BONDING IN MOLECULES PART 2: VB THEORY

General Chemistry I, Lecture Series 10

Pengxin Liu

Reading:

OGB8 §3.10, §3.11

Outline

- Valence Bond Theory (1927)
- Lewis dot structures (1916)
- Hybridization and VSEPR theory (1958)

H_2: Levels of Approximation

H_A, H_B, e_1, e_2

Fix nuclei

e_1, e_2, around H_A, H_B

Molecular Orbital 分子轨道 “共享”

Ignore the other e

H_A, H_B share one e

Linear combination

e sometimes around H_A sometimes around H_B

Valence Bond 价键 “分享”

Avoid the other e

Each H takes one e

Hybridization 杂化 for C, N, O, …

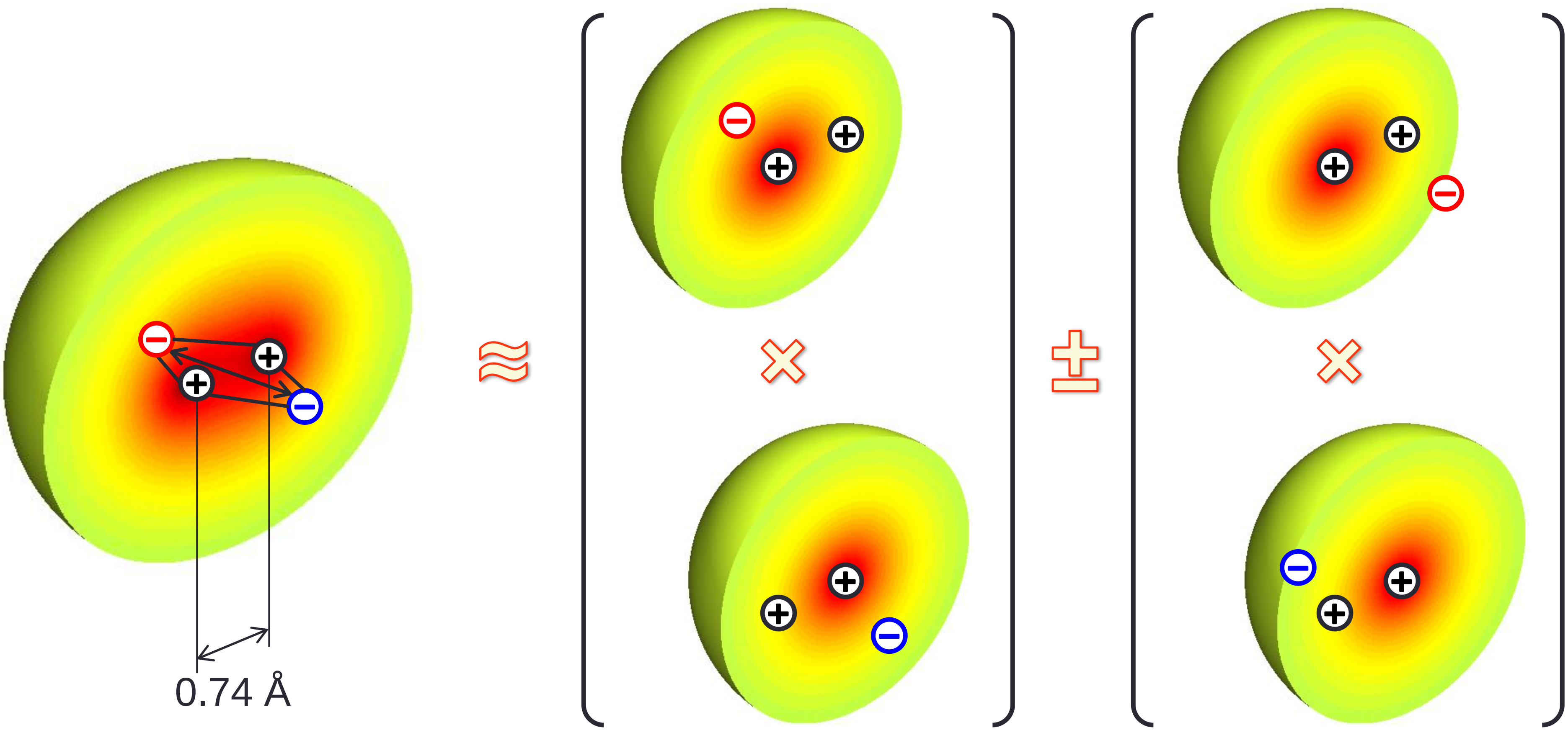
e sometimes in *s* sometimes in *p*

Inspiration of VB theory

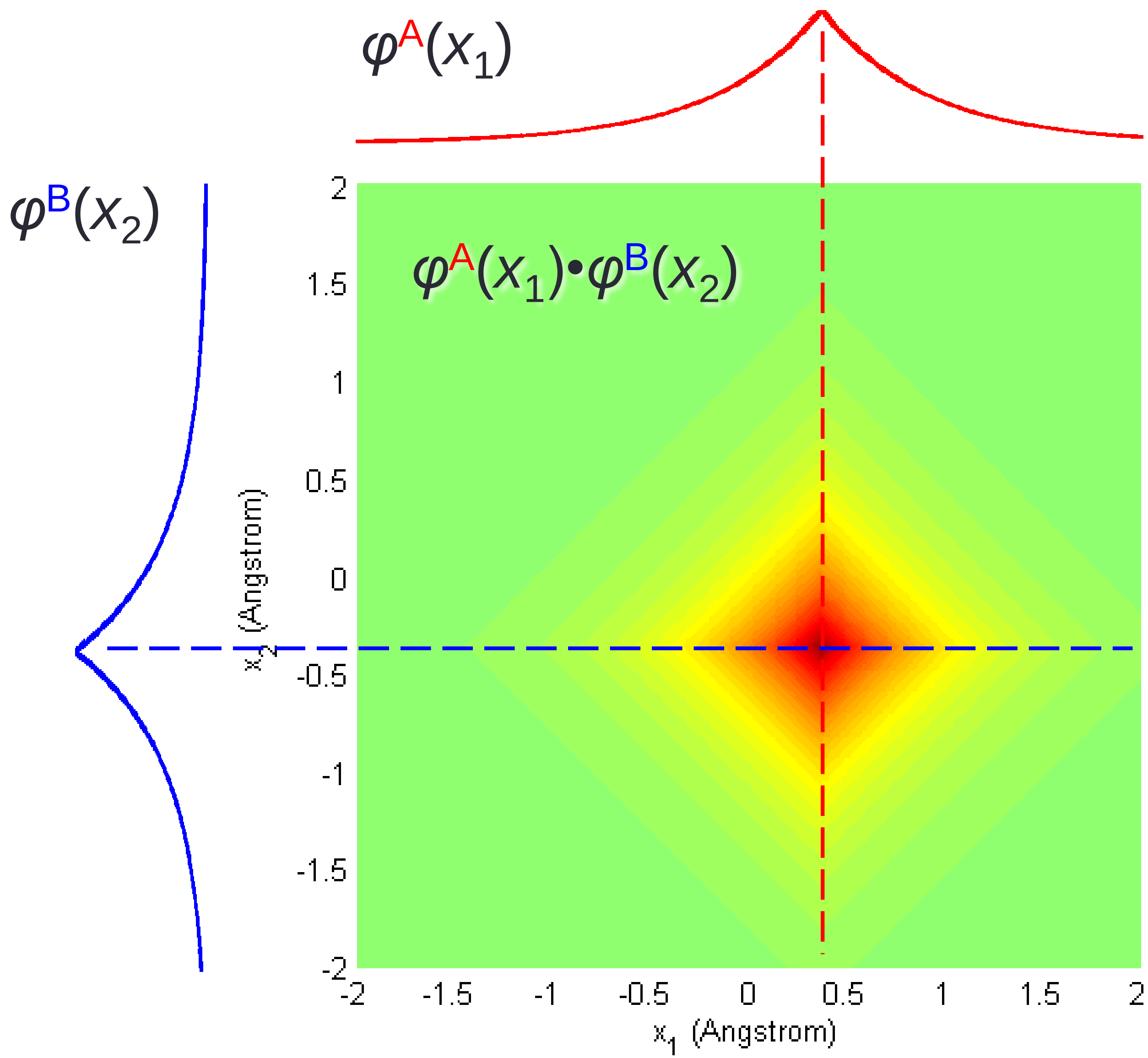
- The characteristics (bond length, bond energy, polarity, etc.) of specific chemical bonds such as O-H, C-C, and C-H do not differ much from molecule to molecule.
- Justification for the Lewis electron pair model.
- Assuming that each participating atom arrives with at least one unpaired electron in an AO

The Valence Bond Theory

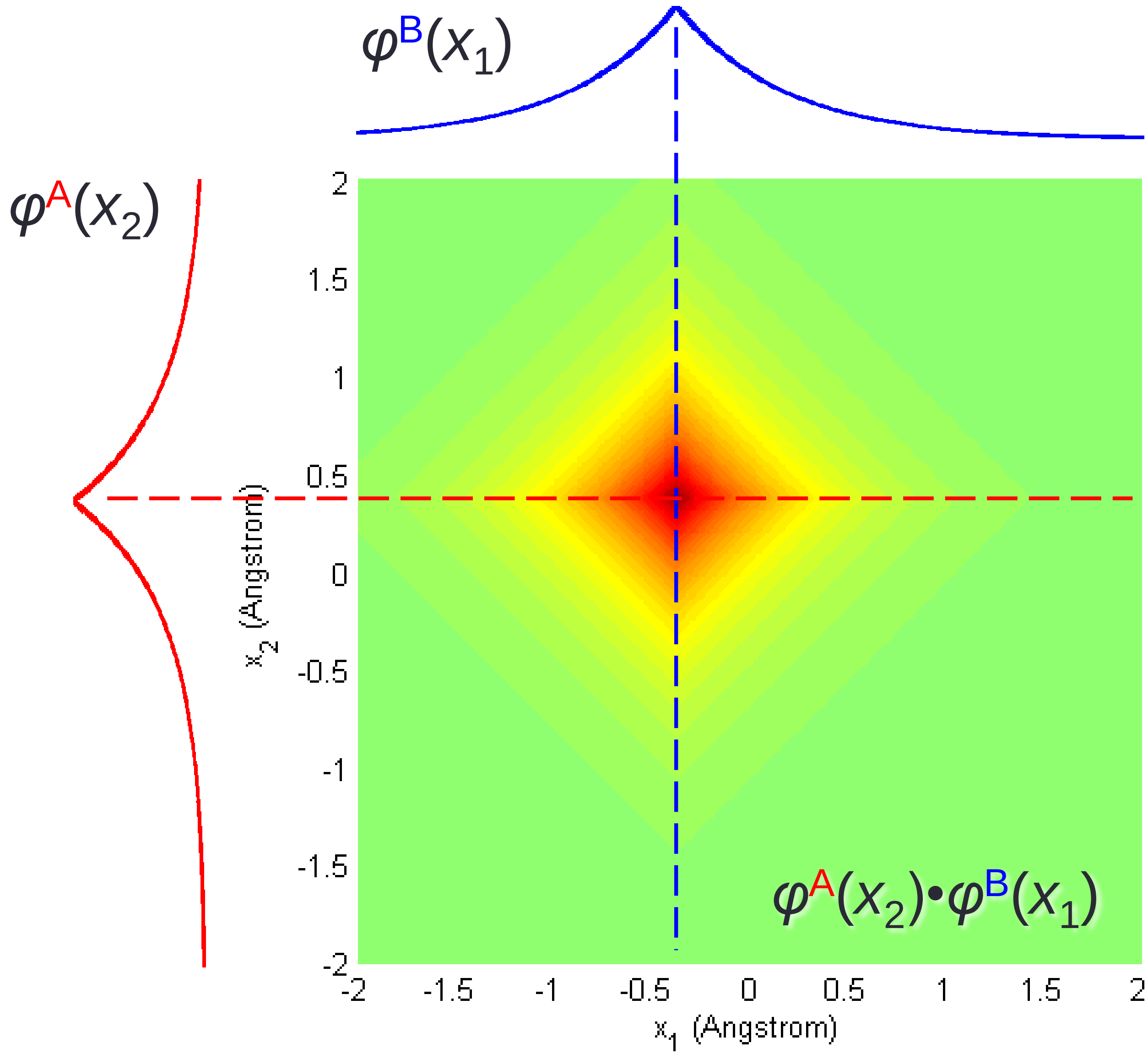
H—H ≈ H$^{\bullet}_{\times}$H or H$_{\times}^{\bullet}$H, but neither H H$^{\bullet}_{\times}$ nor $^{\bullet}_{\times}$H H.



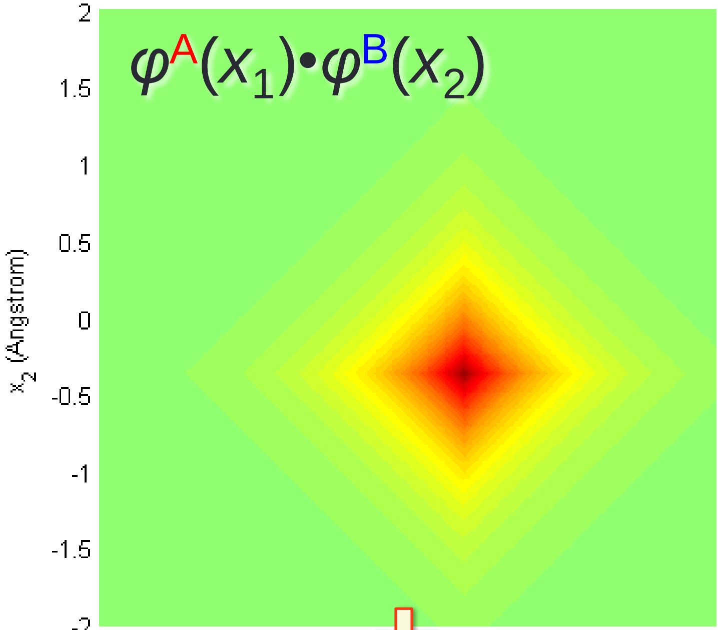
The VB Wavefunction in 1D (1)

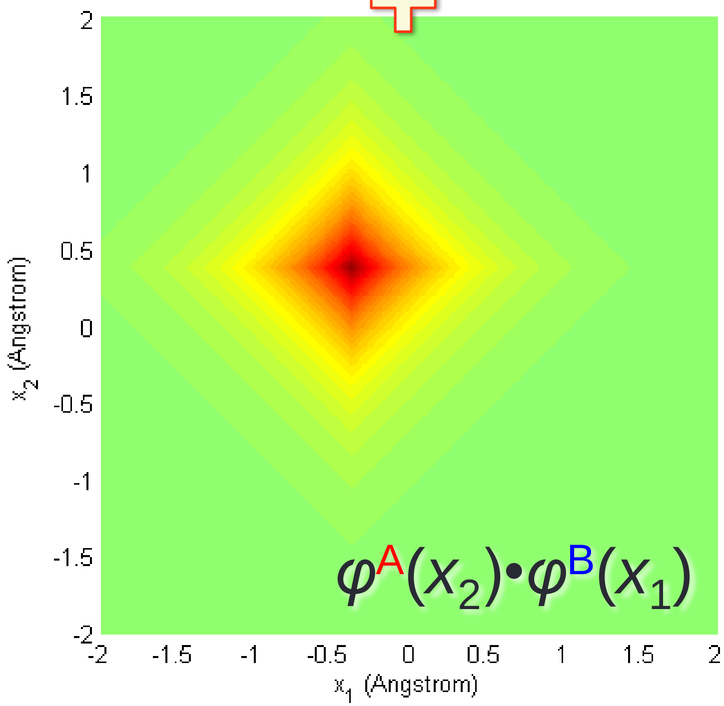


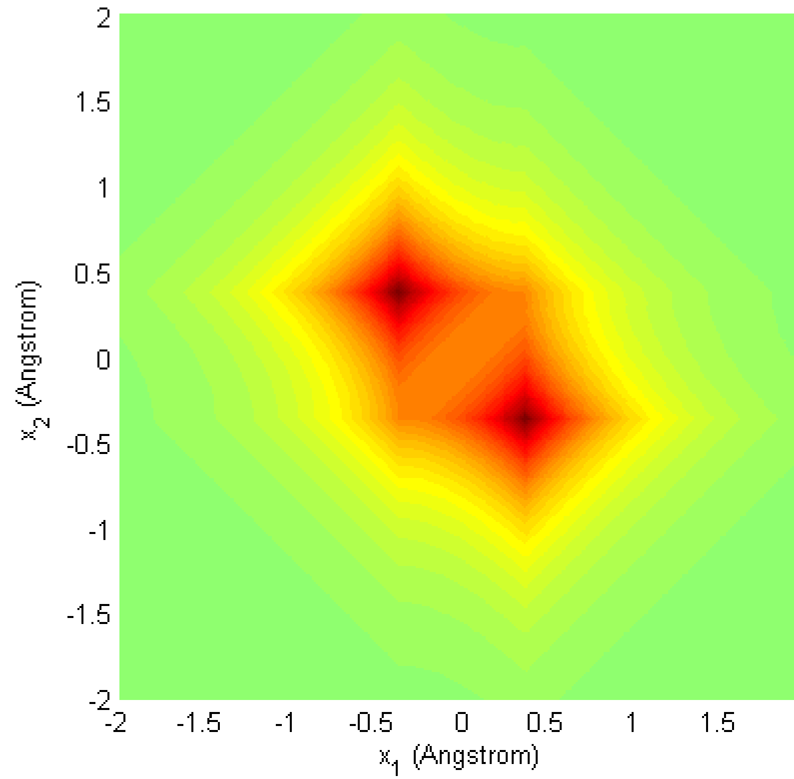
The VB Wavefunction in 1D (2)



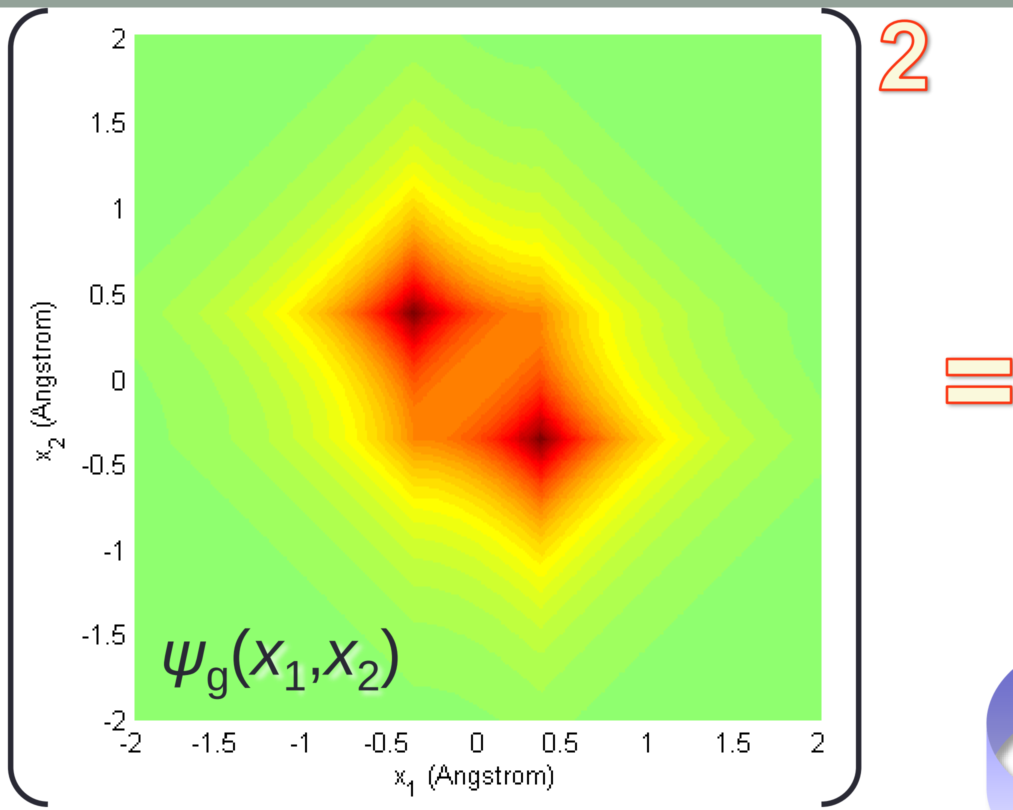
VB Wavefunction (3)

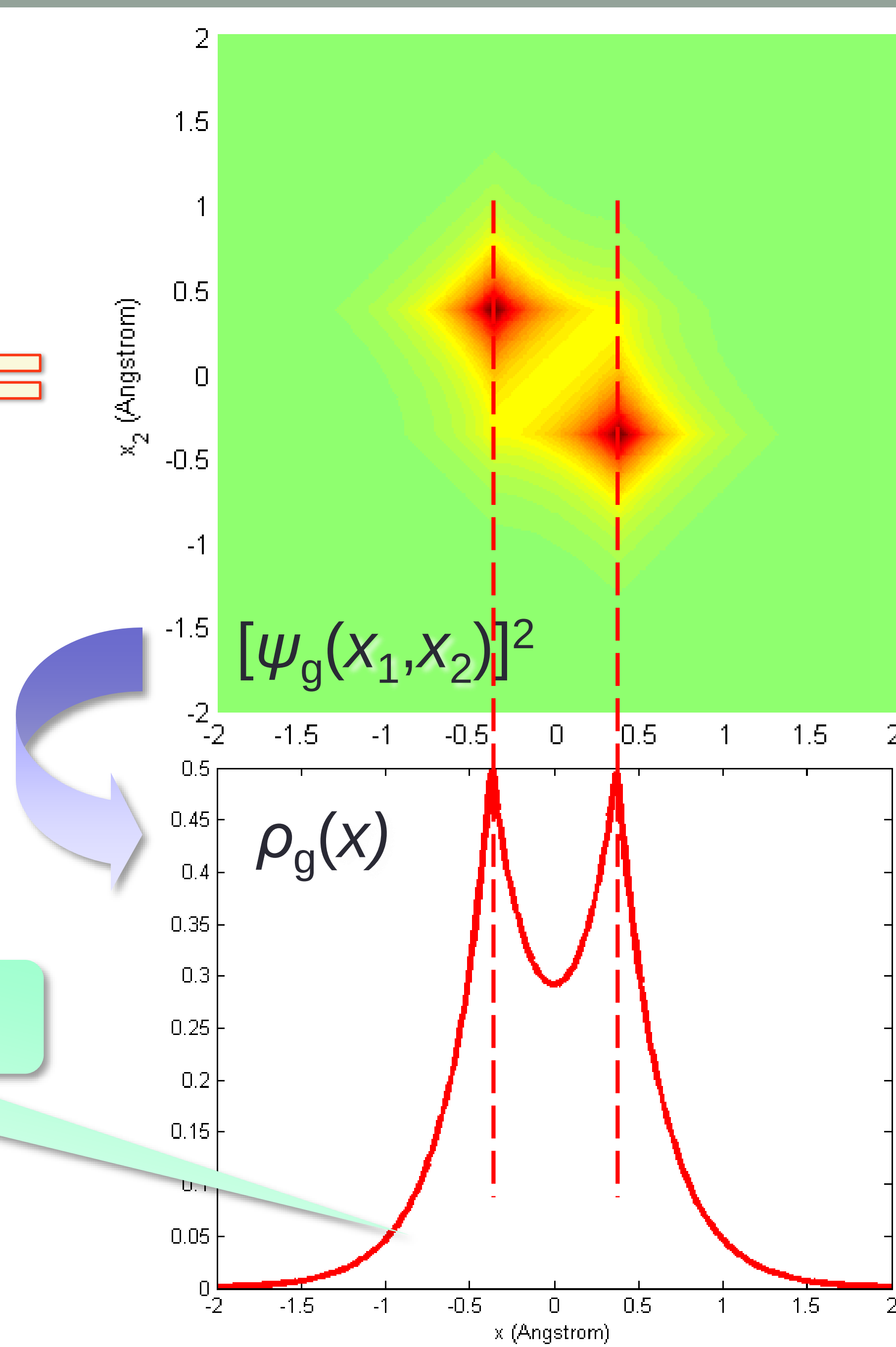






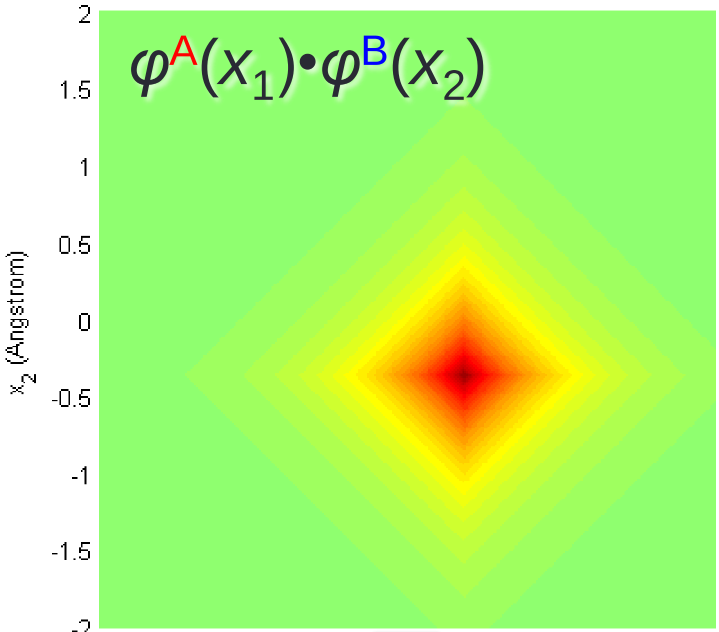
$$\psi_g(x_1,x_2) \approx c_1[\varphi^A(x_1)\bullet\varphi^B(x_2) + \varphi^A(x_2)\bullet\varphi^B(x_1)]$$

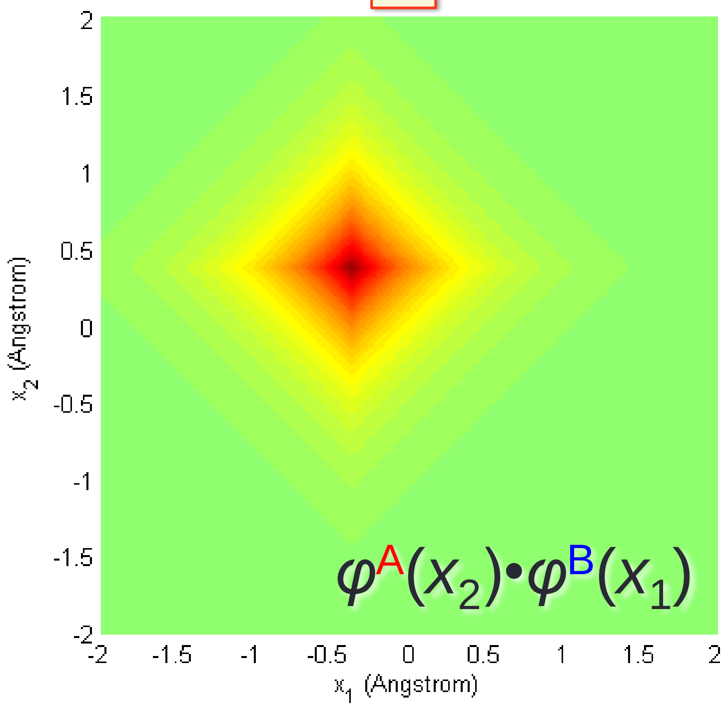


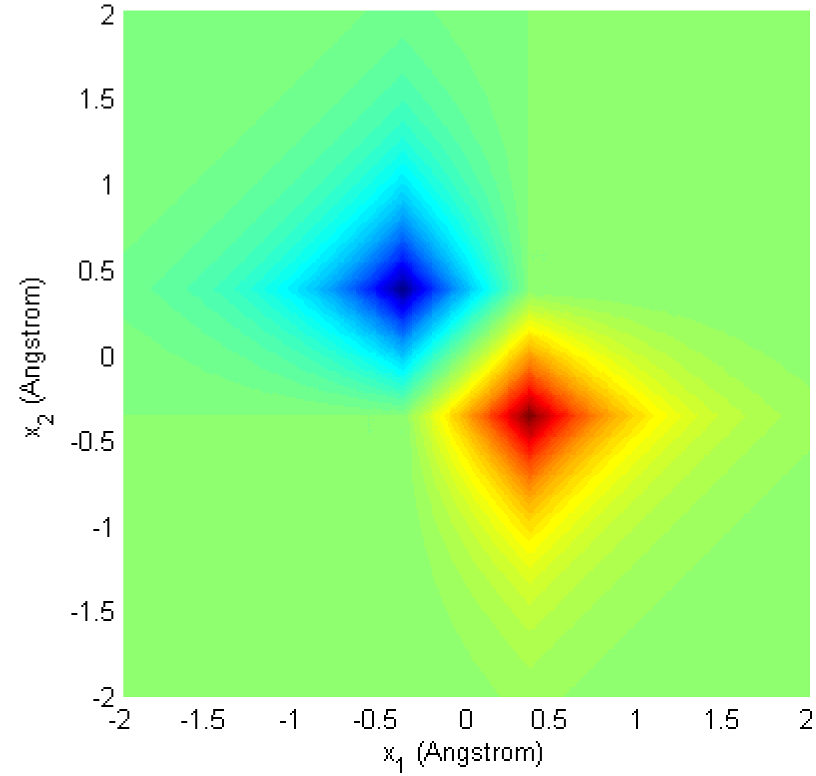


Electron density in 1D

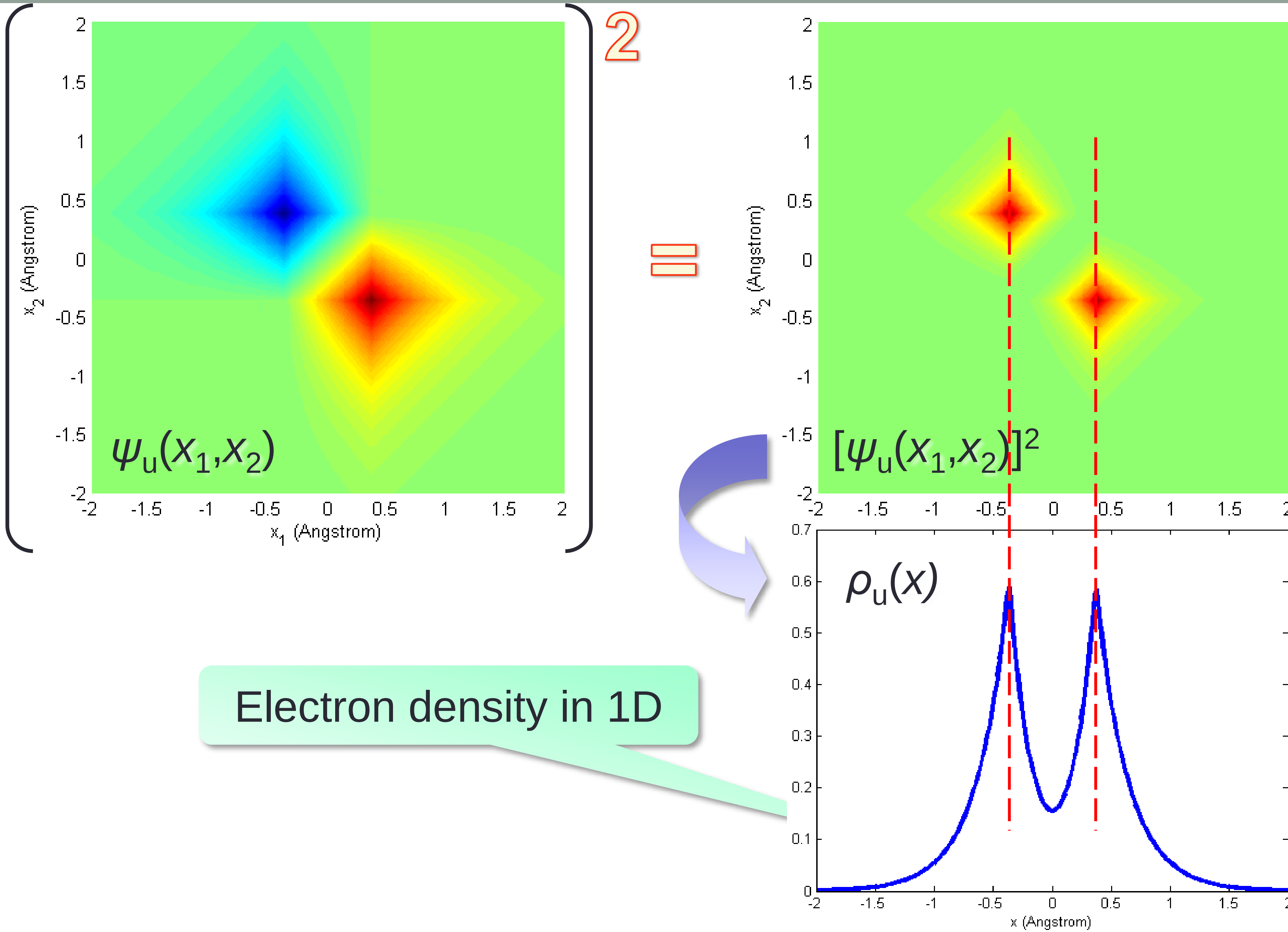
VB Wavefunction (4)





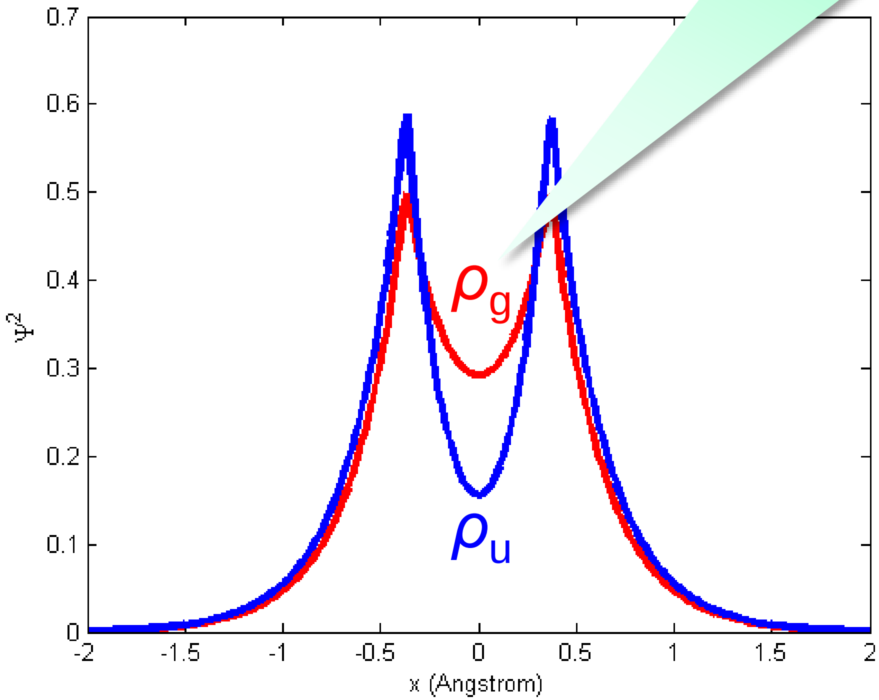


$$\psi_u(x_1,x_2) \approx c_2[\varphi^A(x_1)\cdot\varphi^B(x_2) - \varphi^A(x_2)\cdot\varphi^B(x_1)]$$

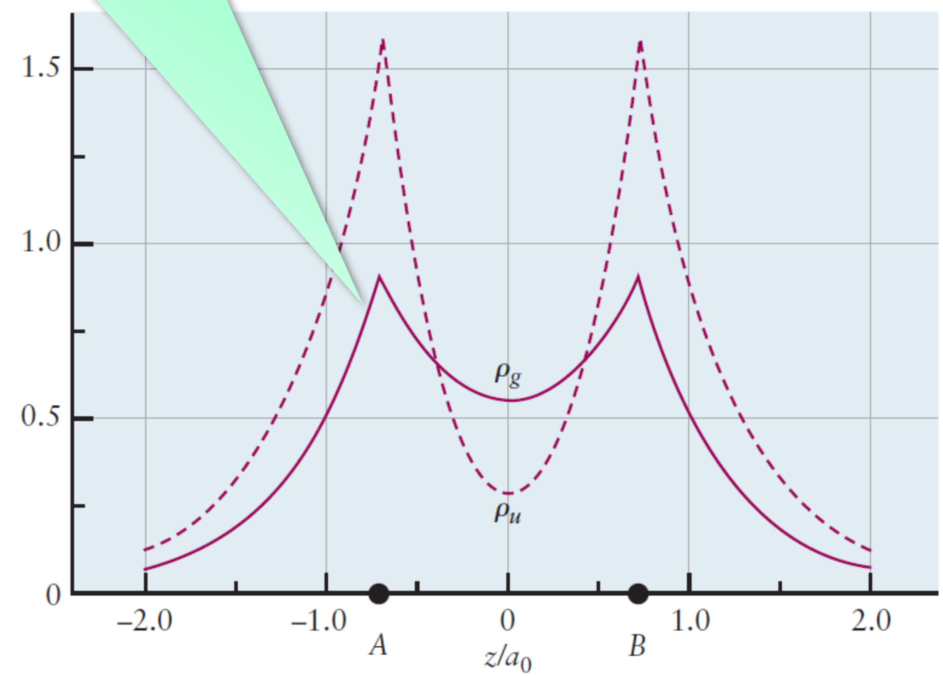

$\psi_u(x_1,x_2)$
2
=
$[\psi_u(x_1,x_2)]^2$
$\rho_u(x)$
x_1 (Angstrom)
x_2 (Angstrom)
x (Angstrom)
Electron density in 1D

Comparison of Density Plots

Bonding orbital σ

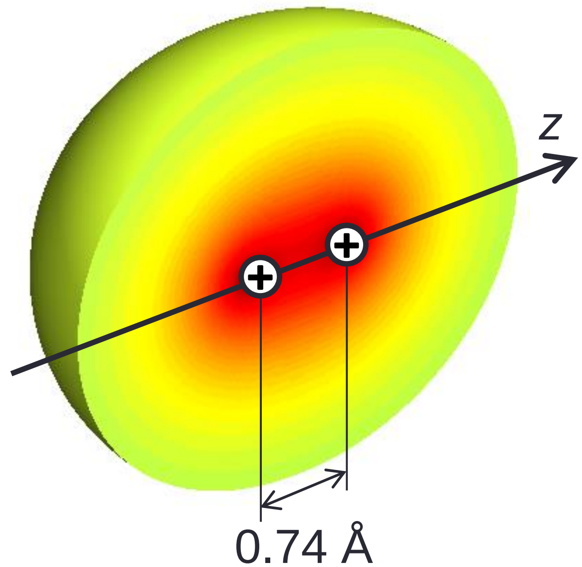


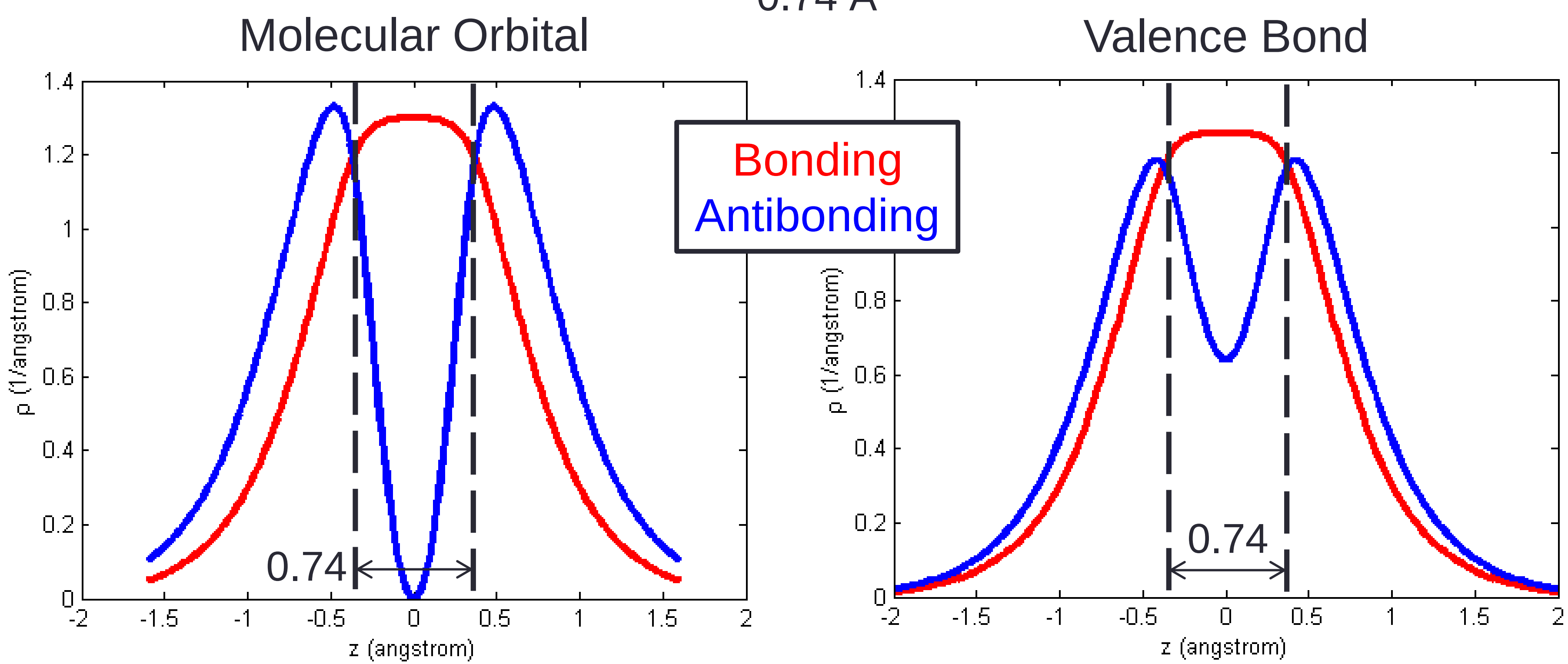
H_2 in one dimension



H_2 in three dimensions

Comparison between MO & VB





MO *vs.* VB Revisited

Molecular Orbital (MO)

- Ignores e-e repulsion
- Electrons wander around
- For orbitals that are
  - Delocalized 离域
  - ‘Fat’
  - Singly occupied

Valence Bond (VB)

- Exaggerates e-e repulsion
- Electrons adhere to the nuclei
- For orbitals that are
  - Localized 定域/局域
  - ‘Tight’
  - Strong

Pros and Cons of VB Theory

- Works best for localized bonds
- Difficult to estimate energy levels
- Complicated programming

- More accurate than MO for σ bonds
- Compatible with hybridization 杂化

$$\psi_g(x_1,x_2) \approx c_1[\varphi^A(x_1)\bullet\varphi^B(x_2) + \varphi^A(x_2)\bullet\varphi^B(x_1)]$$

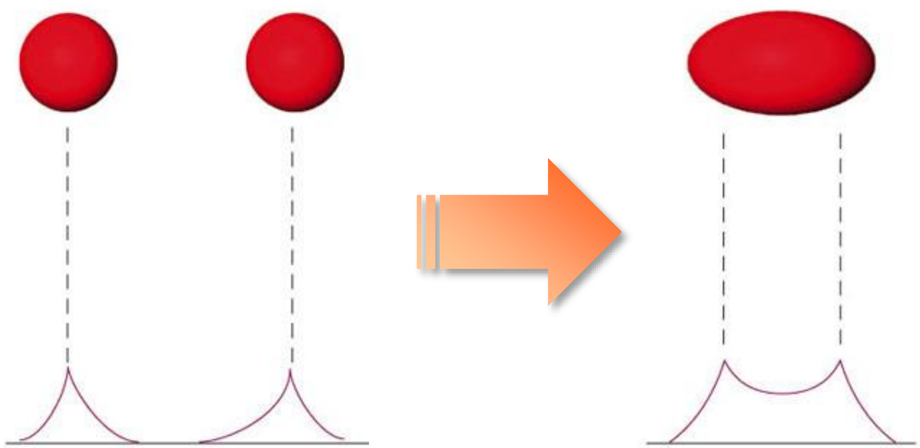
Outline

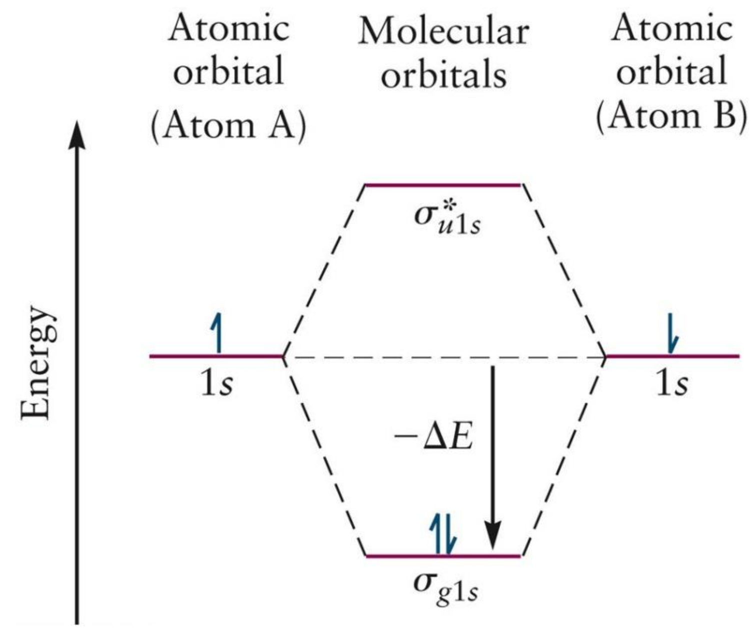
- Valence Bond Theory (1927)
- Lewis dot structures (1916)
- Hybridization and VSEPR theory (1958)

In Practice

Consider	Ignore
• Valence • Bond order • Molecular shape	• Anti-bonding orbitals • Bond energy

Bonding Orbital





VB: Orbital overlap

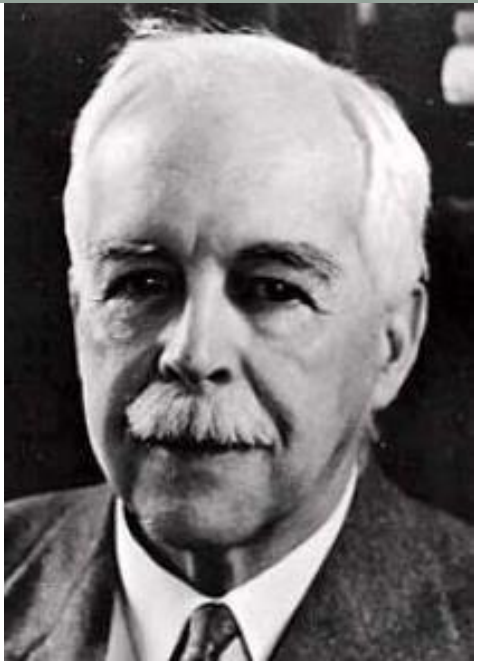
MO: Bonding orbital

H• + •H → H:H or H×•H or H—H

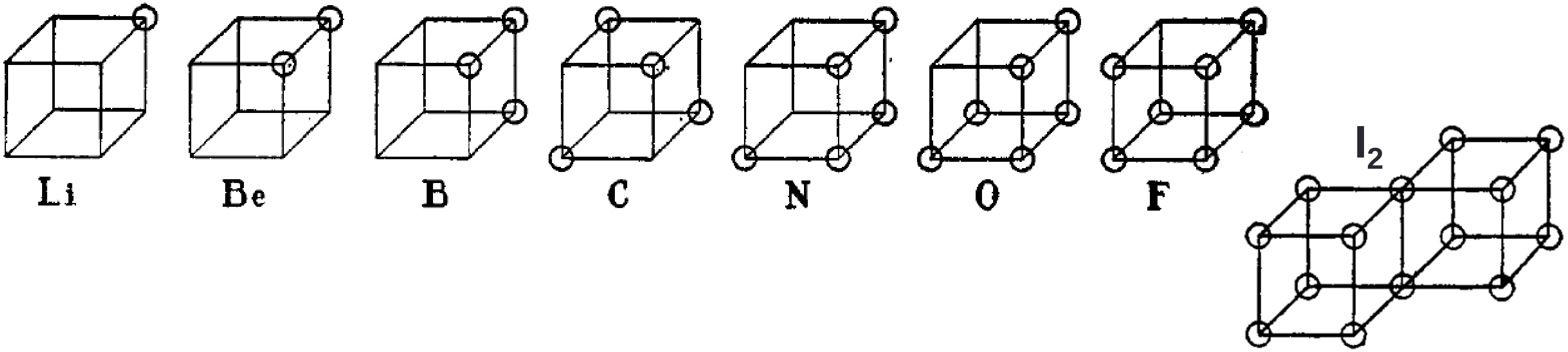
Lewis: Shared electron pair

Lewis Diagram: Rules

1. A shared pair = a covalent bond.
   A lone pair = no bonding.
2. Each atom achieves its own noble-gas shell of electrons.
3. Share as many electrons as possible.



Gilbert N. Lewis
(Berkeley, 1875–1946)



Lewis, G. N. "The Atom and the Molecule", *J. Am. Chem. Soc.* **1916**, *38*, 762–785.

Octet Rule Extension

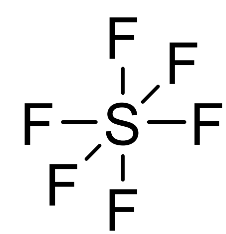
Duet

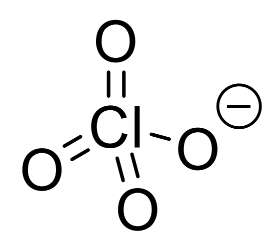
6, 8

Octet 八隅体

1*s*	H							He
2*s*, 2*p*	Li	Be	B	C	N	O	F	Ne
3*s*, 3*p*, 3*d*	Na	Mg	Al	Si	P	S	Cl	Ar
	K	Ca	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	In	Sn	Sb	Te	I	Xe
	Cs	Ba	Tl	Pb	Bi	Po	At	Rn
	Fr	Ra						

8, 10, **12**, 14, …





Correlation

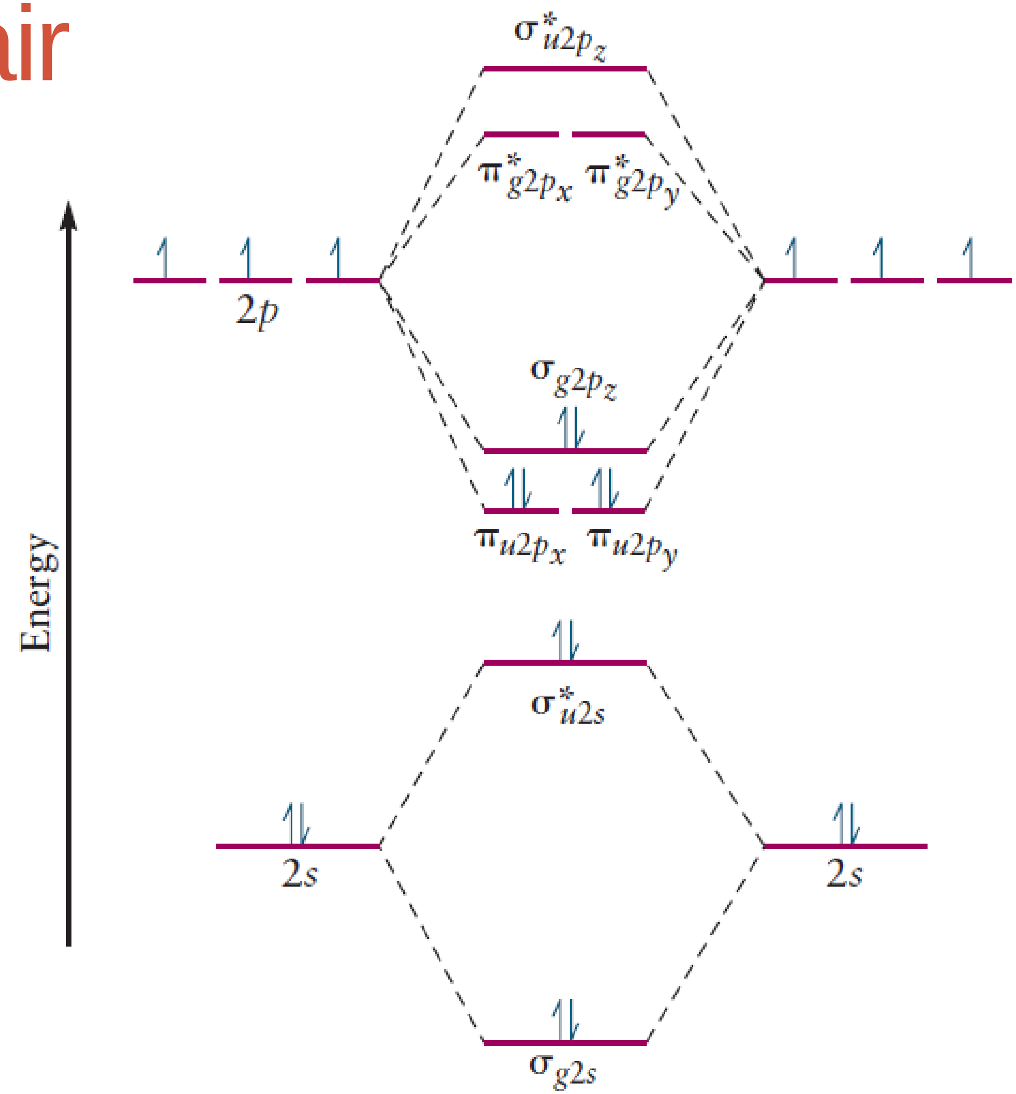
Molecular Orbital	Lewis Dot Structure
Bonding orbital	Shared electron pair
Nonbonding orbital	Lone electron pair
Bonding + antibonding orbitals	2 lone electron pairs
Delocalized orbital	Resonance structures
Two electrons from one atom	Coordinate bond
	Formal charge

Summary: Lone Pair

$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}:$

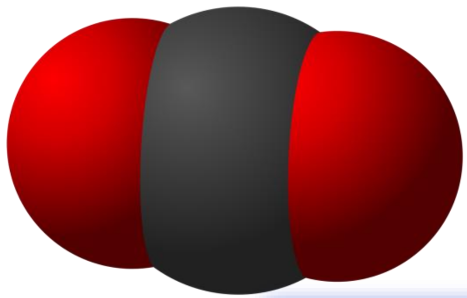
$:N:::N:$ or $:N{\equiv}N:$

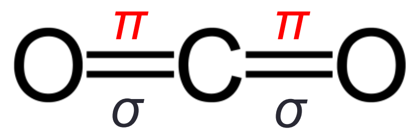
Lewis:
2 lone electron pairs

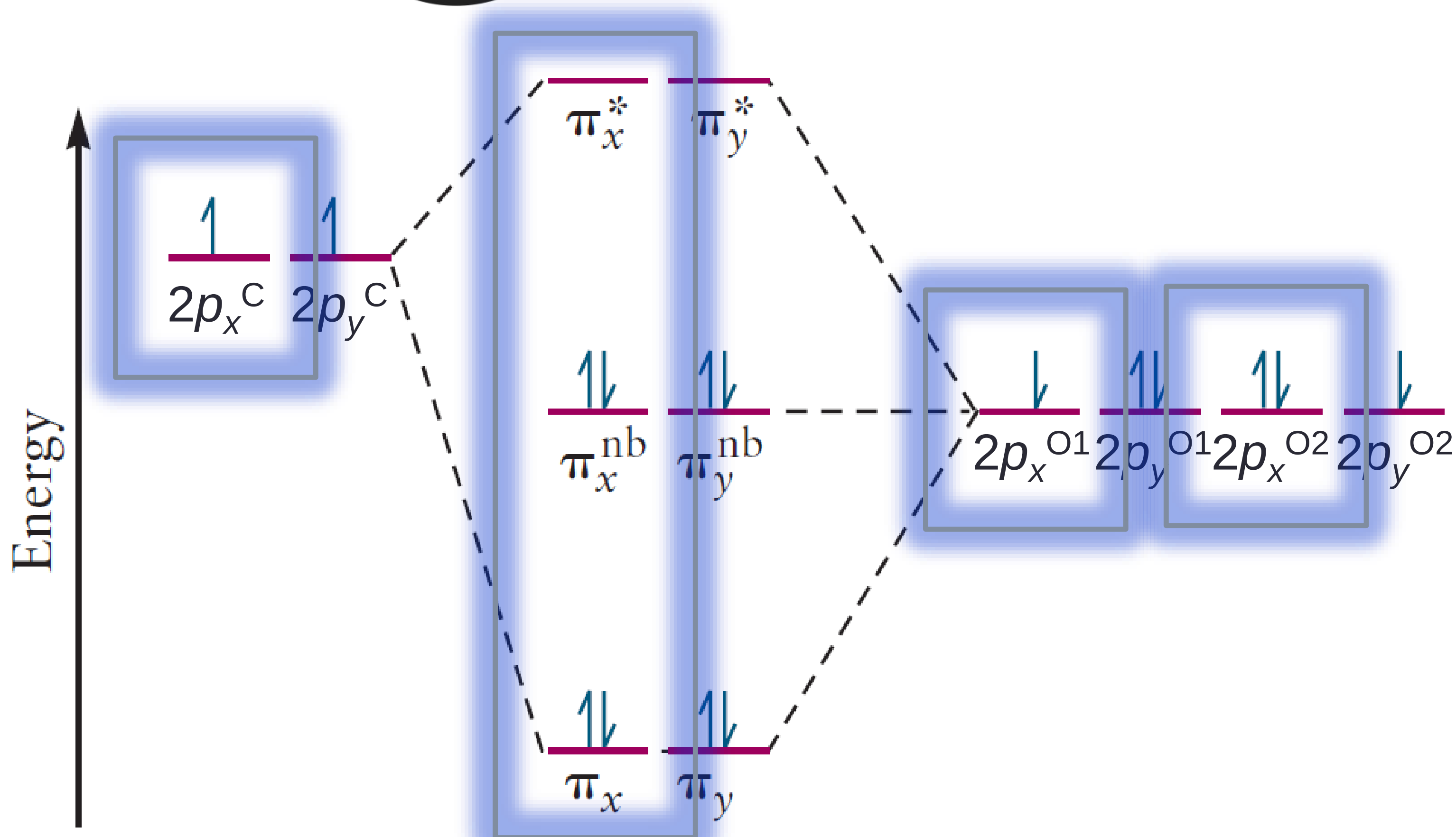


MO: Bonding + antibonding orbitals

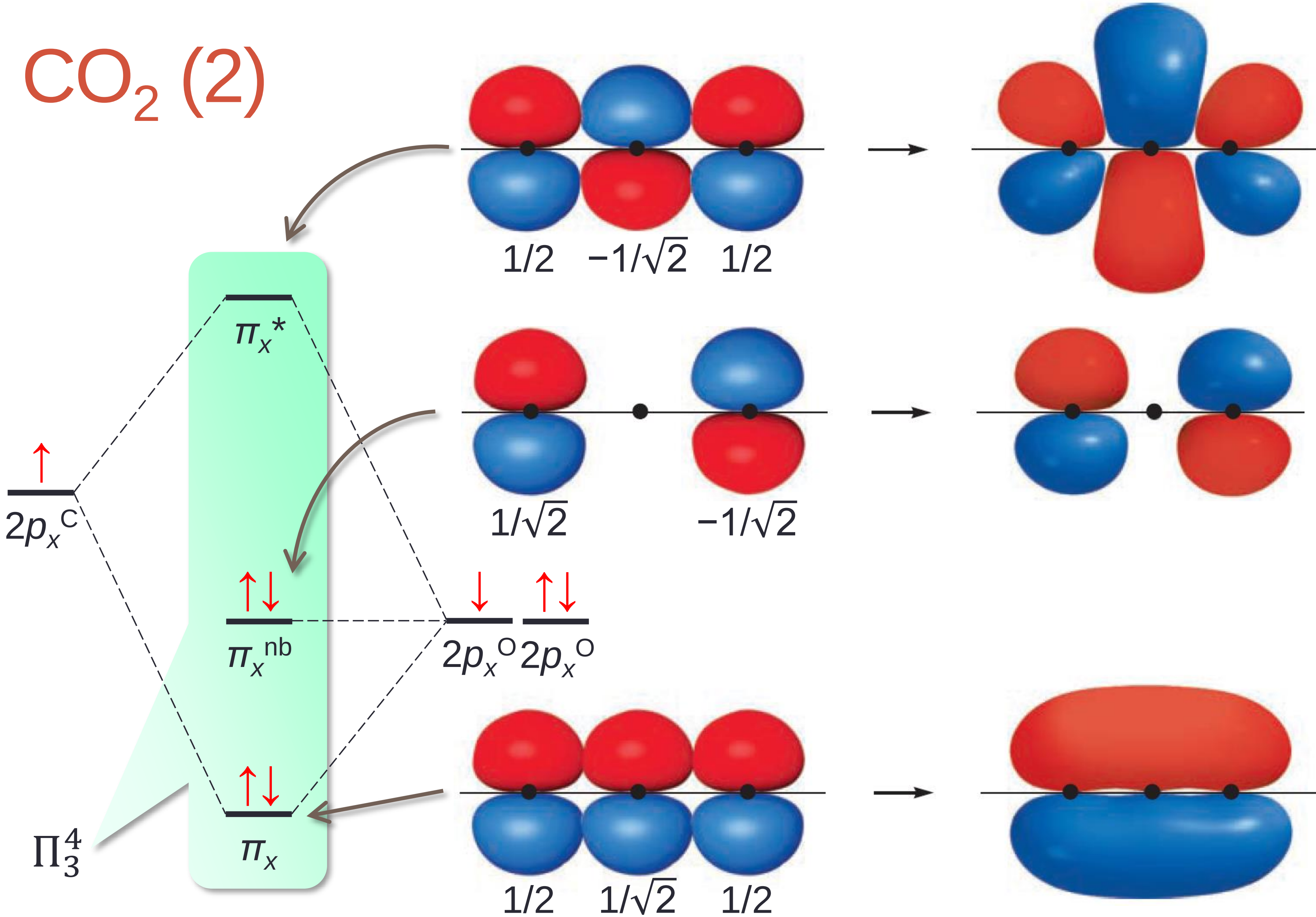
Triatomic Molecules: CO_2 (1)







CO_2 (2)


π_x^*
$2p_x^C$
π_x^{nb}
$2p_x^O$ $2p_x^O$
Π_3^4
π_x
1/2 $-1/\sqrt{2}$ 1/2
$1/\sqrt{2}$ $-1/\sqrt{2}$
1/2 $1/\sqrt{2}$ 1/2

Outline

- Valence Bond Theory (1927)
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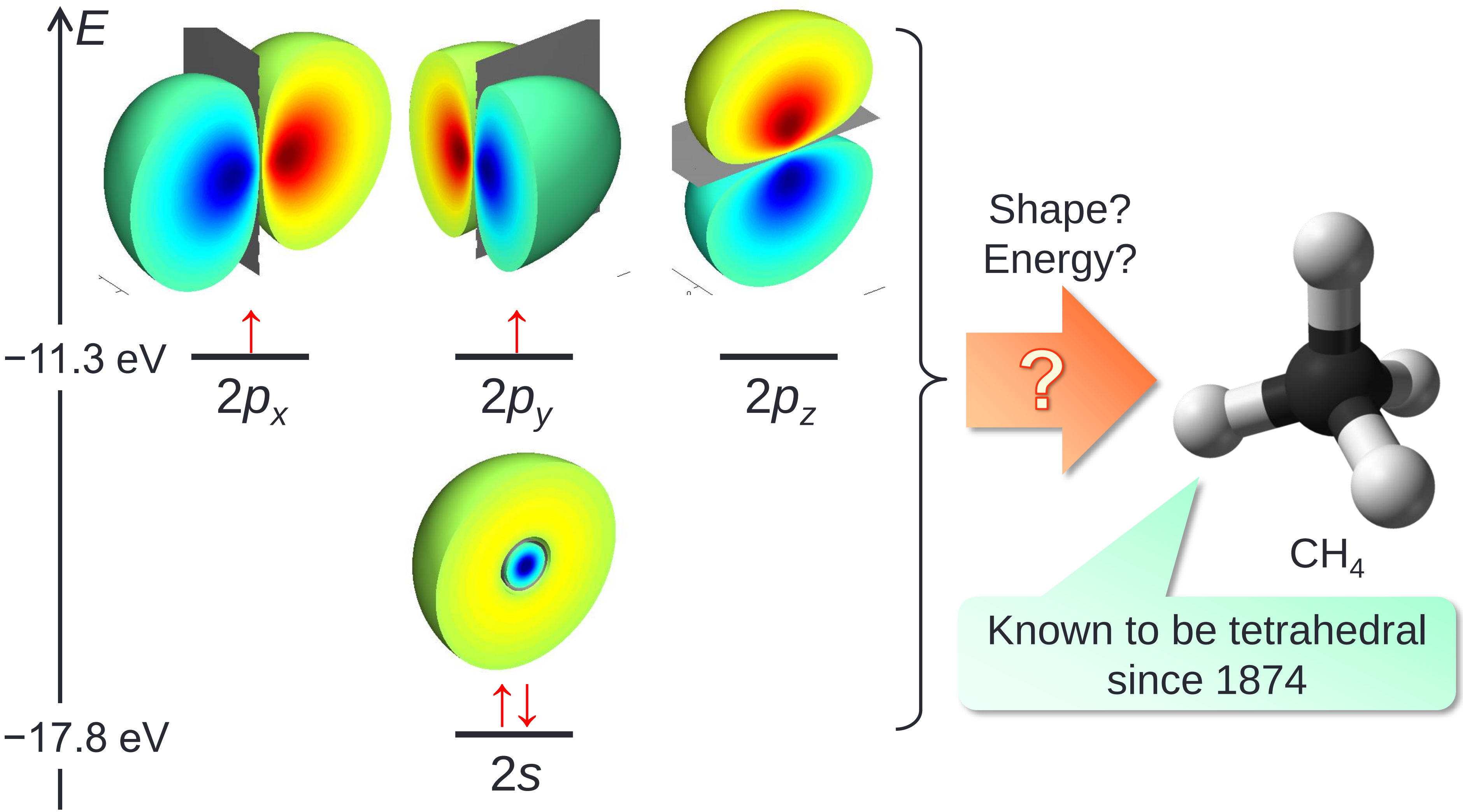
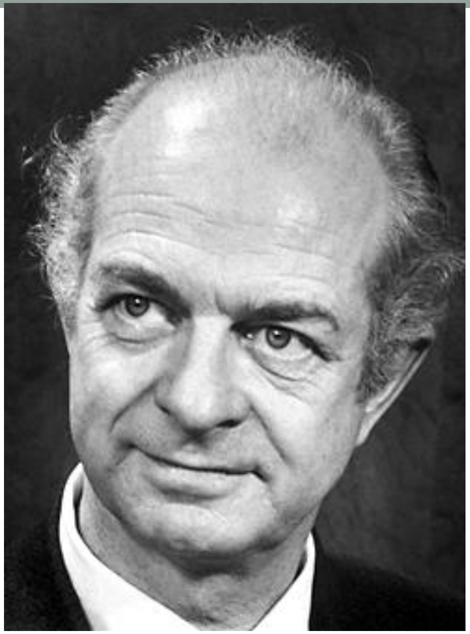
Why Hybridize? (1) CH_4



Pauling's Answer



Linus Pauling
(Caltech, 1901–1994)

E (eV)

−11.3

−17.8

C: $2s^2 2p^2$ + 2× H: $1s^1$ (−13.6) ⟶ $:CH_2$ Carbene

Or better,

E (eV)

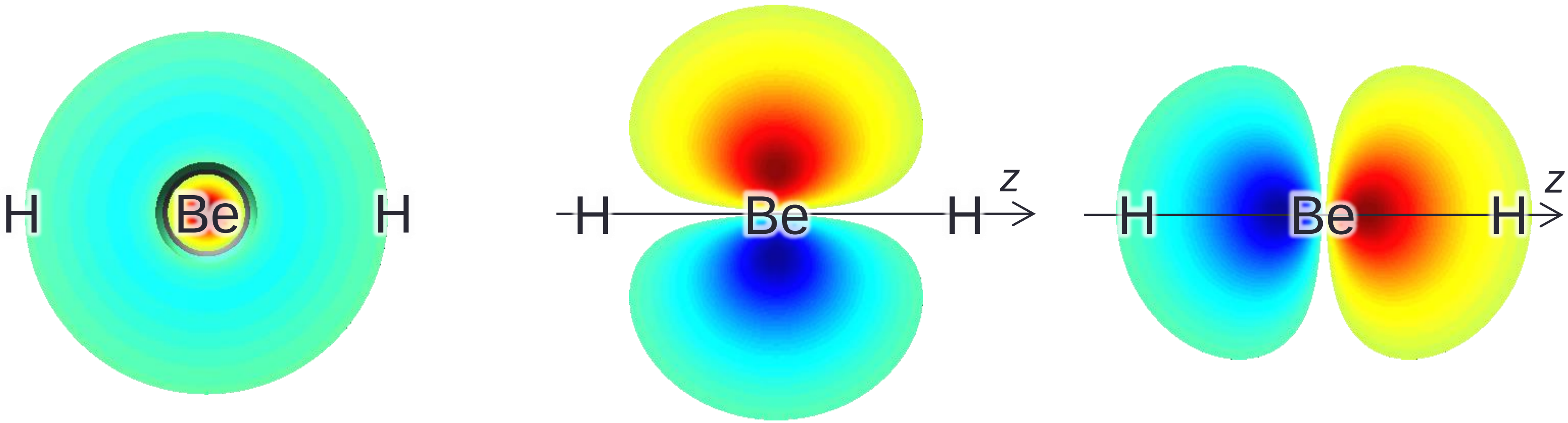
−11.3

−17.8

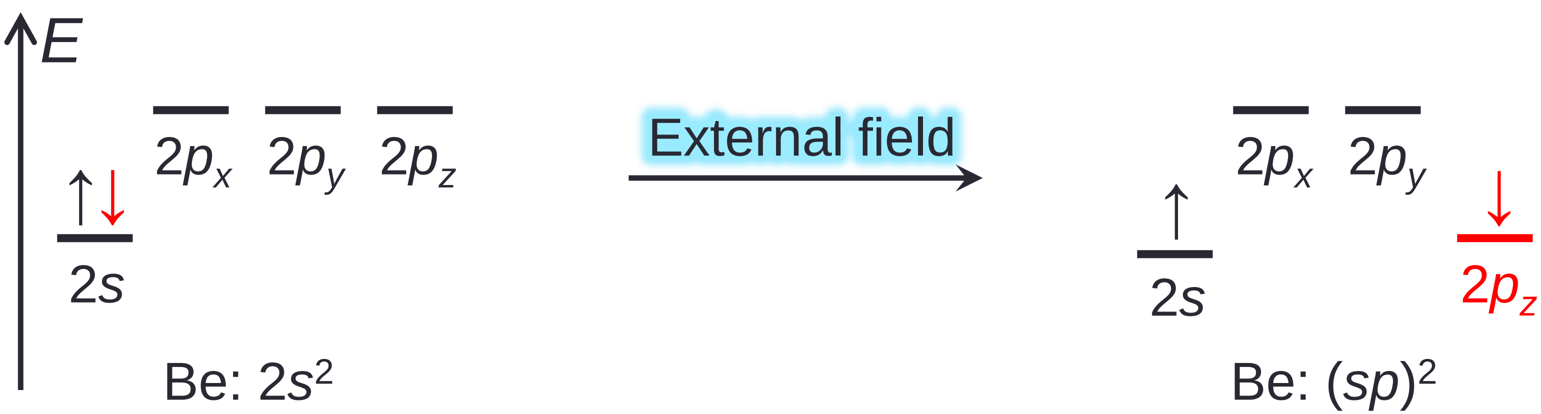
C: $2s^2 2p^2$ $\xrightarrow{\text{Promotion}}$ C: $2s^1 2p^3$ $\xrightarrow{\text{Hybridization}}$ C: $(sp^3)^4$ (−12.9)

+ 4× H $1s^1$ ⟶ CH_4

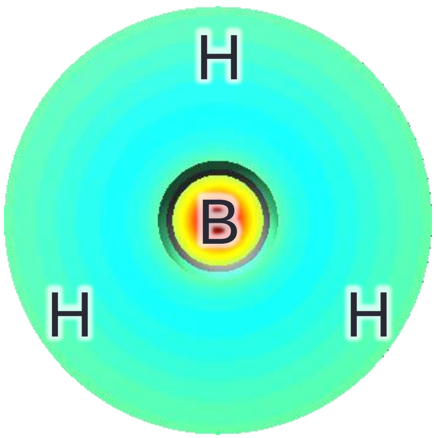
Why Hybridize? (2) BeH_2



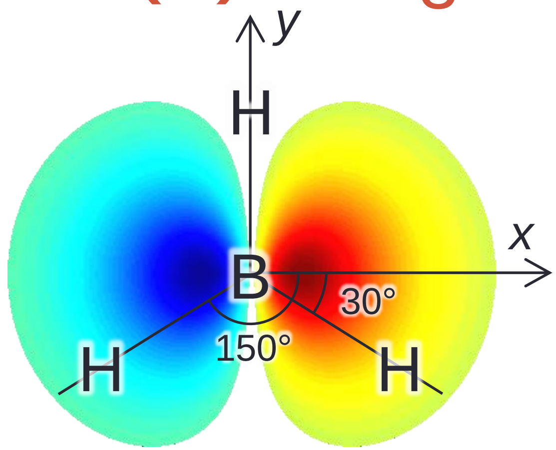
$2s$ $2p_x$, $2p_y$ $2p_z$



Why Hybridize? (2) BH_3



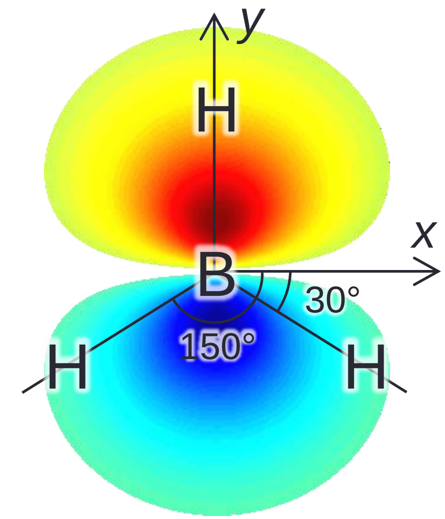
$2s$



$2p_x$

$\cos^2(30°) + \cos^2(150°)$

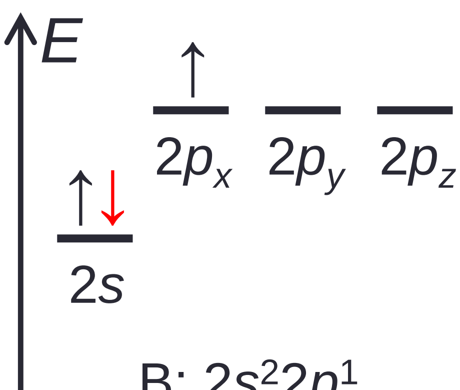
$= 3/2$



$2p_y$

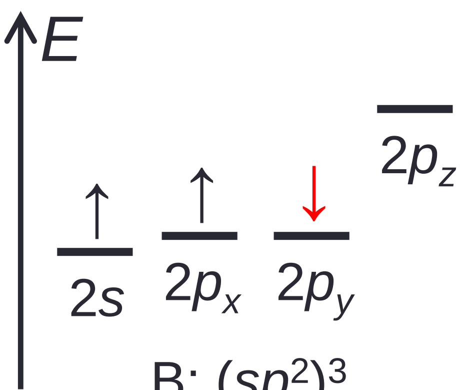
$\sin^2(30°) + \sin^2(150°)$

$+ \sin^2(-90°) = 3/2$



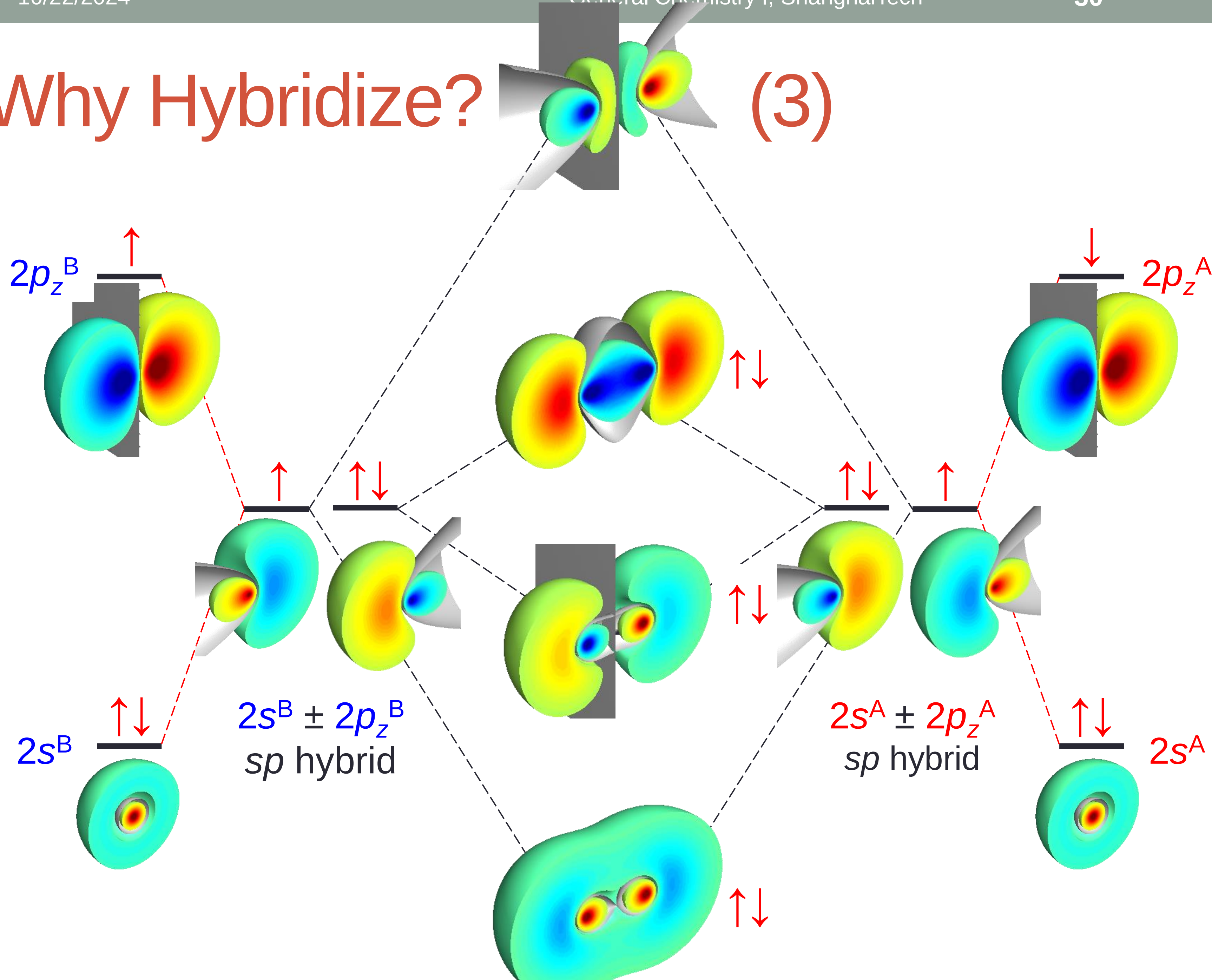
B: $2s^2 2p^1$

External field

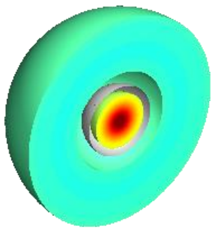


B: $(sp^2)^3$

Why Hybridize? (3)



sp Hybridization



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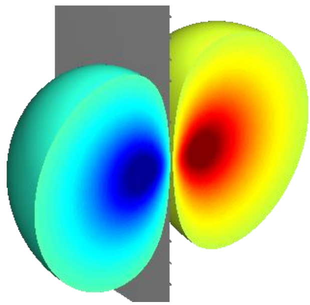

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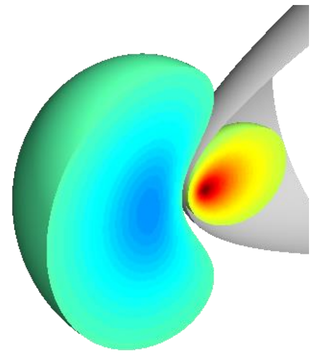
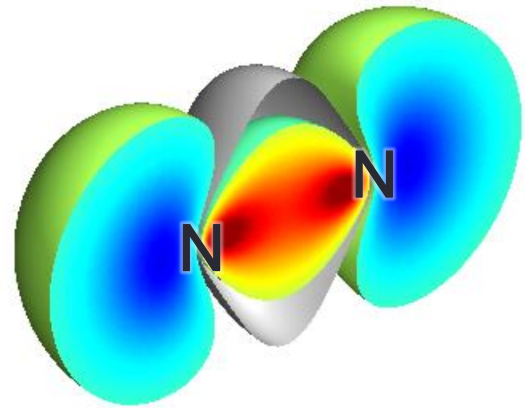
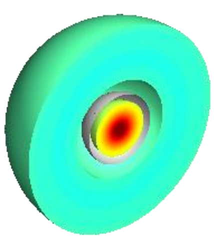




$\frac{1}{\sqrt{2}}s$

$\frac{1}{\sqrt{2}}p_z$

sp hybrid



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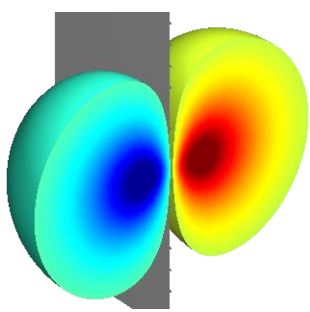

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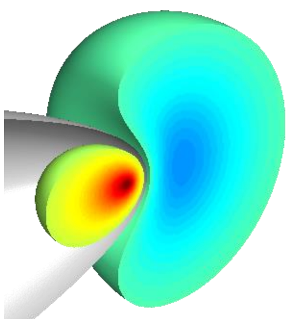
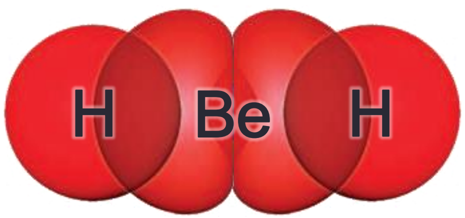
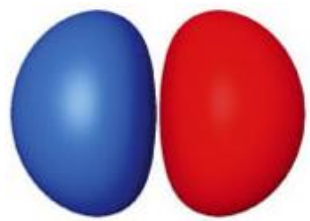
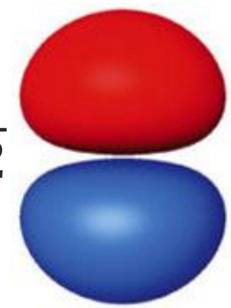
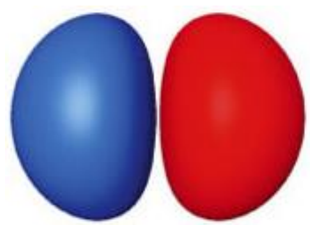
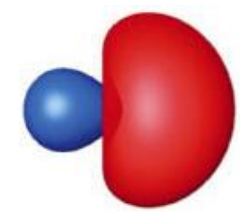


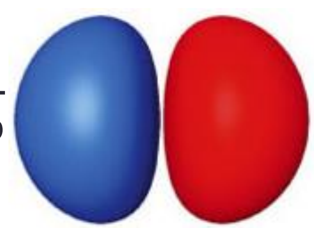
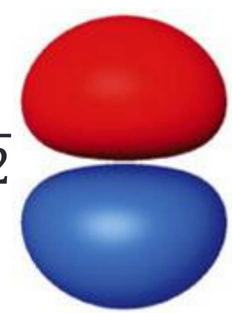


sp^2 Hybridization

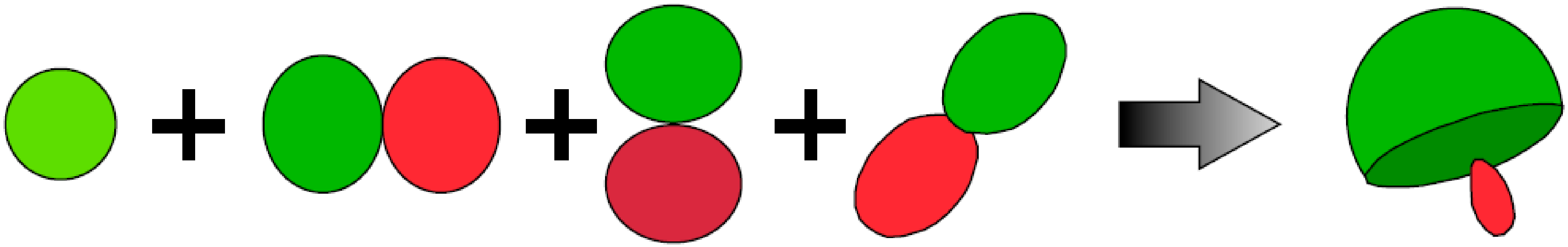
s		p_x		p_y		sp^2 hybrid

$\sqrt{1/3}$  $-\sqrt{1/6}$  $+\sqrt{1/2}$  = 

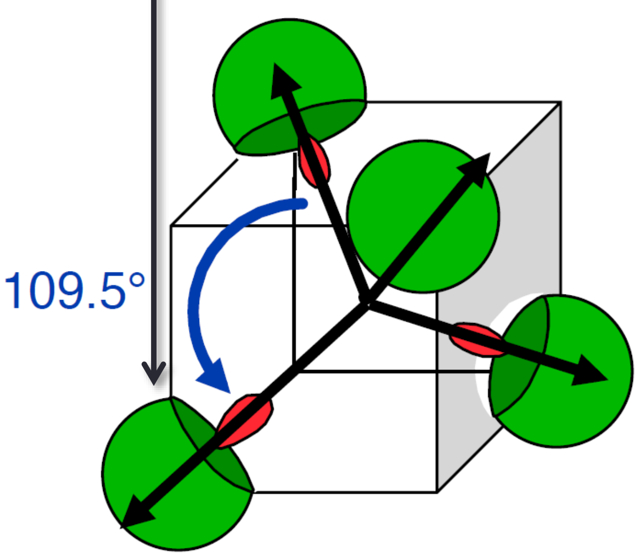
$\sqrt{1/3}$  $+\sqrt{2/3}$  = 

$\sqrt{1/3}$  $-\sqrt{1/6}$  $-\sqrt{1/2}$  = 

sp^3 Hybridization

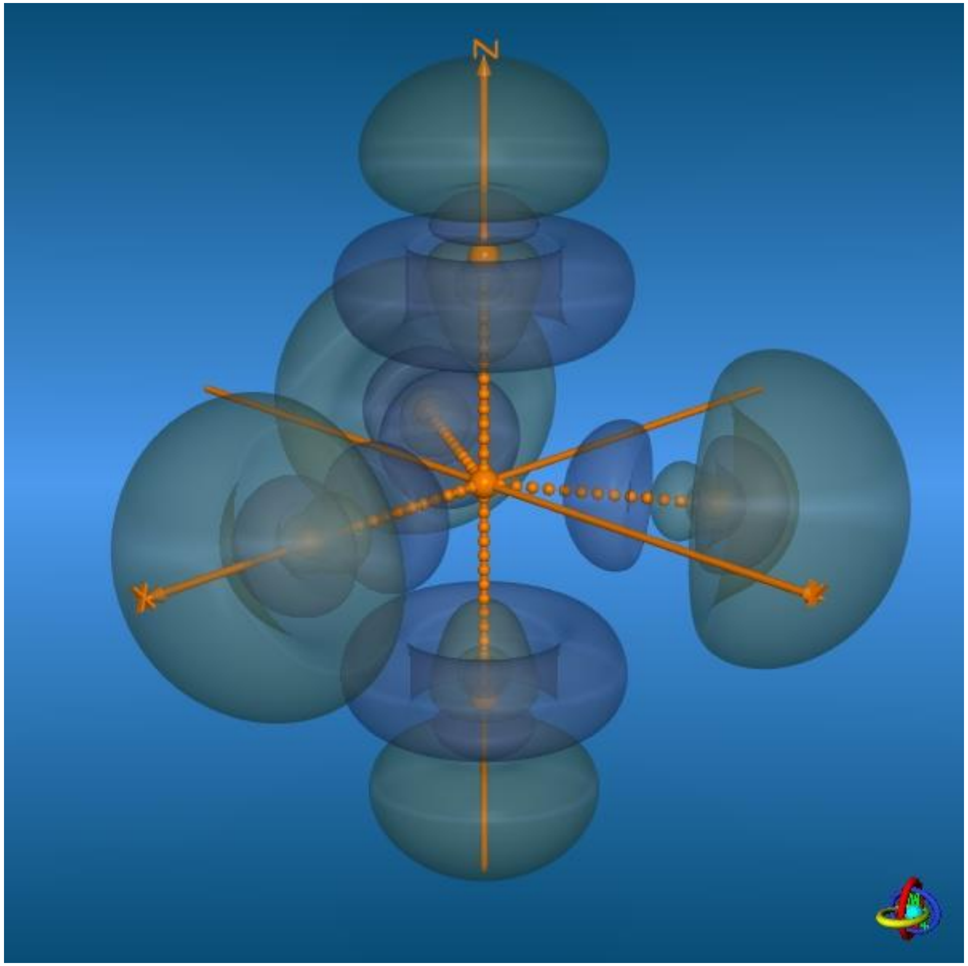


$\sqrt{1/4}$	$\sqrt{1/4}$	$\sqrt{1/4}$	$\sqrt{1/4}$
$\sqrt{1/4}$	$\sqrt{1/4}$	$-\sqrt{1/4}$	$-\sqrt{1/4}$
$\sqrt{1/4}$	$-\sqrt{1/4}$	$\sqrt{1/4}$	$-\sqrt{1/4}$
$\sqrt{1/4}$	$-\sqrt{1/4}$	$-\sqrt{1/4}$	$\sqrt{1/4}$

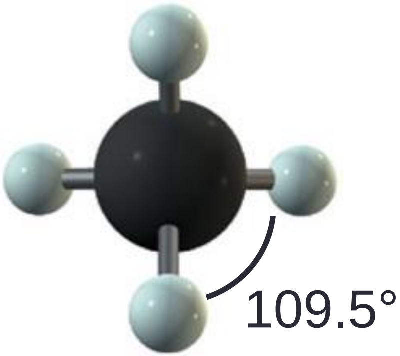


sp^3d Hybridization

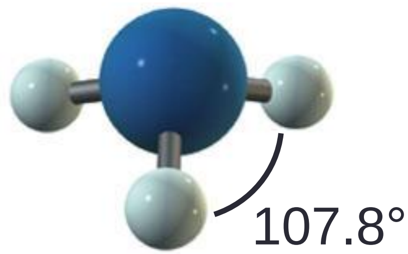
s, p_x, p_y, p_z, d_{z2}



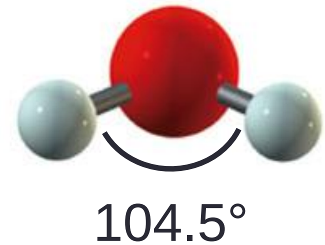
Polyatomic Molecules



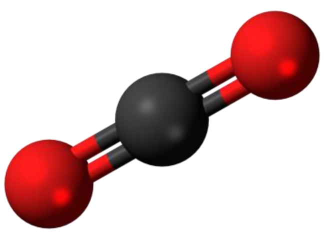
CH_4



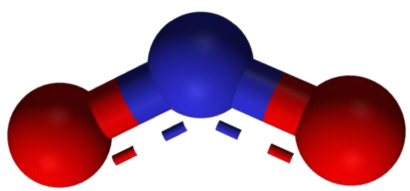
NH_3



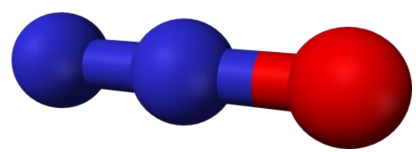
H_2O



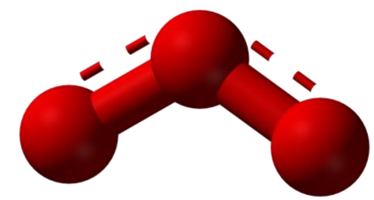
CO_2



NO_2



N_2O

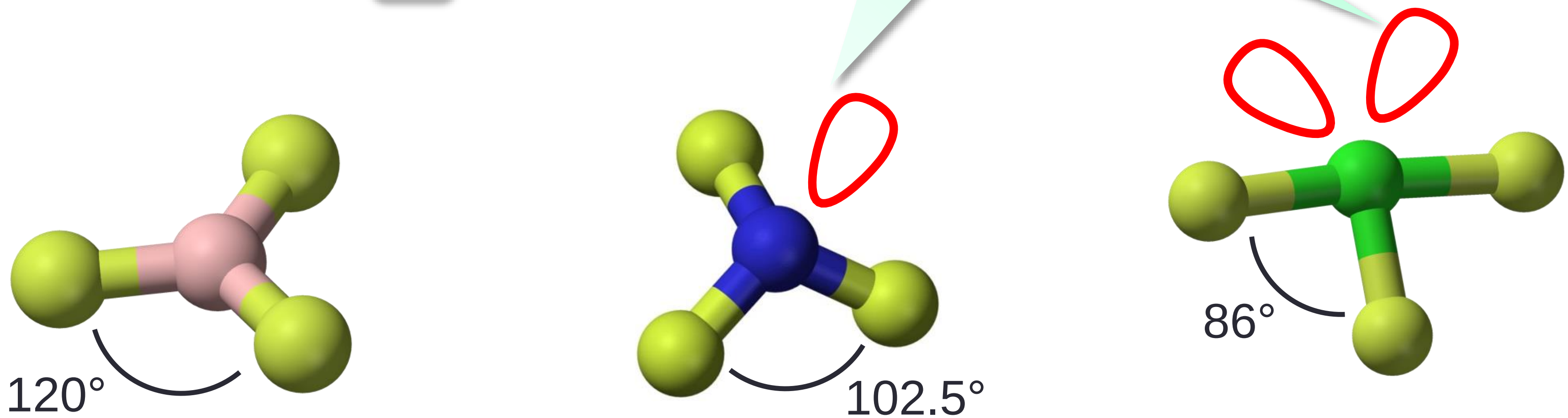


O_3

Molecular Geometry

					He
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr

There's something we can't see!



BF_3 NF_3 BrF_3

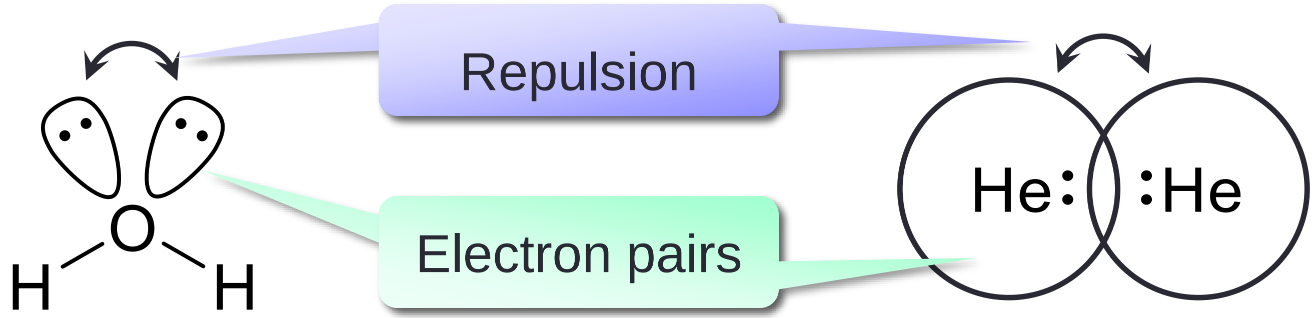
The Valence Shell Electron-Pair Repulsion Theory

Ronald J. Gillespie
(UCL, 1924–)

Ideas based on VB theory:

- Only the valence shell matters
- Shared electron pairs and lone pairs
- Molecular energy ≈
  Bond energies + repulsion energies

Ronald S. Nyholm
(UCL, 1917–1971)

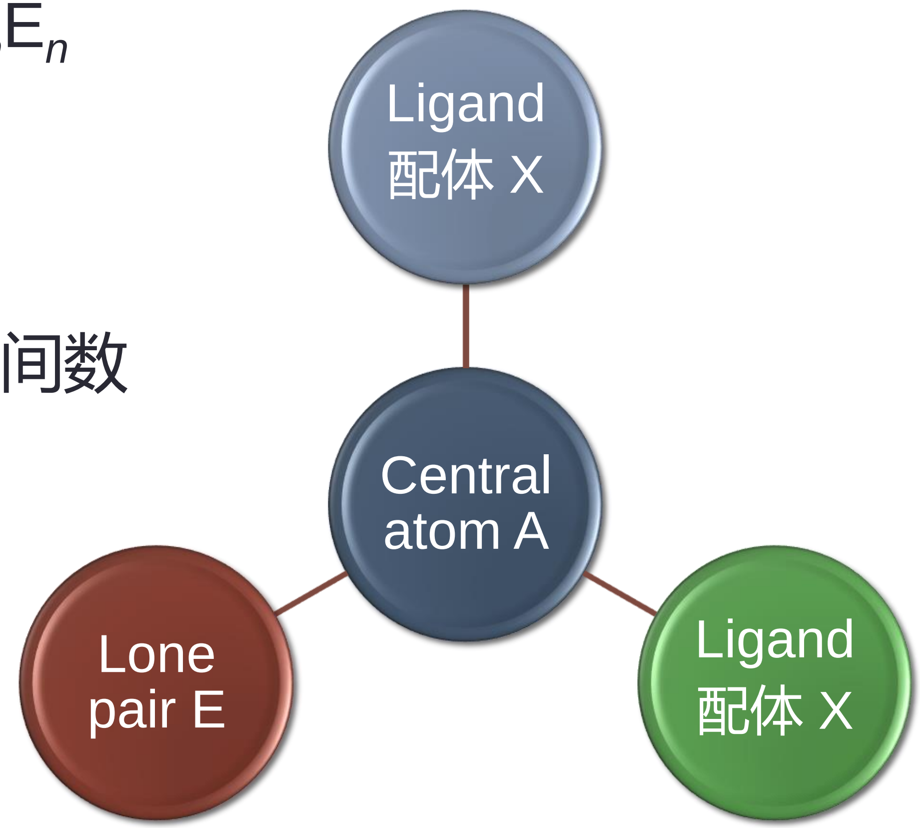


Rules of VSEPR Theory

1. Rewrite a structure as AX_mE_n
   m = number of ligands
   n = number of lone pairs

2. Assign a Steric Number 空间数
   SN = $m + n$

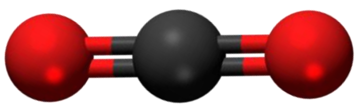
3. Place the ligands and lone pairs on a polyhedron of SN vertexes



4. Size: Lone pair > multiple bonds > shared pair

Example: SN = 2

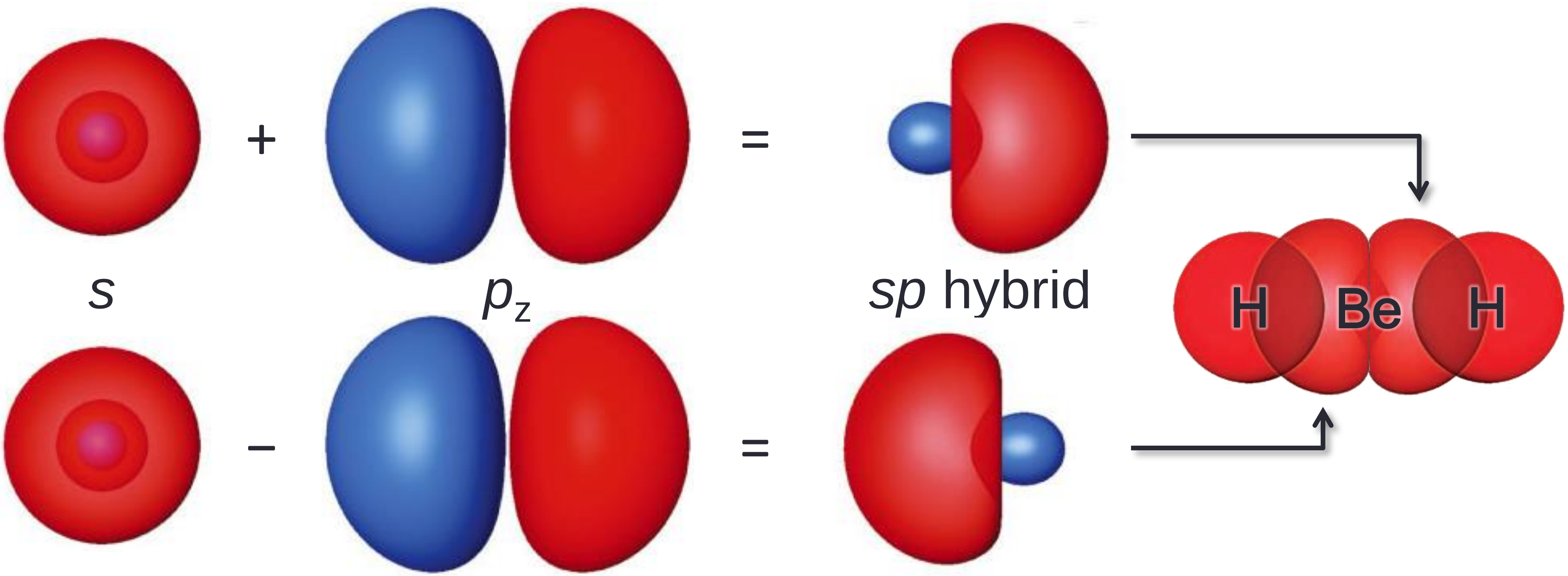
H—Be—H BeH_2: $m = 2$, $n = 0$



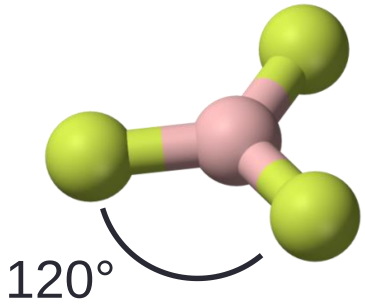
CO_2: $m = 2$, $n = 0$

:N≡N: N_2: $m = 1$, $n = 1$

Linear
直线形

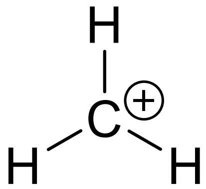


Example: SN = 3



BF_3: m = 3, n = 0 Trigonal planar

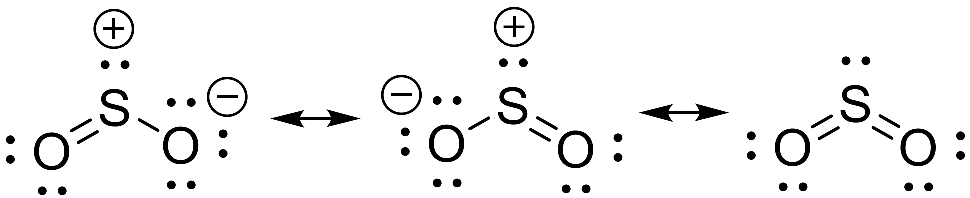
平面三角形



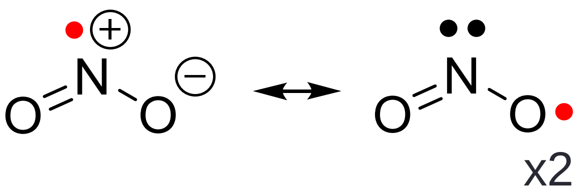
CH_3^+: m = 3, n = 0 Trigonal planar

sp^2 hybrid

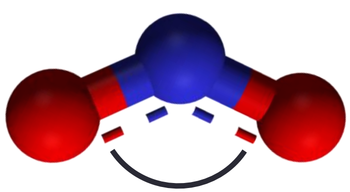
Example: SN = 3



SO_2: m = 2, n = 1
Bent / V-shaped
弯曲形 / V形 / 角形



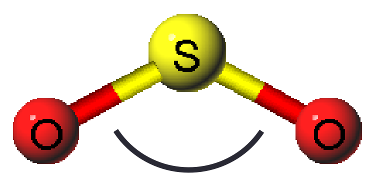
NO_2: m = 2, 0.5 < n < 1 Bent



134°

NO_2

VS



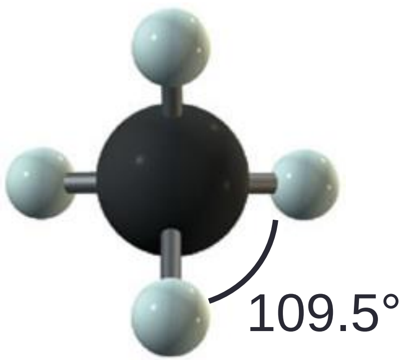
119°

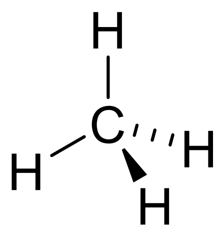
SO_2

117°

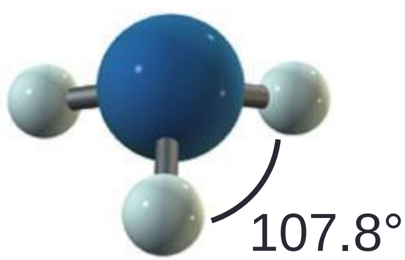
O_3

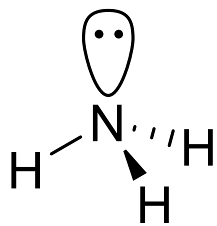
Example: SN = 4



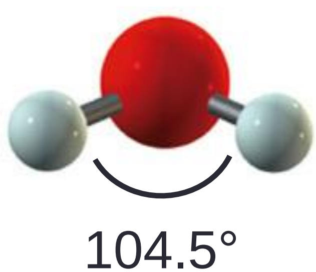


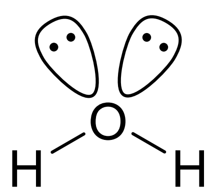
CH_4: m = 4, n = 0 Tetrahedral 四面体





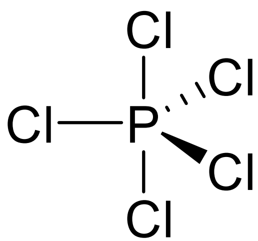
NH_3: m = 3, n = 1 Trigonal pyramidal 三角锥



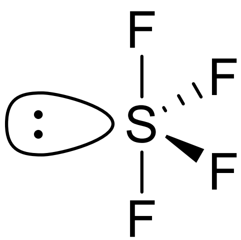


H_2O: m = 2, n = 2 Bent

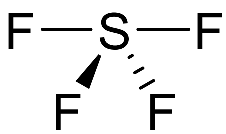
Example: SN = 5

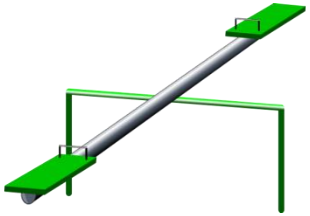


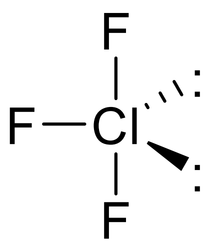
PCl_5: m = 5, n = 0 Trigonal bipyramidal 三角双锥



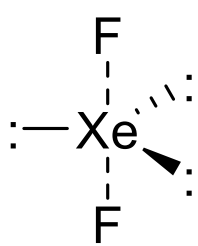
SF_4: m = 4, n = 1 Seesaw 跷跷板







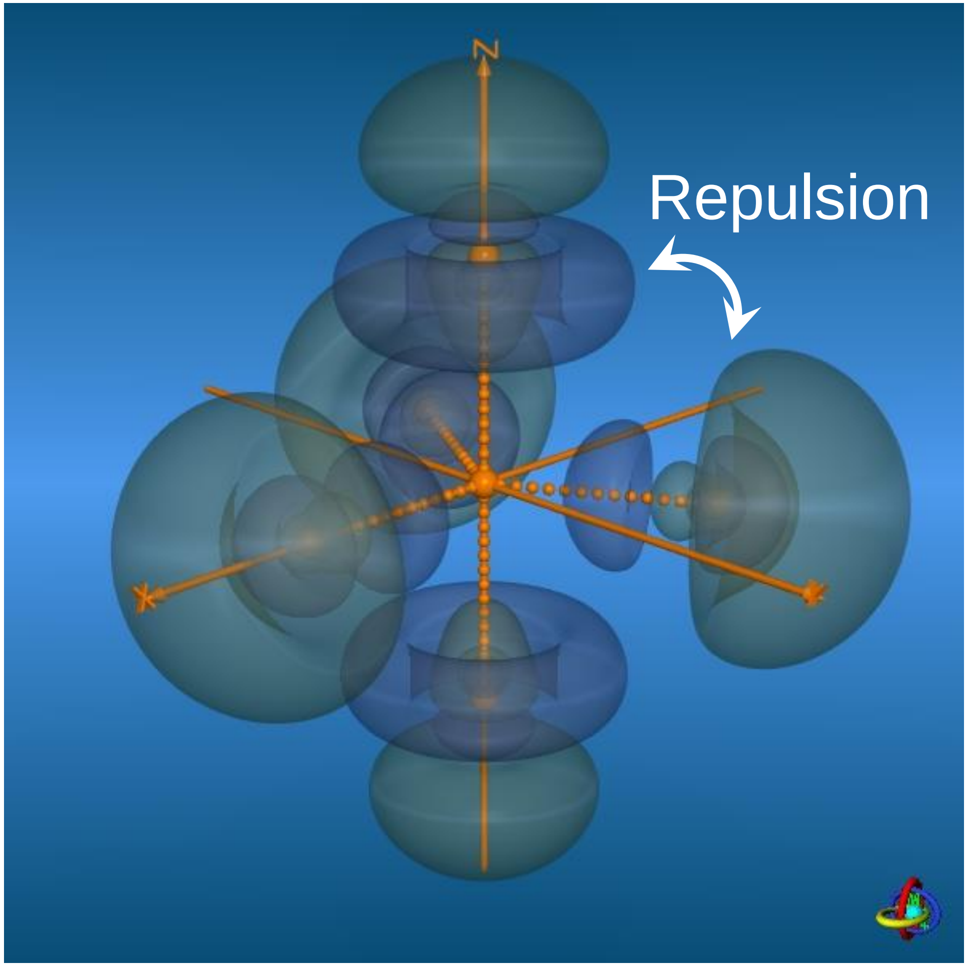
ClF_3: m = 3, n = 2 T-shaped



XeF_2: m = 2, n = 3 Linear

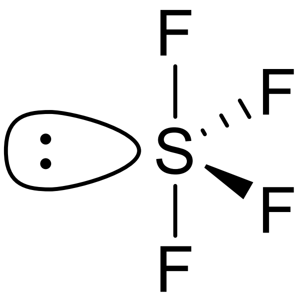
Example: sp^3d Hybridization

s, p_x, p_y, p_z, d_{z2}

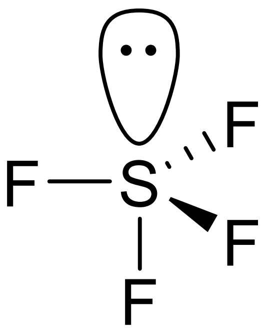


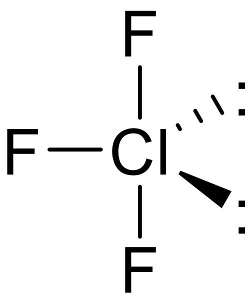
Avoid A–E ⊥ A–E
Minimize A–E ⊥ A–X

Lone Pairs Are Fat

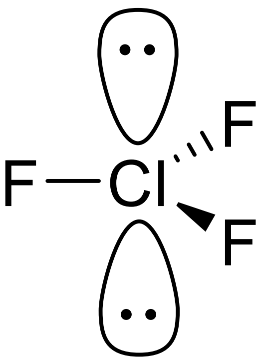


VS



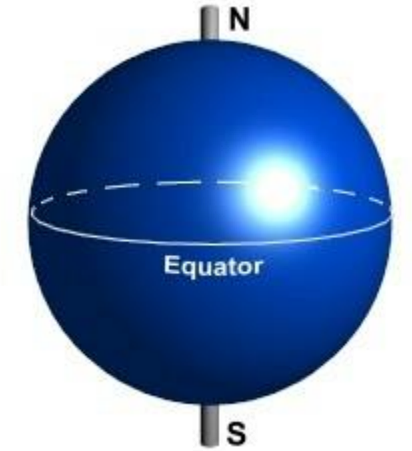


VS



Summary

1. Count the number of lone pairs from Lewis structure
2. Place the lone pairs on equatorial positions
3. Deduce the molecular geometry by ignoring the lone pairs



Simple and intuitive

Compatible with VB theory

Qualitative

Doesn’t work for transition metals

Molecular Orbital (MO)

Valence Bond (VB) / Hybridization

Molecular orbital ← Atomic orbitals (s, p, d) → Hybridized atomic orbital

MO
- Bonding
- Nonbonding
- Antibonding

Correlation diagram

Excited state

Shared / dative
Lone
Repulsive

Electron pair

Lewis dot diagram

Resonance structure

Bond order | Bond type (σ, π, δ) Bond length & energy | Oxid. state Valence

Aufbau principle | Electronic structure of molecules | Formal charges

Conjugated π system | $2^{nd}/3^{rd}$ period | Octet rule | VSEPR

Ligand-field theory | Transition metals | 18-electron rule, Crystal-field theory

Next: Organics

Reading: OGB8 §7