Theoretical methods: Variational methods

For any Hamiltonian one can define:

$$\mathrm{E} = \frac{\int \Psi_{trial}^{*} H \Psi_{trial} d\tau}{\int \Psi_{trial}^{*} \Psi_{trial} d\tau}$$

Trial function can be written on a Basis in Hilbert space:

$$\Psi_{trial} = \sum_{n} c_n \psi_n$$

with $H\psi_n = E_n \psi_n$

Define E_0 as the true ground state of the system: the smallest eigenvalue of H

Consider the integral:

$$I = \int \Psi_{trial}^{*} \left(H - E_0\right) \Psi_{trial} d\tau =$$

$$\sum_{n,n'} c_n^{*} c_{n'} \int \Psi_n^{*} (H - E_0) \Psi_{n'} d\tau =$$

$$\sum_{n,n'} c_n^{*} c_{n'} \left(E_{n'} - E_0\right) \int \Psi_n^{*} \Psi_{n'} d\tau =$$

$$\sum_{n} \left|c_n\right|^2 \left(E_n - E_0\right) \geq 0$$

Since is E_0 is the smallest by definition

$$\int \Psi_{trial}^{*} \left(H - E_0\right) \Psi_{trial} d\tau \geq 0$$

Hence: $\mathrm{E} \geq E_0$

Variation theorem: $E \geq E_0$ for any trial function except for true Ψ_0

Variational methods; another way of looking

For any Hamiltonian one can define:

$$\mathrm{E} = \frac{\int \Psi_{trial}^{*} H \Psi_{trial} d\tau}{\int \Psi_{trial}^{*} \Psi_{trial} d\tau}$$

Starting wave function:

$$\Psi_{trial} = c_0 \Psi_0 + c_1 \Psi_1 + \cdots$$

Hence the trail wave function is close to the ground state, but "contaminated" by contribution from excited states:

The expectation value of the Hamiltonian is then:

$$\mathrm{E} = |c_0|^2 E_0 + |c_1|^2 E_1 + \cdots$$

All stateshave higher energy than E_0:

$$\mathrm{E} \geq \left(|c_0|^2 + |c_1|^2 + \cdots\right) E_0 = E_0$$

Hence:

$$\mathrm{E} \geq E_0$$

Strategy: look for the lowest possible energy in the system

Application of the variational method to the hydrogen atom

Find the optimum form of a trial wave function and a bound to the energy

$$\psi_{trial} = e^{-kr}$$

Simplification: only r-dependence

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

Insert:

(1) $$\int \psi^*_{trial}\psi_{trial}\,d\tau =$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2kr} r^2 dr = \frac{\pi}{k^3}$$

(2) $$\int \psi^*_{trial}\left(\frac{1}{r}\right)\psi_{trial}\,d\tau =$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} e^{-2kr} r\,dr = \frac{\pi}{k^2}$$

(3) $$\int \psi^*_{trial}\nabla^2\psi_{trial}\,d\tau = -\frac{\pi}{k}$$ verify

Hence:

$$\int \Psi^*_{trial} H \Psi_{trial}\,d\tau = \frac{\hbar^2\pi}{2\mu k} - \frac{Ze^2 k}{4\varepsilon_0 k^2}$$

Rayleigh ratio:

$$\mathrm{E} = \frac{\int \Psi^*_{trial} H \Psi_{trial}\,d\tau}{\int \Psi^*_{trial}\Psi_{trial}\,d\tau} = \frac{\hbar^2 k^2}{2\mu} - \frac{Ze^2 k}{4\pi\varepsilon_0}$$

Find minimum value of the Rayleigh ratio
Look for the lowest possible energy:

$$\frac{d\mathrm{E}}{dk} = \frac{\int \Psi^*_{trial} H \Psi_{trial}\,d\tau}{\int \Psi^*_{trial}\Psi_{trial}\,d\tau} = \frac{\hbar^2 k}{\mu} - \frac{Ze^2}{4\pi\varepsilon_0} = 0$$

Solution for the hydrogen atom by the variational method

$$\frac{d\mathrm{E}}{dk} = 0 \qquad \text{if} \qquad k = \frac{Ze^2\mu}{4\pi\varepsilon_0\hbar^2}$$

Hence the best value for the energy is

$$\mathrm{E} = -\frac{Ze^4\mu}{32\pi^2\varepsilon_0^2\hbar^2}$$

(this is the ground state of the H-atom !)

And wave function
(is true wave function for 1s):

$$\psi = e^{-\frac{Ze^2\mu}{4\pi\varepsilon_0\hbar^2}r}$$

Application to the helium atom

Hamiltonian in atomic units (hartree = 2R):

$$\left\{-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_2^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right\}\psi(r_1,r_2)=E\psi(r_1,r_2)$$

Neglecting the repulsion and taking H-orbitals

$$\psi(r_1,r_2)=\psi_{1s}(r_1)\psi_{1s}(r_2)=e^{-Z(r_1+r_2)}$$

The repulsion can be considered as a screening of the charge, thus lowering it: $\alpha < Z$

$$\psi(r_1,r_2)=\psi_{1s}(r_1)\psi_{1s}(r_2)=e^{-\alpha(r_1+r_2)}$$

Calculating the expectation values:

$$\left\langle -\frac{1}{2}\nabla_1^2\right\rangle=\left\langle -\frac{1}{2}\nabla_2^2\right\rangle=\frac{\alpha^2}{2}$$

$$\left\langle -\frac{Z}{r_1}\right\rangle=\left\langle -\frac{Z}{r_2}\right\rangle=-Z\alpha$$

$$\left\langle \frac{1}{r_{12}}\right\rangle=\frac{5}{8}\alpha$$

Again the difficult integral

The variational:

$$\mathrm{E}(\alpha)=\alpha^2-2Z\alpha+\frac{5}{8}\alpha$$

Application to the helium atom: 2

The variational:

$$E(\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha$$

Minimizing:

$$\frac{dE}{d\alpha} = 2\alpha - 2Z + \frac{5}{8} = 0$$

Result for screening (effective charge):

$$\alpha = Z - \frac{5}{16}$$

Energy:

$$E = -\left(Z - \frac{5}{16}\right)^2$$

Energy for helium (Z=2) in hartrees:

1 hartree = 2 R_∞ = 27.2 eV

E = -2.75	for α=2
E = -2.84765	for α=1.6875
E = -2.89112	extra parameter
E = -2.90372	Pekeris (1959) 1078 parameters

E_{exp}= -2.90372

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