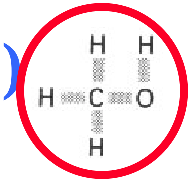
The Essence of Chemistry:
The Covalent Bonding of Atoms

Atkins, Chapter 14

A brief review: Lewis bonding theory (1916)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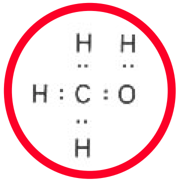
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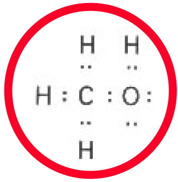
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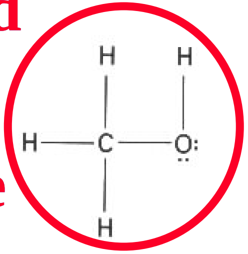
1.) Arrange atoms as found in molecule

2.) Add one electron pair (:) between bonded atoms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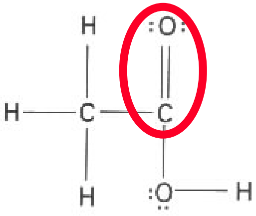
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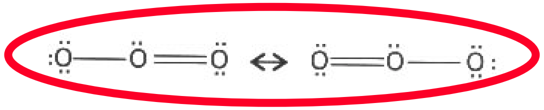
3.) Use remaining electron pairs to complete the octets of all atoms (lone electron pairs!)

4.) Replace bonding electron pairs by bond lines (-)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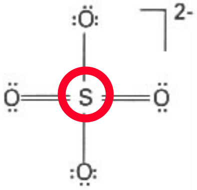
5.) Allow for double and triple bonds

6.) Allow for resonance hybrid (= blend)



7.) Allow for expansion of octet for larger atoms with d orbitals

Further Review: The VSEPR Model to Derive Molecular Geometry

VSEPR= Valence Shell Electron Pair Repulsion

Basic assumption: The valence-shell electron pairs of the central atom adopt positions that maximize their separation (lowest repulsion)

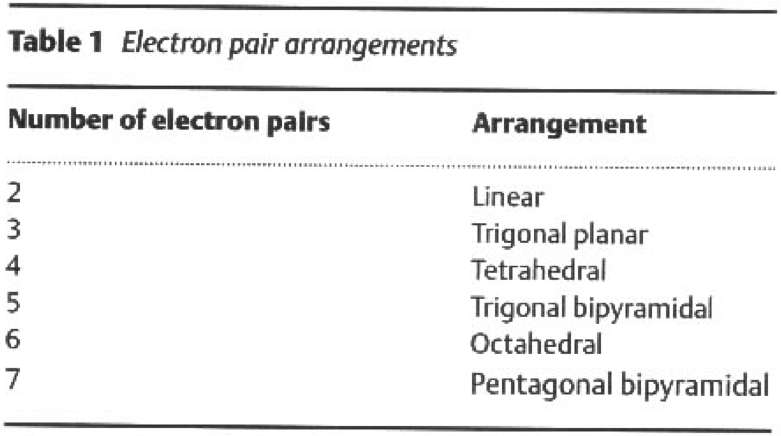
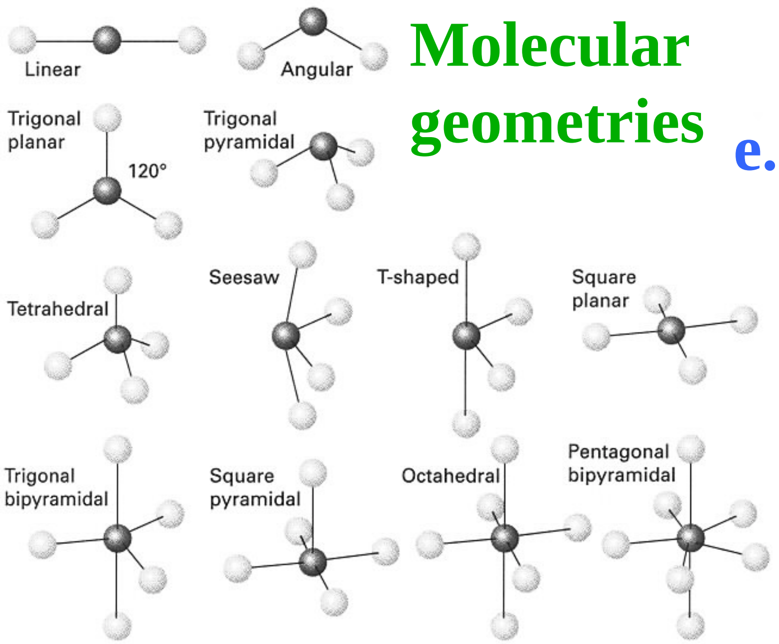


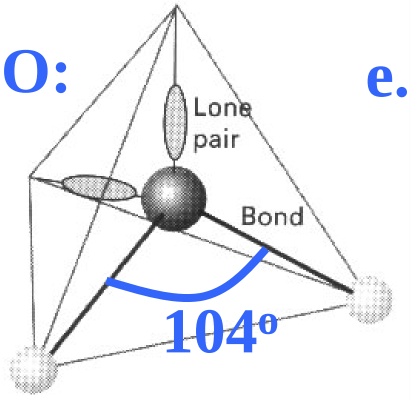
Table 1 *Electron pair arrangements*

Number of electron pairs	Arrangement
2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral
7	Pentagonal bipyramidal

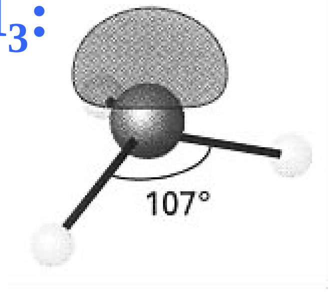
Molecular geometries



e.g., H_2O:

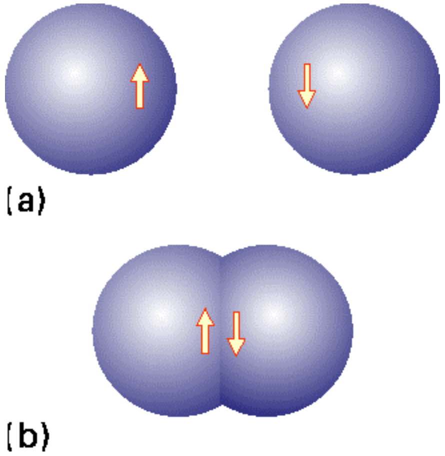


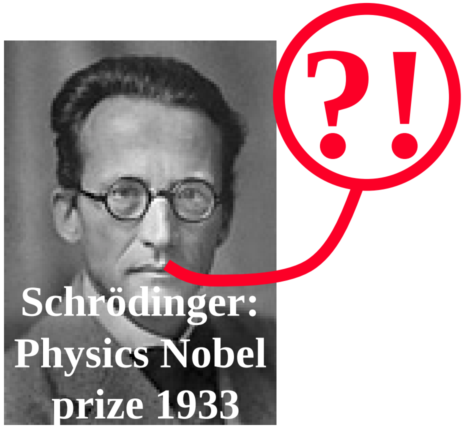
e.g., NH_3:



⇒ Lone electron pairs have greater repelling effect

How Quantum Mechanics can Explain Bonding





Schrödinger: Physics Nobel prize 1933

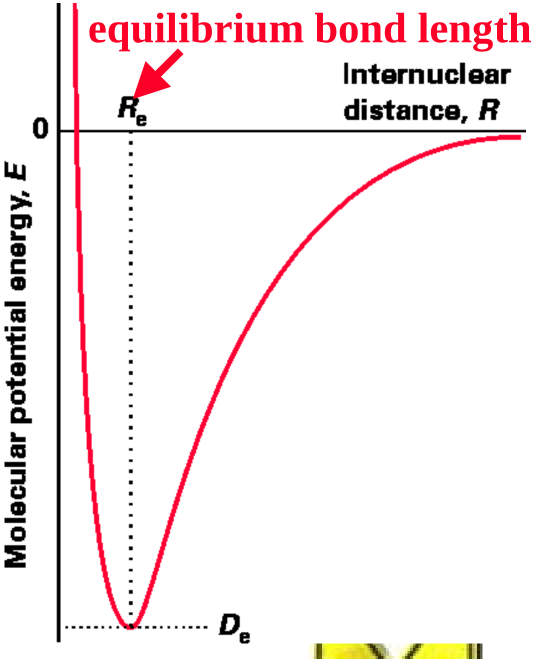
Simplifying the problem: the Born-Oppenheimer approximation = the nuclei are stationary

The basis of bonding: electrons have larger space to roam and become attracted by two nuclei

How does one solve the Schrödinger equation?

- **Valence Bond Theory**
- **Molecular Orbital Theory**

⇒ Solve the Schrödinger equation for a variety of different nuclear distances



⇒ Molecular potential energy curve

Valence Bond (VB) Theory: Older but useful

Electron 1 of atom A, electron 2 of atom B

A and B far apart: $\Psi = \Psi_A(1) \times \Psi_B(2)$ **"Overall wavefunction"**

When A and B come closer: $\Psi = \Psi_A(2) \times \Psi_B(1)$

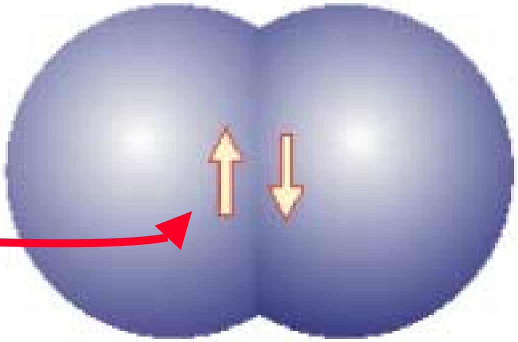
Alternate overall wavefunction, equally likely
(the electrons roam)

⇒ **Valence bond function (wavefunctions of electrons blend):**

$$\Psi(AB) = \Psi_A(1) \times \Psi_B(2) + \Psi_A(2) \times \Psi_B(1)$$

⇒ **Bonds do form because electrons have more space and cannot be distinguished**

⇒ **Bonds are allowed to form because electrons can pair**

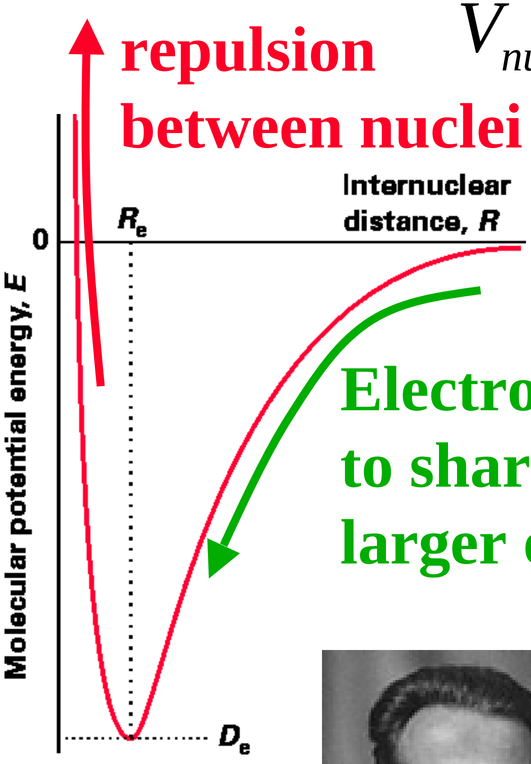


The VB Theory Explains Experimental Data

Explains molecular energy curve:

Coulumbic repulsion between nuclei

$$V_{nuc,nuc} = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}$$



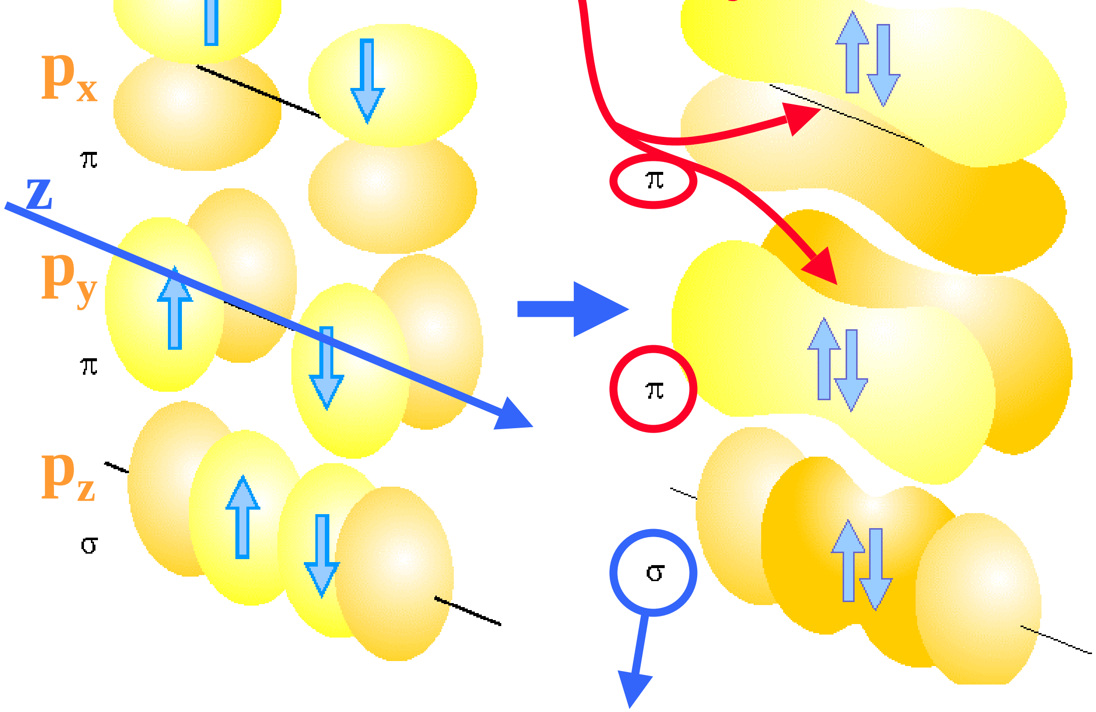
Electrons start to share a larger orbital

Explains bond order:

Example: N_2 = :N≡N:

N: $[He]2s^2 2p_x^{\,1} 2p_y^{\,1} 2p_z^{\,1}$

no e^- density on axis



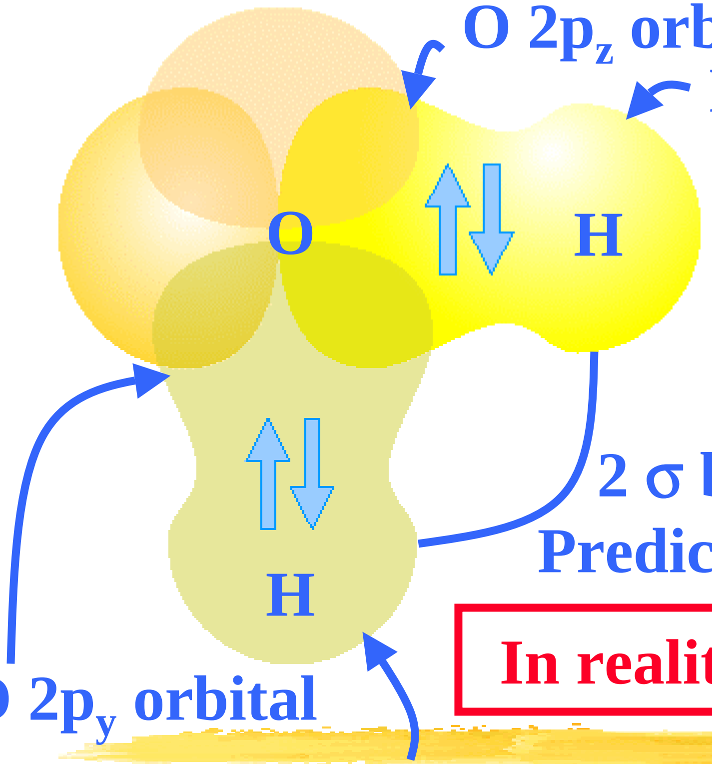
Cylindrically symmetric

Here Comes the Trouble: The VB Theory and Polyatomic Molecules

Example: H_2O
O: $[He]2s^2 2p_x^2 2p_y^1 2p_z^1$
H: $1s^1$

⇒ **Bond angles are poorly predicted**

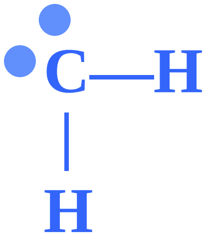
Example: CH_4
C: $[He]2s^2 2p_x^1 2p_y^1$
H: $1s^1$



2 σ bonds
Predicted: 90°

In reality: 104°!

Prediction: CH_2!



⇒ **Bond order is not predicted**