RITZ VARIATION METHOD

Series of trial ψ's ψ_1, ψ_2 ...... corresponding energies E_1, E_2, ... calculated.

Minimum E corresponds to the best ψ

Actual $E < E_{min}$ found

Special case of the above - **LINEAR COMBINATIONS METHOD**

Put $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + ... c_n\psi_n$

Variation method applied to obtain values of c which give *minimum energy* for ψ

1. With n terms in the expression for ψ, the equation for E is of the **nth** order giving **n** values: ground state and excited states.

2. The importance of the contribution of ψ_1, ψ_2, ψ_3 etc. to the actual wavefunction is $c_1: c_2: c_3:$ etc.

3. The greater the overlap between ψ_1, ψ_2 etc. the lower the energy of the corresponding ψ. Thus high overlap leads to a strong bond.

Molecular orbitals: **LINEAR COMBINATION OF ATOMIC ORBITALS** (L.C.A.O.)

$$\psi = c_A\psi_A + c_B\psi_B$$

ψ_A and ψ_B are for **atomic orbitals**

APPLICATION OF THE VARIATION METHOD TO ONE-DIMENSIONAL WELL

An exact solution is straight forward:

$$\psi = (2/L)^{1/2} \sin n\pi x/L$$

but, for sake of illustration, consider trial solutions.

A cubic (over part of its range) might be suitable. One which fits the boundary conditions is

$$\psi_1 = ax^3 - aLx^2$$

Applying the normalisation condition gives

$$a^2 = 105/L^7$$

Using the energy function to evaluate the energy gives

$$E = 7\hbar^2/mL^2$$

A *better solution* might be found using the method of linear combinations. If ψ_1 is a possible solution, the complementary cubic could also be

$$\psi_2 = -ax^3 + 2aLx^2 - aL^2x$$

By symmetry

normalisation condition

$$a^2 = 105/L^7$$

energy

$$E = 7\hbar^2/mL^2$$

Linear combination

A linear combination should give a better wavefunction:

$$\psi_3 = c_1\psi_1 + c_2\psi_2$$

Applying the variation method gives

$$c_1/c_2 = \pm 1$$

(ground state and excited state)

The new wavefunction is much better, i.e. the energy predicted is much closer to that of the exact solution.

	Relative energy $E \times mL^2/\hbar^2$
1st excited state	
Linear combination of cubics	21
Exact	19.6
Ground state	
Single cubic	7
Linear combination of cubics	5
Exact	4.9