Section 5. Variational Method

- First-order perturbation theory can be insufficiently accurate to solve stationary state problems

- Another approximate method, the variational method, can be helpful

- It does not presuppose knowledge of the solutions of a simpler problem

- Particularly useful for calculating the ground state energy

- Start with solutions of the TISE

$$\hat{H}\phi_n = E_n\phi_n$$

orthonormal eigenfunctions

ground state energy

with $E_1 < E_2 < \ldots$

Write any state ψ of the system as

$$\psi = \sum_n c_n\phi_n$$

- Normalisation:

$$\langle\psi|\psi\rangle = \left\langle \sum_m c_m\phi_m \middle| \sum_n c_n\phi_n \right\rangle$$

$$= \sum_m\sum_n c_m^* c_n \langle\phi_m|\phi_n\rangle \qquad = \delta_{mn}$$

$$= \sum_n |c_n|^2 = 1$$

- Expectation value:

$$\left\langle \hat{H} \right\rangle = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle$$

$$= \left\langle \sum_m c_m \phi_m \left| \hat{H} \sum_n c_n \phi_n \right. \right\rangle$$

$$= \sum_m \sum_n c_m^* c_n E_n \underbrace{\left\langle \phi_m \left| \phi_n \right. \right\rangle}$$

$$\boxed{= \delta_{mn}}$$

$$= \sum_n \left| c_n \right|^2 E_n$$

$$\geq E_1 \sum_n \left| c_n \right|^2 = E_1$$

So

$$\boxed{\left\langle \hat{H} \right\rangle = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle \geq E_1}$$

$$\boxed{\text{ground state energy}}$$

If ψ has adjustable parameters, change them to minimise $\left\langle \hat{H} \right\rangle$ to get best approximation to E_1

KNOW OPERATOR $\hat{H}$

GUESS GROUND STATE WAVEFUNCTION

GROUND STATE ENERGY

V
METHOD

IMPROVE WAVEFUNCTION

END WITH AN UPPER BOUND ON THE GROUND STATE ENERGY E_1

Example: Ground state of hydrogen atom

Let's suppose that the ground state corresponds to $\ell = 0$ so that the wavefunction depends only on the radial coordinate $\psi = \psi(r)$ with $\psi(r) \neq 0$. At large distances, the wavefunction must vanish

Trial wavefunction satisfying these boundary conditions is

variational parameter

$$\psi = Ce^{-\alpha r}$$

normalisation constant

Normalisation: $\langle \psi | \psi \rangle = C^2 \int\limits_{0}^{\infty} e^{-2\alpha r} 4\pi r^2 \, dr = 1$

So

$$C = \left(\frac{\alpha^3}{\pi} \right)^{\frac{1}{2}}$$

standard integral:
$$\int\limits_{0}^{\infty} dr \, r^n e^{-ar} = \frac{n!}{a^{n+1}}$$
$a > 0, \; n = 0, 1, 2, \ldots$

For the hydrogen atom, the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

The expectation value for the potential energy

$$\langle\psi|V|\psi\rangle = -C^2\int_0^\infty e^{-\alpha r}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}e^{-\alpha r}4\pi r^2 dr$$

$$= -\frac{\alpha^3}{\pi}\frac{e^2}{\varepsilon_0}\int_0^\infty r\, e^{-2\alpha r}dr$$

$$= -\frac{e^2}{4\pi\varepsilon_0}\alpha$$

In spherical polars

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

The trial wavefunction has no angular dependence, so take $d^3r = 4\pi r^2 dr$. So, the expectation value for the kinetic energy

$$\langle \psi | \hat{T} | \psi \rangle = -\frac{\hbar^2}{2\mu} C^2 4\pi \int\limits_0^\infty dr\, e^{-\alpha r} \frac{d}{dr}\left(r^2 \frac{d}{dr} \right) e^{-\alpha r}$$

$$= \frac{\hbar^2}{2\mu} \alpha^2$$

See problems sheets

Hence

$$\langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{2\mu} \alpha^2 - \frac{e^2}{4\pi\varepsilon_0} \alpha \qquad (1)$$

Minimise wrt α:

$$\frac{d}{d\alpha} \langle \psi | \hat{H} | \psi \rangle = 0$$

$$\Rightarrow \alpha = \frac{e^2 \mu}{4\pi\varepsilon_0 \hbar^2}$$

Substitute into (1) to get upper bound for ground state energy

$$E_1 = -\frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{\mu}{\hbar^2} = -13.6 \text{ eV}$$

This is the actual ground state energy because our trial wavefunction is exact: it is $u_{100}(r)$

In a similar way, the variational method can be used to estimate the ground state energy for the He atom using as a trial function the hydrogen-like wavefunction for the $1s$ orbital

$$\psi(\underline{r}_1, \underline{r}_2) = u_{100}(\underline{r}_1) u_{100}(\underline{r}_2)$$

– see the textbooks for details