement with the sums of 1,3 radii.

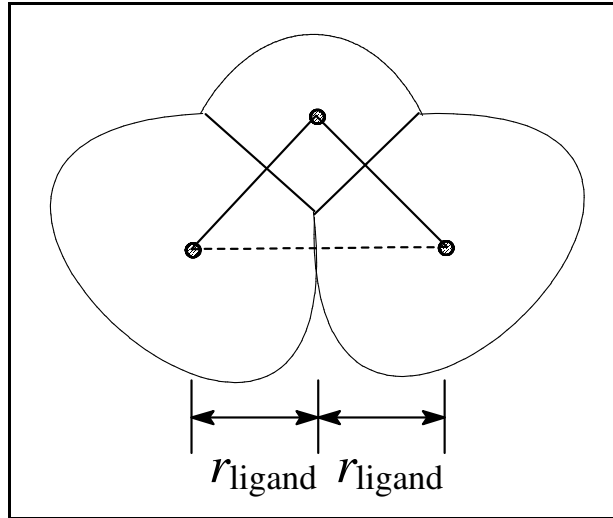


$$d_{\text{O-O}} = 248 \text{ pm} \gg 2r_{\text{O}} = 226 \text{ pm}$$

- ✓ Hargittai⁴ found a relatively constant O-O distance of 248 pm in XYSO_2 compounds, significantly greater than twice the 1,3 radius of oxygen ($2 \times 113 \text{ pm} = 226 \text{ pm}$).
- ☞ The effective radius of a ligand atom depends on the nature of the atom to which it is attached.
- Notion of a constant 1,3 radius is too simple.

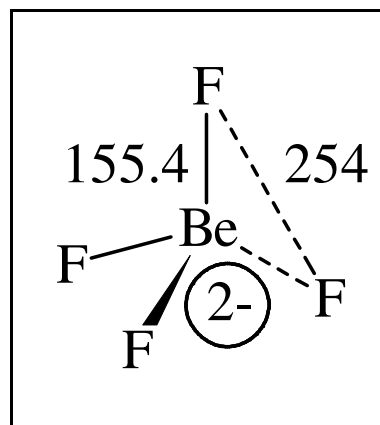
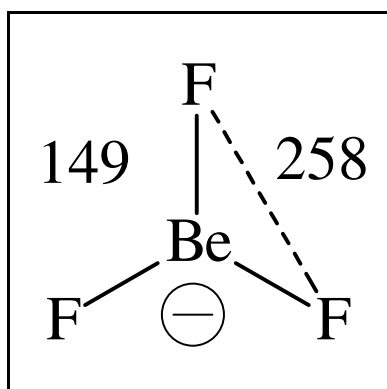
⁴I. Hargittai, *The Structure of Volatile Sulphur Compounds*, Reidel, Dordrecht, 1985.

Ligand Close-Packing (LCP) Model

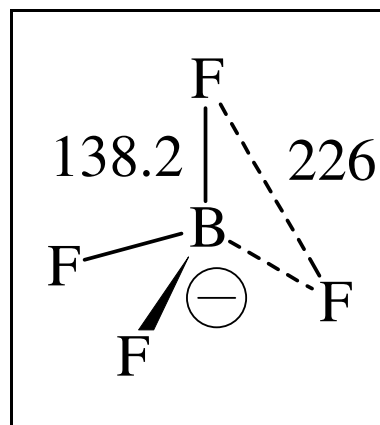
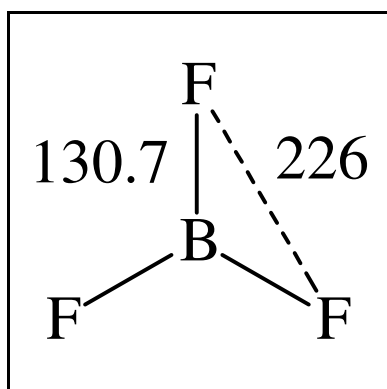


- Gillespie and Robinson developed LCP model beginning in 1997.
- Based on observation of a relatively constant $X\cdots X$ distance in many AX_n compounds, where A and X are specific elements.
- $X\cdots X$ distance is relatively constant even with changing coordination number about A.
- Each ligand is assumed to be touching its neighbor and can be assigned a nonbonded intermolecular ligand radius, called a *ligand radius* for simplicity.
- Bond distances and angles about A result from the relatively constant $X\cdots X$ nonbonding distance maintained by the ligands.

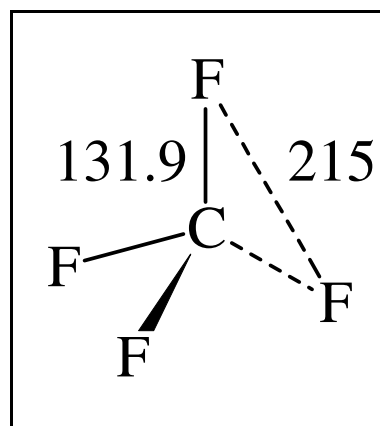
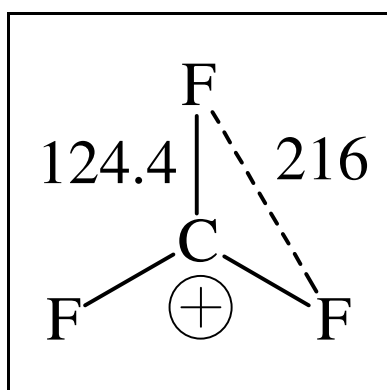
Examples of CN3 and CN4 Molecules with F Ligands



Average $r_F = 128$ pm



Average $r_F = 113$ pm



Average $r_F = 108$ pm

Data Related to Fluorine Ligand Radii⁵

Molecule	CN	A-F (pm)	∠F-A-F (°)	F...F (pm)
BeF ₃ ⁻	3	149	120	258
BeF ₄ ²⁻	4	155.4	109.5	254
			Mean	256
F ₃ B	3	130.7	120	226
F ₂ B-OH	3	132.3	118.0	227
F ₂ B-NH ₂	3	132.5	117.9	227
F ₂ B-Cl	3	131.5	118.1	226
F ₂ B-H	3	131.1	118.3	225
F ₄ B ⁻	4	138.2	109.5	226
F ₃ B-CH ₃ ⁻	4	142.4	105.4	227
F ₃ B-CF ₃ ⁻	4	139.1	109.9	228
F ₃ B-PH ₃	4	137.2	112.1	228
			Mean	226
CF ₃ ⁺	3	124.4	120	216
F ₂ C=CF ₂	3	131.9	112.4	219
F ₂ C=CCl ₂	3	131.5	112.1	218
F ₂ C=CH ₂	3	132.4	109.4	216
F ₂ C=CHF	3	133.6	109.2	218
F ₄ C	4	131.9	109.5	215
F ₃ C-CF ₃	4	132.6	109.8	217
F ₃ C-OF	4	131.9	109.4	215
F ₃ CO ⁻	4	139.2	101.3	215
			Mean	216

⁵Gillespie & Popelier, *ibid.*, p. 119.

Ligand Radii with Different Central Elements^{6,7}

(Revised values for H in blue.)

Ligand	Central Atom			
	Be	B	C	N
H	—	102	94 (CN3)	82
			89 (CN4)	
C	—	137	125	120
N	144	124	119	—
O	133	119	114	—
F	128	113	108	108
Cl	168	151	144	142

⁶Gillespie & Popelier, *ibid.*, p. 121; former values of H with B (110 pm) and C (90 pm) replaced with data of ref. 7.

⁷Revised values for ligand H with central B and C from E. A. Robinson & R. J. Gillespie, *Inorg. Chem.* **2004**, *43*, 2318-2323.

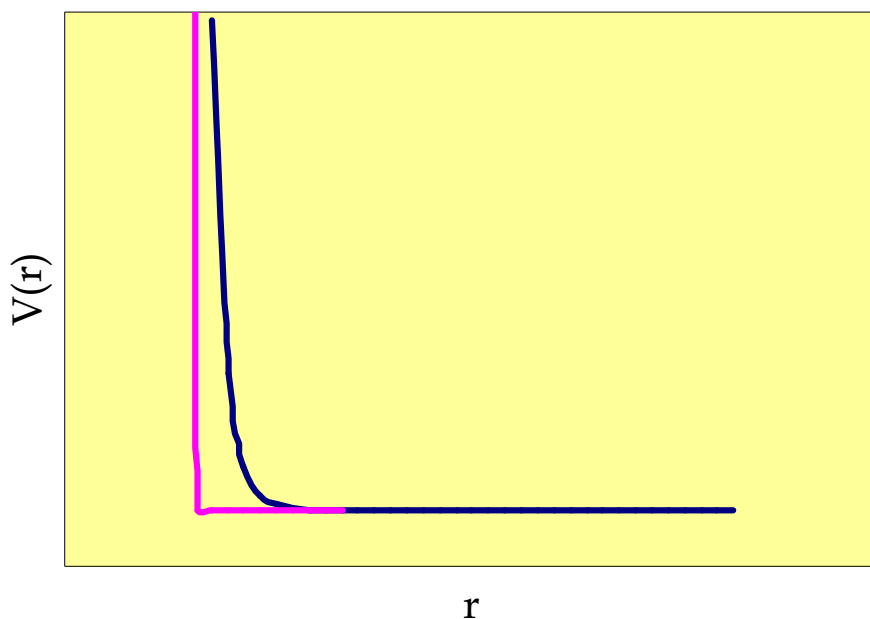
Trends in Ligand Radii

- With less electronegative central atom A, ligand X acquires more electron density (more negative charge), resulting in a larger ligand radius.
- ☞ The ligand radius of a given ligand X decreases as the electronegativity of the central atom A increases (from left to right across the periodic table).
- H ligand radius with central C depends on coordination number, because the ligands *are* close-packed with CN4 but apparently *are not* quite closed packed with CN3.
- H ligand radius with B is independent of coordination number, because boron's low electronegativity makes ligand H bigger, thereby allowing H...H contact for both CN3 and CN4.
- All cases of H bonded to N are CN4 (AX_4 or AX_3E), show relatively constant H...H distances, and presumably have close-packed H ligands.
- Constancy of ligand radius for a given ligand with a given central atom suggests that the ligands are at the limit of their compressibility.

Hard Atom Approximation

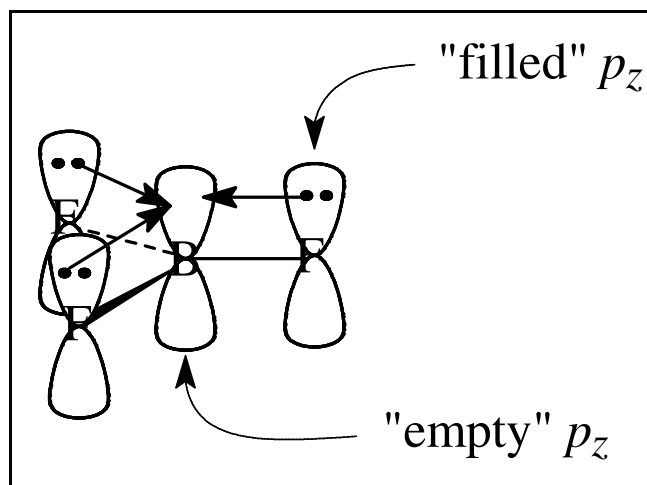
- Ligands bonded to a given central atom act as if they were hard objects that are close-packed.
- “Hardness” of a bonded atom is a consequence of the repulsive potential between two atoms, which is approximated by a function of the form $V = C/r^{12}$.

Repulsive Potential Between Two Non-Bonding Atoms



Bond Length and Coordination Number

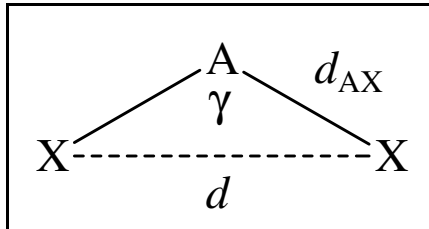
- CN2, with linear geometry, does not involve close packing (i.e., no compression), so A-X length represents a reference “natural” bond length between the two atoms.
- With higher coordination (CN3, CN4, ...), ligand-ligand repulsions prevent X from assuming the shorter “natural” distance from A.
- ☞ Bond lengths for a given A-X bond increase with coordination number.
- Steric model gives a simpler explanation for the shorter bond length in BF_3 (130.7 pm) versus BF_4^- (138.2 pm), without invoking the concept of “back-bonding” between “empty” p_z on B with “filled” p_z orbitals on pendant F atoms.



Back-bonding Model of BF_3

Why Must Bond Length Increase with Coordination?

- Compare AX_3 ($\gamma = 120^\circ$) with AX_4 ($\gamma = 109.5^\circ$), assuming a constant interligand distance $X \cdots X$ of d . What are the A-X bond lengths, d_{AX} , in each case?



- Solving the Law of Cosines for d_{AX}

$$d_{AX} = \frac{d}{2 \sin(\gamma/2)}$$

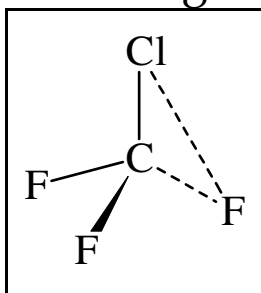
- For CN_3 , $d_{AX3} = 0.57735d$, and for CN_4 , $d_{AX4} = 0.61226d$. Thus, the calculated ratio is $d_{AX4}/d_{AX3} = 1.0605$.

Observed d_{AX4}/d_{AX3} for CN_4 and CN_3 AF_n Compounds

AX_4	d_{AX4} (pm)	AX_3	d_{AX3} (pm)	d_{AX4}/d_{AX3}
BeF_4^{2-}	155.4	BeF_3^-	149	1.04 ₃
BF_4^-	138.2	BF_3	130.7	1.057
CF_4	131.9	CF_3^+	124.4	1.060

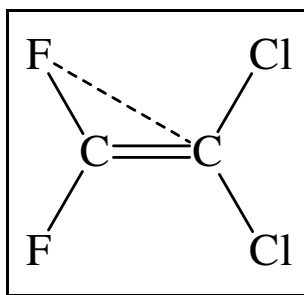
Molecules with Mixed Ligands

- ☞ Interligand distances between two different ligands are given to a very good approximation by the sum of the appropriate ligand radii; i.e., $d_{X...Y} \approx r_X + r_Y$.
- ☞ X...Y distances remain constant in mixed-ligand molecules despite considerable differences in bond lengths and bond angles.
- ☞ Effect of Y on bond angles results from different size of Y and different A-Y bond length.



Observed: $d_{\text{Cl}\dots\text{F}} = 254 \text{ pm}$, $d_{\text{C-Cl}} = 175.1 \text{ pm}$, $d_{\text{C-F}} = 132.8 \text{ pm}$
 $\angle \text{Cl-C-F} = 110.4^\circ$

Calculated: $r_{\text{Cl}} + r_{\text{F}} = (144 + 108) \text{ pm} = 252 \text{ pm}$
 $\angle \text{Cl-C-F} = 109.1^\circ$

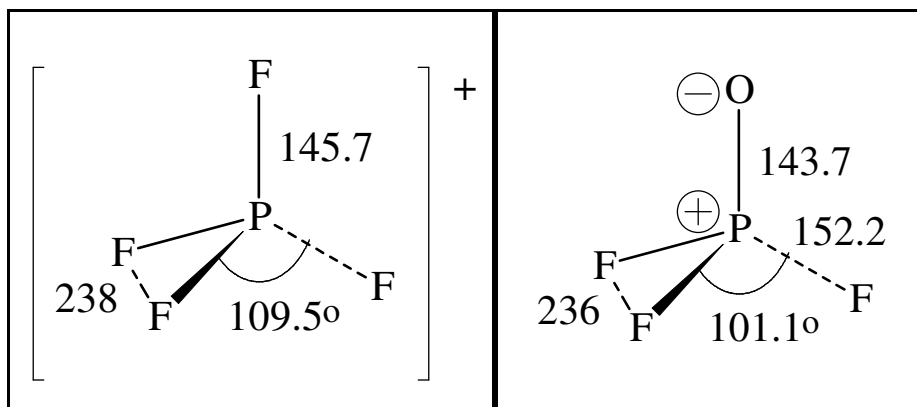
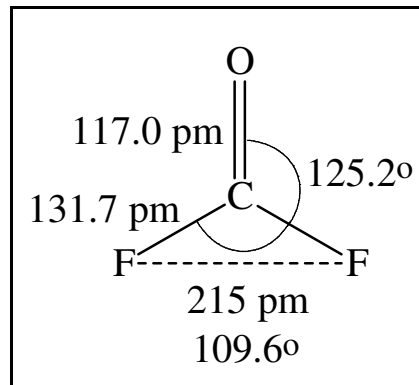
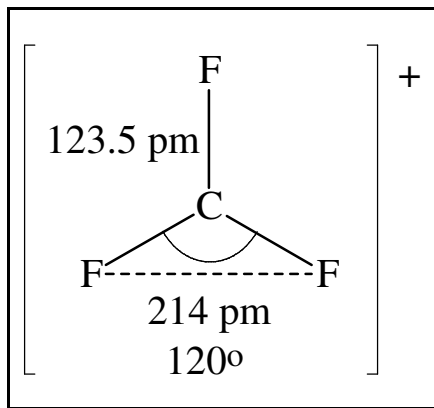


Observed: $d_{\text{C}\dots\text{F}} = 235 \text{ pm}$, $d_{\text{C-C}} = 132.5 \text{ pm}$, $d_{\text{C-F}} = 131.5 \text{ pm}$
 $\angle \text{F-C-C} = 124.1^\circ$

Calculated: $r_{\text{C}} + r_{\text{F}} = (125 + 108) \text{ pm} = 233 \text{ pm}$
 $\angle \text{F-C-C} = 122.3^\circ$

Effect of Shorter Bond on Bond Angle

- Largest effect on bond angle occurs when a ligand is replaced by another ligand of comparable size that forms shorter bonds.



- Ligands with short bonds push away ligands with longer bonds, increasing the angle between short and long bonds, while decreasing the angle between long bonds.

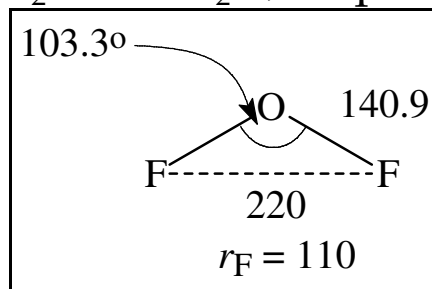
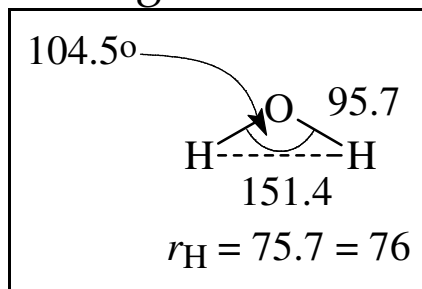
Note : $\text{F}\cdots\text{F}$ distances in PF_4^+ and F_3PO are nearly the same, but in F_3PO the shorter PO bond results in longer PF bonds.

LCP Approach to Molecules with Lone Pairs

- A central atom with lone pairs, which is surrounded by some number of ligands, is not spherical, but rather is polarized to form bond pair and lone pair regions of electron density.
- ☞ Lone pairs act as pseudoligands, spreading out as much as possible and pushing the real ligands into close-packed contact.
- LCP model, with assumption of nearly constant interligand distance, allows quantitative prediction of bond angles when bond lengths are known.

Understanding Small Bond Angle of HOF and HOCl⁸

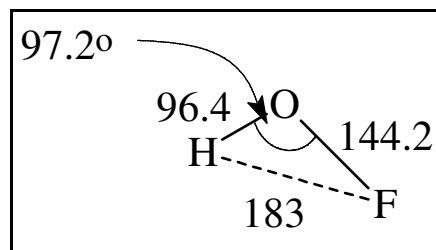
- Ligand radii of H and F with O can be estimated from interligand distances in H₂O and F₂O, respectively.



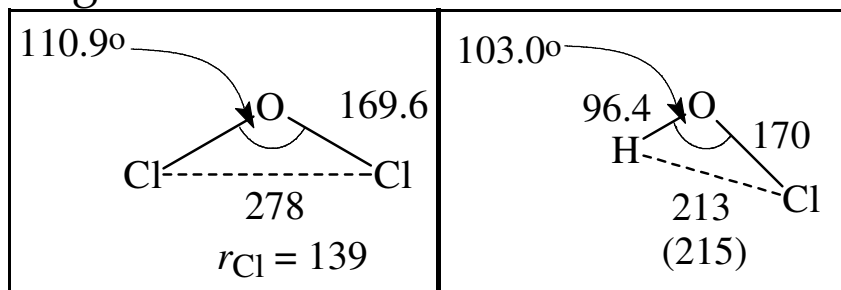
- Predicted interligand distance in HOF is

$$r_H + r_F = (76 + 110) \text{ pm} = 186 \text{ pm}$$

- Actual interligand distance is close to this (183 pm). Given similar bond lengths, the angle is predicted to be smaller than either H₂O or F₂O.



- Similar argument can be made for HOCl.



⁸Data from Table 6 of E. A. Robinson & R. J. Gillespie, *Inorg. Chem.* **2004**, 43, 2318.

Weakly Electronegative Ligands

- With weakly electronegative ligands, central atoms are not well localized into electron pair domains.
 - Bonds are essentially ionic.
 - VSEPR model does not predict shapes.
- Geometries with such ligands are determined by ligand-ligand repulsions.

Examples: linear LiOH and Li₂O

- Bond angles in OX₂E₂ and NX₃E molecules are larger than 109.5° in cases where ligands do not effectively localize electrons on the central atom and in which ligand-ligand interactions govern geometry.

Molecule	∠X-N-X (°)	Molecule	∠X-O-X (°)
NF ₃	102.3	F ₂ O	103.3
NCl ₃	106.8	H ₂ O	104.5
NH ₃	107.2	Cl ₂ O	110.9
N(CH ₃) ₃	110.9	(CH ₃) ₂ O	111.7
N(CF ₃) ₃	117.9	(SiH ₃) ₂ O	144.1
N(SiH ₃) ₃	120.0	((CH ₃) ₃ Si) ₂ O	148
		Li ₂ O	180

Ligand-Ligand Interactions in Molecules with Central Atoms in the Higher Periods (3, 4, ...)

- Central atoms in higher periods are larger, so interligand distances are generally larger.
- Ligands are more compressible with these elements, so ligand radii are less constant.
 - Smallest values occur with CN₆, where ligands are close to the limit of their compressibility.

Ligand Radii (pm) with Some Period 3 Central Elements⁹

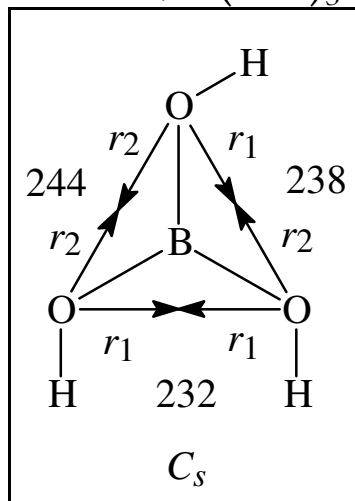
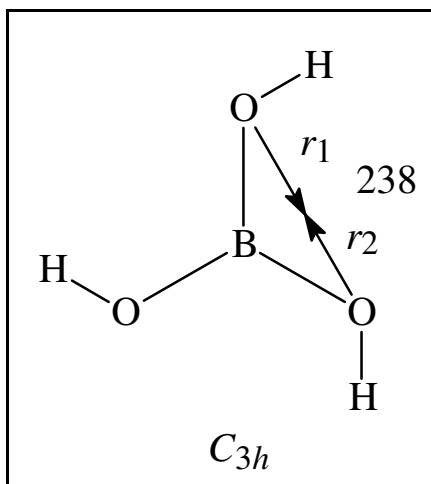
Ligand	CN 6				CN 4			
	Al	Si	P	S	Al	Si	P	S
F	128	120	111	110	135	127	120	118
Cl	160	151	148	145	172	160	156	155
O	134	132	126	121	140	132	126	124

⁹Data of Gillespie & Popelier, *ibid.*, p. 130.

Polyatomic Ligands

- Monatomic or linear ligands have a single ligand radius (e.g., Cl, CN).
- Nonlinear polyatomic ligands (e.g., OH), in which the electronic distribution about the attaching atom is not spherical, may have more than one ligand radius, depending on the direction of interaction.

Example: Geometrical isomers of boric acid, $B(OH)_3$



Ligand radius on the lone-pair side of OH is larger than on the bond-angle side (i.e., $r_1 < r_2$).

Comparison of VSEPR and LCP Models

- VSEPR and LCP are complimentary models.
- Both predict same general geometry for cases where ligands localize central atom valence electrons into pairs.
- LCP provides a better understanding of bond angles, which is nearly quantitative with second period central atom molecules.
- LCP can predict geometry of molecules for which VSEPR does not apply.