Valence Bond Theory (VBT)

* Quantum Mechanical in Nature

VBT was developed in 1920–30's (Linus Pauling)

↳ Chap 5 in Nature of Chemical Bond

↳ 2 Key Concepts (Resonance + Orbital hybridization)

↳ Early development of MOT

↳ Mathematical underpinning for initial chemical computations

↳ A way to describe Lewis' concepts w/ Math (Ψ)

Consider H_2

At Infinite Separation

H_A ..... H_B

$\Psi = \phi_A(1)\,\phi_B(2)$

ϕ_J is H1s on atom J

Decrease Separation

At Small Separation

H_A H_B

Upon interaction, I can't predict which atom hold $e^-(1)$ + which atom holds $e^-(2)$...

Both situations are equally likely ∴ treat true state of system as a superposition of $\Psi_1 + \Psi_2$

$\Psi_1 = \phi_A(1)\,\phi_B(2)$ or $\Psi_2 = \phi_A(2)\,\phi_B(1)$

$\Psi = \Psi_1 + \Psi_2 = \phi_A(1)\,\phi_B(2) + \phi_A(2)\,\phi_B(1)$

Linear Combination of $\Psi_1 + \Psi_2$

$\Psi = \Psi_1 + \Psi_2 = \phi_A(1)\,\phi_B(2) + \phi_A(2)\,\phi_B(1)$ ⇒ Expression for unnormalized H–H

↳ VB Wavefunction for H–H (σ bond)

..... (H ↿⇂ H) .....

↳ Has cylindrical Symmetry about the internuclear AXIS

↳ the σ have zero orbital angular momentum about the internuclear axis.

If we plot PE change for H_2 as we vary the internuclear separation between H_A + H_B:

As $R \to \infty$ $E \to 0$

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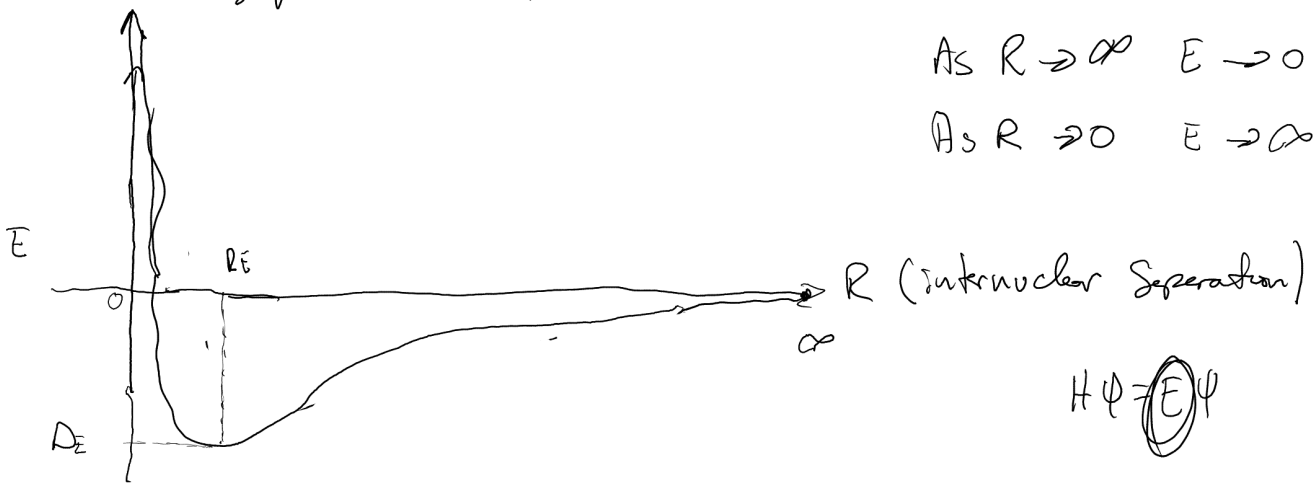


$H\psi = E\psi$

Curve Calculated by varying R + Solving Schrodinger equation at each separation...

R_E = Bonding distance where H-H is most stable

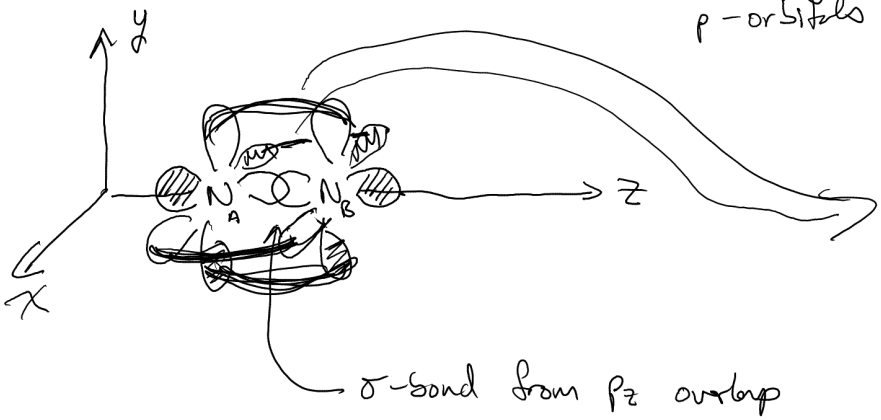
D_E = Max stabilization Energy... How stable the H-H bond is

↳ Delocalization of (1) + (2) is maximal

Lets Consider N_2 ($D_{\infty h}$)

Valence σ config for N: $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

3 singly occupied p-orbitals available for bonding.



$\psi_\pi = \phi_{P_{xA}}(1)\,\phi_{P_{xB}}(2) + \phi_{P_{xA}}(2)\phi_{P_{xB}}(1)$

$\psi_\sigma = \phi_{P_{zA}}(1)\ \phi_{P_{zB}}(2) + \phi_{P_{zA}}(2)\phi_{P_{zB}}(1)$

Overall Bonding → 1 × σ bond, → 2 × π bonds } 3 total bonds

$:N \equiv N:$

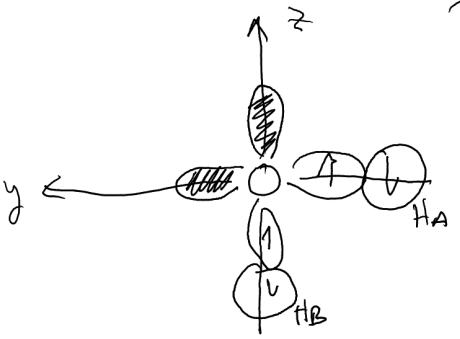
N_A N_B → π bond denoted by a node on the internuclear axis

Polyatomics + VBT

H_2O (C_{2v})

O: $2s^2 2p_x^2 2p_y^1 2p_z^1$ H: $1s^1$

two p orbitals w/ 1 e^- with which to form bonds



Based on this VBT description we predict H–O–H bond angle of 90°...

But experimental value is 104.5°...

Point to major deficiencies in this initial form of VBT

↳ Hybridization can address this issue...

Promotion + Hybridization

Carbon → tetravalent Consider methane (CH_4 → T_d)

C: 4 valence e^- → $2s^2 2p_x^1 2p_y^1$

↳ 2 unpaired e^-

we generate 4 unpaired e^- by "promoting" an e^- from 2s to $2p_z$

$2s^2 2p_x^1 2p_y^1$ —promote→ $2s^1 2p_x^1 2p_y^1 2p_z^1$

4 unpaired e^-

Maximize π_e Eliminate π_c

+ 2 additional bonds!

CH_4 → 4 × 1S H orbitals

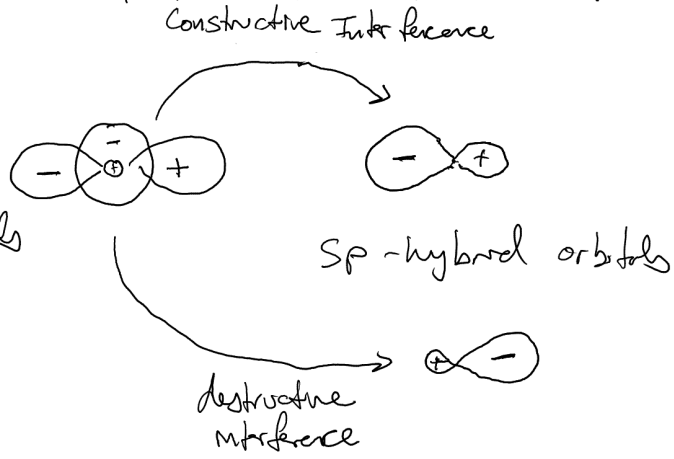
↳ this electronic config gives 2 types of bonds

$1\times \phi_{2s}(1)\phi_{1s}(2) + \phi_{2s}(2)\phi_{1s}(1)$

$3\times \phi_{2p}(1)\phi_{1s}(2) + \phi_{2p}(2)\phi_{1s}(2)$

Hybridization – Developed w/ the recognition that bond + AOs are ψ

↳ Interference between AOs

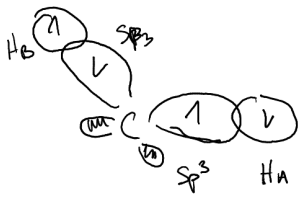


2 linear combinations of 2s + 2px to deliver 2 x sp-hybrid orbitals

LCAO – linear combination of atomic orbitals to deliver hybrid orbitals

$$\psi_1 = s + p_x + p_y + p_z$$
$$\psi_2 = s - p_x - p_y + p_z$$
$$\psi_3 = s - p_x + p_y - p_z$$
$$\psi_4 = s + p_x - p_y - p_z$$

} 4 identical sp^3 hybrids



CH_4 does NOT have 4 identical C–H bonds...

Molecular Orbital Theory