

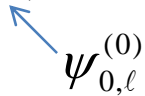
Degenerate PT

When two zeroth-order states are degenerate (or near degenerate), cannot use simple PT.

Degenerate PT designed to deal with such cases

Suppose the energy level of interest is r -fold degenerate

$$H^{(0)} |0, \ell\rangle = E_0^{(0)} |0, \ell\rangle, \quad \ell = 1, 2, \dots, r$$

$$\psi_{0,\ell}^{(0)}$$


$$\phi_{0,i}^{(0)} = \sum_{\ell=1}^r c_{i\ell} \psi_{0,\ell}^{(0)}$$

$$\psi_i = \phi_{0,i}^{(0)} + \lambda \psi_{0,i}^{(1)}$$

$$E_i = E_0^{(0)} + \lambda E_{0,i}^{(1)}$$

$$H\psi_i = E_i\psi_i \longrightarrow$$

$$H^{(0)}\phi_{0,i}^{(0)} = E_0^{(0)}\phi_{0,i}^{(0)} \quad \left| \begin{array}{l} \lambda^0 \\ \lambda^1 \end{array} \right.$$

$$\left(H^{(0)} - E_0^{(0)} \right) \psi_{0,i}^{(1)} = \left[E_{0,i}^{(1)} - H^{(1)} \right] \phi_{0,i}^{(0)}$$

$$\psi_{0,i}^{(1)} = \underbrace{\sum_{\ell} a_{\ell} \psi_{0,\ell}^{(0)}}_{\text{deg zeroth order states}} + \underbrace{\sum' a_n \psi_n^{(0)}}_{\text{sum over other zeroth order states}}$$

Insert into previous equation and multiply by $\langle 0,k|$

$$\sum_{\ell} c_{i\ell} \left\{ E_{0,i}^{(1)} S_{k\ell} - H_{k\ell}^{(1)} \right\} =$$

$$\rightarrow \left| H_{k\ell}^{(1)} - E_{0i}^{(1)} S_{k\ell} \right| = 0$$

Exactly the same result we would get from a variational treatment using the r degenerate zeroth-order levels.

Variational Method

$$\varepsilon = \frac{\langle \psi_{trial} | H | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle}$$

$$\varepsilon \geq \cancel{E_0}$$

true energy

If ψ_{trial} has one or more parameters α, β, \dots

$$\frac{\partial \varepsilon}{\partial \alpha} = 0, \quad \frac{\partial \varepsilon}{\partial \beta} = 0, \quad \dots \quad \text{to minimize the energy}$$

As a special case

$$\psi_{trial} = \sum_i c_i \psi_i \quad \longleftarrow \quad \text{linear variational problem}$$

$$\frac{\partial \varepsilon}{\partial c_i} = 0 \rightarrow$$

$$\sum_i c_i (H_{ik} - \varepsilon S_{ik}) = 0 \Rightarrow |H_{ik} - \varepsilon S_{ik}| = 0$$

In some cases, $S_{ik} = \delta_{ik}$

$n \times n$ matrix $\rightarrow n$ values of ε_i , n vectors

Suppose H depends on some parameter P

Hellmann – Feynman Theorem $\frac{dE}{dP} = \left\langle \frac{\partial H}{\partial P} \right\rangle$

Suppose ψ is normalized for all P

$$\begin{aligned} E(P) &= \langle \psi(P) | H(P) | \psi(P) \rangle \\ \frac{dE}{dP} &= \left\langle \frac{\partial \psi}{\partial P} | H | \psi \right\rangle + \left\langle \psi | H | \frac{\partial \psi}{\partial P} \right\rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle \\ &= E \left\langle \frac{\partial \psi}{\partial P} | \psi \right\rangle + E \left\langle \psi | \frac{\partial \psi}{\partial P} \right\rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle \\ &= E \frac{d}{dP} \langle \psi | \psi \rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle \\ &= \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle \end{aligned}$$

Suppose $H = H^0 + Px \rightarrow \frac{\partial H}{\partial P} = x$

$$\frac{dE}{dP} = \langle x \rangle$$

But there is a catch. We have assumed ψ is the exact wavefunction

If ψ is approximate, there are errors due to Hellmann-Feynman Theorem

time-dep. PT

$$H = H^{(0)} + H^{(1)}(t)$$

$$\text{e.g., } H = H^{(0)} + 2H^{(1)} \cos \omega t$$

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Now consider the special case of a two-level system

$$\left[\begin{array}{l} \psi_1^{(0)} \rightarrow E_1^{(0)} \rightarrow \Psi_1^{(0)}(t) = \psi_1^{(0)} e^{-iE_1^{(0)}t/\hbar} \\ \psi_2^{(0)} \rightarrow E_2^{(0)} \rightarrow \Psi_2^{(0)}(t) = \psi_2^{(0)} e^{-iE_2^{(0)}t/\hbar} \end{array} \right]$$

In the absence of the
time-dep. perturbation

$$\begin{aligned} \Psi(t) &= a_1(t)\Psi_1^{(0)}(t) + a_2(t)\Psi_2^{(0)}(t) \\ \left[H^{(0)} + H^{(1)}(t) \right] \left[a_1\Psi_1^{(0)} + a_2\Psi_2^{(0)} \right] \\ &= i\hbar \frac{\partial}{\partial t} \left[a_1\Psi_1^{(0)} + a_2\Psi_2^{(0)} \right] \end{aligned}$$

$$H^{(1)}(t) \left[a_1 \Psi_1^{(0)} + a_2 \Psi_2^{(0)} \right] = i\hbar \left[\frac{\partial a_1}{\partial t} \Psi_1^{(0)} + \frac{\partial a_2}{\partial t} \Psi_2^{(0)} \right]$$

$$\begin{aligned} & a_1 H^{(1)}(t) |1\rangle e^{-iE_1^{(0)}t/\hbar} + a_2 H^{(1)}(t) |2\rangle e^{-iE_2^{(0)}t/\hbar} \\ &= i\hbar \left[\dot{a}_1 |1\rangle e^{-iE_1^{(0)}t/\hbar} + \dot{a}_2 |2\rangle e^{-iE_2^{(0)}t/\hbar} \right] \end{aligned}$$

multiply on left by $\langle 1 |$



$$a_1 \langle 1 | H^{(1)}(t) |1\rangle e^{-iE_1^{(0)}t/\hbar} + a_2 \langle 1 | H^{(1)}(t) |2\rangle e^{-iE_2^{(0)}t/\hbar} = i\hbar \dot{a}_1 e^{-iE_1^{(0)}t/\hbar}$$

$$a_1 H_{11}^{(1)}(t) e^{-iE_1^{(0)}t/\hbar} + a_2 H_{12}^{(1)}(t) e^{-iE_2^{(0)}t/\hbar} = i\hbar \dot{a}_1 e^{-iE_1^{(0)}t/\hbar}$$

$$a_1 H_{11}^{(1)}(t) + a_2 H_{12}^{(1)}(t) e^{-i\omega t} = i\hbar \dot{a}_1, \quad \hbar\omega = E_2^{(0)} - E_1^{(0)}$$

if the diagonal elements are 0

$$a_2 H_{12}^{(1)}(t) e^{-i\omega t} = i\hbar \dot{a}_1$$

$$a_1 H_{21}^{(1)}(t) e^{+i\omega t} = i\hbar \dot{a}_2$$

if no perturbation

$$\dot{a}_1 = 0 = \dot{a}_2$$

$$\Psi(t) = a_1(0)\psi_1(0)e^{-iE_1^{(0)}t/\hbar} + a_2(0)\psi_2(0)e^{-iE_2^{(0)}t/\hbar}$$

system is frozen at initial composition

Consider a constant perturbation

$$H_{12}^{(1)}(t) = \hbar V$$

$$H_{21}^{(1)}(t) = \hbar V^*$$

$$\left. \begin{aligned} \dot{a}_1 &= \frac{1}{i\hbar} a_2 \hbar V e^{-i\omega t} \\ \dot{a}_2 &= \frac{1}{i\hbar} a_1 \hbar V^* e^{+i\omega t} \end{aligned} \right] \quad \begin{aligned} \dot{a}_1 &= -i a_2 V e^{-i\omega t} \\ \dot{a}_2 &= -i a_1 V^* e^{+i\omega t} \end{aligned}$$

$$\frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = -i \begin{pmatrix} 0 & V e^{-i\omega t} \\ V^* e^{i\omega t} & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

$$a_2 = (A e^{i\Omega t} + B e^{-i\Omega t}) e^{i\omega t/2}, \quad \Omega = \frac{1}{2} \sqrt{\omega^2 + 4|V|^2}$$

if at $t = 0$, $a_2 = 0$, $a_1 = 1$

$$a_1(t) = \left[\cos \Omega t + \frac{i\omega t}{2\Omega} \sin \Omega t \right] e^{-i\omega t/2}$$

$$a_2(t) = -\frac{i|V|}{\Omega} [\sin \Omega t] e^{i\omega t/2}$$

Can solve by finding the eigenvalues and eigenvectors that correspond to the matrix

$$P_1(t) = |a_1|^2$$

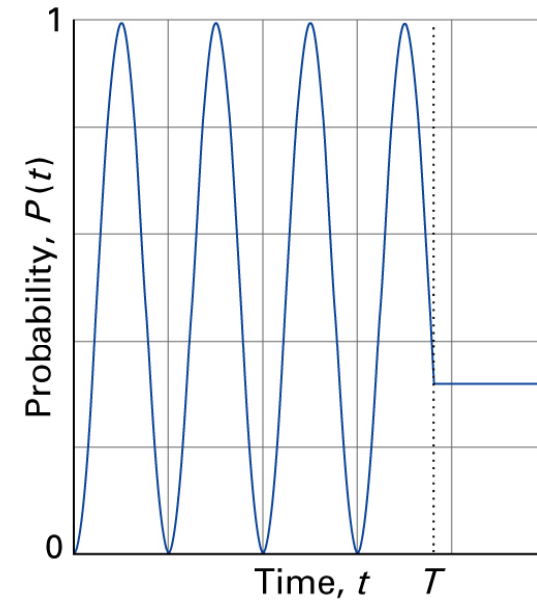
$$P_2(t) = |a_2|^2$$

$$P_2(t) = \frac{4|V|^2}{\omega^2 + 4|V|^2} \sin^2 \frac{1}{2} (\omega^2 + 4|V|^2)^{1/2} t$$

Rabi formula

if the two states are degenerate

$$P_2(t) = \sin^2 |V| t$$

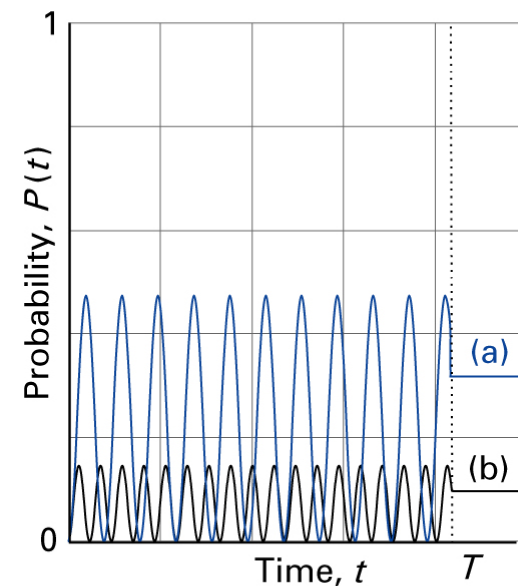


System simply oscillates between the two states

if $\omega^2 \gg 4|V|^2$

$$P_2(t) = \left[\frac{2|V|}{\omega} \right]^2 \sin^2 \frac{1}{2} \omega t \ll 1$$

small probability that the perturbation will drive system into $|2\rangle$



Skip sections 6.13, 6.14, 6.15, 6.16

Einstein transition probabilities

Stimulated absorption $W_{f \leftarrow i} = B_{if} \rho_{rad} (E_{fi})$

Stimulated emission $W_{f \rightarrow i} = B_{fi} \rho_{rad} (E_{fi})$

$$W_{f \rightarrow i}^{spont} = A_{fi}$$

$$W_{f \rightarrow i} = A_{fi} + B_{fi} \rho_{rad} (E_{fi})$$

$$A_{fi} = \frac{8\pi\hbar\nu_{fi}^3}{c^3} B_{fi}$$

$W = \text{rate}$

$$B_{if} = B_{fi} = \frac{|\mu_{fi}|^2}{6\epsilon_0\hbar^2}$$

$$N_i W_{f \leftarrow i} = N_f W_{i \rightarrow f}$$

$$\frac{N_f}{N_i} = e^{-E_n/kT}$$

The two equations
Inconsistent

Sorted out by
Einstein – need to
consider **spontaneous**
emission

Lifetime + energy

$$\Psi = \psi e^{-iEt/\hbar} \quad \text{for an eigenstate}$$

$$|\Psi|^2 = |\psi|^2, \quad \text{Independent of } t$$

But if a state decays in time, its energy is not precise

$$\Psi = \psi e^{-iE_r t/\hbar} e^{-t/2\tau} = \psi e^{-iE_r t/\hbar} e^{-\frac{\Gamma t}{2\hbar}} = \psi e^{-i\left(E_r - \frac{i\Gamma}{2}\right)t/\hbar}$$

$$\tau = \hbar / \Gamma$$

exponentially decaying state \Leftrightarrow complex energy (the energy has a width)

$$e^{-iEt/\hbar - t/2\tau} = \int g(E') e^{-iE't/\hbar} dE'$$

$$g(E') = \frac{\hbar / 2\pi\tau}{(E - E')^2 + (\hbar / 2\tau)^2}$$

$$\tau \delta E \approx \frac{\hbar}{2}$$

The shorter the lifetime, the greater the width

“uncertainty-like” principle