

Atomic Units

It is often convenient to write equations and carry out calculations in atomic units.

quantity	atomic unit	symbol	S.I.
mass	electron mass	m_e	9.109×10^{-31} kg
length	Bohr radius	a_0	52.92×10^{-12} m
charge	electron charge	e	1.602×10^{-19} C
energy	Hartree	H	2625 kJ mol ⁻¹ 27.2 eV
velocity	speed of light	c	2.998×10^8 m s ⁻¹
angular momentum		\hbar	1.0546×10^{-34} J s

e.g for the H atom

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \Rightarrow \quad -\frac{1}{2} \nabla^2 - \frac{Z}{r} \text{ a.u.}$$

$$E_n = -\frac{Ze^4\mu}{2\hbar^2(4\pi\epsilon_0)^2} \cdot \frac{1}{n^2} \quad \Rightarrow \quad -\frac{1}{2} \cdot \frac{Z}{n^2} \text{ a.u.}$$

The Born-Oppenheimer Approximation

The full Hamiltonian for a molecule is

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_e^2 - \frac{1}{2} \sum_k \frac{m}{M_k} \nabla_k^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_i \sum_j \frac{1}{r_{ij}} + \sum_{k1} \sum_{k2} \frac{Z_{k1} Z_{k2}}{r_{k1k2}}$$

electrons
nuclei
el–nucl.
electron
pairs of

pairs
pairs
nuclei

Ψ_{int} has $3(n+N-1)$ coordinates – impossible to solve exactly.

The **Born-Oppenheimer Approximation** states that electronic motion is so fast that nuclei can be considered fixed.

The Schrödinger equation can then be solved (usually approximately) for the *electronic* wavefunction for fixed nuclear distances. The plot of *electronic* energy as a function of *nuclear* distances is called the **potential energy surface**.

The P.E. surface represents the potential within which the nuclei move. Motion of nuclei on this surface corresponds to molecular vibration. (Rotation is considered as a special case of vibration in which internuclear distances are fixed.)

The B.O. Approximation is another example of simplifying a Q.M. problem by **separation of variables**.

$$\Psi_{\text{tot}} = \Psi_{\text{el}} \Psi_{\text{vib}} \Psi_{\text{rot}} \quad E_{\text{tot}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}$$

A molecule is stable if its energy < the energy of separate atoms.

The Electron Pair Bond

Consider two independent electrons with wavefunctions

$\psi_a(1), \psi_b(2)$; and $E = E_a + E_b$. electron repulsion ignored

Since $\psi_a(1)\psi_b(2)$ is indistinguishable from $\psi_b(1)\psi_a(2)$
possible total wavefunctions are:

$$\Psi_S = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)]$$

$$\Psi_A = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]$$

For any point between the nuclei where $\vec{r}(1) \approx \vec{r}(2)$

$\psi_a(1) \approx \psi_a(2)$, $\psi_b(1) \approx \psi_b(2)$

$$\Rightarrow \Psi_A \approx 0, \quad \Psi_S \approx \sqrt{2}\psi_a(1)\psi_b(2)$$

For points outside the internuclear region, either

$$\psi_a \approx 0 \text{ or } \psi_b \approx 0 \quad \Rightarrow \quad \Psi_S \approx 0$$

i.e. Ψ_S represents bond formation with a pair of electrons
between nuclei.

To satisfy the **Pauli Principle** the total wavefunction,
including the spin part ϕ , must be **antisymmetric**. Thus,

$$\Psi_0 = \Psi_S \phi_A = \frac{1}{2}[\psi_a\psi_b + \psi_b\psi_a][\alpha\beta - \beta\alpha]$$

The spins are paired in the bond. This is the essence of the
Valence Bond Method.

H₂ : Valence Bond Approach

For an electron pair in the bonding orbital,

$$\Psi_0 = \Psi_S \phi_A = \frac{1}{2}[a(1)b(2) + b(1)a(2)][\alpha\beta - \beta\alpha]$$

where a and b represent the 1s wavefunctions in H atoms A and B.

$$\begin{aligned} \hat{H} &= \underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}}}_{\hat{H}_a(1)} - \underbrace{\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}} - \frac{1}{r_{a2}}}_{\hat{H}_b(2)} + \frac{1}{r_{12}} \left\{ + \frac{1}{R_{ab}} \right\} \\ &= \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}_{ab}(1,2) \\ &= E_{1s} + E_{1s} + E_{12} \end{aligned}$$

$$E_{12} = \frac{\langle \Psi | \hat{H}_{ab} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{J + K}{1 + S^2}$$

where **Coulomb integral** $J = \langle ab | \hat{H}_{ab} | ab \rangle$

exchange integral $K = \langle ab | \hat{H}_{ab} | ba \rangle$

overlap integral $S = \langle a | b \rangle$

Note: $\langle ab | ba \rangle \equiv \int a(1)b(1)d\tau_1 \cdot \int b(2)a(2)d\tau_2 = S^2$

Extensions to the Valence Bond Method

The pure valence bond wavefunction is covalent – each atom contributes one electron to the bond between them, and these atoms are shared equally.

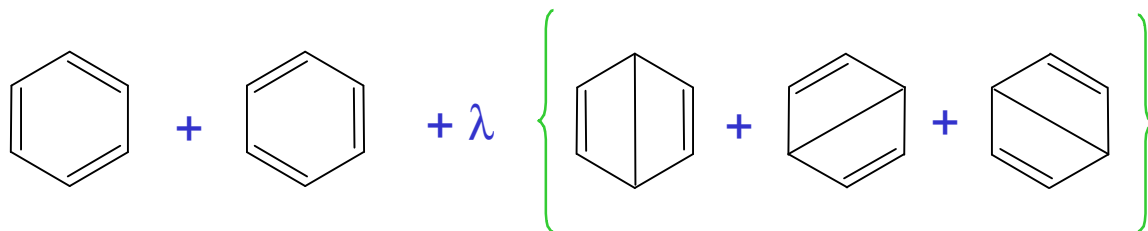
An improved wavefunction has some “ionic” terms:

$$\Psi_{\text{space}} = N \{ ab + ba + \lambda [aa + bb] \}$$

where λ is a variational parameter.

This concept can be generalized to include all possible arrangements of electron pairs, including other covalent structures.

e.g. benzene

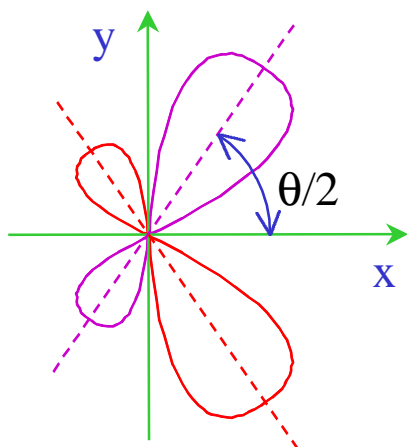


Often it is useful to make an electron pair bond from atomic orbitals that are themselves combinations of atomic orbitals centred on the *same* atom. These are called **hybrid orbitals**.

Hybrid Orbitals

A **hybrid orbital** contains contributions from more than one atomic orbital centred on the same atom.

e.g. Construct hybrids from oxygen s, p_x and p_y orbitals in H_2O .



$$h_1 = a\psi_s + b\psi_p(\theta/2)$$

$$h_2 = a\psi_s + b\psi_p(-\theta/2)$$

where $\psi_p(\theta/2) = \psi_{px} \cos(\theta/2) + \psi_{py} \sin(\theta/2)$

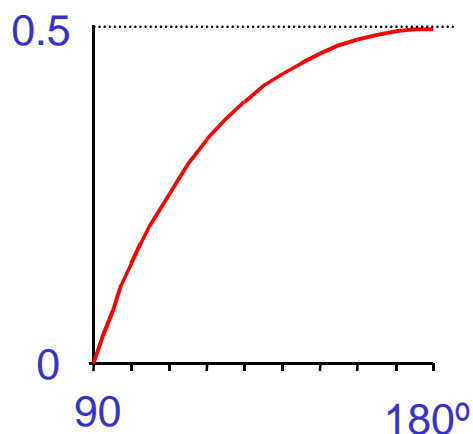
$$\psi_p(-\theta/2) = \psi_{px} \cos(\theta/2) - \psi_{py} \sin(\theta/2)$$

but since $\langle h_1 | h_1 \rangle = 1$, $a^2 + b^2 = 1$

and $\langle h_1 | h_2 \rangle = 0$, $a^2 + b^2 \cos^2(\theta/2) - b^2 \sin^2(\theta/2) = 0$

$$\Rightarrow a^2 = \frac{\cos \theta}{(\cos \theta) - 1}$$

The s character of the hybrid increases as the bond angle changes from 90° to 180° .



Hybridization – Special Cases

sp

$$\left. \begin{aligned} h_1 &= a\psi_{2s} + b\psi_{2px} \\ h_2 &= a'\psi_{2s} + b'\psi_{2px} \end{aligned} \right\}$$

$$\langle h_1 | h_1 \rangle = 1 \quad \langle h_1 | h_2 \rangle = 0 \quad \Rightarrow \quad a^2 + b^2 = 1, \quad aa' + bb' = 0$$

$$a = a' = b = -b' = \frac{1}{\sqrt{2}}$$

sp²

$$a^2 = \frac{1}{3} \quad b^2 = \frac{2}{3}$$

$$\left. \begin{aligned} h_1 &= \frac{1}{\sqrt{3}}\psi_{2s} - \sqrt{\frac{2}{3}}\psi_{2px} \\ h_2 &= \frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{6}}\psi_{2px} - \frac{1}{\sqrt{2}}\psi_{2py} \\ h_3 &= \frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{\sqrt{6}}\psi_{2px} + \frac{1}{\sqrt{2}}\psi_{2py} \end{aligned} \right\}$$

aligned along x

angled

sp³

$$a^2 = \frac{1}{4} \quad b^2 = \frac{3}{4}$$

$$h_1 = \frac{1}{2}\psi_{2s} - \frac{\sqrt{3}}{2}\psi_{2px} \quad \text{etc. } \text{OR}$$

$$\left. \begin{aligned} h_1 &= \frac{1}{2}[\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz}] \\ h_2 &= \frac{1}{2}[\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz}] \\ h_3 &= \frac{1}{2}[\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz}] \\ h_4 &= \frac{1}{2}[\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz}] \end{aligned} \right\}$$

aligned towards

corners of a cube