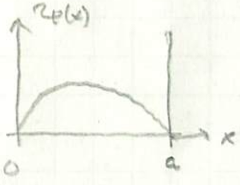
Observation

For the infinite square well, we know the ground state wave function:

$$\psi_1(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{\pi x}{a}\right)$$

w/ energy

$$E_1 = \frac{\pi^2\hbar^2}{2ma^2}$$



Take the similarly shaped $\psi(x) = -\sqrt{\frac{30}{a^5}}\,x\,(x-a)$, ? What is $\langle \hat{H} \rangle$ for this state?

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m}\sqrt{\frac{30}{a^5}}\,[2]$$

so

$$\langle \hat{H} \rangle = \int_0^a \psi^* H \psi\, dx = \frac{10\hbar^2}{2ma^2}$$

that's close to E_1, a little over since $10 > \pi^2 \approx 9$.

the "variational principle" is based on the idea that any $\psi(x)$ (w/ appropriate b.c.s) has the property that

$$\langle \hat{H} \rangle \geq E_{gs} \leftarrow \text{ground state energy associated w/ } \hat{H}.$$

given Hamiltonian $\hat{H}$.

We can then engineer $\psi(x)$ to achieve tight bounds.

to show: given $\hat{H}$ + some $|\psi\rangle$ (normalized), $\langle\psi|\hat{H}|\psi\rangle \geq E_{gs}$

Suppose you had the complete set $|\psi_j\rangle$ w/

$$\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle$$

Any $|\psi\rangle$ can be expanded in the basis $\{|\psi_j\rangle\}_{j=1}^{\infty}$, so

$$|\psi\rangle = \sum_{j=1}^{\infty} c_j |\psi_j\rangle \quad \text{w/} \quad \sum_{j=1}^{\infty} |c_j|^2 = 1 \text{ (normalized)}$$

+

$$\hat{H}|\psi\rangle = \sum_{j=1}^{\infty} c_j \hat{H}|\psi_j\rangle = \sum_{j=1}^{\infty} c_j E_j |\psi_j\rangle$$

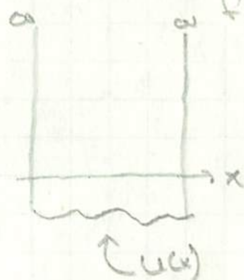
then:

$$\langle\psi|\hat{H}|\psi\rangle = \sum_{j=1}^{\infty} |c_j|^2 E_j \geq \sum_{j=1}^{\infty} |c_j|^2 E_{gs} = E_{gs}\sum_{j=1}^{\infty}|c_j|^2 = E_{gs}$$

$$\downarrow$$

$$\langle \hat{H} \rangle \geq E_{gs}$$

Example: For an infinite sq. well that has a bumpy floor; we could take



$$\psi(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{\pi x}{a}\right)$$, the g.s. of the well as our "trial" wave function, then

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\psi''(x) + U(x)\psi(x)$$

has energy expectation value:

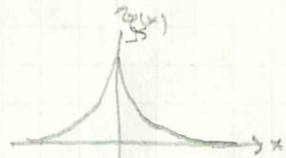
$$\langle \hat{H} \rangle = \underbrace{\int_0^a \psi^*(x)\left[-\frac{\hbar^2}{2m}\psi''(x)\right]dx}_{=\frac{\pi^2\hbar^2}{2ma^2}} + \underbrace{\int_0^a \psi^*(x)U(x)\psi(x)\,dx}_{=\langle\psi^0|U|\psi^0\rangle}$$

in this case, we've recovered the prediction of 1st order time-dependent perturbation theory.

The real power of the approach comes in varying parameters in the trial wave function.

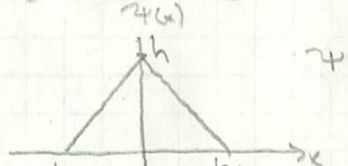
example: For the "delta well" $U(x) = -\alpha\delta(x)$, we have ground state

$$\psi_{gs}(x) = \frac{\sqrt{m\alpha}}{\hbar}\, e^{-m\alpha|x|/\hbar^2}$$



w/ energy $E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$.

Use the trial wave-function:



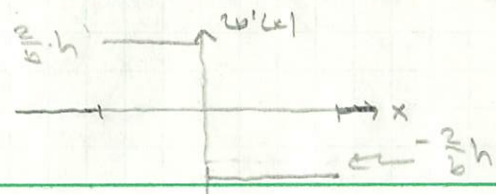
$$\psi(x) = \begin{cases} 0 & x<-b/2,\ x>b/2 \\ \frac{2}{b}hx + h & -b/2<x<0 \\ -\frac{2}{b}hx + h & 0<x<b/2 \end{cases}$$

normalization gives: $\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = \frac{1}{3} b h^2 = 1$

so $h = \sqrt{3/b}$.

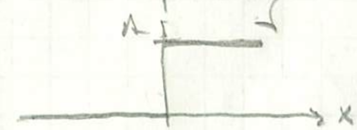
The $\hat{H}$ here is $\hat{H} = -\frac{\hbar^2}{2m}\psi''(x) - \alpha\delta(x)\psi$,

& a sketch of ψ' looks like:



& the 2nd derivative is; noting that

$f(x) = A\theta(x)$



has derivative

$f'(x) = A\delta(x)$, so

$$\psi''(x) = \frac{2h}{b}\delta(x+b/2) - \frac{4h}{b}\delta(x) + \frac{2h}{b}\delta(x-b/2)$$

& then

$$\langle\psi|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty}\psi(x)\psi''(x)\,dx + \int_{-\infty}^{+\infty}|\psi(x)|^2(-\alpha\delta(x))\,dx$$

$$= -\frac{\hbar^2}{2m}\left[-\frac{4h}{b}\cdot h\right] - \alpha\cdot h^2$$

$$\langle\hat{H}\rangle = \frac{3}{b}\left[\frac{2\hbar^2}{bm} - \alpha\right]$$

now let's minimize

$$\frac{d\langle\hat{H}\rangle}{db} = -\frac{3}{b^2}\left[\frac{2\hbar^2}{bm} - \alpha\right] + \frac{3}{b}\left[-\frac{2\hbar^2}{b^2 m}\right] = 0$$

or

$$\frac{2\hbar^2}{m} - \alpha b + \frac{2\hbar^2}{m} = 0 \Rightarrow b = \frac{4\hbar^2}{\alpha m}$$

then

$$\langle\hat{H}\rangle = \frac{3\alpha m}{4\hbar^2}\left[\frac{2\hbar^2\alpha m}{4\hbar^2 m} - \alpha\right]$$

$$= -\frac{3m\alpha^2}{4\hbar^2} + \frac{3m\alpha^2}{8\hbar^2} = -\frac{3m\alpha^2}{8\hbar^2}$$

A Minimization Problem

It's good to pick trial wave functions w/ multiple parameters, then you have more options for minimizing, but the minimization problem becomes more difficult:

For $\psi(\alpha, \beta)$, the expectation value is a fnc. of α & β:

$$f(\alpha, \beta) \equiv \langle \psi | \hat{H} | \psi \rangle$$

we can minimize $f(\alpha, \beta)$ using "steepest descent" – the α-β grad. of $f(\alpha,\beta)$ gives dir. of greatest increase so $-\nabla f$ gives dir. of greatest <u>decrease</u>

iterate $\vec{V} = -\frac{\partial f}{\partial \alpha}\hat{\alpha} - \frac{\partial f}{\partial \beta}\hat{\beta}$

$$\alpha\hat{\alpha} + \beta\hat{\beta} \leftarrow \alpha\hat{\alpha} + \beta\hat{\beta} + \epsilon\hat{V}$$

this can often be done numerically.

Use a Basis

"Any" function (that vanishes at $x=0, a$) can be written as a linear combination of

$$\psi_j(x) \equiv \sqrt{\frac{2}{a}} \sin\left(\frac{j\pi x}{a}\right)$$

make your trial wave-function a linear combo.:

$$\psi(x) = \sum_{j=1}^{n} c_j \psi_j(x) \quad \text{w/ "parameters"} \quad \{c_j\}_{j=1}^{n}$$

or $|\psi\rangle = \sum_{j=1}^{n} c_j |\psi_j\rangle$.

So

$$\langle \psi | \hat{H} | \psi \rangle = \underbrace{\frac{1}{\langle \psi | \psi \rangle}}_{\text{normalization}} \sum_{j,k}^{n} c_j^* c_k \underbrace{\langle \psi_j | \hat{H} | \psi_k \rangle}_{\equiv H_{jk}}$$

$$= \frac{1}{\sum_{\ell=1}^{n} c_\ell^* c_\ell} \sum_{j,k}^{n} c_j^* c_k H_{jk}$$

so take

$$\frac{\partial \langle \hat{H} \rangle}{\partial c_u^*} = -\frac{c_u}{\left(\sum_{\ell=1}^{n} c_\ell^* c_\ell\right)} \langle \hat{H} \rangle + \frac{1}{\sum_{\ell=1}^{n} c_\ell^* c_\ell} \sum_{k=1}^{n} H_{uk} c_k = 0$$

or

$$\sum_{k=1}^{n} H_{uk} c_k = \langle \hat{H} \rangle c_u \quad \text{for } u = 1 \to n$$

$$\Downarrow$$

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

Find e-vals of $\mathbb{H}$ – that gives $\langle \hat{H} \rangle$ – pick the <u>smallest</u> e-val. of $\mathbb{H}$.