1st order perturbat° theory is insufficient for stationary state pbs

↓

variational method

↳ does not presuppose knowledge of solut° for simpler pbs

↳ particularly useful for calc ground state energy

- Start TISE : $\hat{H}\phi_n = E_n \phi_n$ $\qquad \psi = \sum_n c_n \phi_n$

  $E_1 < E_2 < \dots$

- Normalisat° :
$$\langle \psi | \psi \rangle = \langle \sum_m c_m \phi_m | \sum_n c_n \phi_n \rangle$$
$$= \sum_m \sum_n c_m^* c_n \underbrace{\langle \phi_m | \phi_n \rangle}_{= \delta_{mn}}$$
$$= \sum_n |c_n|^2$$
$$= 1$$

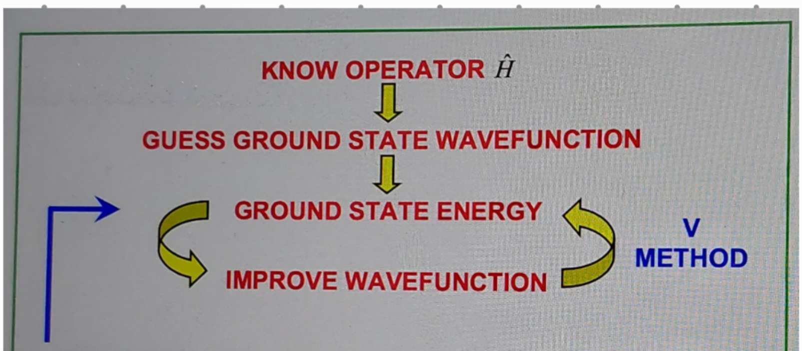
- Expectat° val :
$$\langle \hat{H} \rangle = \langle \psi | \hat{H} | \psi \rangle$$
$$= \langle \sum_m c_m \phi_m | \hat{H} \sum_n c_n \phi_n \rangle$$
$$= \sum_m \sum_n c_m^* c_n E_n \underbrace{\langle \phi_m | \phi_n \rangle}_{= \delta_{mn}}$$
$$= \sum_n |c_n|^2 E_n$$
$$\geq E_1 \sum_n |c_n|^2 = E_1$$

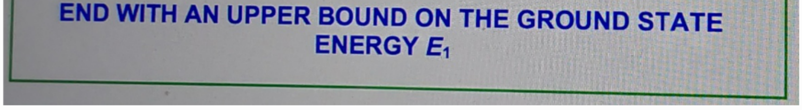
↓

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

ground state E

minimise $\langle \hat{H} \rangle$ → best E_1 approx




END WITH AN UPPER BOUND ON THE GROUND STATE ENERGY E_1

Ex Ground state of hydrogen atom

Ground state $l = 0 \Rightarrow \psi = \psi(r) \not{f}\ 0$

variational param

Trial wavef° satisfies BC: $\psi = Ce^{-\alpha r}$

normalisat° const

Normalisat°: $\langle\psi|\psi\rangle = C^2\int_0^\infty e^{-2\alpha r}\,4\pi r^2 dr = 1$

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

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

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

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

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

$$\langle\psi|\hat{T}|\psi\rangle = \frac{-\hbar^2}{2\mu}C^2 4\pi\int_0^\infty dr\, e^{-\alpha r}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)e^{-\alpha r}$$

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

Hence

$$\langle\psi|\hat{H}|\psi\rangle = \frac{\hbar^2}{2\mu}\alpha^3 - \frac{e^2}{4\pi\varepsilon_0}\alpha \quad ①$$

Minimise w.r.t 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:

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