

Lecture 5; CH 101: Inorganic Chemistry

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&

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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	1 H Hydrogen 1.00794	Atomic # Symbol Name Atomic Mass																2 He Helium 4.002602	
	<div><div><div>C Solid</div><div>Hg Liquid</div><div>H Gas</div><div>Rf Unknown</div></div><div><div>Alkali metals</div><div>Alkaline earth metals</div><div>Lanthanoids</div><div>Actinoids</div><div>Transition metals</div><div>Poor metals</div><div>Other nonmetals</div><div>Noble gases</div></div></div>																		
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											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	
3	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050											13 Al Aluminium 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948	
4	19 K Potassium 39.0983	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 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	
5	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 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293	
6	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57–71		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 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)
7	87 Fr Francium (223)	88 Ra Radium (226)	89–103		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	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	118 Uuo Ununoctium (294)

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

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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 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	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 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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

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

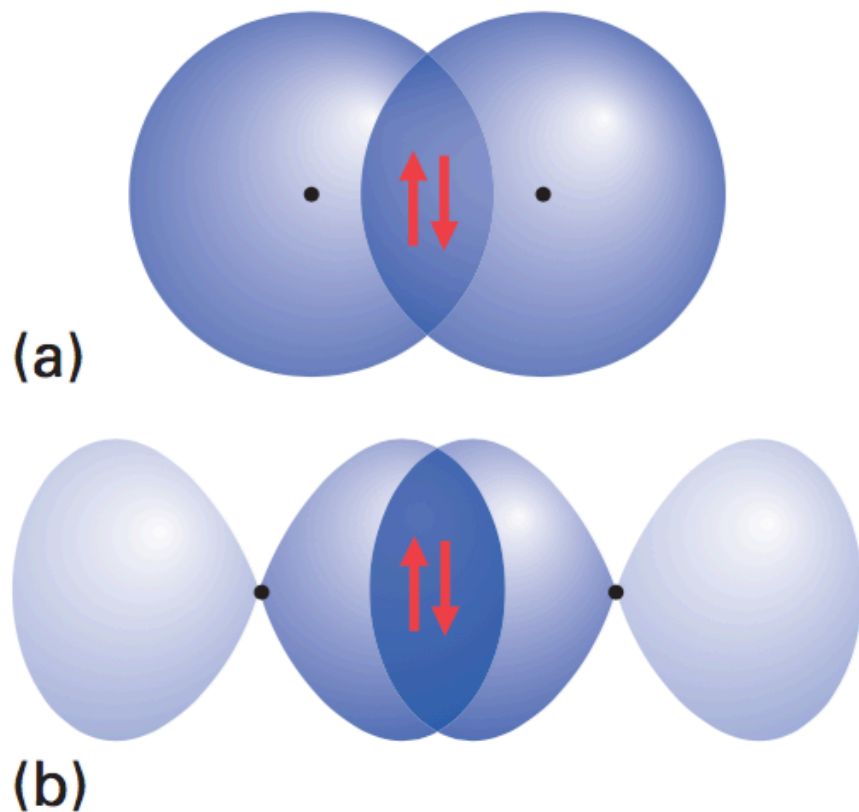
When atoms are close, an equally valid description

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

Proper description is an linear combination

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

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

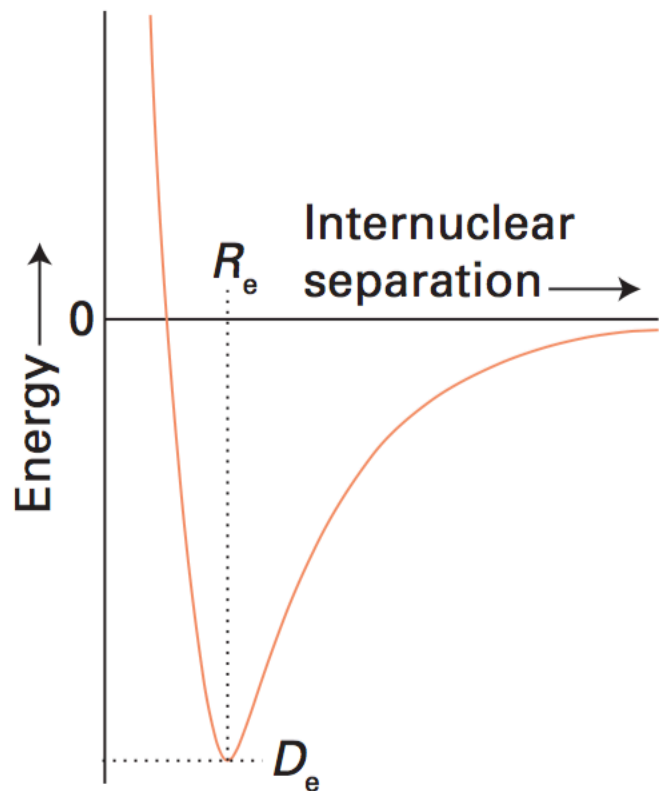
Constructive interference – enhancement in amplitude of wavefunction in internuclear region

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

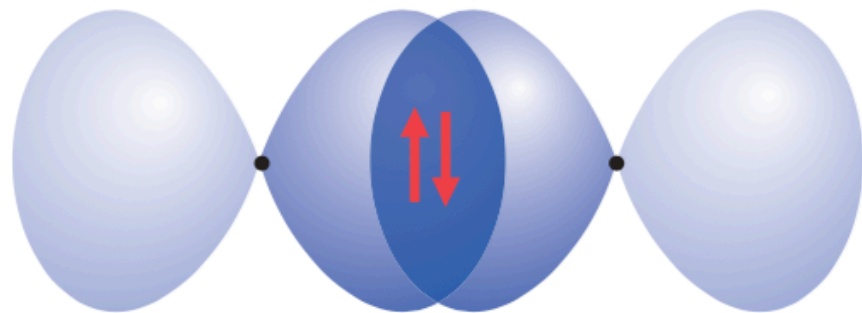
Each electron free to migrate to other atoms

Lowering of energy is countered by columbic repulsion

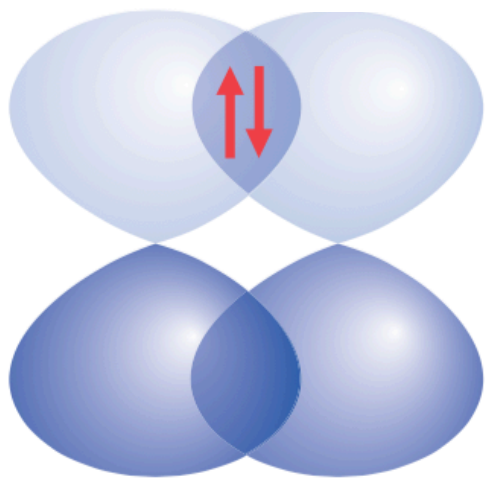
Deeper the minima, the stronger is the bond

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 N_2 : $2s^2 2p_z^1 2p_y^1 2p_x^1$

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

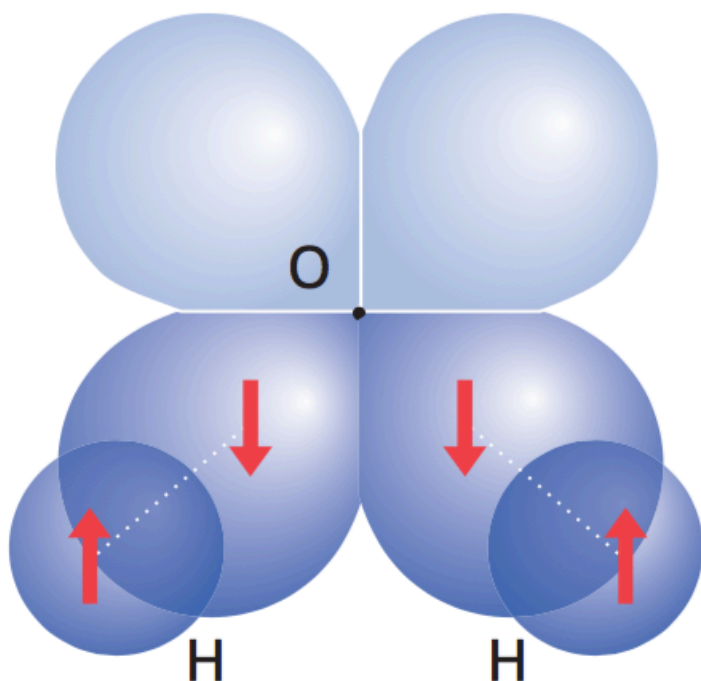
Envisage rotation of bond around the internuclear axis; If wavefunction remains unchanged, then bond is σ . If signs of lobes interchange then it is a π -bond

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 H₂O. There are two σ bonds formed by pairing electrons in O2p and H1s 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

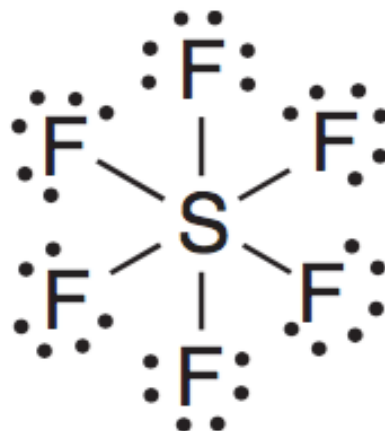
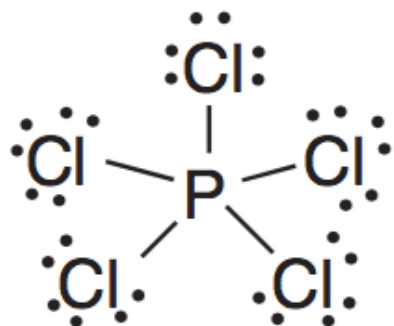
Characteristic feature of group 14 elements

Relieves 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

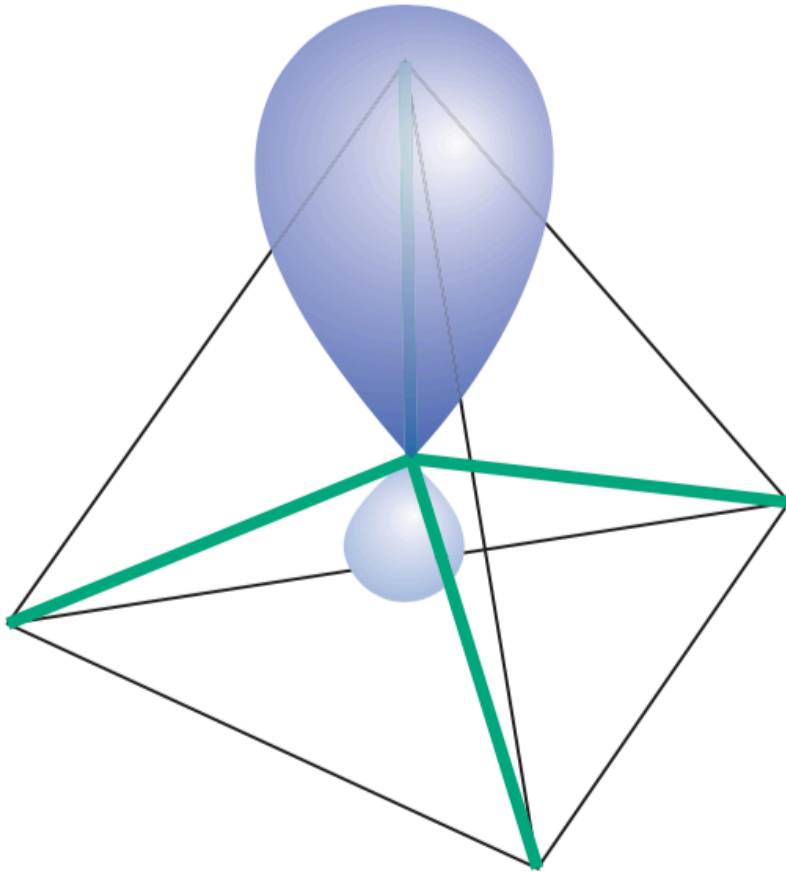
Real reason for rarity of hypervalence in period 2: geometrical difficulty

MO theory provides better understanding

Structure & Bonding : VBT - *Hybridization*

Not all C-H bonds in CH₄ 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	~ <i>p</i>	335	112.0

^a McWeeny, R. *Coulson's Valence*; Oxford University: London, 1979; p 204.
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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) - Equatorial

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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Structure & Bonding : VBT – *Bent's Rule*

PCl_3F_5 – More electronegative F occupies axial position!!

Bond angles in CH_2F_2