Using Symmetries to Diagonalize H

- Showed how to solve general problem — given H — characteristic eqn.

- But practically, we almost always either
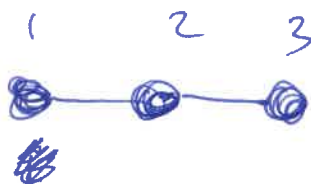
  ① Solve numerically

    or

  ② Use symmetries to ~~find~~ answer more quickly.

Example

3-site system, e^- can be at any site.

1 2 3

$$E_i = \langle \phi_i | H | \phi_i \rangle, \quad i = 1, 2, 3$$

hopping or
tunelling interaction

(real)

$$-\Delta = \langle 1 | H | 2 \rangle = \langle 2 | H | 3 \rangle$$

$$0 = \langle 1 | H | 3 \rangle$$

$$H = \begin{pmatrix} E_0 - \Delta & 0 \\ -\Delta & E_0 & -\Delta \\ 0 & -\Delta & E_0 \end{pmatrix}$$

Symmetry of system?

— Cyclical rotation? No $1 \to 2$ adds extra
(Keep sites same, but shift $\bar{e}$) interaction.

— Interchage of population ~~between~~ between ~~site~~ 1 & 3.
electron w.f.

— Equivalently parity transform.

— In this basis $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = |1\rangle$,

what is Π transformation matrix?

$$\Pi = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

— Recall, we can think of a ~~symmetry~~ transform U as being a symmetry when

$$|\psi\rangle \xrightarrow{\text{time evolve}} |\psi(t)\rangle$$

$\downarrow U \qquad\qquad\qquad \downarrow U$

$$U|\psi\rangle \xrightarrow[\text{time evolve}]{} \text{same as when}$$

If $[H,\Pi] = 0$, $\Pi|\psi_i\rangle = \pi_i|\psi_i\rangle$

then H acting on $|\psi_i\rangle$

either ① returns $|\psi_i\rangle$ or ② carries

$|\psi_i\rangle$ to another state with same definite

π_i

- If there is a degeneracy in Π, then

we can pick a basis which simultaneously

diagonalizes, e.g. basis vectors are eigenvectors

of both Π & H

$$-\left(e^{-iHt}\right)U_\phi|\psi\rangle = U_\phi e^{-iHt}|\psi\rangle$$

$$\Rightarrow [U,H] = 0 \quad \text{if } U_\phi \text{ is a symmetry.}$$

- Should be case here. Lets check.

$$\Pi H = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} \mathcal{E}_\phi & -\Delta & 0 \\ -\Delta & \mathcal{E}_\phi & -\Delta \\ 0 & -\Delta & \mathcal{E}_\phi \end{pmatrix}$$

$$= \begin{pmatrix} 0 & -\Delta & \mathcal{E}_\phi \\ -\Delta & \mathcal{E}_\phi & -\Delta \\ \mathcal{E}_\phi & -\Delta & 0 \end{pmatrix}$$

$$H\Pi = \begin{pmatrix} \mathcal{E}_\phi & -\Delta & 0 \\ -\Delta & \mathcal{E}_\phi & -\Delta \\ 0 & -\Delta & \mathcal{E}_\phi \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & -\Delta & \mathcal{E}_\phi \\ -\Delta & \mathcal{E}_\phi & -\Delta \\ \mathcal{E}_\phi & -\Delta & 0 \end{pmatrix}$$

$$\Rightarrow [H, \Pi] = 0 \checkmark$$

-OK, so how do we use Π symmetry to solve problem?

- H & Π must be "simultaneously diagonalizable"

    i.e. can choose basis of e.v.'s which is simlt. e.v. of each op.

- E.v.'s of Π?

    One state with $\Pi = -1$: $|v_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$

    Two states with $\Pi = +1$: $|v_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$

    $|v_3\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$

- $|v_1\rangle$ must be an e.v. of H. verify easily. see below

    E.v. of H

    $|\varphi_1\rangle = |v_1\rangle$

    Check: $H|v_1\rangle = \varepsilon |v_1\rangle$ ✓

- $|v_2\rangle$ & $|v_3\rangle$ are only e.v.'s if we got lucky.

    Check. $H|v_3\rangle = \begin{pmatrix} -\Delta \\ \varepsilon_m \\ -\Delta \end{pmatrix} \neq \varepsilon_3 |v_3\rangle$

    $H|v_3\rangle = \alpha|v_2\rangle + \beta|v_3\rangle$

- But we now just have a 2D problem.

- Only one state w/ $\Pi = -1$:

$$|\sigma_1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \implies H|\sigma_1\rangle = E_1|\sigma_1\rangle$$

$$|\psi_1\rangle = |\sigma_1\rangle \xleftarrow{} \text{evect of } \Pi$$

$$\uparrow \text{ evect of } H$$

- Two states w/ $\Pi = +1$

$$|\sigma_2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$$

$$H|\sigma_2\rangle \cancel{\neq E_2|\sigma_2\rangle}$$

$$= \alpha|\sigma_2\rangle + \beta|\sigma_3\rangle \cancel{\neq E_2|\sigma_2\rangle}$$

- Lets find H matrix in subspace

of $|\sigma_2\rangle, |\sigma_3\rangle$

- $$H|\sigma_3\rangle = \begin{pmatrix} -\Delta \\ \cancel{\varepsilon} \\ \Delta \end{pmatrix}$$

$$|\sigma_3\rangle = |\psi_3\rangle$$

evect of Π e.vect of H

$$\langle v_3 | H | v_3 \rangle = \mathcal{E}$$

~~$\langle v_1 | H | v_3 \rangle = 0$ as it should~~

$$\langle v_2 | H | v_3 \rangle = \frac{1}{\sqrt{2}} \cdot 2\Delta = -\sqrt{2}\Delta$$

$$H | v_2 \rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \mathcal{E} \\ -2\Delta \\ \mathcal{E} \end{pmatrix}$$

$$\langle v_2 | H | v_2 \rangle = \frac{1}{2} \left(2\mathcal{E} \right) = \mathcal{E}$$

$$\Rightarrow \quad H = \begin{pmatrix} \mathcal{E} & -\sqrt{2}\Delta \\ -\sqrt{2}\Delta & \mathcal{E} \end{pmatrix} \begin{array}{l} | v_2 \rangle \\ | v_3 \rangle \end{array}$$

$$\overbrace{\qquad}^{|v_2\rangle \quad |v_3\rangle}$$

Note: 3 different bases we can use.

We know answer:

$$| \varphi_2 \rangle = \frac{1}{\sqrt{2}} \left(| v_2 \rangle + | v_3 \rangle \right) = \frac{1}{2} \begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix} = \frac{1}{2} \left(|1\rangle + \sqrt{2}|2\rangle + |3\rangle \right)$$

$$| \varphi_3 \rangle = \frac{1}{\sqrt{2}} \left(| v_2 \rangle - | v_3 \rangle \right) = \frac{1}{2} \begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix} = \frac{1}{2} \left(|1\rangle - \sqrt{2}|2\rangle + |3\rangle \right)$$

___

$\Rightarrow$ No need to solve char. eq. Recognizing parity symmetry allows us to find e.v.s' of H pretty easily.

Energy spectrum:

$$H |\sigma_i\rangle = \underset{E_{i}}{\overset{E}{\cancel{}}} |\sigma_i\rangle$$

$$\parallel$$

$$|\varphi_i\rangle$$

$$H |\varphi_2\rangle = (\overset{(E-\sqrt{2}\Delta)}{\cancel{}}) |\varphi_2\rangle$$

$$H |\varphi_3\rangle = (\overset{E+\sqrt{2}\Delta}{\cancel{}}) |\varphi_2\rangle$$

On degeneracies

① ~~~~ No energy degeneracies. ⇒ Each energy eigenstate
must have ~~~~~~~ well-defined parity.

② There is a parity degeneracy in the
positive parity manifold. ⇒ H can mix
the two states of positive parity.

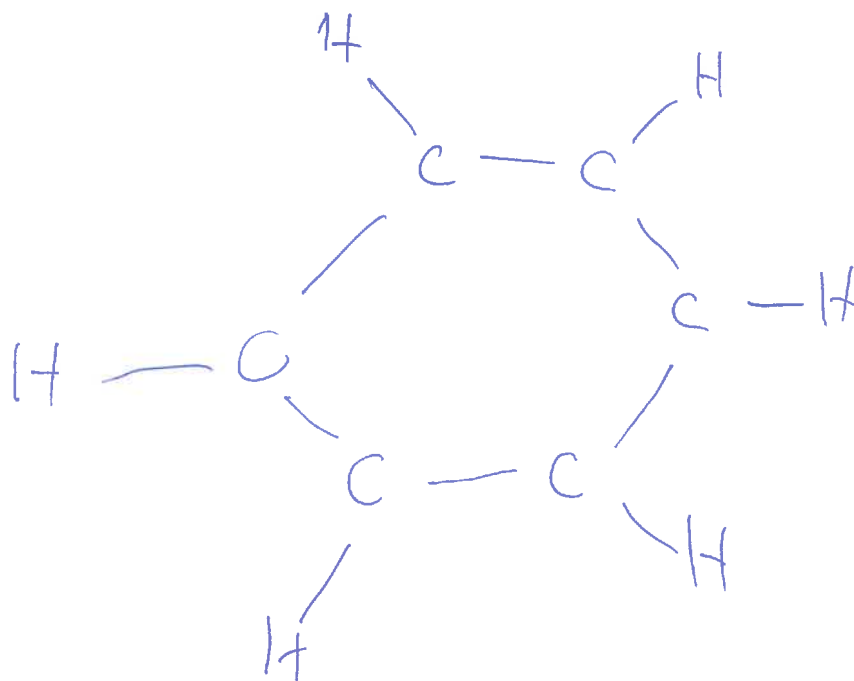But it is also possible to simultaneously
diagonalize H & M, & we have done that
by ~~~~~~ using the ~~ basis of energy
eigenstates.

Now consider cyclic molecule

$$1 \quad 2 \quad 3$$

N

For $N = 6$, this models benzene C_6H_6

$$
\begin{array}{c}
H \quad\quad\quad H \\
C - C \\
H - C \quad\quad\quad C - H \\
C - C \\
H \quad\quad\quad H
\end{array}
$$

which has one delocalized e^- per

C atom

For general N

$$H = \begin{pmatrix} E_a & -\Delta & & & -\Delta \\ -\Delta & E_a & & \text{O} & \\ & & \ddots & & \\ & \text{O} & & \ddots & \Delta \\ -\Delta & & & -\Delta & E_a \end{pmatrix}$$

← Energy of one electron. (No e^- on e^- interactions)

For example N=4

$$H = \begin{pmatrix} E_a & -\Delta & 0 & -\Delta \\ -\Delta & E_a & -\Delta & 0 \\ 0 & -\Delta & E_a & 0 \\ -\Delta & 0 & -\Delta & E_a \end{pmatrix}$$

– We can guess at some e.vects, eg. $|v_1\rangle = \begin{pmatrix} 1 \\ \vdots \\ 1 \end{pmatrix}$

$$H |v_1\rangle = (E - 2\Delta)|v_1\rangle$$

– But more systematic approach is to use
by one unit
rotation ∧ symmetry

– for N=4, this is 90°

Let R be the operator which shifts the n location in the ring by one unit.

$$R = \begin{pmatrix} 0 & 1 & & & & \\ 0 & 0 & 1 & & & \\ 0 & 0 & 0 & 1 & & \\ & & & \ddots & & \\ & & & & 0 & 1 \\ 1 & 0 & & & & 0 & 0 \end{pmatrix},$$

For $N=4$,

$$R = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

— This is clearly a symmetry of problem,

so $[R, H] = 0$ (could verify)

— $\Rightarrow R \& H$ can be simult. diagonalized

— Easy to find e.vects. of R:

$$|v_{(\alpha)}\rangle = \begin{pmatrix} 1 \\ \alpha \\ \alpha^2 \\ \vdots \\ \alpha^{N-1} \end{pmatrix} \qquad R|v_{(\alpha)}\rangle = \alpha |v_{(\alpha)}\rangle$$

Obviously works for all but last row. (R shifts everything by 1 unit, & we pick up an α)
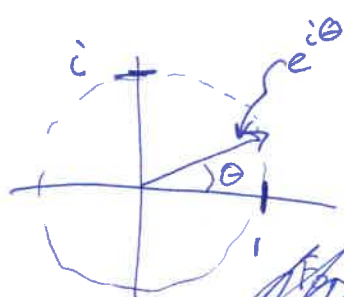
To fulfil last row condition,

~~[scribbled out]~~

~~nth row~~

α is an Nth root of unity: (m is wrapping factor)

$$\alpha^N = 1 \quad , \text{ or } \quad \alpha = e^{2\pi i m / N} \quad , \quad m = 0,1,2..$$

(Think of rotating unit vector in complex plane. For $m=1$, N rotations of $e^{2\pi i / N}$ will give $e^{2\pi i} = 1$. (One rotation of 360°)

For $m = 2$, 720° in N steps)

— There are N independent roots (solutions) corresponding to $m = 0 \ldots N-1$. Once $m \geq N$ we are repeating values of α.

— For $N = 4$

$90°$ rotation of 1 with each row $\quad$ $180°$ rot /row

$$|v_0\rangle = \frac{1}{\sqrt{4}} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \qquad |v_1\rangle = \begin{pmatrix} 1 \\ i \\ -1 \\ i \end{pmatrix} \qquad |v_2\rangle = \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} \qquad |v_3\rangle = \begin{pmatrix} 1 \\ -i \\ -1 \\ i \end{pmatrix}$$

$m=0$ $\qquad$ $m=1$

✳✳ Notice — electron density is shared

equally between sites. But there is 1-site a phase difference which varies from one eigenstate to the other.

$|v_0\rangle$ looks like this

$\psi_1 \quad \psi_2 = \psi_1$
○   ○

○   ○ $\psi_3 = \psi_1$

I am describing the phase of the electron w.f. localized at different points in space.

The $|v_1\rangle$ eigenstate is composed of 4 localized waves all with the same phase.

However $|v_2\rangle$ looks like

$\psi_1 \quad \psi_2 = i\psi_1$
○   ○

$\psi_4 = -i\psi_1 \quad \psi_3 = -\psi_1$
○   ○

We shall see that the site-to-site phase shift determines the eigenenergy. (This is just like the double well case, where the 180° phase-shifted eigenstate has higher energy)

~~Now check~~ ~~equally between sites. But these~~

~~is a different phase shift~~ ~~R has a~~

- So we see that

set of N non-deg. e.vects

$\Rightarrow$ Each one must be e.vect of

H.

~~Check~~ Find e.v.

And that phase shift of w.f.
determines energy of state

$$H \, |\sigma_m\rangle = \uparrow \begin{pmatrix} \cdots & 0 & 0 & \Delta & E_0 & \Delta & 0 & \cdots \end{pmatrix} \begin{pmatrix} \vdots \\ \alpha^{j-1} \\ \alpha^j \\ \alpha^{j+1} \\ \vdots \end{pmatrix} \quad \begin{array}{l}(j+1)\text{th} \\ \leftarrow \text{row}\end{array}$$

$(j+1)$~~th~~ row

$$= \begin{pmatrix} \vdots \\ \alpha^j \left[E_0 + \Delta(\alpha + \alpha^{-1}) \right] \\ \vdots \end{pmatrix} \quad \begin{array}{l}(j+1)\text{th} \\ \leftarrow \text{row}\end{array}$$

$\alpha = e^{2\pi i m / N}$

$\alpha^{-1} = e^{-2\pi i m / N}$

$$\Rightarrow H \, |\sigma_m\rangle = \left[E_0 + \Delta(\alpha + \alpha^{-1}) \right] |\sigma_m\rangle$$

$$= \left[E_0 + 2\Delta \cos \frac{2\pi m}{N} \right] |\sigma_m\rangle$$

- For the 4-state system we have

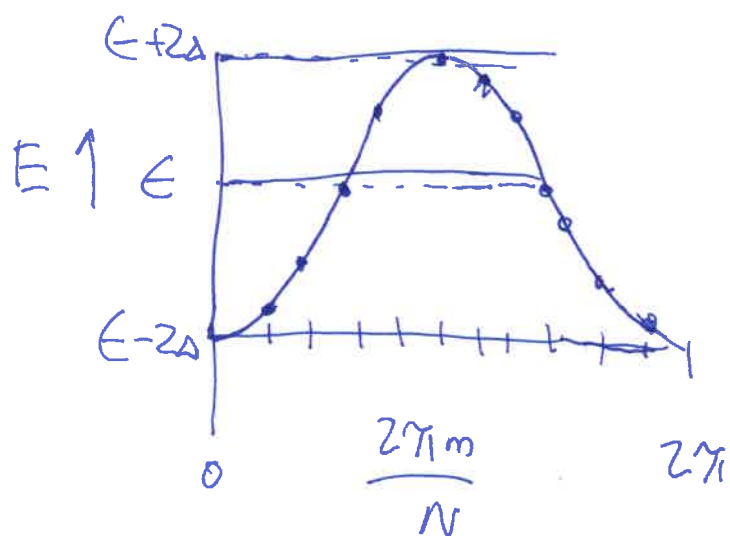$$E_0 = \epsilon - 2\Delta \qquad E_1 = \epsilon \qquad E_2 = \epsilon + 2\Delta \qquad E_3 = \epsilon$$

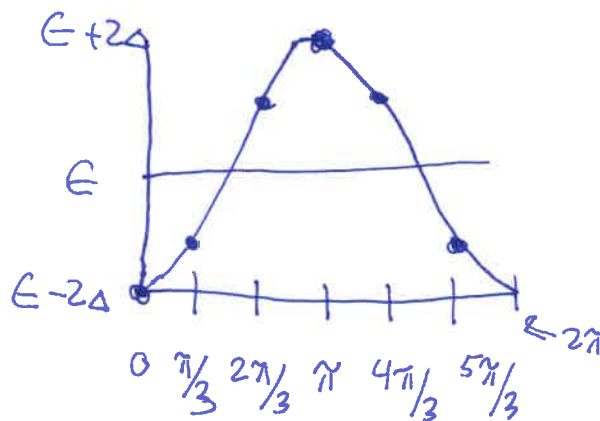$\uparrow$ m=0 $\qquad\qquad \uparrow$ m=1

(Lowest energy state has zero site-to-site phase shift)

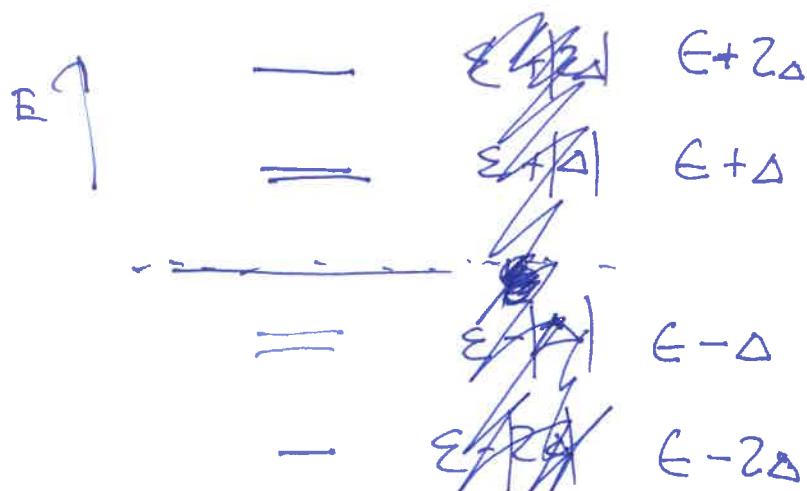- For N-state system, we get energies along equally spaced slices of a cosine curve
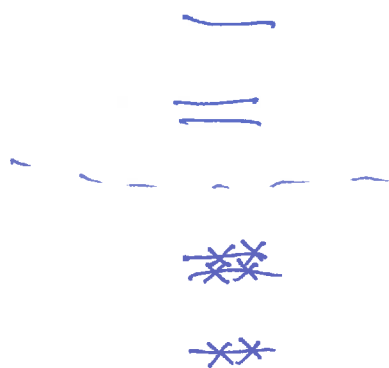
The dots represent the allowed energies

For benzene (N=6)

We obtain the spectrum

$$E \uparrow$$

	$\mathcal{E}\langle \cancel{\uparrow\downarrow}\rangle$	$\mathcal{E}+2_\Delta$
	$\mathcal{E}\langle \cancel{\Delta}\rangle$	$\mathcal{E}+\Delta$
	$\mathcal{E}\langle \cancel{\Delta}\rangle$	$\mathcal{E}-\Delta$
	$\mathcal{E}\langle \cancel{\uparrow\downarrow}\rangle$	$\mathcal{E}-2_\Delta$

There are 6 free electrons. Using Pauli exclusion, they fill up the lowest 3 ~~sta~~ levels. :

— We find a ~~bond~~ bond energy of $\Delta E = \cancel{-8_\Delta}$

$$(\cancel{2x-2_\Delta + 4x-\Delta}) \quad -8_\Delta$$

$$(2x-2_\Delta + 4x-\Delta)$$

or $-\frac{4}{3}|\Delta|$ per electron due to hopping. (or as some chemists say "resonance") between sites.

— Recall bonds happen b/c e^- can spread out & lower zero-point energy.