A. A Formal and Exact Approach

- Turn TISE[+] $\hat{H}\psi = E\psi$ into a huge Matrix problem

What for?

- Finding eigenvalues/eigenvectors of a huge matrix is a standard problem of computational physics [numerical package]
- Starting point for developing/understanding approximations

[+] TISE stands for Time-independent Schrödinger Equation.

$$\hat{H}\psi = E\psi \quad \text{(A1)}$$

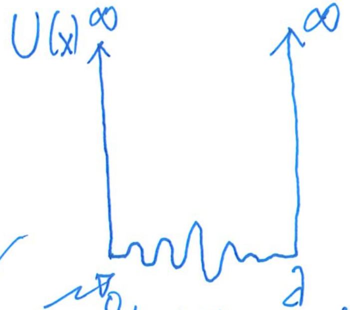
Often, know the equation but can't solved it analytically (解析解)

- But, still possible to solve TISE exactly (精確解) OR almost exactly by numerical approaches (computationally)
- Inspect QM problem and domain (region of space)
- Choose a (convenient) set of "basis functions"

  $\{\phi_1, \phi_2, \phi_3, \ldots, \phi_i, \phi_j, \ldots\}$ (often infinitely many)

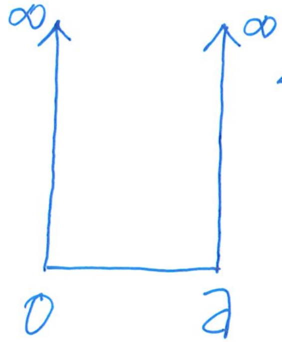
  such that any other function (especially eigenstates ψ in Eq.(1)) can be expanded in terms of $\underbrace{\{\phi_i\}}_{\text{Symbol means the whole set}}$

Want some examples to help follow the math?



rough $U(x)$ inside well

but TISE solutions $\psi_n(x)$ must vanish outside well ($\because U \to \infty$ there)



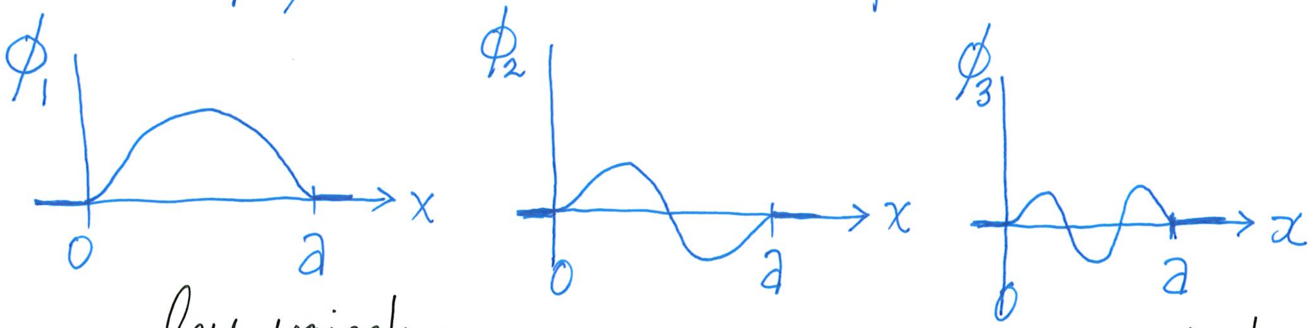
We know $\{\phi_n(x) \leftrightarrow E_n\}$ $\underbrace{n = 1, 2, 3, \cdots}_{\text{infinite of them!}}$

$\hat{H}\psi = E\psi$ expects $\{\psi_n(x) \leftrightarrow E_n\}$ (infinite of them)

$$\psi(x) = \sum_i a_i \, \phi_i(x) \quad \text{(exact)} \quad \text{(A2)}$$

The eigenfunctions of the hard-to-solve problem CAN BE expressed in terms of a linear combination of a known (your choice) basis set of functions $\{\phi_i(x)\}$ (problem becomes: Find a_i's)

More physical sense to keep in tool box



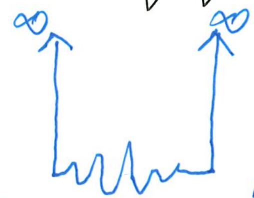
... (basis functions)

— less wriggling ——————— more wriggling →

$$\psi = \sum_i a_i \phi_i$$

less wriggling → $\psi_1 = \underbrace{a_1^{(1)}}_{\text{big}}\phi_1 + \underbrace{a_2^{(1)}}_{\text{small}}\phi_2 + \underbrace{a_3^{(1)}}_{\text{tiny}}\phi_3 + (\text{negligible})$

more wriggling → $\psi_4 = \underbrace{a_1^{(4)}}_{\text{tiny, tiny}}\phi_1 + \underbrace{a_2^{(4)}}_{\text{tiny}}\phi_2 + \underbrace{a_3^{(4)}}_{\text{small}}\phi_3 + \underbrace{a_4^{(4)}}_{\text{big}}\phi_4 + \underbrace{a_5^{(4)}}_{\text{small}}\phi_5 + (\text{negligible})$

ψ_4's energy E_4 is higher than ψ_1's energy E_1 for the 

problem

$$\hat{H}\psi = E\psi \quad (A1)$$ <u>to solve for</u> <u>$E_i \leftrightarrow \psi_i$</u> (many solutions)

- Expand $\underset{\text{unknown}}{\psi} = \sum_i \underset{\text{many unknowns}}{a_i}\, \phi_i$ ← known [your choice] (A2) (Exact in principle)

- Substitute Eq. (A2) into Eq. (A1):

$$\sum_i a_i \hat{H} \phi_i = E \sum_i a_i \phi_i$$ (equivalent to Eq. (A1), TISE)

- (i) left multiply by (any) ϕ_j^*, (ii) integrate over all coordinates

$$\sum_i \underset{\text{unknowns}}{a_i} \underbrace{\int \phi_j^* \hat{H} \phi_i \, d\tau}_{\text{known}} = \underset{\text{unknowns}}{E} \sum_i \underset{\text{unknowns}}{a_i} \underbrace{\int \phi_j^* \phi_i \, d\tau}_{\text{known}} \quad (A3)$$

$\int$, $d\tau$ ← symbols for integrating over all coordinates

known ($\because$ $\hat{H}$ & $\{\phi_i\}$ are known)

$\hat{H}$ ↑ the problem; $\{\phi_i\}$ ↑ your choice

- Functions $\{\phi_i\}$ can <u>always</u> be chosen to be <u>normalized</u>
- For generality, <u>NOT</u> assuming $\{\phi_i\}$ to be orthogonal

  [Why not? Can't do it for some TISE problems, e.g. molecules]

See Eq.(A3), there are $\underbrace{\int \phi_j^* \, \phi_i \, d\tau}$ $= \langle \phi_j | \phi_i \rangle$ (Dirac notation)

- take ϕ_j & ϕ_i, form an integral
- it is <u>a number</u>! (many #'s for $i, j = 1, 2, \cdots$)
- This number can be labelled by j and i

<u>Call</u> $\boxed{\int \phi_j^* \phi_i \, d\tau \equiv S_{ji}}$ (A4) OR $\langle \phi_j | \phi_i \rangle \equiv S_{ji}$

$\boxed{S_{ii} = \int \phi_i^* \phi_i \, d\tau = 1 \text{ (normalized), but } S_{ji} \neq 0 \text{ in general for } i \neq j}$

(<u>in general</u>)

There are also $\underbrace{\int \phi_j^* \hat{H} \phi_i \, d\tau}_{\text{a quantity of unit "energy" labelled by } j \text{ and } i} = \langle \phi_j | \hat{H} | \phi_i \rangle$

<u>Call</u> $\boxed{\int \phi_j^* \hat{H} \phi_i \, d\tau \equiv H_{ji}}$ (A5) (know $\hat{H}$ and $\{\phi_i\}$, then let the computer does the integrals H_{ji})

$\therefore$ Eq. (A3) becomes

$$\boxed{\sum_i H_{ji} a_i = E \sum_i S_{ji} a_i} \quad \text{OR} \quad \boxed{\sum_i (H_{ji} - E S_{ji}) a_i = 0} \qquad \text{(A6)}$$

equivalent (等價) to TISE (Eq. (A1))

- Eq. (A1) is an energy eigenvalue problem
- Schrödinger form: TISE is a differential equation
- Equivalent form in Eq. (A6): <u>turned TISE into a Matrix problem</u>

<u>Refresher</u>: Matrix $\overleftrightarrow{M}$ multiplies into a column vector

$$\underbrace{\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix}}_{2\times 2}\underbrace{\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}}_{2\times 1} = \underbrace{\begin{pmatrix} M_{11}a_1 + M_{12}a_2 \\ M_{21}a_1 + M_{22}a_2 \end{pmatrix}}_{2\times 1}$$

same

Inspect: $M_{11}a_1 + M_{12}a_2 = \sum_{i=1,2} M_{1i}a_i$ — (i) (first row)

$M_{21}a_1 + M_{22}a_2 = \sum_{i=1,2} M_{2i}a_i$ — (ii) (second row)

So, $j=1$, $\sum_{i=1,2} M_{ji}a_i$ is (i)

$j=2$, $\sum_{i=1,2} M_{ji}a_i$ is (ii)

$\therefore \sum_{i=1,2} M_{ji}a_i$ (for various j) is a matrix multiplying into a column vector

Back to Eq.(A6): $\sum_i (H_{ji} - ES_{ji})\, a_i = 0$

It is...

Key Result

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = 0 \qquad \text{(A7)}$$

(same as (A6))

- General so far, leave S_{ji} general, equivalent to TISE (thus EXACT)
- Typically, $\left(\begin{smallmatrix} \cdot & \cdot & \cdot \\ \cdot & \ddots & \\ \cdot & & \cdot \end{smallmatrix}\right)$ is $\underline{\infty \times \infty \text{ Matrix}}$ ($\because$ Infinitely many ϕ_i's)
- TISE unknowns are E and ψ (many pairs)
- Eq.(A7): E and $\begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$ are unknowns (many pairs)

Useful Skill

Next time, when you see $H\psi = E\psi$

and when you think about a basis set $\{\phi_i\}$, the next thing pops up should be

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = 0$$

AND

$$\left| \quad \text{Determinant} \quad \right| = 0$$ gives (many) values of E

Refresher: Hermitian Operators

$$\boxed{\int f^* \hat{A}\, g\, d\tau = \int g (\hat{A} f)^* d\tau = \left(\int g^* \hat{A} f\, d\tau\right)^* \quad \text{for Hermitian } \hat{A}}$$

any f and g

- Hamiltonian $\hat{H}$ is Hermitian (allowed energies are real)

$$\underbrace{\int \phi_j^* \hat{H} \phi_i \, d\tau}_{H_{ji}} = \underbrace{\left(\int \phi_i^* \hat{H} \phi_j \, d\tau\right)^*}_{H_{ij}^*} \tag{A8}$$

Matrices obeying this relation are called Hermitian Matrices

(ji)-element = complex conjugate of (ij)-element

$\therefore$ Only need to calculate half of matrix elements ← Not too bad!

and $H_{ii} = H_{ii}^* \Rightarrow$ H_{ii} are real (diagonal elements are real)

Similarly, $\boxed{S_{ji} = S_{ji}^* \; (\because \text{"}\hat{1}\text{" is Hermitian})}$ ← Not too bad!

Back to (A7), $\underbrace{\begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}}_{}$ is obviously a "solution", but $\psi = \sum_i a_i \phi_i = 0$ (particle disappears!)
→ trivial solution

- For non-trivial solutions, requires determinant

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \qquad (A9)$$

- Plug in a value of E, LHS gives a value, but may not be zero
  $\Rightarrow$ Eq. (A9) is not satisfied $\Rightarrow$ Wrong E (then try again...)

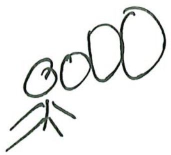
$\therefore$ Eq. (A9) is an equation for allowed values of E

$|\infty \times \infty| = 0 \Rightarrow \underbrace{\text{infinite many}}_{\text{not surprising (c.f. 1D well, harmonic oscillator, ...)}}$ allowed E

Formal vs Practical

$\hat{H}$ (a problem that has ∞ many E's) $\leftrightarrow$ Needs an infinite basis $\{\phi_i\}$

$\Rightarrow \underset{\text{with } E \text{ inside}}{|\infty \times \infty|} = 0 \Rightarrow$ infinitely many E's (Formal)

- But if we only need five lowest E's, then  think like a physicist!

include $\{\phi_i,\ i = 1, 2, \cdots \underbrace{10}_{\text{say}}\}$ (less wriggling $\leftrightarrow$ lowest energy)

$\Rightarrow |10 \times 10| = 0 \Rightarrow 10$ values of E (then $\underbrace{\text{pick lowest five}}_{\text{Done! Approximately!}}$)

Meaning:

Truncating $\infty \times \infty$ into $\underset{(10\times 10)}{N \times N}$ problems! (An art and a science!) (Practical)

Take-Home Passage

- For a problem (defined by $\hat{H}$), choose a set $\{\phi_i\}$, TISE becomes Eq. (A7) in Matrix Form. Matrix elements are $(H_{ji} - ES_{ji})$.
- Exact and general (Eq. (A7))
- Cleverer choice(s) of $\{\phi_i\}$ $\leftrightarrow$ shorter computing time
- Carry Eq. (A7) with you. Will use it many times.
- Practically, truncate to smaller size (guided by physical sense)

Basically Done!

Simplified Form of Eq.(A7)

- If $\{\phi_i\}$ give $\int \phi_j^* \phi_i \, d\tau = 0$ (orthogonal) OR ≈ 0, for $j \neq i$ (approximately orthogonal) (an approximation often made)

note condition

and $\int \phi_i^* \phi_i \, d\tau = 1$ (normalized), then Eq.(6) becomes (i.e. $\langle \phi_j | \phi_i \rangle = \delta_{ji}$)

$$\sum_j H_{ji} a_i = E \sum_j \underbrace{S_{ji}}_{\delta_{ji}} a_i = E a_j \qquad (A10)$$

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \qquad (A11)^{+}$$

which is clearly an eigenvalue problem of the matrix H_{ji} (Hermitian)

$^{+}$ Eq.(A11) can be obtained directly from Eq.(A7) by setting $S_{ii} = 1$ & $S_{ji} = 0$ ($j \neq i$)

- Used a basis $\{\phi_i\}$ to construct the matrix $\overleftrightarrow{H}$ (Recall)

- Keep in mind that

there is a basis set usually not shown explicitly

$$\begin{array}{c|c} & \begin{array}{cccc} |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle & \cdots \end{array} \\ \begin{array}{c} \langle\phi_1| \\ \langle\phi_2| \\ \langle\phi_3| \\ \vdots \end{array} & \underbrace{\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}}_{\text{A big Matrix } \overleftrightarrow{H}} \end{array} \quad \text{and} \quad \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \begin{array}{c} |\phi_1\rangle \\ |\phi_2\rangle \\ |\phi_3\rangle \\ \vdots \end{array} \qquad (A12)$$

meaning

$$\psi = a_1\phi_1 + a_2\phi_2 + a_3\phi_3 + \cdots$$

H_{ij} depends on $\hat{H}$ AND $\underbrace{\{\phi_i\}}_{}$

many choices [some more convenient or obvious]

∴ Eq.(A11), if valid, says TISE is equivalent to finding eigenvalues & eigenvectors of $\overleftrightarrow{H}$

"Cleverest"† Choice

$$\hat{H}\psi_i = E_i \psi_i$$

eigenstates of $\hat{H}$ energy eigenstates

Choose the basis set to be $\{\psi_i\}$, then $\int \psi_j^* \underbrace{\hat{H}\psi_i}_{E_i\psi_i} d\tau = E_i \underbrace{\int \psi_j^* \psi_i d\tau}_{\text{orthonormal}}$

$= E_i \delta_{ij}$

Meaning: $H_{ii} = E_i$; $H_{ij} = 0$ $(i \neq j)$

$$\therefore \overleftrightarrow{H} = \begin{pmatrix} E_1 & & & 0 \\ & E_2 & & \\ & & E_3 & \\ 0 & & & \ddots \end{pmatrix}$$

is <u>diagonal</u> & <u>elements are eigenvalues</u>

- If Eq. (A11) is valid, solving Eq. (A11) is equivalent to "diagonalizing the matrix $\overleftrightarrow{H}$" in (A12), i.e. changing (looking for) the basis from $\{\phi_i\}$ ($\overleftrightarrow{H}$ not diagonalize) to $\{\psi_i\}$ ($\overleftrightarrow{H}$ is diagonalized)

† Perhaps silliest! If we know $\{\psi_i\}$, we don't need to treat the whole treatment!

- Finally, if $\infty \times \infty$ or $N \times N$ is scary, <u>don't worry</u>.
- Get yourself familiar with a simple case
  - focus on two functions ϕ_i and ϕ_j (forget the others)

So only H_{ii}, H_{ij}, H_{ji}, H_{jj}

$$\begin{pmatrix} H_{ii} - ES_{ii} & H_{ij} - ES_{ij} \\ H_{ji} - ES_{ji} & H_{jj} - ES_{jj} \end{pmatrix}$$ in Eq. (A7)

and

$$\begin{pmatrix} H_{ii} - E & H_{ij} \\ H_{ji} & H_{jj} - E \end{pmatrix}$$ in Eq. (A11)

Involve Only 2×2 Matrices (simple)

or eigenvalue problem of $\begin{pmatrix} H_{ii} & H_{ij} \\ H_{ji} & H_{jj} \end{pmatrix}$

$\therefore$ Knowing how to treat 2×2 matrices is useful in many QM problems
[Any everyone can handle 2×2 matrices!]

You should know[+] how to solve

$$\begin{vmatrix} H_{ii} - ES_{ii} & H_{ij} - ES_{ij} \\ H_{ji} - ES_{ji} & H_{jj} - ES_{jj} \end{vmatrix} = 0 \quad \text{for } E \qquad \text{(quadratic equation of E)}$$

OR simpler

$$\begin{vmatrix} H_{ii} - E & H_{ij} \\ H_{ji} & H_{jj} - E \end{vmatrix} = 0 \quad \text{for } E \qquad \text{(also quadratic equation of E)}$$

[+] If you know how to do this, we immediately understand much about chemical bonding, effect of external field on atoms, and formation of bands and band gaps in solid! It really worths the effort.

One Page Summary: TISE $\longleftrightarrow$ Huge Matrix Problem

defines problem $\rightarrow$ $\hat{H}\psi = E\psi$

to solve

choose a complete set of basis functions $\{\phi_i\}$ (your choice)

$$\psi = \sum_i a_i \phi_i$$

to solve

$$H_{ji} \equiv \int \phi_j^* \hat{H} \phi_i \, d\tau$$

$$S_{ji} \equiv \int \phi_j^* \phi_i \, d\tau$$

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = 0 \qquad \text{(A7)}$$

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \qquad \text{(A9)}$$

becomes a computational physics problem!

equation giving allowed energies E

Summary

- Eq. (A7) & (A11) [if valid] are key results
- They are starting points for understanding molecules (bonding), solids (energy bands).
- Convenient for numerical approaches
- Convenient for developing & understanding approximation methods
- QM TISE problems are related to Matrix Math (Heisenberg/Born)

The effectiveness of the method depends strongly on a good choice of $\{\phi_i\}$, which requires good physical sense.