Variational Principle - Use a Basis

Suppose you have a basis set of states: $|\psi_j\rangle$ such that any $|\psi\rangle$ has:

$$|\psi\rangle = \sum_{j=1}^{N \leftarrow \text{truncate}} c_j |\psi_j\rangle \qquad (*)$$

we'll leave these un-normalized for now, but then we need to divide by $\langle\psi|\psi\rangle$ to get $\langle\hat{H}\rangle$:

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

(aside - that's fine think of the sq. well w/ $\psi_j(x) = A\sin(j\pi x/a)$, we have

$$\int_0^a \psi_j(x)\hat{H}\psi_j(x)\,dx = \frac{j^2\pi^2\hbar^2}{2ma^2}A^2$$

so

$$\langle\hat{H}\rangle = \frac{\langle\psi_j|\hat{H}|\psi_j\rangle}{\underbrace{\langle\psi_j|\psi_j\rangle}_{=A^2}} = \frac{j^2\pi^2\hbar^2}{2ma^2} \checkmark$$
)

Using $(*)$ as our "trial wave function,"

$$f(c) \equiv \langle\hat{H}\rangle = \left[\sum_{\ell=1}^{N} c_\ell^* c_\ell\right]^{-1} \sum_{j,k=1}^{N} c_k^* c_j \underbrace{\langle\psi_k|\hat{H}|\psi_j\rangle}_{\equiv H_{kj}}$$

the c_u^*-gradient of this eqn. is:

$$\frac{\partial f}{\partial c_u^*} = -\left[\sum_{\ell=1}^{N} c_\ell^* c_\ell\right]^{-2} \cdot c_u \sum_{j,k=1}^{N} c_k^* c_j H_{kj} + \left[\sum_{\ell=1}^{N} c_\ell^* c_\ell\right]^{-1} \sum_{j,k=1}^{N} \delta_{uk} c_j H_{kj}$$

or:

$$\frac{\partial f}{\partial c_u^*} = \frac{-c_u f(c)}{\sum_{\ell=1}^{N} c_\ell^* c_\ell} + \frac{1}{\sum_{\ell=1}^{N} c_\ell^* c_\ell} \sum_{j=1}^{N} H_{uj} c_j = 0 \leftarrow \text{minimize.}$$

the eqns we need to solve, for $\{c_u\}_{u=1}^{N}$ is:

$$\sum_{j=1}^{N} H_{uj} c_j = c_u \langle\hat{H}\rangle, \qquad u = 1 \rightarrow N$$

writing this out in matrix form, we need $\vec{c}$ & $\langle\hat{H}\rangle$ such that:

$$\mathbb{H}\vec{c} = \langle\hat{H}\rangle\vec{c},$$

an eigenvalue problem for the matrix $\mathbb{H}$ - the e-vals are the ground state energy estimates - the minimizing one is the smallest...

1st Excited State Energy Estimate

How would we use the variational principle to estimate the 1st excited state energy?

Suppose you knew the ground state $|\psi_1\rangle$ of $\hat{H}$, construct the trial wave-function, & project out $|\psi_1\rangle$:

$$|\psi\rangle \longrightarrow |\psi\rangle - \langle\psi_1|\psi\rangle|\psi_1\rangle$$

so that $\langle\psi_1|\psi\rangle = \langle\psi_1|\psi\rangle - \langle\psi_1|\psi\rangle\langle\psi_1|\psi_1\rangle = 0$ ✓

then for normalized $|\psi\rangle$ w/

$$|\psi\rangle = \sum_{j=2}^{\infty} c_j|\psi_j\rangle \qquad (\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle)$$

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{j=2}^{\infty}|c_j|^2 E_j \geq E_2 \overbrace{\sum_{j=2}^{\infty}|c_j|^2}^{1} = \underbrace{E_2}_{\text{1st excited state energy}}$$

so for $\langle\psi_1|\psi\rangle = 0$, $\langle\psi|\hat{H}|\psi\rangle \geq E_2$, & we hope to find a minimum $\langle\hat{H}\rangle$ using parameters, etc.

How should we find a $|\psi_1\rangle$ estimate?

You could use (*) w/ the $\vec{c}$ you get from the $\mathbb{H}$-eval problem. Here's another approach:

"Wick Rotation"

The time-dependent Schrödinger eqn. is:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (\circ)$$

w/ b.c. $\psi \xrightarrow[r\to\infty]{} 0$.

We normally take $\Psi = \psi(\vec{r})\cdot T(t)$, then $(\circ)$ is

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + U = \underbrace{i\hbar\frac{\dot{T}}{T}}_{=E}$$

and $\dot{T} = -\frac{iE}{\hbar}T \Rightarrow T = e^{-iEt/\hbar}$, oscillatory.

$$\Psi = \psi(\vec{r})e^{-iEt/\hbar}$$

& for $\psi_j(\vec{r})$, w/

$$-\frac{\hbar^2}{2m}\nabla^2\psi_j + U\psi_j = E_j\psi_j,$$

the general solution is a superposition.

$$\Psi(\vec{r},t) = \sum_{j=1}^{\infty} c_j\psi_j(\vec{r})e^{-iE_jt/\hbar}$$

w/ c_j set by the initial condition: $\Psi(\vec{r},0) = \psi_0(\vec{r})$.
← given.

If we "complexify time" (a "Wick rotation") taking $s = it$, we have

$$\frac{\partial\Psi}{\partial t} = \frac{\partial\Psi}{\partial s}\cdot\frac{\partial s}{\partial t} = \frac{\partial\Psi}{\partial s}\cdot i$$

Schrödinger's eqn. becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U\Psi = -\hbar\frac{\partial\Psi}{\partial s}$$

Now, separation of variables, w/ $\Psi = \psi(\vec{r})S(s)$, gives:

$$-\frac{\hbar^2}{2m}\frac{\nabla^2\psi}{\psi} + U = \underbrace{-\hbar\frac{S'}{S}}_{=E}$$

the ... s-independent wave eqn. is $-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi$ as always, but now:

$$-\frac{\hbar S'}{S} = E \Rightarrow S' = -\frac{E}{\hbar}S \Rightarrow S = e^{-E/\hbar\, s}.$$

the general solution is given by:

$$\Psi(\vec{r},s) = \sum_{j=1}^{\infty} c_j\psi_j(\vec{r})e^{-E_js/\hbar}$$

? What happens here as $s\to\infty$?

As "time" (s) goes on, the term w/ the smallest decay constant dominates. Since

$E_1 < E_2 < \cdots$ (ideally)

the ground state dominates:

$$\Psi \xrightarrow[s\to\infty]{} c_1 \psi_1 e^{-E_1 s/\hbar}$$

giving you a way to approximate the ground state — primarily a numerical technique.

Galerkin Method(s)

How would we solve (working in D=1)

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + U\Psi = -\hbar\frac{\partial\Psi}{\partial s} \quad \text{w/ } \psi(x,0) = \psi_0(x) \text{ given?}$$

Pick a basis set $\{\psi_j(x)\}_{j=1}^{\infty}$ that satisfies the relevant b.c.

Then $\Psi(x,s) = \sum_{j=1}^{\infty} a_j(s)\psi_j(x)$

Putting this expansion in to the PDE,

$$\sum_{j=1}^{\infty} a_j(s)\left[-\frac{\hbar^2}{2m}\psi_j''(x) + U(x)\psi_j(x)\right] = -\hbar\sum_{j=1}^{\infty} a_j'(s)\psi_j(s)$$

mult. by $\psi_k^*(x)$ & int. $x: -\infty \to \infty$

$$\sum_{j=1}^{\infty} a_j(s) \underbrace{\langle \psi_k | \hat{H} | \psi_j \rangle}_{=H_{kj}} = -\hbar\frac{da_k(s)}{ds}$$

so we need to solve:

$$\frac{da_k(s)}{ds} = -\frac{1}{\hbar}\sum_{j=1}^{\infty} H_{kj}\, a_j(s) \quad \text{for } k = 1 \to \infty$$

in matrix form:

$$\frac{d\vec{a}}{ds} = -\frac{1}{\hbar}\mathbb{H}\vec{a}$$

the "solution" here is: $\vec{a}(s) = e^{-\frac{1}{\hbar}\mathbb{H}s}\,\vec{a}_0 \ldots$