

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) Theorem: Blind Guess can only be bigger or equal to E_{GS} .

▪ Knowing what it says

• Given \hat{H} (a quantum problem)

• Make a guess (arbitrary) on a wavefunction $\phi(x)$ or $\phi(\vec{r})$
 [meant to be a guess on the ground state wavefunction]

Key idea
 ↙ ↘

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

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

↑ if ϕ is normalized

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

↑ inequality

↑ Actual ground state energy (not known)

Meaning: Guess any ϕ , $\langle \hat{H} \rangle_{\phi}$ can only be bigger OR equal to E_{GS}

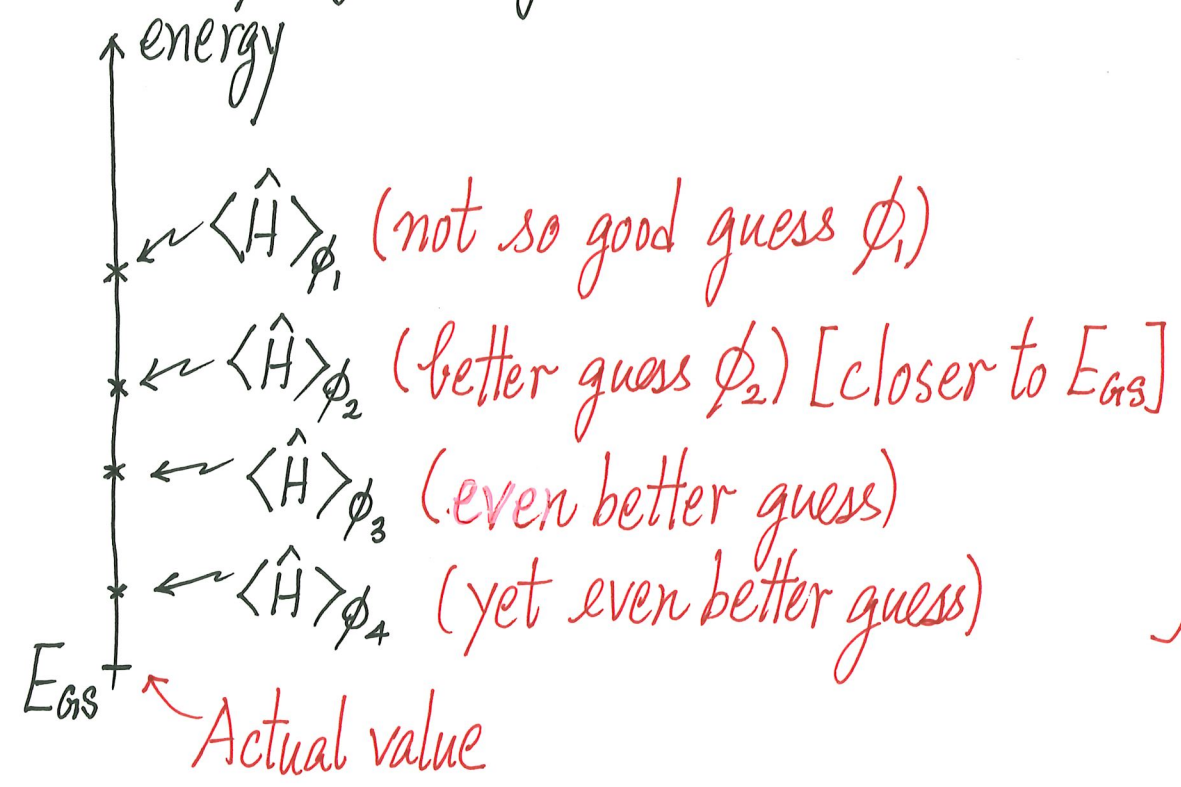
one-sided!

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

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

• Strategy of using the theorem

Idea



Make many trials $\phi_1, \phi_2, \dots, \phi_N$
N trials

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

(b) Proof of the Theorem

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

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)

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

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

But $\sum_n E_n |a_n|^2 \geq E_{\text{GS}} \sum_n |a_n|^2$ (Key step, because $E_n \geq E_{\text{GS}}$ 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 $\langle \hat{H} \rangle_{\phi} = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_{GS} \quad (B2)$

Name: The Guess wavefunction is called the trial wavefunction

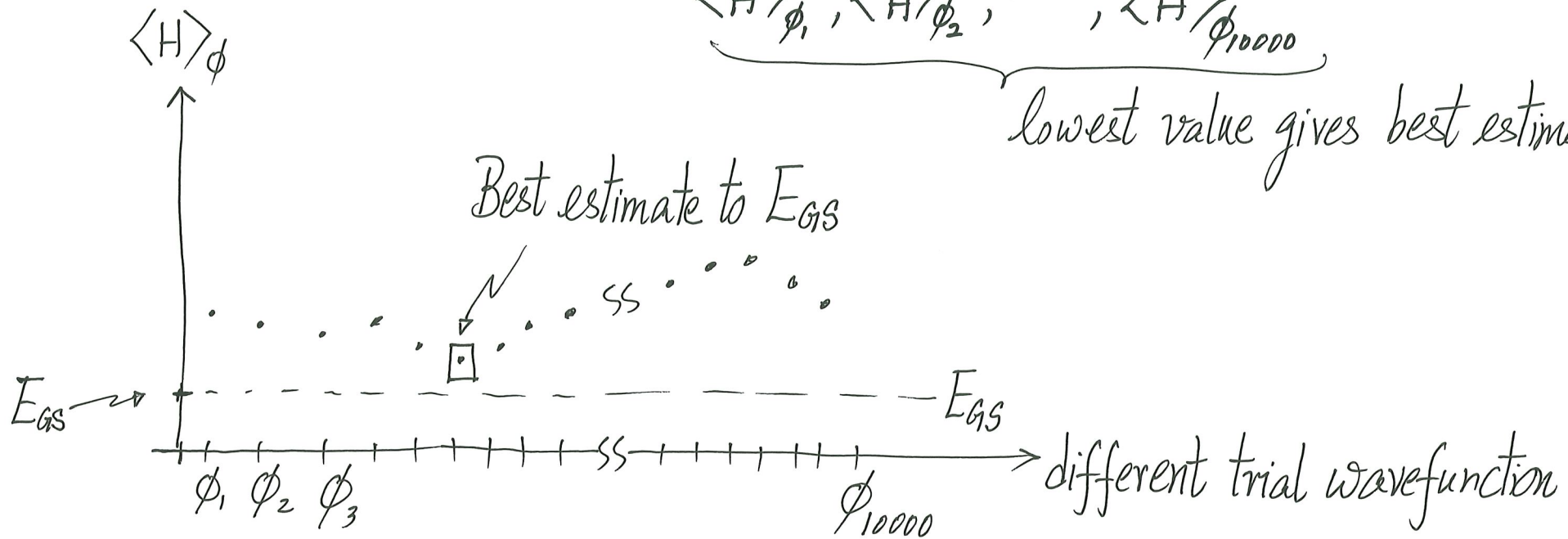
implicitly mean that we should keep on trying different ϕ 's

⁺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 Methodvarying the trial wavefunctionMake different guesses $\phi_1, \phi_2, \dots, \phi_{10000}$ (say)

$$\begin{array}{c} \downarrow \quad \downarrow \quad \quad \quad \downarrow \\ \langle H \rangle_{\phi_1}, \langle H \rangle_{\phi_2}, \dots, \langle H \rangle_{\phi_{10000}} \end{array}$$

lowest value gives best estimate



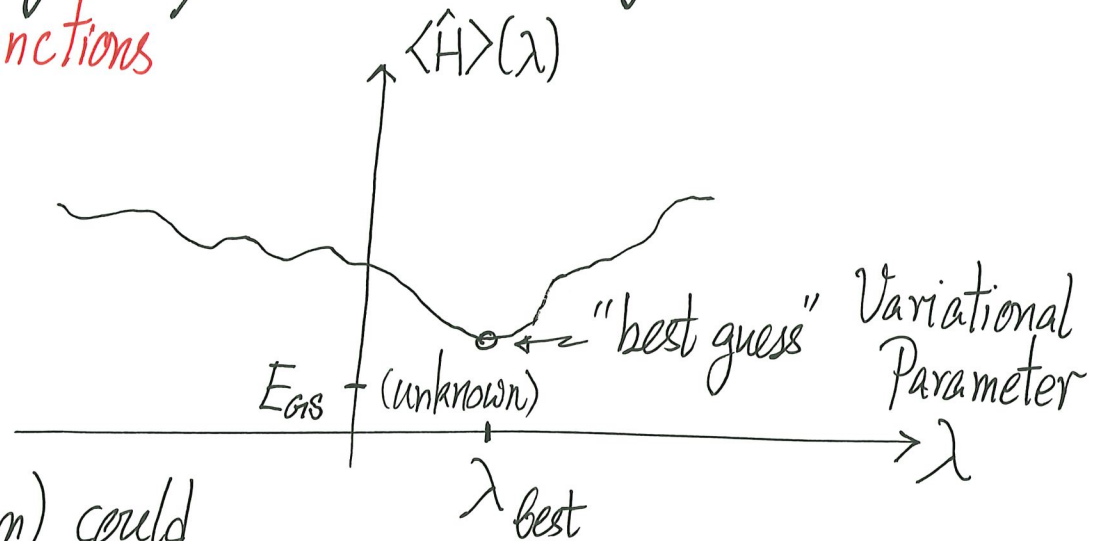
- How to try infinitely many trial wavefunctions?
 - Introduce parameter(s) [called variational parameter(s)] into the trial wavefunction

- $\phi_\lambda(x)$ 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 $\Rightarrow \langle \hat{H} \rangle_{\text{minimum}} \geq E_{\text{GS}}$



- 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

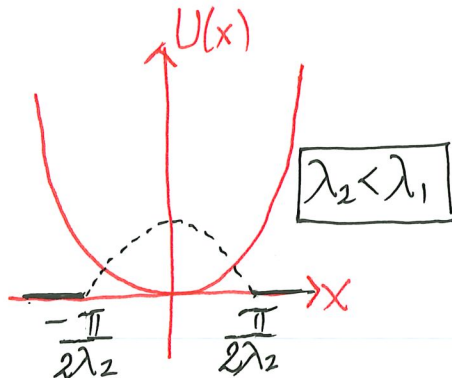
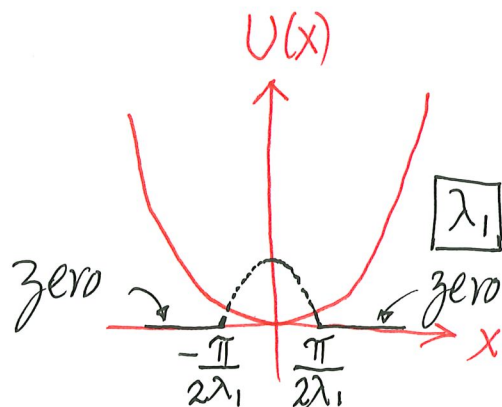
$$(i) \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \underbrace{\frac{1}{2} K x^2}_{U(x)} \quad (\text{Harmonic Oscillator}) \quad (\text{analytically solvable})$$

[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

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



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

[†] Please don't!

Think like a physicist!

Small $\lambda \Rightarrow$ Narrow $\phi(x) \rightarrow \langle \hat{U} \rangle$ low
 $\rightarrow \langle \hat{T} \rangle$ high

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

large $\lambda \Rightarrow$ Wide $\phi(x) \rightarrow \langle \hat{U} \rangle$ high
 $\rightarrow \langle \hat{T} \rangle$ 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.

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

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

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

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

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

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

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

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

Best Estimate of E_{0s} based on $\phi(x)$ is:

$$\frac{\hbar^2}{2m} \lambda_{best}^2 + \left(\frac{\pi^2}{24} - \frac{1}{4}\right) \frac{K}{\lambda_{best}^2} = \frac{\hbar^2}{2m} \lambda_{best}^2 = \frac{1}{2} \hbar \sqrt{\frac{K}{m}} \left[2^{3/2} \left(\frac{\pi^2}{24} - \frac{1}{4}\right)^{1/2} \right] = \frac{1}{2} \hbar \omega (1.14) \geq \frac{1}{2} \hbar \omega$$

AM (B11)

Actual E_{0s}
↓

Not bad!

This is as good as $\phi(x) \sim \cos \lambda x$ can do in estimating E_{0s} of Oscillator

How to do better?

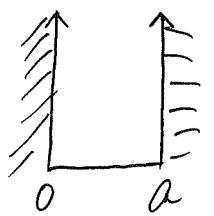
- more elaborate trial wavefunction $\phi(x)$
- better insight into the form of actual G.S. wavefunction

• Try $\phi_{trial}(x) \sim e^{-\lambda x^2}$
on harmonic oscillator

Gaussian wavefunction with λ
tuning the spread (width)

[You did it in QM I]

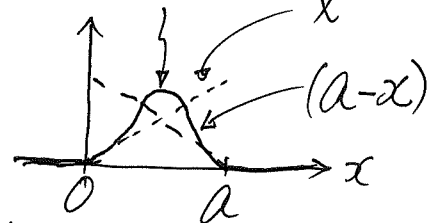
(ii) Infinite 1D Well (Ex.) $E_{GS} = \frac{\pi^2 \hbar^2}{2ma^2} = \frac{\hbar^2}{8ma^2}$



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 $0 < x < a$: $x(a-x)$? x looks OK! How about $x^2(a-x)^2$?
also looks OK!



How about $\phi_{\text{trial}}(x) = C_1 x(a-x) + C_2 x^2(a-x)^2$?

C_1 & C_2 are variational parameters

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

(Ex.) Compare $\phi_{\text{trial}}(x)$ 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

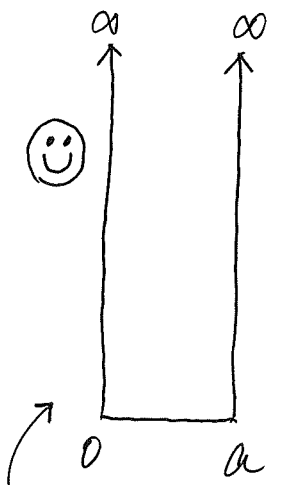
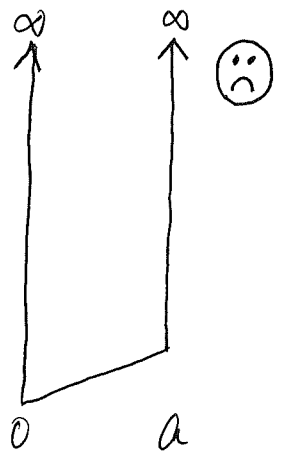
- Hydrogen atom ground state energy

$\phi_{\text{trial}} \sim e^{-\lambda r^2}$ (which is wrong, as we know $R_{00}(r)$)

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

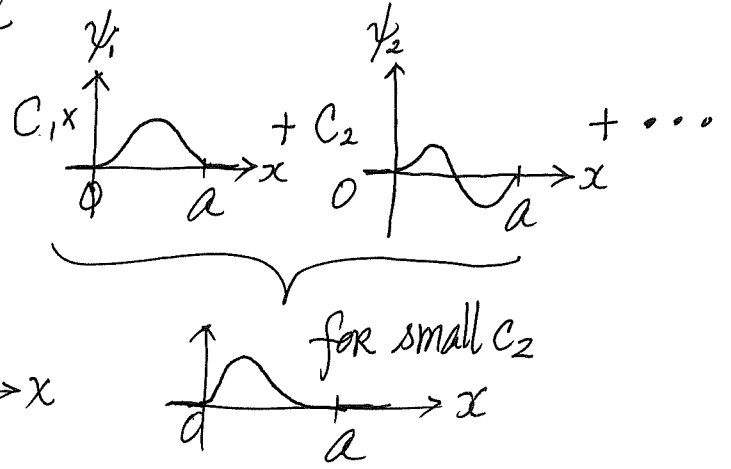
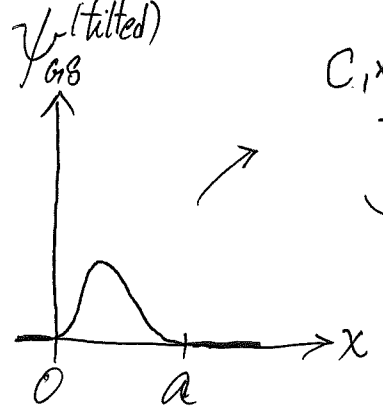
$\phi_{\text{trial}} \sim e^{-\lambda r^2}$ (which is wrong)

Tilted Wells



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

"Quantum Sense"



for small c_2

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

OR $\phi(x) = c_1 \psi_1(x) + c_2 \psi_2(x) + \dots + c_{137} \psi_{137}(x)$ 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 $\phi_{\text{trial}} = \sum_{i=1}^N c_i \psi_i$ and the formal & exact treatment in Section A. But what is it?

(e) Trial wavefunctions of form $\phi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n$

- c_1, c_2, \dots, c_n as variational parameters (can be complex in general)
- $\phi_1, \phi_2, \dots, \phi_n$ are known, carefully chosen

- $\phi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n$

- linear combination of $\{\phi_i\}$ ($i=1, \dots, n$)

- meant to mimic ground state wavefunction of a problem \hat{H}

- Consider the simplest case

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

and see how the variational calculation proceeds

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

$$\begin{aligned} \text{Numerator: } \langle \phi | \hat{H} | \phi \rangle &= \int \overbrace{(c_1^* \phi_1^* + c_2^* \phi_2^*)}^{\phi^*} \hat{H} \overbrace{(c_1 \phi_1 + c_2 \phi_2)}^{\phi} d\tau \quad [4 \text{ terms}] \\ &= c_1^* c_1 H_{11} + c_1^* c_2 H_{12} + c_2^* c_1 H_{21} + c_2^* c_2 H_{22} \end{aligned}$$

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

$$\begin{aligned} \text{Denominator: } \langle \phi | \phi \rangle &= \int (c_1^* \phi_1^* + c_2^* \phi_2^*) (c_1 \phi_1 + c_2 \phi_2) d\tau \\ &= c_1^* c_1 S_{11} + c_1^* c_2 S_{12} + c_2^* c_1 S_{21} + c_2^* c_2 S_{22} \end{aligned}$$

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

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

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

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

Eg. (B4) [this is the variational method]

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

[take[†] c_1^* and c_2^* as variational parameters] (B4')

- 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)

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

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

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

[†] 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

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0$$

(B6) [Start to look familiar, see Sec. A]

Rewrite Eq. (B6) in Matrix Form:

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

This is the equation to solve for E and the best c_1 & c_2 values.

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

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \Rightarrow \text{Multiple (two) roots} \Rightarrow \text{Lowest one is an estimate to } E_{\text{GS}} \quad (\text{Done!})$$

(B8) of E

↳ 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 $\phi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_n \phi_n$? Jump to [Ex.]

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


[an $n \times n$ problem]

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

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} - ES_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} = 0 \quad (\text{B10}) \quad \left[\text{An } n^{\text{th}} \text{ order equation for } E \right]$$

$\mathcal{F}(E) = 0$ 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 truncation of Eq. (A7) (thus an approximation)
 - If $\{\phi_1, \phi_2, \dots, \phi_n\}$ are increasingly wiggling (thus ϕ_1 least wiggling and most resembles GS wavefunction), may use lowest values 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  (6x6 problem)
- Must take in... for $\phi_{\text{trial}} = c_1 \phi_1 + c_2 \phi_2$ OR $\phi_{\text{trial}} = \sum_{i=1}^n c_i \phi_i$,
start with (B7) [OR (B8)] OR (B9) [(B10)]

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