

Comparison of Molecular Orbital & Valence Bond Theories

MO = LCAO

VB

Both Theories:

- based on Schrödinger Eqtn $\leftarrow \Psi$ (of $3 \times n$ coordinates)
- Use approximation for multi e^- molecules \leftarrow # of electrons
- Give bond lengths with 10% error
- Underestimate ΔE_d (\leftarrow overestimate molecular energies)

Simple MO ~~Theory~~ ^{Approach}

Simple VB Approach

Each e^- in Ψ_{MO} (x, y, z) ^{one e^-}

Each bonding pair: Ψ_{VB} ($x_1, y_1, z_1, x_2, y_2, z_2$) ^{two e^-}

All e^- move independently

e^- pairs move in correlated way

Each Ψ_{MO} is LCAO

Ψ_{AO} 's are hybridized (LCAO-one atom)

Bonds span all atom

Bond involves 2 atoms only

Some Ψ_{MO} are on one atom only

Non-bonding e^- in AO's (hybridized)

Polar bond mean $|c_j(\text{atom A})| > |c_j(\text{atom B})|$

Polar bond not explained

Advantages:

- Calc electron density

- Can consider one bond at a time

" excited states (energies)

Predicting spectra (λ of light absorbed)

Explain delocalized bonding (π)

- Bonding corresponds to Lewis structure

Major deficiencies (simple theories)

Non-intuitive beyond diatomic

Requires lots of computing

No correlated motions

Fixable: more calculations

No polar bonds

Too much correlation between electrons

Fixable