Variation (Rayleigh-Ritz) Method

Hamiltonian

Claim: for any function f: $E_{gs} \leq \dfrac{\langle f|H|f\rangle}{\langle f|f\rangle}$

actual ground state energy

Pf: expand f in terms of the eigenfunctions of H: $H\phi_i = E_i\phi_i$; $f = \sum c_i \phi_i$

$$\frac{\langle f|H|f\rangle}{\langle f|f\rangle} = \frac{\sum |c_i|^2 E_i}{\sum_j |c_j|^2} \quad ; \quad \text{Let } P_i = \frac{|c_i|^2}{\sum_j |c_j|^2}$$

Note: $\sum P_i = 1 \leftarrow$ "weights"

Then $\dfrac{\langle f|H|f\rangle}{\langle f|f\rangle} = \sum P_i E_i \leftarrow$ weighted average of eigen energies must be greater than smallest in sum.

Certainly the smallest E_i in sum is ground state

so $E_{gs} \leq \dfrac{\langle f|H|f\rangle}{\langle f|f\rangle}$

IF we are sure $c_{gs} = 0$ then

$$E_{1st\ excited} \leq \frac{\langle f|H|f\rangle}{\langle f|f\rangle}$$

possible for example if gs known to be even & f is odd or gs known to be $\ell = 0$ (s) and f is $\ell = 1$ (p)

Seek the lowest upper bound on E_{gs} ... pick f that depends on some parameters $(a, b, c \ldots)$

Then select the parameter values which produce the smallest value of $\dfrac{\langle f|H|f\rangle}{\langle f|f\rangle}$ ... setting $\partial_a = 0$ etc is a common way to do such minimizations — or use Mathematica FindMinimum ... but that requires a starting guess.

$E_{gs} \le \dfrac{\langle f|H|f\rangle}{\langle f|f\rangle}$ is not useful unless the bound is close... in this case "quadratically" close:

actual ground state

Let $f = \phi + \varepsilon g$ — f is "nearly" ϕ ... how close is bound?

$$\frac{\langle f|H|f\rangle}{\langle f|f\rangle} = \frac{\langle\phi|H|\phi\rangle + \varepsilon^* \langle g|\underbrace{H|\phi\rangle}_{E_{gs}|\phi\rangle} + \varepsilon \underbrace{\langle\phi|H}_{E_{gs}\langle\phi|}|g\rangle + \varepsilon^2\langle g|H|g\rangle}{\langle\phi|\phi\rangle + \varepsilon^*\langle g|\phi\rangle + \varepsilon\langle\phi|g\rangle + \varepsilon^2\langle g|g\rangle}$$

$$= \frac{E_{gs}\left(\langle\phi|\phi\rangle + \varepsilon^*\langle g|\phi\rangle + \varepsilon\langle\phi|g\rangle\right) + \varepsilon^2\langle g|H|g\rangle}{\langle\phi|\phi\rangle + \varepsilon^*\langle g|\phi\rangle + \varepsilon\langle\phi|g\rangle + \varepsilon^2\langle g|g\rangle}$$

add & subtract the needed term

$$= E_{gs} + \frac{-E_{gs}\,\varepsilon^2\langle g|g\rangle + \varepsilon^2\langle g|H|g\rangle}{\langle\phi|\phi\rangle + \varepsilon^*\langle g|\phi\rangle + \varepsilon\langle\phi|g\rangle + \varepsilon^2\langle g|g\rangle}$$

$$= E_{gs} + \varepsilon^2 \frac{\langle g|H - E_{gs}|g\rangle}{\langle\phi|\phi\rangle + \underbrace{\varepsilon^*\langle g|\phi\rangle + \varepsilon\langle\phi|g\rangle}_{\text{FYI} = 2\,\mathrm{Re}(\varepsilon\langle\phi|g\rangle)} + \varepsilon^2\langle g|g\rangle}$$

if ε is "small" correction will be small

Useful fact for $\langle f| \frac{-\hbar^2}{2m}\partial_x^2 |f\rangle = \frac{\hbar^2}{2m}\langle\partial_x f|\partial_x f\rangle$ as p operator is hermitian

Typical notation:

$KE = \frac{\hbar^2}{2m}\langle\partial_x f|\partial_x f\rangle$

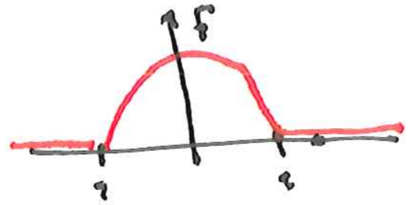
$PE = \langle f|V|f\rangle$

$N = \langle f|f\rangle$

seek $\dfrac{KE + PE}{N}$

Example: SHO: $H = -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2} m\omega^2 x^2$

$$f = \begin{cases} (a^2 - x^2) & \text{for } |x| < a \\ 0 & \text{for } |x| > a \end{cases}$$



$$KE = \frac{\hbar^2}{2m}\, 2\int_0^a (f')^2\, dx = \frac{\hbar^2}{2m}\, 2\int_0^a (-2x)^2\, dx = \frac{4\hbar^2}{m}\frac{a^3}{3}$$

even so $\int_{-a}^{a} = 2\int_0^a$

$a^4 - 2a^2x^2 + x^4$

$$PE = \frac{1}{2} m\omega^2\, 2\int_0^a x^2 f^2\, dx = m\omega^2 \int_0^a x^2 (a^2 - x^2)^2\, dx$$

$$= m\omega^2 \left\{ a^4 \frac{a^3}{3} - 2a^2 \frac{a^5}{5} + \frac{a^7}{7} \right\} = m\omega^2 a^7 \left\{ \frac{1}{3} - \frac{2}{5} + \frac{1}{7} \right\}$$

$\frac{35 - 42 + 15}{105}$

$$= m\omega^2 a^7 \frac{8}{105}$$

$$N = 2\int_0^a (a^2 - x^2)^2\, dx = 2\left\{ a^5 - 2a^2 \frac{a^3}{3} + \frac{a^5}{5} \right\}$$

$$= 2a^5 \left\{ 1 - \frac{2}{3} + \frac{1}{5} \right\} = \frac{16}{15} a^5$$

$$\frac{KE + PE}{N} = \frac{\frac{\hbar^2}{2m}\frac{8}{3}a^3 + \frac{1}{2} m\omega^2 a^7 \frac{16}{105}}{\frac{16}{15} a^5}$$

call this x

$$= \frac{1}{2}\hbar\omega \left[\frac{\hbar}{m\omega}\frac{8}{3} a^{-2} + \boxed{\frac{m\omega}{\hbar} a^2}\frac{16}{105} \right] \frac{15}{16}$$

$$= \frac{1}{2}\hbar\omega \left[\frac{8}{3}\frac{1}{x} + \frac{16}{105} x \right] \frac{15}{16}$$

set $[\ ]' = 0 = -\frac{8}{3}\frac{1}{x^2} + \frac{16}{105} \rightarrow x^2 = \frac{8}{3}\frac{105}{16} \rightarrow x = 4.18$

plug in that x: $\left[\frac{8}{3}\frac{1}{x} + \frac{16}{105} x \right] \frac{15}{16} = 1.20$

Exact answer would be 1 → 20% over estimate

SHO 1^{st} excited trial wavefunction : $f = x\, e^{-bx}$

→ see Mathematica

$$KE \Rightarrow \frac{\hbar^2}{4bm} = \frac{\hbar^2}{2m}\langle f'|f'\rangle$$

$$PE = \frac{3}{4}\frac{m\omega^2}{b^5} = \frac{1}{2}m\omega^2\langle f|x^2|f\rangle$$

$$N = \frac{1}{2b^3} = \langle f|f\rangle$$

cell x

$$\frac{KE+PE}{N} = \frac{b^2\hbar^2}{2m} + \frac{3m\omega^2}{2b^2} = \frac{3}{2}\hbar\omega\left[\frac{1}{3}\frac{b^2\hbar}{m\omega} + \frac{m\omega}{b^2\hbar}\right]$$

$$= \frac{3}{2}\hbar\omega\left[\frac{1}{3}x + \frac{1}{x}\right]$$

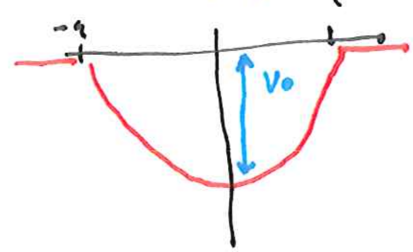
$$[\ \ ]' = \frac{1}{3} - \frac{1}{x^2} = 0 \Rightarrow x^2 = \sqrt{3} \qquad \left[\frac{1}{3}x + \frac{1}{x}\right] = 1.15$$

15% too high

Using Mathematica look at $-\frac{\hbar^2}{2m}\partial_x^2 + \begin{Bmatrix} V_0(x^2-a^2)/a \\ 0 \end{Bmatrix}$

V(x)

Go to dimensionless coordinates



$x' = \frac{x}{a}$

unit $e = \frac{\hbar^2}{2ma^2}$; $E' = E/e$, $V_0' = \frac{V_0}{e}$

$$\Rightarrow -\partial_{x'}^2 + \begin{Bmatrix} V_0'(x'^2-1) \\ 0 \end{Bmatrix} = E'$$

For $V_0' = 25$; $\psi = e^{-bx^2}$ estimate $E_{gs} = -20.0073$

$\psi = e^{-b|x|}$ $= -18.42$

"exact" $= -20.0095$

$\psi = x\, e^{-bx^2}$ estimate 1^{st} excited $= -10.1132$

$\psi = x\, e^{-b|x|}$ $= -8.9333$

"exact" $= -10.15765$

For $V_0' = -7.5$: $\psi = e^{-bx^2}$ estimate $E_{gs} = -4.8176$

$\psi = e^{-b|x|}$ $= -4.2903$

"exact" $= -4.83523$

$\psi = x e^{-bx^2}$ estimate 1^{st} excited $= -.062705$

$\psi = x e^{-b|x|}$ $= -.29188$

"exact" $= -.3724$