Time-Independent Perturbation Theory

We had: $(\hat{H}^0 + \lambda\hat{H}')|\psi_j\rangle = E_j|\psi_j\rangle$ (*)

w/ $\hat{H}^0|\psi_j^0\rangle = E_j^0|\psi_j^0\rangle$, $\langle\psi_k^0|\psi_j^0\rangle = \delta_{jk}$,

+ $|\psi_j\rangle = |\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \lambda^2|\psi_j^2\rangle + \cdots$

$E_j = E_j^0 + \lambda E_j^1 + \lambda^2 E_j^2 + \cdots$

putting these into (*):

$(\hat{H}_0 + \lambda\hat{H}')(|\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \lambda^2|\psi_j^2\rangle + \cdots)$

$= (E_j^0 + \lambda E_j^1 + \lambda^2 E_j^2 + \cdots)(|\psi_j^0\rangle + \lambda|\psi_j^1\rangle + \lambda^2|\psi_j^2\rangle + \cdots)$

+ collecting in powers of λ:

λ^0: $\hat{H}^0|\psi_j^0\rangle = E_j^0|\psi_j^0\rangle$

λ^1: $\hat{H}^0|\psi_j^1\rangle + \hat{H}'|\psi_j^0\rangle = E_j^0|\psi_j^1\rangle + E_j^1|\psi_j^0\rangle$

λ^2: $\hat{H}^0|\psi_j^2\rangle + \hat{H}'|\psi_j^1\rangle = E_j^0|\psi_j^2\rangle + E_j^1|\psi_j^1\rangle + E_j^2|\psi_j^0\rangle$

⋮

From the λ^1 eqn., we learned (hitting both sides w/ $\langle\psi_j^0|$)

$$E_j^1 = \langle\psi_j^0|\hat{H}'|\psi_j^0\rangle$$

+ (hitting both sides w/ $\langle\psi_k^0|$ w/ $k \neq j$),

$$|\psi_j^1\rangle = \sum_{\substack{k=0\\ \neq j}}^{\infty} \frac{\langle\psi_k^0|\hat{H}'|\psi_j^0\rangle}{E_j^0 - E_k^0}|\psi_k^0\rangle$$

- for now, we'll assume $E_j^0 \neq E_k^0$ for $j \neq k$.
- How about the $|\psi_j^0\rangle$ component of $|\psi_j^1\rangle$?

remember: $E_j = E_j^0 + E_j^1$, +

$|\psi_j\rangle = |\psi_j^0\rangle + |\psi_j^1\rangle$

already have the $|\psi_j^0\rangle$ contribution.

- $|\psi_j^0\rangle + |\psi_j^1\rangle$ is not, in general normalized.

Moving on to the λ^2 eqn – we'll again hit both sides w/ $|\psi_j^0\rangle$

$$\underbrace{\langle\psi_j^0|\hat{H}^0|\psi_j^2\rangle}_{=E_j^0\langle\psi_j^0|\psi_j^2\rangle \text{ cancels w/}} + \langle\psi_j^0|\hat{H}'|\psi_j^1\rangle = E_j^0\langle\psi_j^0|\psi_j^2\rangle + E_j^1\underbrace{\langle\psi_j^0|\psi_j^1\rangle}_{=0 \text{ - no } |\psi_j^0\rangle \text{ in } |\psi_j^1\rangle} + E_j^2\overbrace{\langle\psi_j^0|\psi_j^0\rangle}^{=1}$$

we get:

$$E_j^2 = \langle\psi_j^0|\hat{H}'|\psi_j^1\rangle$$

$$= \sum_{\substack{k=0\\ \neq j}}^{\infty} \frac{\langle\psi_k^0|\hat{H}'|\psi_j^0\rangle}{E_j^0 - E_k^0}\underbrace{\langle\psi_j^0|\hat{H}'|\psi_k^0\rangle}_{=(\langle\psi_k^0|\hat{H}'|\psi_j^0\rangle)^*}$$

$$= \sum_{\substack{k=0\\ \neq j}}^{\infty} \frac{|\langle\psi_k^0|\hat{H}'|\psi_j^0\rangle|^2}{E_j^0 - E_k^0}$$

next, you get the eigenstate corrections, then on to the λ^3 eqn ...

Degeneracy in One Dimension

In one dimension, energies are "never" degenerate – we always have $E_j \neq E_k$ for $j \neq k$.

Proof by contradiction: Suppose you had 2 solutions to Schrödinger's eqn:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2} + U\psi_1 = E\psi_1 \quad \& \quad -\frac{\hbar^2}{2m}\frac{d^2\psi_2}{dx^2} + U\psi_2 = E\psi_2$$

multiply the 1st eqn by ψ_2, the 2nd by ψ_1 & subtract:

$$-\frac{\hbar^2}{2m}\left[\frac{d^2\psi_1}{dx^2}\psi_2 - \frac{d^2\psi_2}{dx^2}\psi_1\right] = 0 = -\frac{\hbar^2}{2m}\frac{d}{dx}\left[\frac{d\psi_1}{dx}\psi_2 - \frac{d\psi_2}{dx}\psi_1\right]$$

so that $\psi_1'\psi_2 - \psi_2'\psi_1 = K$ a constant

(+) at spatial infinity $\psi_1 \xrightarrow[x\to\infty]{} 0$, $\psi_2 \xrightarrow[x\to\infty]{} 0$, so $K=0$, &

$$\frac{\psi_1'}{\psi_1} = \frac{\psi_2'}{\psi_2} \Rightarrow \frac{d}{dx}\log\psi_1 = \frac{d}{dx}\log\psi_2$$

$$\Downarrow$$

$$\log\psi_1 = \log\psi_2 + A \quad \leftarrow \text{const of int.}$$

$$\Downarrow$$

$$\psi_1 = \psi_2 e^A$$

Finally, the normalization condition is:

$$\int_{-\infty}^{+\infty}|\psi_1|^2dx = 1 = \int_{-\infty}^{+\infty}|\psi_2|^2dx$$

$$\parallel$$

(o) $$|e^A|^2\int_{-\infty}^{+\infty}|\psi_2|^2dx = |e^A|^2 = 1$$

if $A = i\varphi$, then ψ_1 & ψ_2 differ by a pure phase (& hence are not different).

← "Exceptions" – there are two notable exceptions to this rule

1. Free particle solutions: $-\frac{\hbar^2}{2m}\psi''(x) = E\psi(x)$ has:

$$\psi_1(x) = e^{ipx/\hbar} \quad \& \quad \psi_2(x) = e^{-ipx/\hbar} \quad (p = \sqrt{2mE})$$

representing left & right-travelers. 2 solutions w/ the same energy ... ?

We made 2 explicit assumptions in our "proof" (+) & (o), the free particle solution violates (o)

The Hamiltonian here has translation symmetry, since

$$[\hat{H}, \hat{T}] = 0 \quad \text{(\& almost always does, in higher dimension)}$$

& symmetry could lead to degeneracy: if $|\psi\rangle$ has $\hat{H}|\psi\rangle = E|\psi\rangle$, then:

$$\hat{T}\hat{H}|\psi\rangle = E\,\hat{T}|\psi\rangle$$

$$\hat{H}\hat{T}|\psi\rangle = E\,\hat{T}|\psi\rangle$$

so that $|\psi\rangle$ & $\hat{T}|\psi\rangle$ have the same energy.

But here, we can see, that $\psi = e^{i/\hbar\, px}$ &

$$\hat{T}\psi = e^{i/\hbar\, p(x-a)} = e^{-i/\hbar\, pa}\psi$$

are really the same state (differing only by a pure phase). So no degeneracy there.

parity is also a symmetry of the Hamiltonian:

$$[\hat{\Pi}, \hat{H}] = 0$$

& so if you have $\hat{H}|\psi\rangle = E|\psi\rangle$, you <u>also</u> have:

$$\hat{H}\hat{\Pi}|\psi\rangle = E\hat{\Pi}|\psi\rangle,$$ $|\psi\rangle$ & $\hat{\Pi}|\psi\rangle$

have the same energy.

But for $\psi_1 = e^{ipx/\hbar}$, $\hat{\Pi}\psi_1 = e^{-ipx/\hbar} = \psi_2$

i.e. here, $\hat{\Pi}\psi_1$ is not the same state (up to constant phase) as ψ_1.

While both $[\hat{\Pi}, \hat{H}] = 0$ & $[\hat{T}, \hat{H}] = 0$, & so you can find simultaneous eigenstates of $\{\hat{\Pi}, \hat{H}\}$, or $\{\hat{T}, \hat{H}\}$, you <u>cannot</u> find simultaneous eigenstates of all three, $\{\hat{\Pi}, \hat{T}, \hat{H}\}$, since

$$[\hat{\Pi}, \hat{T}] \neq 0$$

so - to get degeneracy, you need (at least) 2 op.s that commute w/ $\hat{H}$, but not each other.

2. Bead on a wire: $\psi(0) = \psi(2\pi)$

$$-\frac{\hbar^2}{2mR^2}\frac{d^2\psi(\phi)}{d\phi^2} = E\psi(\phi)$$

this is almost exactly like the free particle, let $p = \sqrt{2mE}$, then

$$\psi_1 = e^{ipR\phi} \qquad \psi_2 = e^{-ipR\phi}$$

This time, the wave functions are normalizable - so what is the obstruction? (+)

we have $\psi(\phi)$ w/ $\phi \in [0, 2\pi)$, so the domain is different. Now, free.

$$\psi_1'\psi_2 - \psi_2'\psi_1 = ipR\psi_1\psi_2 + ipR\psi_1\psi_2 = 2ip$$

this was the constant K, which we set to zero

Once again, we have $[\hat{H}, \hat{\Pi}] = 0$ & $[\hat{H}, \underset{\text{in }\phi}{\hat{T}}] = 0$

but $[\hat{\Pi}, \hat{T}] \neq 0$

so there must be a simultaneous state of $\{\hat{H}, \hat{\Pi}\}$ & a simultaneous state of $\{\hat{H}, \hat{T}\}$ that have the same energy, but are <u>not</u> the same state (since $[\hat{\Pi}, \hat{T}] \neq 0$) - that <u>is</u> degeneracy.