

Lecture 2; CH 101: Inorganic Chemistry

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Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																				
1 H Hydrogen 1.00794	2 He Helium 4.002602	3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 Na Sodium 22.98976928	6 Mg Magnesium 24.3050	7 Alkali metals	8 Alkaline earth metals	9 Lanthanoids	10 Transition metals	11 Poor metals	12 Other nonmetals	13 Noble gases	14 Metals	15 Nonmetals	16 K Potassium 39.0983	17 Ar Argon 39.948	18 Kr Krypton 83.798																																																				
1 C Solid	2 Hg Liquid	3 H Gas	4 Rf Unknown	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797	11 S Sulfur 32.065	12 P Phosphorus 30.973762	13 Se Selenium 78.96	14 Br Bromine 79.904	15 As Arsenic 74.92180	16 Se Selenium 78.96	17 Kr Krypton 83.798	18 Xe Xenon 131.293	19 Zr Zirconium 91.224																																																			
20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.887	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.548	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92180	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Tl Thallium 118.710	51 Sn Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.50447	54 Xe Xenon 131.293	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57-71 89-103	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.9866569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)	87 Fr Francium (223)	88 Ra Radium (226)	104 Rf Rutherfordium (281)	105 Db Dubnium (282)	106 Sg Seaborgium (286)	107 Bh Bohrium (284)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium (294)	118 Uuo Ununoctium (294)
57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.984	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92353	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9686	72 Ac Actinium (227)	73 Th Thorium 232.03606	74 Pa Protactinium 231.03588	75 U Uranium 238.02691	76 Np Neptunium (237)	77 Pu Plutonium (244)	78 Am Americium (243)	79 Cm Curium (247)	80 Bk Berkelium (247)	81 Cf Californium (251)	82 Es Einsteinium (252)	83 Fm Fermium (257)	84 Md Mendelevium (258)	85 No Nobelium (259)	86 Lr Lawrencium (262)																																								

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Molecular Structure & Bonding

- Lewis Structures

Covalent bond: formed when two neighboring atoms share an electron pair

Single bond - A shared electron pair A:B A—B

Double bond - Two shared electron pairs A::B A= B

Triple bond - Three shared electron pairs A:::B A≡ B

Lone pair - An unshared valence electron pair A:

Diagram that shows the patterns of bonds and lone pairs in a molecule

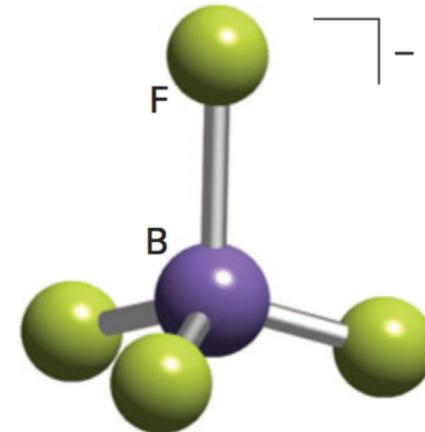
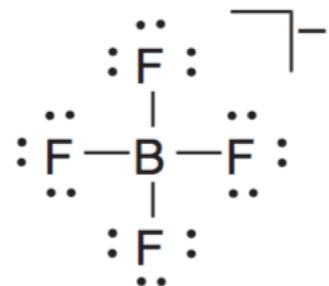
Molecular Structure & Bonding

- Lewis Structures

Diagram that shows the patterns of bonds and lone pairs in a molecule

Does not portray the shape of species

Does not show the geometry of the molecule



Molecular Structure & Bonding

– Octet Rule

Atoms **share** electron pairs until they have acquired an **octet** of valence electrons

Provides a convenient method to **construct** Lewis structures

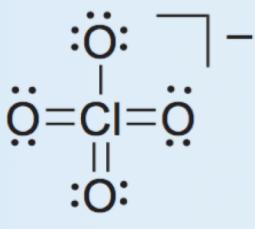
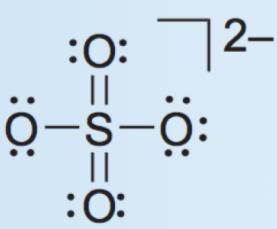
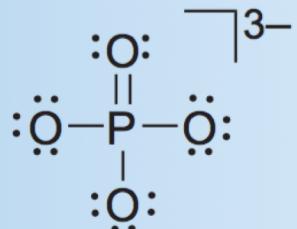
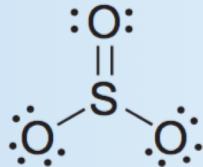
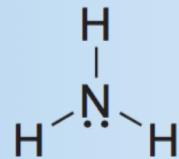
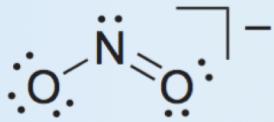
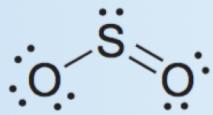
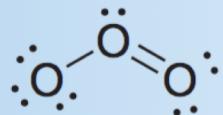
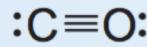
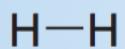
Decide: Number of electrons to be included

Arrange: Chemical symbols

Distribute: Electron pairs until each atom has an octet

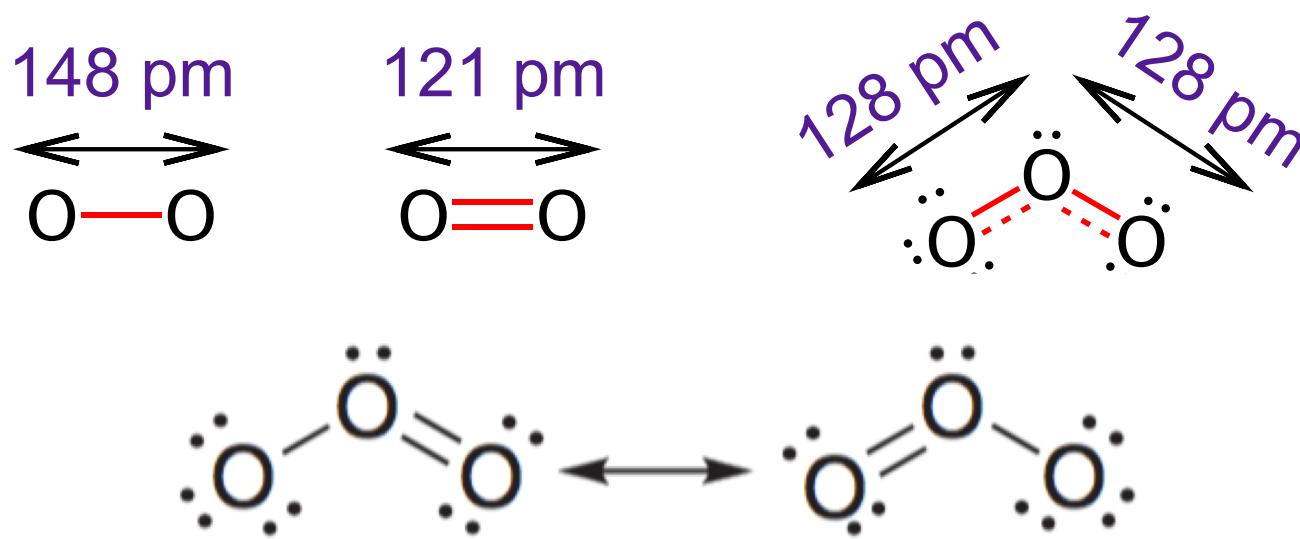
Molecular Structure & Bonding

- Lewis Structures



Structure & Bonding – Resonance

A single Lewis structure often provides an inadequate description of the molecule



Actual structure is the average of all possible Lewis structures corresponding to a given atomic arrangement

Structure & Bonding – Resonance

Actual wavefunction,

$$\psi = \psi(\text{O}-\text{O}=\text{O}) + \psi(\text{O}=\text{O}-\text{O})$$

Two structures have identical energies, hence equal contribution

Blended structure of two or more Lewis structures is called the resonance hybrid

Structures differ only in allocation of electrons

No resonance in structures where atoms lie in different positions (SOO & OSO)

Structure & Bonding – Resonance

Resonance averages the bond characteristics

Energy of resonance hybrid is lower than that of any single contributing structure

Lewis structures with similar energies provide greatest resonance stabilization

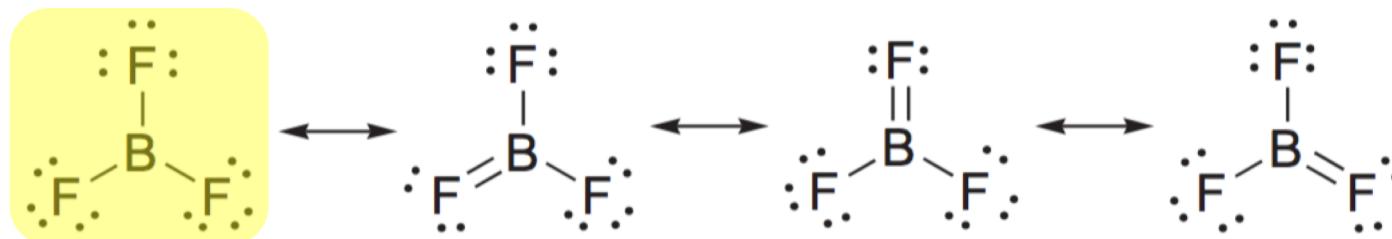
All the structures of the same energy contribute equally to the overall structure.

The greater the energy difference between two Lewis structures, the smaller the contribution of the higher energy structure.

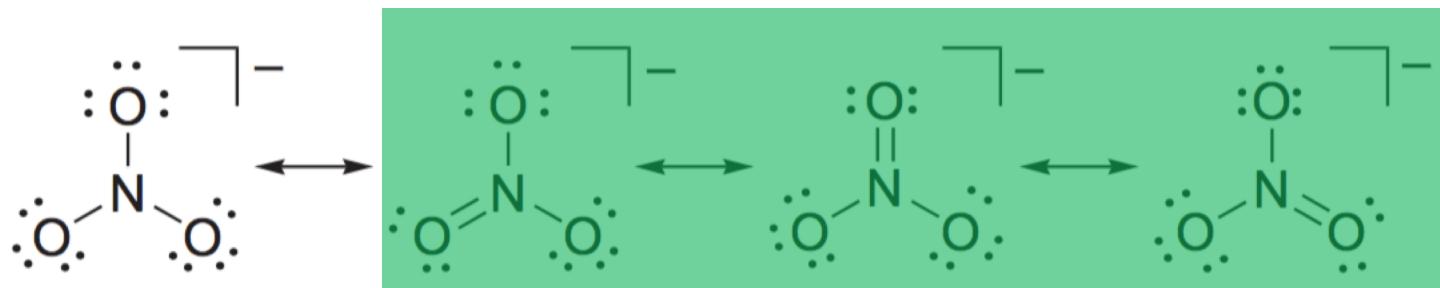
Structure & Bonding – Resonance



Equal Contribution



Unequal



Unequal

Structure & Bonding – VSEPR Model

Regions of enhanced electron density take up positions as far apart as possible – Minimize repulsion

Number of electron regions	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

Structure & Bonding – VSEPR Model

Regions of enhanced electron density governs the **shape** of the molecule

Arrangement of atoms determines the **name of the shape**

Shape	Example
Linear	HCN, CO ₂
Angular	H ₂ O, O ₃
Trigonal planar	BF ₃ , SO ₃
Trigonal pyramidal	NH ₃
Tetrahedral	CH ₄
Square planar	XeF ₄
Square pyramidal	Sb(Ph) ₅
Trigonal bipyramidal	PCl ₅
Octahedral	SF ₆

Structure & Bonding – VSEPR Model

Write down the Lewis structure of the molecule

Identify the central atom

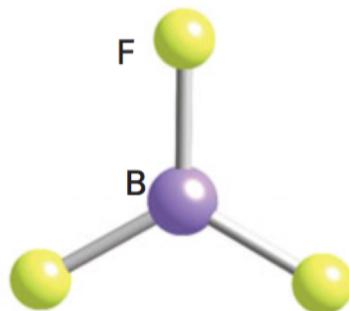
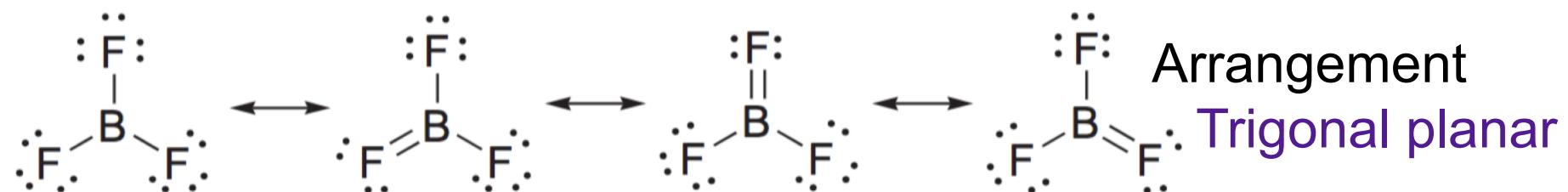
Count the number of lone pairs and atoms carried by the central atom

To achieve lowest energies lone pair regions take positions as far apart as possible

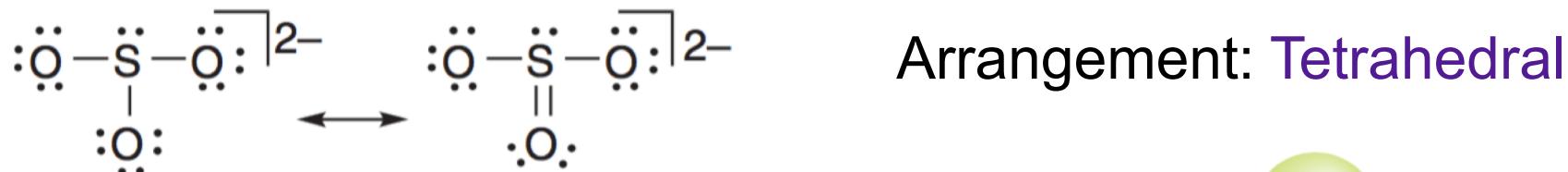
Identify the basic shape of the molecule

Name the shape of the molecule based on number/location of atoms

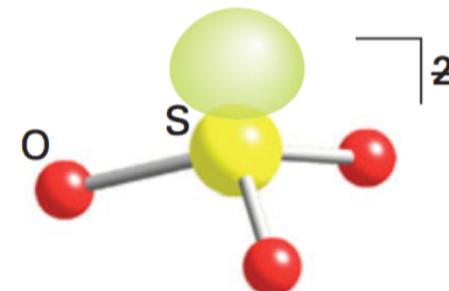
Structure & Bonding – VSEPR Model



Name of the shape
Trigonal planar

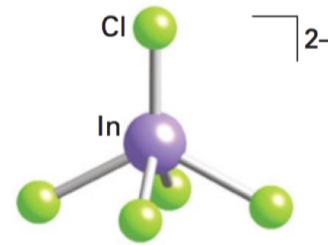
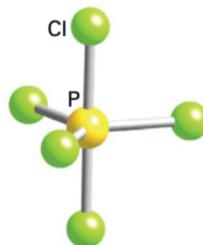


Name of the shape: Trigonal pyramidal



Structure & Bonding – VSEPR Model

A square-pyramidal arrangement is only slightly higher in energy than a trigonal-bipyramidal arrangement



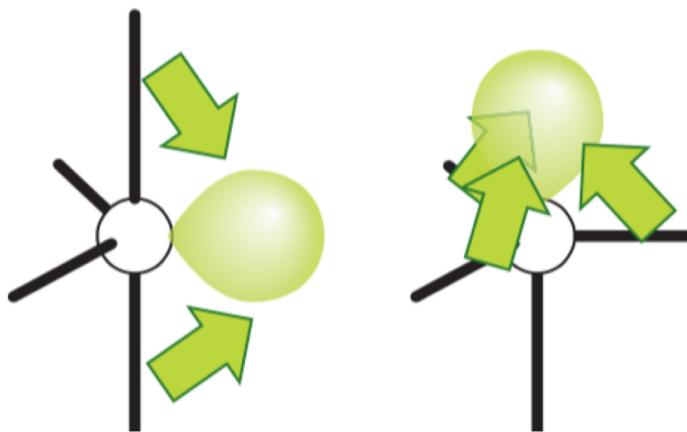
In p block, seven-coordination is dominated by pentagonal-bipyramidal structures (IF_7^-)

Lone pairs are stereochemically less influential when they belong to heavy p-block elements.

SeF_6^{2-} and TeCl_6^{2-} ions, for instance, are octahedral (Lone pairs on Se and Te are **stereochemically inert** and are usually in the non-directional s orbitals.)

Structure & Bonding – VSEPR Model

lone pair/lone pair > lone pair/bonding region > bonding region/bonding region



CH_4 109.5

NH_3 107

H_2O 104.5

Structure & Bonding : Valence Bond Theory

First quantum mechanical theory of bonding

Considers interaction of atomic orbitals

Two-electron wavefunction for two widely separated H atoms

$$\psi = \chi_A(1)\chi_B(2)$$

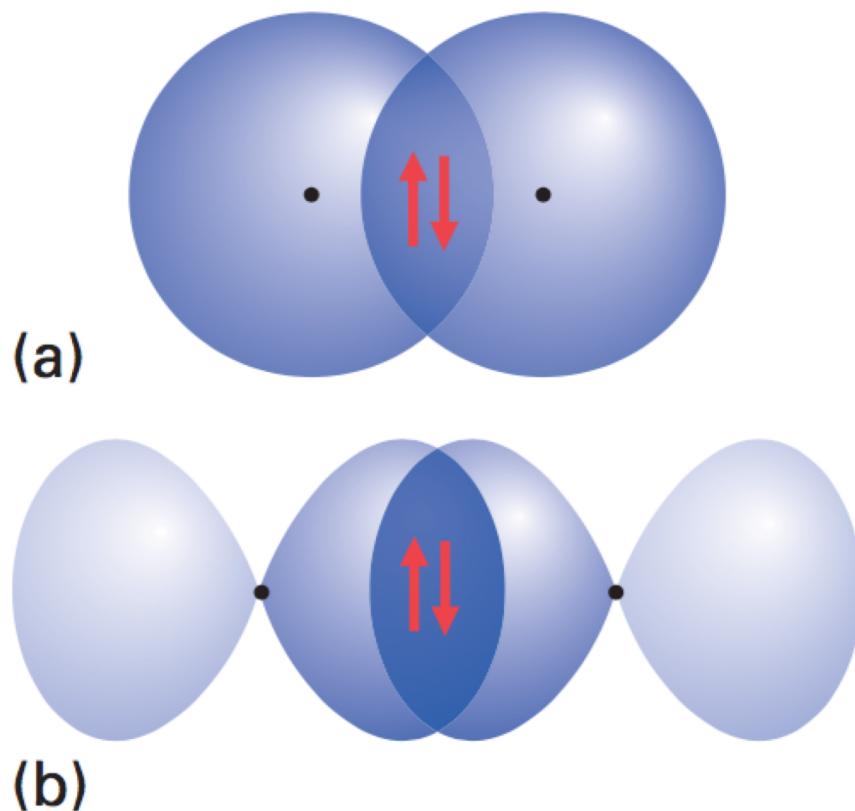
When atoms are close, an equally valid description

$$\psi = \chi_B(2)\chi_A(1)$$

Proper description is a linear combination

$$\psi = \chi_A(1)\chi_B(2) + \chi_A(2)\chi_B(1) \text{ } (\sigma\text{-bond})$$

Structure & Bonding : Valence Bond Theory



The formation of a σ bond from
(a) s orbital overlap, (b) p orbital overlap.
A σ bond has cylindrical symmetry around
the internuclear axis.

Structure & Bonding : Valence Bond Theory

Formation of bond: High probability of finding electrons between two nuclei

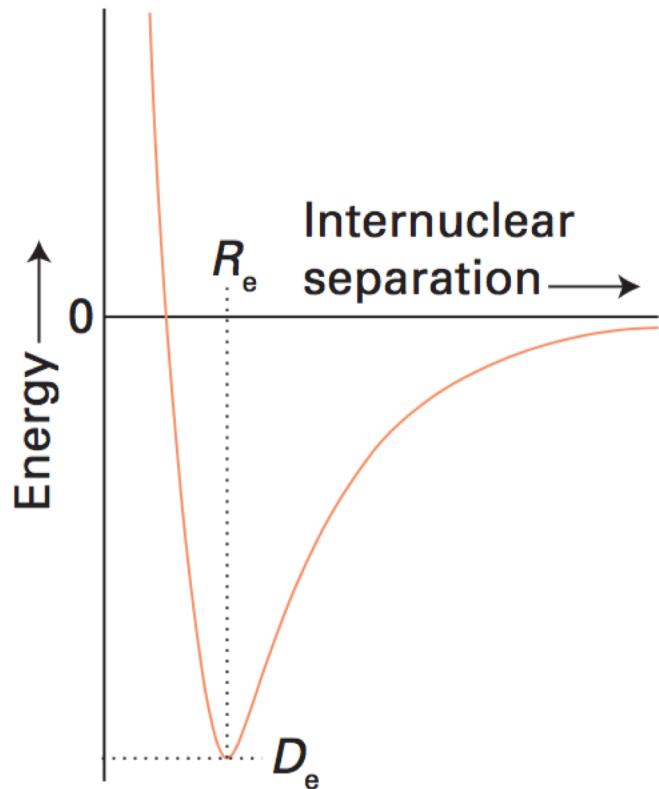
Constructive interference – enhancement in amplitude of wavefunction in internuclear region

VB wavefunction formed by spin-pairing of electrons in the two contributing orbitals

σ -bond has cylindrical symmetry about internuclear axis

Electrons in a σ -bond have zero orbital angular momentum about the axis

Structure & Bonding : Valence Bond Theory



A molecular potential energy curve showing how the total energy of a molecule varies as the internuclear separation is changed.

Structure & Bonding : Valence Bond Theory

When within bonding distance, energy falls below the two separated atoms

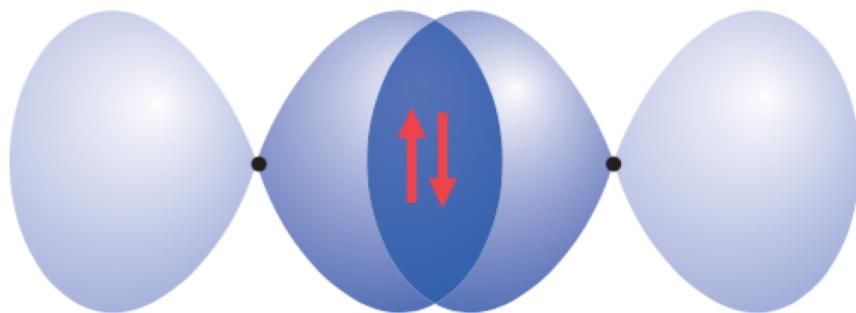
Each electron free to migrate to other atoms

Lowering of energy is countered by columbic repulsion

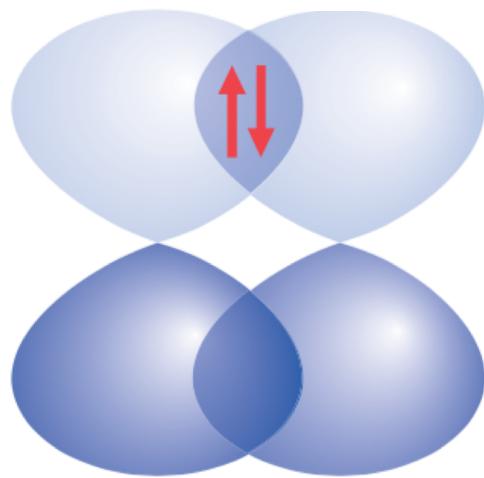
Deeper the minima, the stronger is the bond

Steepness of the curve is an indication of the “stiffness” of the bond and governs the vibrational frequency of the bond

Structure & Bonding : Valence Bond Theory



The formation of a σ bond from



The formation of a π bond.

Structure & Bonding : Valence Bond Theory

Outer electronic configuration of N₂: $2s^2 2p_z^1 2p_y^1 2p_x^1$

A σ -bond formed by spin pairing of electrons in $2p_z$

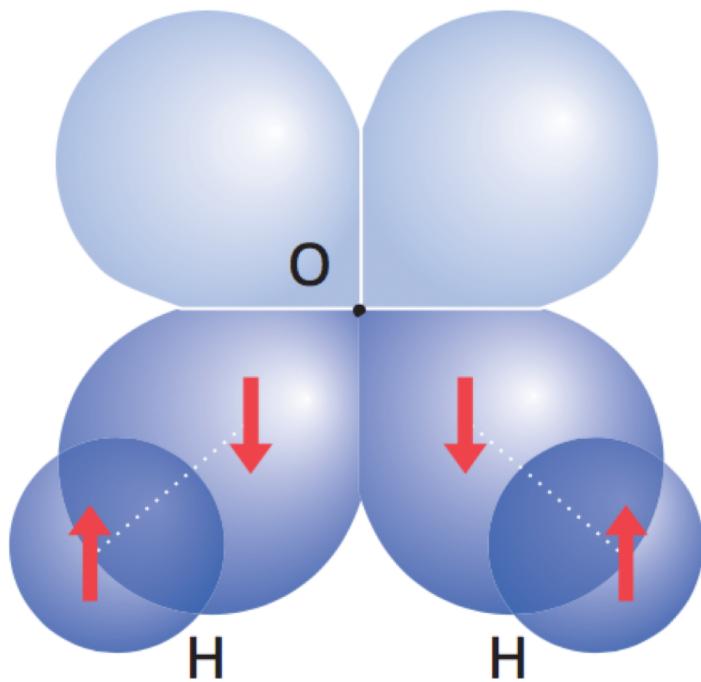
Envisage rotation of bond around the internuclear axis;
If wavefunction remains unchanged, then bond is σ . If
signs of lobes interchange then it is a π -bond

Remaining p do not have cylindrical symmetry about
internuclear axis

Spin pairing occurs by a side-by-side approach to yield
a π -bond. In total: 1 σ -bond + 2 π -bonds

An electron in a π -bond has one unit of orbital
momentum about the internuclear axis

Structure & Bonding : Valence Bond Theory



The VB description of H_2O . There are two σ bonds formed by pairing electrons in $\text{O}2\text{p}$ and $\text{H}1\text{s}$ orbitals. This model predicts a bond angle of 90° .

Structure & Bonding : Valence Bond Theory

Each σ - bond in a polyatomic molecule is formed by the spin pairing of electrons in any neighboring atomic orbitals with cylindrical symmetry about the relevant internuclear axis

π -bonds are formed by pairing electrons that occupy neighbouring atomic orbitals of the appropriate symmetry.

Bond angle in H_2O and NH_3 is not 90° but 104.5° and 107° respectively

Another limitation is the inability to account for the tetravalence of carbon

Structure & Bonding : VBT - *Promotion*

Structure & Bonding : VBT - *Promotion*

Excitation of an electron to an orbital of higher energy during the course of bond formation

Not a “real process”, but an contribution to overall energy change that occurs during bond formation

Requires energy but worthwhile

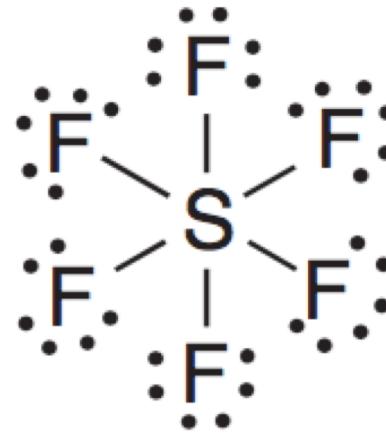
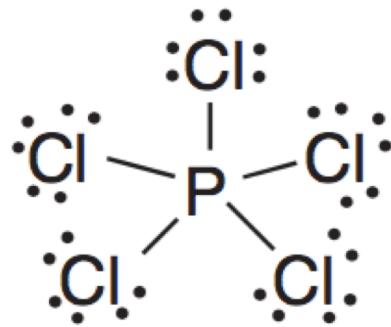
Characteristic feature of group 14 elements

Relives electron-electron repulsion as promotion occurs between ns and np

Promotion is energetically less favorable as one moves down the group (Pb and Sn prefer divalency)

Structure & Bonding : VBT - Hypervalence

Hypervalence and octet expansion occurs for elements following period 2



Traditional explanation: Low-lying un-filled d -orbitals

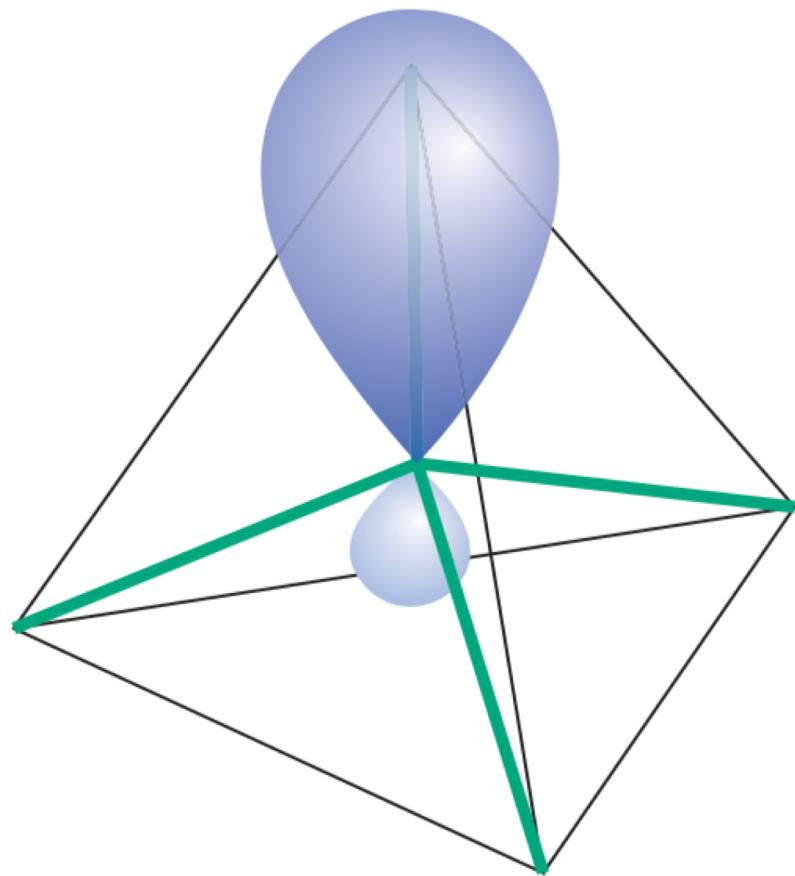
Real reason for rarity of hypervalence in period 2: geometrical difficulty

MO theory provides better understanding

Structure & Bonding : VBT - Hybridization

Not all C-H bonds in CH_4 are equivalent!!

Structure & Bonding : VBT - Hybridization



One of the four equivalent sp^3 hybrid orbitals. Each one points towards a different vertex of a regular tetrahedron.

Structure & Bonding : VBT - Hybridization

Hybrid orbitals formed by interference or mixing of $2s$ and $2p$ orbitals

Specific linear combinations that give rise to four equivalent hybrid orbitals are

$$h_1 = s + p_x + p_y + p_z \quad h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z \quad h_4 = s + p_x - p_y - p_z$$

Each hybrid built from one s and three p , hence sp^3

Angle between axis of hybrid orbitals is 109.47°

Constructive interference results in pronounced directional character and enhanced amplitude in internuclear region

Structure & Bonding : VBT - Hybridization

Bond strength of an sp^3 hybrid is greater than for an s or p orbital alone

This helps in repaying promotion energy

Because each sp^3 hybrid orbital has the same composition, all four σ -bonds are identical apart from their orientation in space

Hybrid orbitals are formed when atomic orbitals on the same atom interfere;

Specific hybridization schemes correspond to each local molecular geometry.

Structure & Bonding : VBT - Hybridization

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, pd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	$sp^2d^2, sd^4, pd^4, p^3d^2$
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

Structure & Bonding : VBT – Hybridization

Strength of bond proportional to extent of overlap of atomic orbitals

Pure s and pure p provide inefficient overlap compared to hybrid orbitals $sp > sp^2 > sp^3 \gg p$

Molecule	Hybridization	C—H bond energy (kJ mol ⁻¹)	C—H bond length (pm)
H—C≡C—H	<i>sp</i>	500	106.1
H ₂ C=CH ₂	<i>sp</i> ²	400	108.6
CH ₄	<i>sp</i> ³	410	109.3
CH radical	$\sim p$	335	112.0

• McWeeny, R. *Coulson's Valence*; Oxford University: London. 1979; p 204.
Used with permission.

Structure & Bonding : VBT – Hybridization

In the case of sp^3d hybrids, the resulting orbitals are not equivalent

Three orbitals directed trigonally form one set of equivalent orbitals (sp^2) - Equitorial

Two orbitals directed linearly (perpendicular to the plane of the first three) form second set of two equivalent orbitals (dp) – Axial

Bond angles are different!! (PF_5)

Structure & Bonding : VBT – Hybridization

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Two orbitals directed linearly (perpendicular to the plane of the first three) form second set of two equivalent orbitals (dp) – Axial

Bond angles are different!! (PF_5)

Structure & Bonding : VBT – Bent's Rule

PCl_3F_2 – More electronegative F occupies axial position!!

Bond angles in CH_2F_2

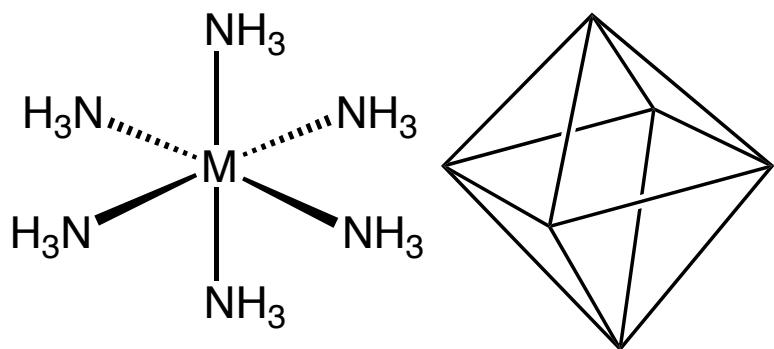
A Brief Review of Co-ordination Chemistry

❖ Co-ordination compound (complex)

An assembly of metal atom(s) and organic and/or inorganic groups (“Ligands”)

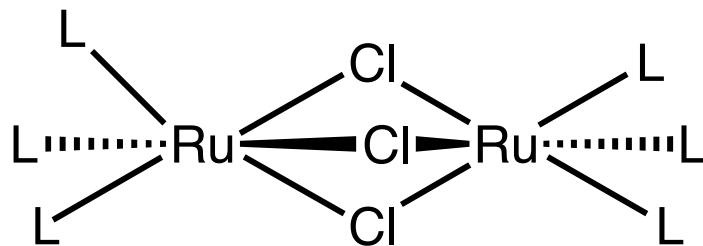
❖ Metal bound to non-carbon ligands –

Werner complexes

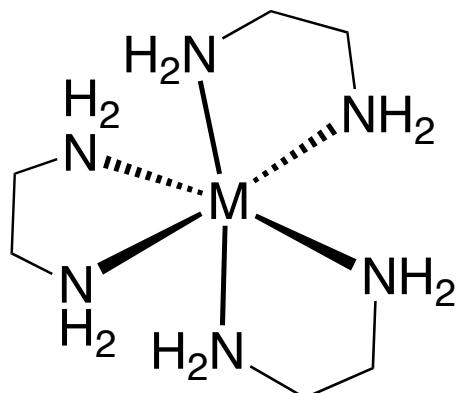


Lone pair on N donated to M
M is a polyvalent Lewis acid

- ❖ Ligands can have donor atoms having more than one lone pair



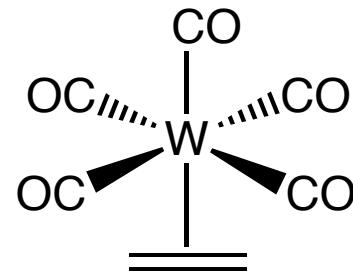
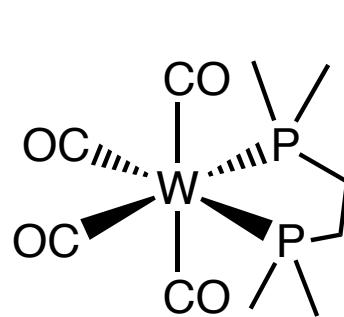
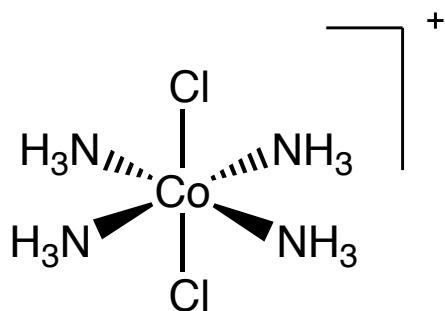
- ❖ There are also ligands which have more than one donor atoms



Very stable and less easily displaced compared to monodentate ligands

- ❖ Metal bound to organic ligands –
Organometallic complexes (M-C bond)
- ❖ Metal bound to organic ligands –
Metallo-organic complexes (M-XC bond, X= N, O)

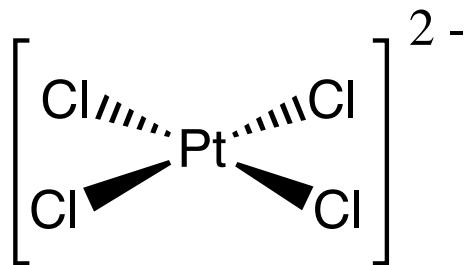
- ❖ Co-ordination number
Number of groups bound to the central atom



❖ Oxidation state; $OS(M) = C_{tot} - L_{tot}$

C = Total charge of complex

L = Total charge of ligands

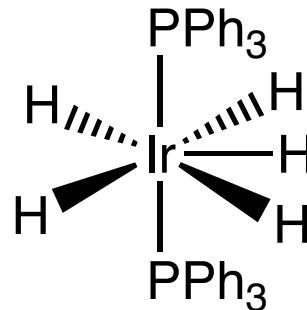


$$C = -2$$

$$L = 4 \times (-1) = -4$$

$$OS = -2 - (-4) = 2$$

How about $K_4[Fe(CN)_6]$ or



Actually oxidation state is only a formality

Bonding: Valence Bond Theory

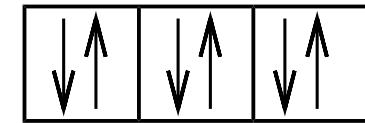
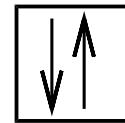
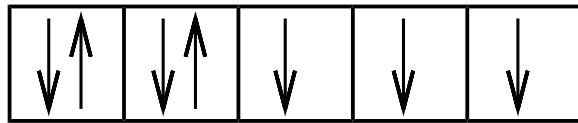
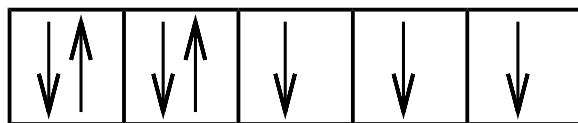
Overlapping of AOs of participating atoms

Filled orbital of ligand with empty orbital of metal

Geometry based on hybridization of metal ion

Bonding: Valence Bond Theory

Geometry of $[\text{CoCl}_4]^{2-}$



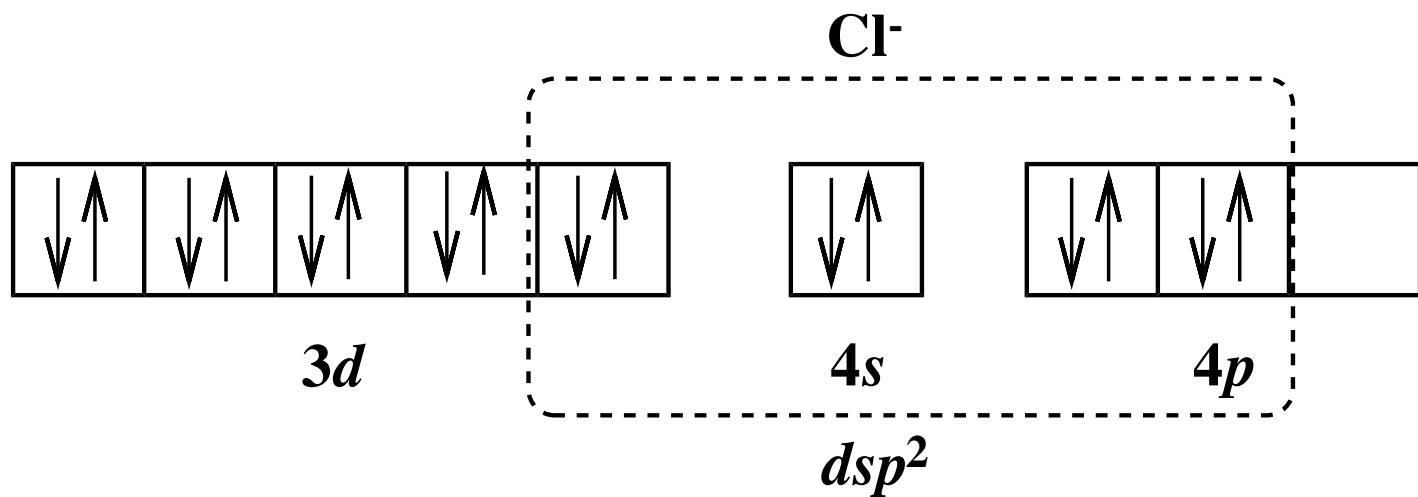
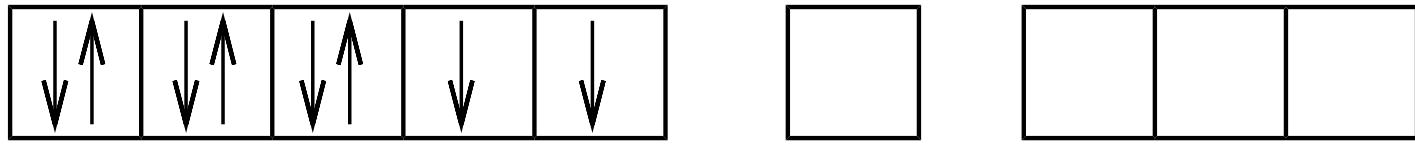
Cl^-

sp^3

4 co-ordinate, tetrahedral, paramagnetic

Bonding: Valence Bond Theory

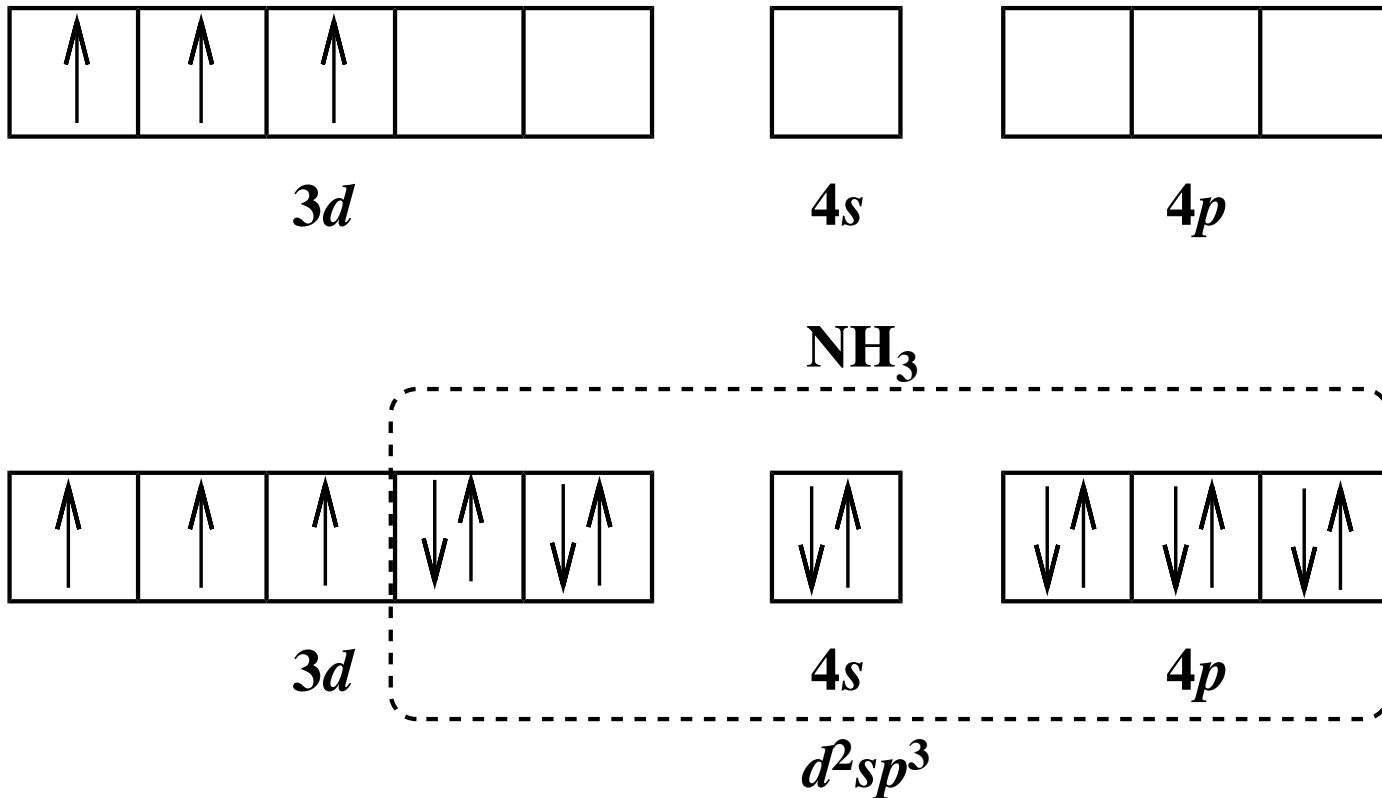
Geometry of $[\text{NiCN}_4]^{2-}$



4 co-ordinate, square planar, diamagnetic

Bonding: Valence Bond Theory

Geometry of $[\text{Cr}(\text{NH}_3)_6]^{3+}$



6 co-ordinate, octahedral, paramagnetic

Bonding: Valence Bond Theory

Geometry of $[\text{CoF}_6]^{3-}$ Vs. $[\text{Co}(\text{CN})_6]^{3-}$