B. Variational Method

- An approximation for "guessing" at the Ground State Energy (E_{GS}) of a system defined by Hamiltonian $\hat{H}$ (a very humble task!)
- But very powerful! It is applicable to the physics of
  - atoms
  - molecules
  - solids
  - superconductivity
  - Many-electron systems [e.g. Hartree approximation of molecules, solids]
- And easy to apply
  - But result can be nice or lousy

(a) <u>Theorem</u>: <u>Blind Guess can only be bigger or equal to E_{GS}.</u>

- Knowing what it says
  - Given $\hat{H}$ (a quantum problem)
  - Make a guess (arbitrary) on a wavefunction $\phi(x)$ or $\phi(\vec{r})$ 1D 2D, 3D
    [meant to be a guess on the ground state wavefunction]

Key idea

- Evaluate expectation value $\langle \hat{H} \rangle_\phi$ ← stress that $\langle \cdots \rangle$ is taken w.r.t. ϕ

$$\langle \hat{H} \rangle_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = \int \phi^* \hat{H} \phi \, d\tau \quad \text{(B1)}$$

if ϕ is normalized

Theorem says $\langle \hat{H} \rangle_\phi \geq E_{GS}$ (B2)

inequality

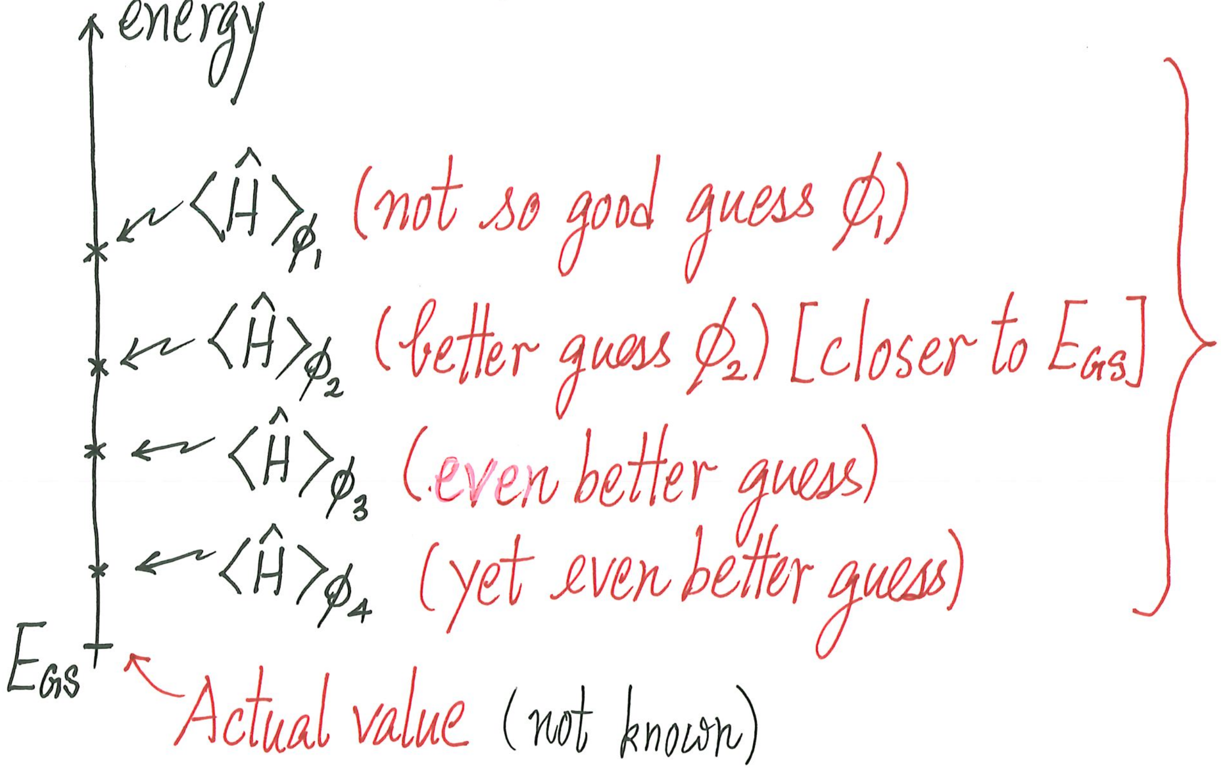
Actual ground state energy (not known)

Meaning: Guess any ϕ, $\langle \hat{H} \rangle_\phi$ can only be $\underbrace{\text{bigger OR equal to}}_{\text{one-sided!}}$ E_{GS}

- When does $\langle \hat{H} \rangle_\phi \overset{\text{equal!}}{\overset{?}{=}} E_{GS}$?

  Guess (ϕ) the correct ground state wavefunction! (Lucky)

- Strategy of using the theorem



Idea

Make many trials

$\phi_1, \phi_2, \ldots, \phi_N$

N trials

Min $\langle \hat{H} \rangle_\phi$ is the best estimate (closest) of E_{GS}

(b) Proof of the Theorem

TISE: $\hat{H}\psi_n = E_n \psi_n$ [can't solve analytically]

But we know that the energy eigenstates $\{\psi_n\}$ (not known) can be used to express any function [your guess ϕ]

Guess ϕ: Can always write $\phi = \sum_n a_n \psi_n$ (exact relation)

(i) $$\int \phi^* \phi \, d\tau = \sum_n \sum_m a_n^* a_m \int \psi_n^* \psi_m \, d\tau = \sum_n \sum_m a_n^* a_m \delta_{nm} = \sum_n |a_n|^2$$

(ii) $$\int \phi^* \hat{H} \phi \, d\tau = \sum_n \sum_m a_n^* a_m \int \psi_n^* \underbrace{\hat{H} \psi_m}_{E_m \psi_m} d\tau = \sum_n \sum_m a_n^* a_m E_m \delta_{nm} = \sum_n E_n |a_n|^2$$

But $\sum_n E_n |a_n|^2 \geq E_{GS} \sum_n |a_n|^2$ (Key step, because $E_n \geq E_{GS}$ as E_{GS} is the lowest energy eigenvalue)

$$\therefore \langle \hat{H} \rangle_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq \frac{E_{GS} \sum_n |a_n|^2}{\sum_n |a_n|^2} \geq E_{GS} \quad \text{Done!} \quad (B2)$$

[In Chinese[+], 亂猜，只會猜高了!]

Dirac Notation $\langle \hat{H} \rangle_\phi = \dfrac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_{GS}$ (B2)

Name: The Guess wavefunction is called the $\underbrace{\text{trial wavefunction}}$

implicitly mean that we should keep on trying different ϕ's

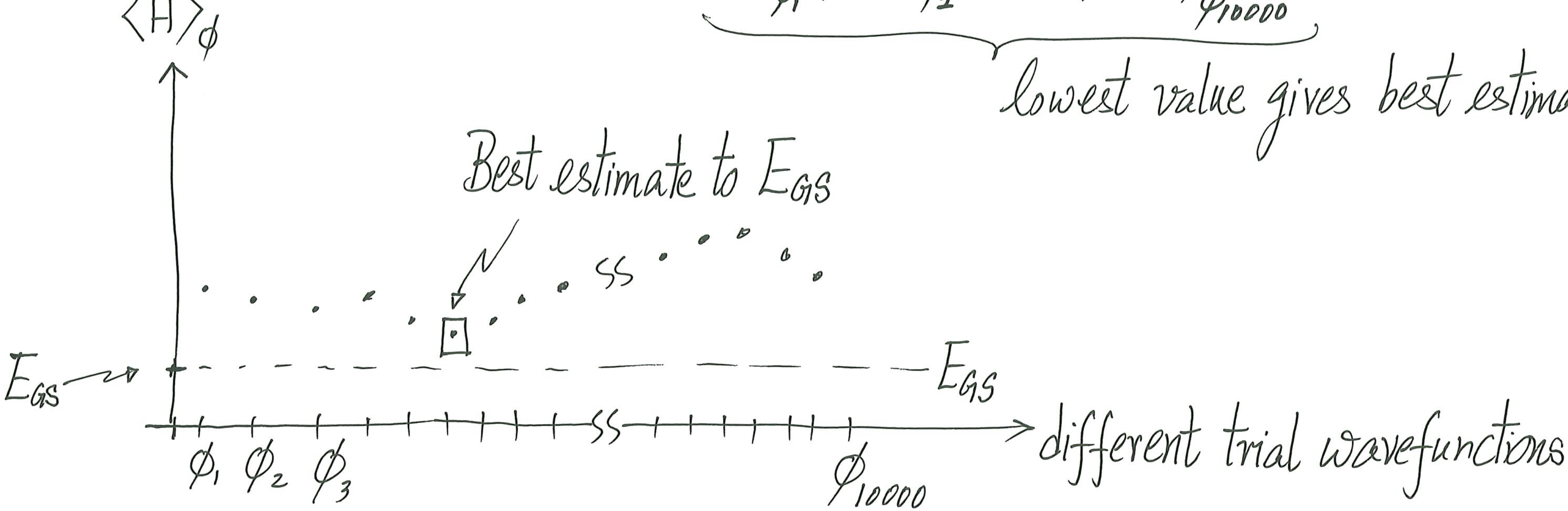
[+] In Cantonese,「亂估都唔會估低咗」，因為…真的 E_{GS} 已低無可低，是很Quantum的原因!

(c) Variational Method

Make different guesses $\overbrace{\phi_1,\ \phi_2,\ \cdots,\ \phi_{10000}}^{\text{varying the trial wavefunction}}$ (say)

$$\begin{array}{ccccc} \phi_1, & \phi_2, & \cdots, & \phi_{10000} \\ \downarrow & \downarrow & & \downarrow \\ \end{array}$$

$$\underbrace{\langle H\rangle_{\phi_1},\ \langle H\rangle_{\phi_2},\ \cdots,\ \langle H\rangle_{\phi_{10000}}}_{\text{lowest value gives best estimate}}$$



- How to try infinitely many trial wavefunctions?
  - Introduce parameter(s) [called variational parameter(s)] into the trial wavefunction

- $\phi_\lambda(x)$ OR $\phi_{\lambda,\beta}(x)$ [e.g. for 1D problems] OR more parameters

  [one value of λ corresponds to one trial wavefunction]

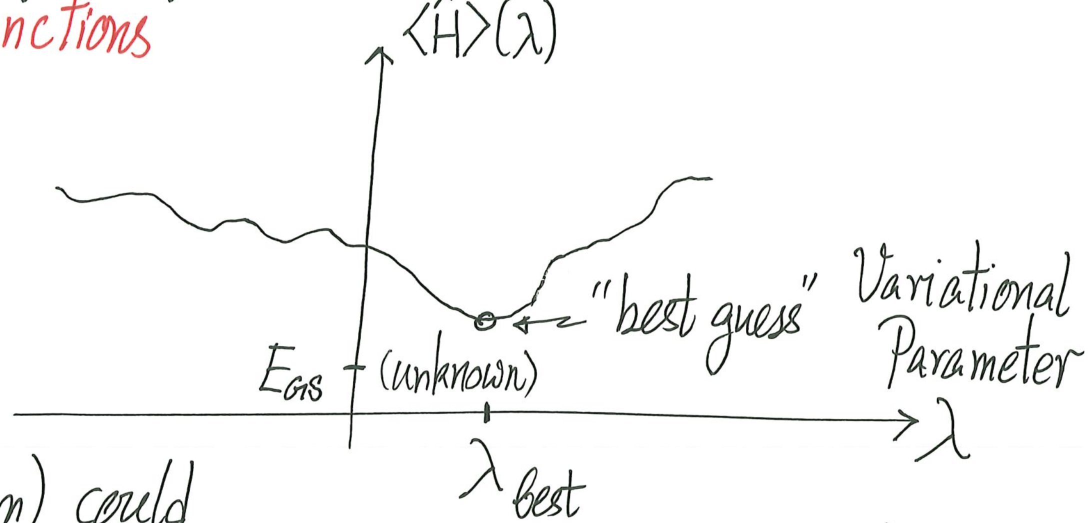
- Evaluate $\langle \hat{H} \rangle_\phi \Rightarrow \langle \hat{H} \rangle(\lambda)$ OR $\langle \hat{H} \rangle(\lambda,\beta)$

  function of λ

- Vary λ $\Rightarrow$ $\langle \hat{H} \rangle$ is minimized by some value of λ

  thus trying many wavefunctions

Best Estimate $\langle \hat{H} \rangle_{minimum} \geq E_{GS}$

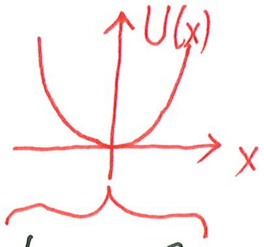


- Similarly for $\phi_{\lambda,\beta}$ OR $\phi_{\lambda,\beta,\gamma}$

- A cleverer trial wavefunction (form) could give an estimate closer to the actual E_{GS}

(see examples)

(d) Examples



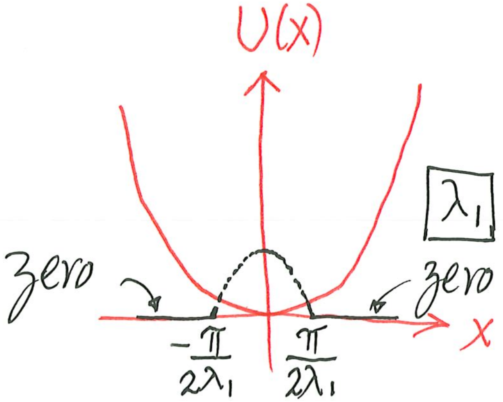
(i) $\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}Kx^2$ (Harmonic Oscillator) (analytically solvable)

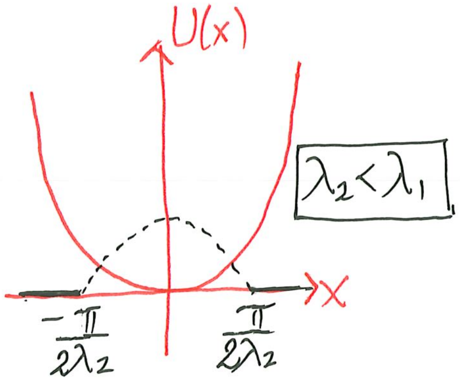
[Pretend we don't know [forgot[†]] the analytic solutions]

The Art of guessing a reasonable trial wavefunction ("quantum sense")

- G.S. (actual) is symmetric about $x=0$, has no nodes

Take $\phi_\lambda(x) = \begin{cases} \cos\lambda x & \text{for } \frac{-\pi}{2\lambda} < x < \frac{\pi}{2\lambda} \\ 0 & \text{otherwise} \end{cases}$





- width of $\phi(x)$ is adjusted by λ
- λ plays the role of variational parameter

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† Please don't!

Think like a physicist!

$\nearrow$ large $\lambda \Rightarrow$ Narrow $\phi(x)$ $\nearrow \langle \hat{U} \rangle$ low

$\searrow \langle \hat{T} \rangle$ high

$\Downarrow$

$\langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{U} \rangle$ may not be low!

$\searrow$ small $\lambda \Rightarrow$ Wide $\phi(x)$ $\nearrow \langle \hat{U} \rangle$ high

$\searrow \langle \hat{T} \rangle$ low

$\Downarrow$

$\langle \hat{H} \rangle = \langle \hat{T} \rangle + \langle \hat{U} \rangle$ may not be low!

$\therefore$ Expect some value λ_{best} that compromises $\langle \hat{T} \rangle$ and $\langle \hat{U} \rangle$ and gives minimum $\langle \hat{H} \rangle$

Now, let's fill in the Math for this physical picture.

To get $\langle \hat{H} \rangle_\phi$, need $\langle \phi | \hat{H} | \phi \rangle$ and $\langle \phi | \phi \rangle$

$$\int_{-\frac{\pi}{2\lambda}}^{\frac{\pi}{2\lambda}} \phi^* \phi \, dx = \int_{-\frac{\pi}{2\lambda}}^{\frac{\pi}{2\lambda}} \cos^2 \lambda x \, dx = \frac{\pi}{2\lambda}$$ [goes into denominator in $\langle \hat{H} \rangle$]

$$\int_{-\frac{\pi}{2\lambda}}^{\frac{\pi}{2\lambda}} \cos \lambda x \overbrace{\left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} K x^2 \right]}^{\hat{H}} \cos \lambda x \, dx = \frac{\pi \hbar^2}{4m} \lambda + \left(\frac{\pi^3}{48} - \frac{\pi}{8} \right) \frac{K}{\lambda^3} \quad \text{(Ex.)}$$

$$\langle \hat{H} \rangle_\phi (\lambda) = \frac{\hbar^2}{2m} \lambda^2 + \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \frac{K}{\lambda^2} \quad \text{(true for any } \lambda)$$

emphasize that it is evaluated w.r.t. ϕ

The theorem says: $E_{GS} \leq \frac{\hbar^2}{2m} \lambda^2 + \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \frac{K}{\lambda^2}$ (any λ)

For Best (tightest) estimate of E_{GS}: make RHS smallest

$$\frac{d}{d\lambda} \left[\frac{\hbar^2}{2m} \lambda^2 + \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \frac{K}{\lambda^2} \right] \Bigg|_{\lambda = \lambda_{best}} = 0$$ determines λ_{best}

$$\Rightarrow \lambda_{best}^4 = \frac{2mK}{\hbar^2} \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \quad \text{(Ex.)}$$

Best Estimate of E_{GS} based on $\phi(x)$ is:

Actual E_{GS}

$$\frac{\hbar^2}{2m}\lambda_{best}^2 + \left(\frac{\pi^2}{24}-\frac{1}{4}\right)\frac{K}{\lambda_{best}^2} = \frac{\hbar^2}{2m}\lambda_{best}^2 = \frac{1}{2}\hbar\sqrt{\frac{K}{m}}\left[2^{3/2}\left(\frac{\pi^2}{24}-\frac{1}{4}\right)^{1/2}\right] = \underbrace{\frac{1}{2}\hbar\omega(1.14)}_{\text{Not bad! (14\% higher)}} \geq \frac{1}{2}\hbar\omega$$

This is as good as $\underbrace{\phi(x) \sim \cos\lambda x}_{\text{this particular form}}$ can do in estimating E_{GS} of Oscillator

How to do better?

- more elaborate trial wavefunction $\phi(x)$
- better insight into the form of actual G.S. wavefunction
  - Try $\phi_{trial}(x) \sim e^{-\lambda x^2}$ on harmonic oscillator

Gaussian wavefunction with λ tuning the spread (width)

[c.f. exact solution solved in QM I]

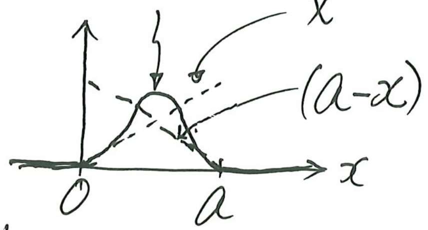
(ii) Infinite 1D Well (Ex.) $E_{GS} = \dfrac{\pi^2\hbar^2}{2ma^2} = \dfrac{h^2}{8ma^2}$

Think like a physicist (who forgot how to solve the easiest QM problem!)

- GS wavefunction should vanish at $x=0$ and $x=a$, and symmetric about $x=\frac{a}{2}$

  How about...

  for $0<x<a$: $x(a-x)$? looks OK! How about $\underbrace{x^2(a-x)^2}_{\text{also looks OK!}}$?



How about $\phi_{trial}(x) = c_1 x(a-x) + c_2 x^2(a-x)^2$? (see (e))

c_1 & c_2 are variational parameters

(Ex.) Result: $E_{min} = 0.125002\,\dfrac{h^2}{ma^2} > \dfrac{h^2}{8ma^2}$ only by a tiny bit!

(Ex.) Compare $\phi_{trial}(x)$ with best values c_1 & c_2 with exact form $\sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$.

(iii) Some Standard Exercises

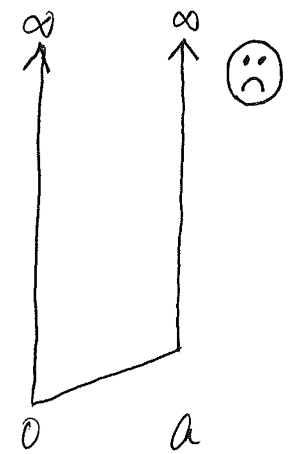
- Hydrogen atom ground state energy

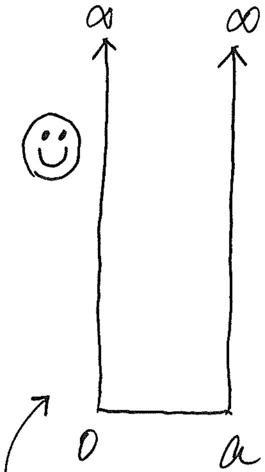
$$\phi_{\text{trial}} \sim e^{-\lambda r^2} \quad \text{(which is wrong, as we know } R_{10}(r)\text{)}$$

- $U(x) = \frac{1}{2}Kx^2 + \frac{1}{2}K'x^4$ (oscillator with quadratic & quartic terms)

$$\phi_{\text{trial}} \sim e^{-\lambda r^2} \quad \text{(which is wrong)}$$

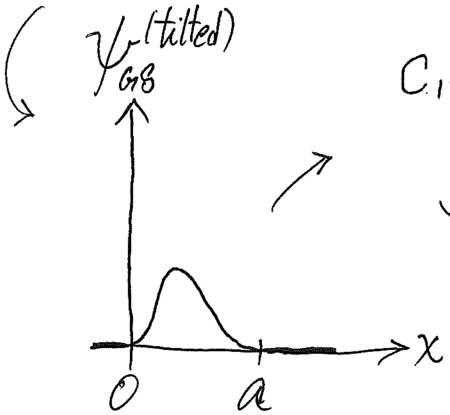
- Tilted Wells

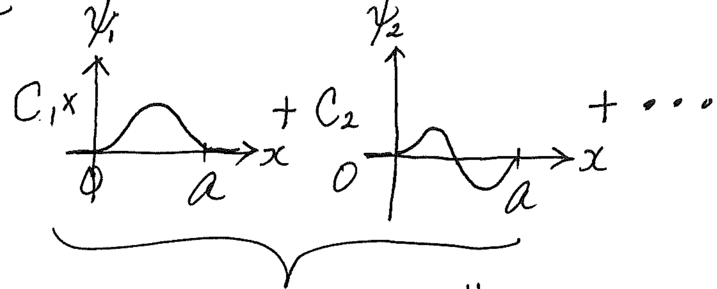




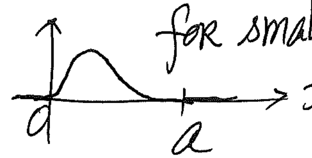
know everything $\{\psi_i\}$ and $\{E_i\}$

"Quantum Sense"





for small c_2



(c_1, c_2 as variational parameters)

$\therefore$ $\phi(x) = c_1 \psi_1(x) + c_2 \psi_2(x)$ is reasonable

variational parameters

OR $\phi(x) = c_1 \psi_1(x) + c_2 \psi_2(x) + \cdots + c_{137} \psi_{137}(x)$ will work better

variational parameters

How about ...

$$\phi(x) = \sum_{i=1}^{\infty} c_i \psi_i(x) \;?$$

This is an exact relation, as $\{\psi_i\}$ is a complete set!

What is the end result?

Turn TISE into an $\infty \times \infty$ Matrix (see Section A) (Done!)

$\therefore$ Must be some relation between approximated $\phi_{trial} = \sum_{i=1}^{n} c_i \psi_i$ and the formal & exact treatment in Section A. But what is it?

(e)[†] Trial wavefunctions of form $\phi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n$

- $c_1, c_2, \cdots, c_n$ as variational parameters (can be complex in general)
- $\phi_1, \phi_2, \cdots, \phi_n$ are known, carefully chosen
- $\phi = c_1\phi_1 + c_2\phi_2 + \cdots + c_n\phi_n$
  - linear combination of $\{\phi_i\}$ $(i=1,\cdots,n)$
  - meant to mimic ground state wavefunction of a problem $\hat{H}$
- Consider the simplest case

$$\phi = c_1\phi_1 + c_2\phi_2 \quad \text{(B3)}$$ [end result can be easily generalized]

and see how the variational calculation proceeds

[†] Key concept here, with very useful result

Evaluate $\langle \hat{H} \rangle_\phi \equiv \dfrac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = \dfrac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$

Numerator: $\langle \phi | \hat{H} | \phi \rangle = \int \overbrace{(c_1^* \phi_1^* + c_2^* \phi_2^*)}^{\phi^*} \hat{H} \overbrace{(c_1 \phi_1 + c_2 \phi_2)}^{\phi} d\tau$ [4 terms]

$= c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22}$

[where $H_{ij} = \int \phi_i^* \hat{H} \phi_j \, d\tau$ and $H_{ij} = H_{ji}^*$ ($\hat{H}$ is Hermitian)]

Denominator: $\langle \phi | \phi \rangle = \int (c_1^* \phi_1^* + c_2^* \phi_2^*)(c_1 \phi_1 + c_2 \phi_2) \, d\tau$

$= c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22}$

[where $S_{ij} = \int \phi_i^* \phi_j \, d\tau = S_{ji}^*$ (Old friends, see Section A)]

$$\therefore \langle \hat{H} \rangle_\phi (c_1, c_2) \equiv E(c_1, c_1^*, c_2, c_2^*) = \frac{c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22}}{c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22}} \qquad (B4)$$

emphasizing $\langle \hat{H} \rangle_\phi$ is fn of c_1 & c_2

May skip this in 1st reading

Aside: For those who like to see things done in matrices

$$\langle\phi|\hat{H}|\phi\rangle = (c_1^* \quad c_2^*)\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22}\end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = c_1^*c_1H_{11} + c_1^*c_2H_{12} + c_2^*c_1H_{21} + c_2^*c_2H_{22}$$

Because $\phi = c_1\phi_1 + c_2\phi_2 \Rightarrow \phi$ is $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$ in the basis of ϕ_1, ϕ_2

$\hat{H}$ becomes $\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22}\end{pmatrix}$ with $H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau = \langle\phi_j|\hat{H}|\phi_i\rangle$ in the basis of ϕ_1, ϕ_2

Similarly,

$$\langle\phi|\phi\rangle = (c_1^* \; c_2^*)\begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22}\end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$ in general with $S_{ij} = \int \phi_i^* \phi_j d\tau$

$$= c_1^*c_1 S_{11} + c_1^*c_2 S_{12} + c_2^*c_1 S_{21} + c_2^*c_2 S_{22}$$

Only if ϕ_i, ϕ_j are orthonormal, then $\langle\phi|\phi\rangle = (c_1^* \; c_2^*)\begin{pmatrix} 1 & 0 \\ 0 & 1\end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = |c_1|^2 + |c_2|^2$

Next, find best values of c_1 and c_2 such that E is minimized

[this is the variational method]

Eq. (B4)

$$\hookrightarrow c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22} = E \cdot (c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22}) \quad (B4')$$

[take† c_1^* and c_2^* as variational parameters]

- Take $\frac{\partial}{\partial c_1^*}$ on both sides of (B4') and set $\frac{\partial E}{\partial c_1^*} = 0$ (best value would minimize E)

$$\Rightarrow \boxed{c_1 H_{11} + c_2 H_{12} = E\,(c_1 S_{11} + c_2 S_{12})} \quad (B5a)$$

- Take $\frac{\partial}{\partial c_2^*}$ on both sides of (B4') and set $\frac{\partial E}{\partial c_2^*} = 0$

$$\Rightarrow \boxed{c_1 H_{21} + c_2 H_{22} = E\,(c_1 S_{21} + c_2 S_{22})} \quad (B5b)$$

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† Take c_1, c_1^*, c_2, c_2^* as independent, we could have taken c_1 and c_2. We could even take real and imaginary parts of c_1 and c_2. The end result is the same. (Try it out)

Eqs. (B5a) and (B5b) together give

$$(H_{11} - ES_{11})\, c_1 + (H_{12} - ES_{12})\, c_2 = 0$$
$$(H_{21} - ES_{21})\, c_1 + (H_{22} - ES_{22})\, c_2 = 0 \qquad \text{(B6)}$$

[Start to look familiar, see Sec.A]

Rewrite Eq.(B6) in <u>Matrix Form</u>:

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \qquad \text{(B7)}$$

(<u>Key Result</u>)

This is the <u>equation to solve for E and the best c_1 & c_2 values</u>.

Non-trivial solution to c_1 & c_2 requires (2x2 problem)

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \qquad \text{(B8)}$$

$\Rightarrow$ Multiple (two) roots of E $\Rightarrow$ <u>Lowest one is an estimate to E_{GS}</u>

(Done!)

Each root $\Rightarrow$ value of c_1 & c_2

Important Remarks and Extensions

- Next time, see $\phi = c_1\phi_1 + c_2\phi_2$, start with Eq. (B7) [Don't derive it again!]
- How about $\phi = c_1\phi_1 + c_2\phi_2 + \cdots c_n\phi_n$? Jump to [Ex.]

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2n}-ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0 \qquad \text{(B9)}$$

[an $n \times n$ problem]

Non-trivial solution to $(c_1, c_2, \cdots, c_n)$ requires $|\text{Determinant}| = 0$

The form $(H_{ij} - E_{ij})$ of the matrix elements should remind you of the huge matrix when we turn TISE into a matrix problem by using a complete set of basis functions.

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2n}-ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{vmatrix} = 0 \quad \text{(B10)}$$

[An n^{th} order equation for E]

$\to$ $\mathcal{F}(E) = 0$ with $\mathcal{F}(E)$ having E^n as the highest power

$\Rightarrow$ n roots for E and lowest one is best estimate to E_{GS} (Done!)

- Getting some understanding and useful result free!
  - Eq. (B9) has the same form as Eq. (A7), which is exact
  - Eq. (B9) is a <u>truncation</u> of Eq. (A7) (thus an approximation)
  - If $\{\phi_1, \phi_2, \ldots, \phi_n\}$ are increasingly wiggling (thus ϕ_1 least wiggling and most resembles GS wavefunction), may use lowest value<u>s</u> of E as approximated GS energy and excited state energies!

- Truncating the exact $\infty \times \infty$ problem in Eq. (A7) to retain the less wiggling n basis and thus $n \times n$ problem is backed-up theoretical by variational method.
- (B8) and (B10) will be used to understand bonding in H_2, O_2, ... and in benzene  (6×6 problem)
- Must take in... for $\phi_{trial} = c_1 \phi_1 + c_2 \phi_2$ OR $\phi_{trial} = \sum_{i=1}^{n} c_i \phi_i$, start with (B7) [OR (B8)] OR (B9) [(B10)]

Ex: Try tilted well problem on p. AM-B13