A brief review: Lewis bonding theory (1916)

1.) Arrange atoms as found in molecule
2.) Add one electron pair (:) between bonded atoms
3.) Use remaining electron pairs to complete the octets of all atoms (lone electron pairs!)
4.) Replace bonding electron pairs by bond lines (-)
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)

**Molecular geometries** e.g., H$_2$O:

![Diagram of H$_2$O molecular geometry with a bond angle of 104°]

**Molecular geometries** e.g., NH$_3$:

![Diagram of NH$_3$ molecular geometry with a bond angle of 107°]

⇒ Lone electron pairs have greater repelling effect
How Quantum Mechanics can Explain Bonding

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

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

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

How does one solve the Schrödinger equation?

• Valence Bond Theory
• Molecular Orbital Theory

⇒ 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)

\( \Rightarrow \) Valence bond function (wavefunctions of electrons blend):

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

\( \Rightarrow \) Bonds do form because electrons have more space and cannot be distinguished

\( \Rightarrow \) Bonds are allowed to form because electrons can pair
The VB Theory Explains Experimental Data

Explains molecular energy curve:

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

Coulombic repulsion between nuclei

Electrons start to share a larger orbital

Example: \( \text{N}_2 = :\text{N}\equiv\text{N}: \)
\( \text{N}: [\text{He}]2s^22p_x^12p_y^12p_z^1 \)

Explains bond order:

Cylindrically symmetric

no e\textsuperscript{-} density on axis
Here Comes the Trouble: The VB Theory and Polyatomic Molecules

Example: \( \text{H}_2\text{O} \)

- **O**: \([\text{He}]2s^22p_x^22p_y^21p_z^1\)
- **H**: \(1s^1\)

⇒ Bond angles are poorly predicted

In reality: 104°!

Example: \( \text{CH}_4 \)

- **C**: \([\text{He}]2s^22p_x^12p_y^1\)
- **H**: \(1s^1\)

Prediction: \( \text{CH}_2 \)!

⇒ Bond order is not predicted

Example: \( \text{O}_2 \)

- **O**: \(2p_z\) orbital
- **H**: \(1s\) orbital

⇒ 2 σ bonds

Predicted: 90°

In reality: 104°!