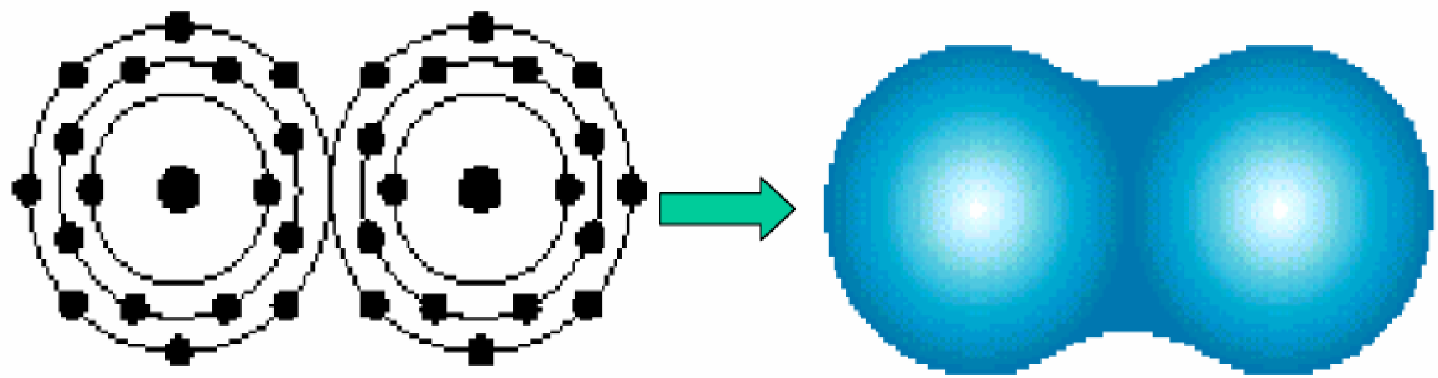
Quantum Mechanics

The interactions between atoms are governed by the **quantum mechanical** behaviour of the electrons.



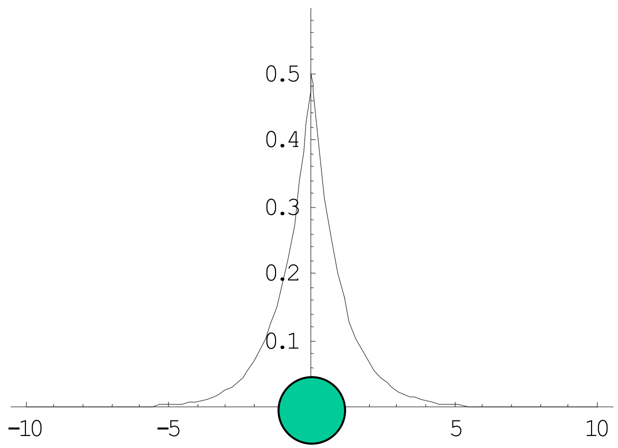
Lets look in the simplest way at the reason for the formation of a chemical bond…

The H Atom

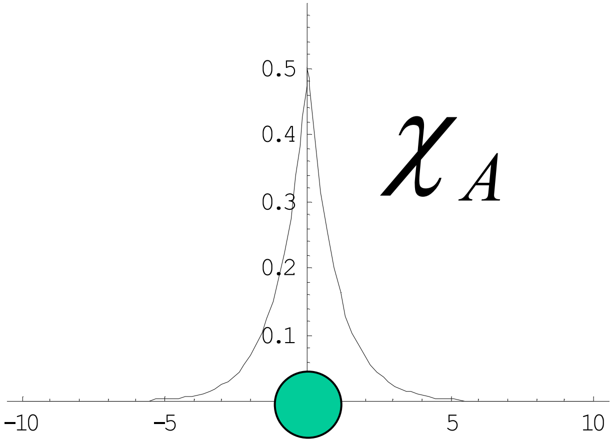
$$H\chi(r) = E\chi(r)$$

$$\chi(r) = Ae^{-\alpha r}$$

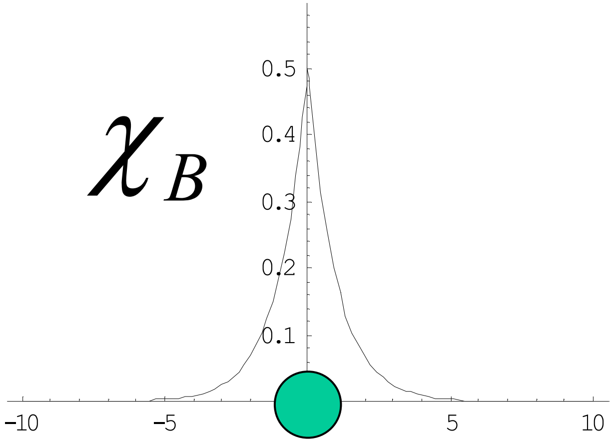
$$\rho(r) \sim A^2 r e^{-2\alpha r}$$



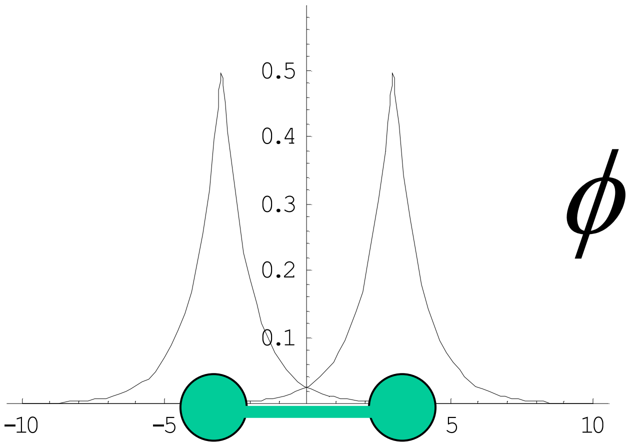
What is the wavefunction of H_2?



χ_A



χ_B

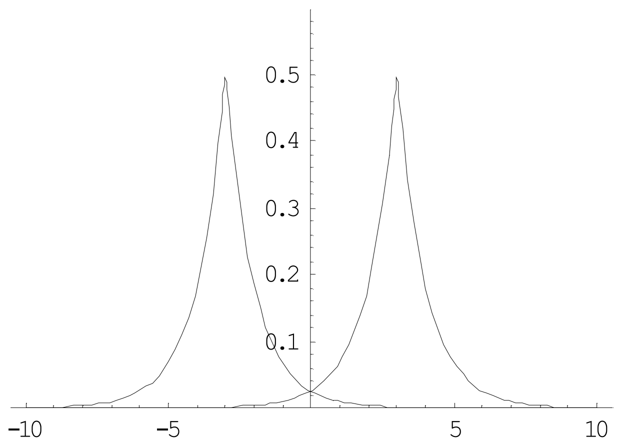


$\phi = ???$

A Linear Combination of Atomic Orbitals ?

In the simplest approximation we can guess that the molecular wavefunction can be built as a combination of the atomic wavefunctions.

(called: LCAO, Huckel, Tight Binding…)



$$\phi = c_A \chi_A + c_B \chi_B$$

To Solve for the Molecular Wavefunction

Take our approximation;

$$\phi(r) = c_A \chi_A(r) + c_B \chi_B(r)$$

And insert it into the Schroedinger equation

$$H\phi = E\phi$$

Solving to find c_A and c_B....

Some assumptions to make life easy !

Orbitals are normalised

Ignore orbital overlaps

$$\int \chi_A{}^2 dr = \int \chi_B{}^2 dr = 1$$

$$\int \chi_A \chi_B dr = 0$$

Plug it in….

$$H(c_A\chi_A + c_B\chi_B) = E(c_A\chi_A + c_B\chi_B)$$

Standard trick: multiply both sides by χ_A (or χ_B) and integrate over all space.
This converts an operator (or differential) equation into an algebraic equation….

$$\int \chi_A H(c_A\chi_A + c_B\chi_B)dr = E\int \chi_A(c_A\chi_A + c_B\chi_B)dr$$

And we get .....

$$\int \chi_A H(c_A\chi_A + c_B\chi_B)dr = E\int \chi_A(c_A\chi_A + c_B\chi_B)dr$$

$$c_A\int \chi_A H\chi_A dr + c_B\int \chi_A H\chi_B dr = Ec_A$$

Or if we multiplied by χ_B we get,

$$c_A\int \chi_B H\chi_A dr + c_B\int \chi_B H\chi_B dr = Ec_B$$

The right hand side was easy because of the normalisation and non-overlapping assumptions.

The left hand side depends on the details of the Hamiltonian (H)…so lets avoid the details…

Matrix Elements (or "Integrals")

$$c_A \int \chi_A H \chi_A dr + c_B \int \chi_A H \chi_B dr = E c_A$$
$$c_A \int \chi_B H \chi_A dr + c_B \int \chi_B H \chi_B dr = E c_B$$

Lets not *do* the integrals – just give them names !

$$\alpha = \int \chi_A H \chi_A dr = \int \chi_B H \chi_B dr$$ "on-site interaction"

$$\beta = \int \chi_A H \chi_B dr$$ "inter-site interaction"

So the Shroedinger equation reduces to:

$$\alpha c_A + \beta c_B = E c_A$$
$$\beta c_A + \alpha c_B = E c_B$$

Note: Typically α and β are negative

Solving for c_A, c_B and E

$$\alpha c_A + \beta c_B = E c_A$$
$$\beta c_A + \alpha c_B = E c_B$$

Not simple 2x2 linear equations as the right hand sides also contain the unknowns; so rewrite as

$$(\alpha - E) c_A + \beta c_B = 0$$
$$\beta c_A + (\alpha - E) c_B = 0$$

These equations have a solution when;

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

Which is an equation we can solve …

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)^2 - \beta^2 = 0$$
$$\alpha - E = \pm\beta$$
$$E = \alpha + \beta,\ \alpha - \beta$$

Two possible energies – for each there is a wavefunction…

Substitute in E to find the c_A and c_B

$$\alpha c_A + \beta c_B = E c_A$$
$$\beta c_A + \alpha c_B = E c_B$$

E=α+β => c_A=c_B

E=α-β => c_A=-c_B

NB: The important thing for now is the relative size of C_A and C_B the absolute values are determined by normalising φ

To Summarise

The two solutions;

$$E = \alpha - \beta \quad ; \quad c_A = 1, c_B = -1$$
$$E = \alpha + \beta \quad ; \quad c_A = 1, c_B = 1$$

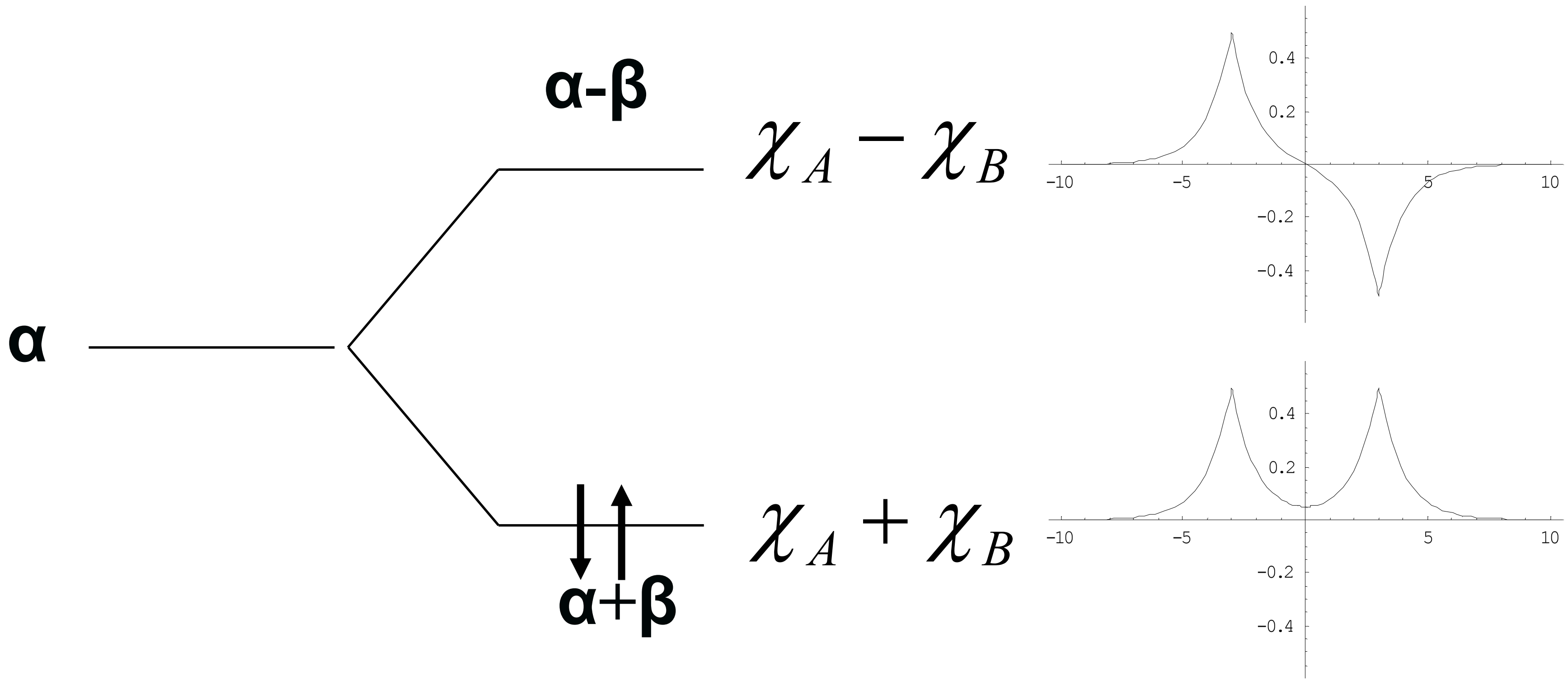
So the wavefunctions are;

$$\phi = \chi_A + \chi_B$$

or

$$\phi = \chi_A - \chi_B$$

Pictorially…



Which is the chemical bond…

Remember: β is negative

For a bigger molecule

4 identical atoms generates a 4x4 problem

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

This terms computational labs will involve calculations of atoms based on these ideas.

(also: 3^{rd} year QM lectures)

Matrices

A Matrix is simply and array of elements… eg:

$$\mathbf{A} = \begin{pmatrix} 1 & -2 & 4 \\ 3 & 10 & 6 \\ 1 & -9 & 41 \end{pmatrix}$$

Elements can be labelled as we did for determinants..

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$