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

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

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 $\underbrace{\{\phi_i\}}_{\text{Symbol means the whole set}}$

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

to solve for $E_i \leftrightarrow \psi_i$ (many solutions)

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

- Substitute Eq. (2) into Eq. (1):

$$\sum_i a_i \hat{H}\phi_i = E \sum_i a_i \phi_i$$

(equivalent to Eq.(1), TISE)

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

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

symbols for integrating over all coordinates

- 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. (3), 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>!
- This number can be labelled by j and i

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

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

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

$\therefore$ Eq. (3) becomes

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

equivalent to TISE (Eq. (A1))
(等價)

- 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
- Typically, $\left(\because\right)$ is $\underline{\infty \times \infty \text{ Matrix}}$ ($\because$ Infinitely many ϕ_i's)
- TISE unknowns are E and ψ (many pairs)
- Eq.(7): E and $\begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$ are unknowns (many pairs)

- $\begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$ is obviously a "solution", but $\psi = \sum_i a_i \phi_i = 0$ (particle disappears!)
  $\rightarrow$ trivial solution

- For non-trivial solutions, requires determinant

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & \cdots \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & \cdots \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \qquad (A8)$$

- Plug in a value of E, LHS gives a value, but may not be zero
  $\Rightarrow$ Eq. (A8) is not satisfied $\Rightarrow$ Wrong E (then try again...)

$\therefore$ Eq. (A8) 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

- Practically, truncate into $N \times N$ size (approximation), then

$$\left| N \times N \right| = 0 \Rightarrow N \text{ values of allowed energy}$$

Take-home Message

- Choose a set of $\{\phi_i\}$, TISE becomes Eq.(A7) in Matrix form
- Completely general up to here, thus Eq.(A7) is exact
- Cleverer choice(s) of $\{\phi_i\}$ can shorten computing time
- Take Eq.(A7) in, we shall use it many times

Further questions

- Is H_{ji} related to H_{ij}? If yes, how? [$\hat{H}$ is a Hermitian operator]
- How about S_{ji} and S_{ij}?

Refresher: Hermitian Operators

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

any f and g

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

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

$H_{ji} = H_{ij}^*$ ← (A9) Matrices obeying this relation are called Hermitian Matrices

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

$\therefore$ Only need to calculate half of matrix elements

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

Similarly, $S_{ji} = S_{ji}^*$ ($\because$ "$\hat{1}$" is Hermitian)

Simplified Form of Eq.(A7)

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

  and $\int \phi_i^* \phi_i \, d\tau = 1$, then Eq.(6) becomes

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

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

which is clearly <u>an eigenvalue problem</u> of <u>the matrix H_{ji}</u>

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

Further Remarks

- Eq. (A7) OR Eq. (A11) (if valid) is the starting point in understanding electronic states in <u>molecules</u> (molecular orbitals) and in <u>solids</u> (energy bands)
- Starting point for <u>computational</u> approaches
- <u>Truncation</u> : Want lowest 10 eigenvalues E, truncate to 500×500
  (an approximation) may not affect the lowest eigenvalues
- If Eq. (A11) is valid, allowed energies E are eigenvalues of

$$\overleftrightarrow{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \qquad (A12)$$

- QM TISE problems are related to Matrix Mathematics (<u>Heisenberg</u>/<u>Born</u>)

- Need a basis $\{\phi_i\}$ to construct the matrix $\overleftrightarrow{H}$ (Recall)
- <u>Keep in mind</u> that

there is a basis set

$$\begin{array}{c|cccc} & |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle & \cdots \\ \hline \langle\phi_1| & H_{11} & H_{12} & H_{13} & \cdots \\ \langle\phi_2| & H_{21} & H_{22} & H_{23} & \cdots \\ \langle\phi_3| & H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{array} \quad \text{and} \quad \begin{array}{cc} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} & \overbrace{\begin{matrix} |\phi_1\rangle \\ |\phi_2\rangle \\ |\phi_3\rangle \\ \vdots \end{matrix}} \end{array} \qquad (A13)$$

meaning

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

H_{ij} depends on $\hat{H}$ <u>AND</u> $\underbrace{\{\phi_i\}}_{\text{many choices [some more convenient or obvious]}}$

"Cleverest" Choice

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

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

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

is diagonal & elements are eigenvalues

- 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)

- 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}

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

and

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

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!]