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

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

$\left|0,\ell\right\rangle \leftarrow \psi_{0,\ell}^{(0)}$

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

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

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

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

$$H^{(0)}\phi_{0,i}^{(0)} = E_0^0\phi_{0,i}^{(0)} \qquad \Big| \quad \lambda^0$$

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

$$\psi_{0,i}^{(1)} = \underbrace{\sum_{\ell} a_{\ell} \psi_{0,\ell}^{(0)}}_{} + \underbrace{\sum{}' a_n \psi_n^{(0)}}_{}$$

deg zeroth order states

sum over other zeroth order states

Insert into previous equation and multiply by <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

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

$\varepsilon \geq E_0$ ← true energy

If ψ_{trial} has one or more parameters $\alpha, \beta, \ldots$

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

As a special case

$$\psi_{trial} = \sum_i c_i \psi_i$$ ← linear variational problem

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

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

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

n x n matrix → *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*

$$E(P) = \langle \psi(P) | H(P) | \psi(P) \rangle$$

$$\frac{dE}{dP} = \left\langle \frac{\partial \psi}{\partial P} | H | \psi \right\rangle + \left\langle \psi | H | \frac{\partial \psi}{\partial P} \right\rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle$$

$$= E \left\langle \frac{\partial \psi}{\partial P} | \psi \right\rangle + E \left\langle \psi | \frac{\partial \psi}{\partial P} \right\rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle$$

$$= E \frac{d}{dP} \langle \psi | \psi \rangle + \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle$$

$$= \left\langle \psi \left| \frac{\partial H}{\partial P} \right| \psi \right\rangle$$

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*

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

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

$$\begin{bmatrix} \psi_1^{(0)} \rightarrow E_1^{(0)} \rightarrow \Psi_1^{(0)}(t) = \psi_1^{(0)} e^{-iE_1^{(0)} t/\hbar} \\ \psi_2^{(0)} \rightarrow E_2^{(0)} \rightarrow \Psi_2^{(0)}(t) = \psi_2^{(0)} e^{-iE_2^{(0)} t/\hbar} \end{bmatrix}$$

In the absence of the time-dep. perturbation

$$\Psi(t) = a_1(t)\Psi_1^{(0)}(t) + a_2(t)\Psi_2^{(0)}(t)$$

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

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

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

$$a_1 H^{(1)}\left|1\right\rangle e^{-iE_1^{(0)}t/\hbar} + a_2 H^{(1)}(t)\left|2\right\rangle e^{-iE_2^{(0)}t/\hbar}$$

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

multiply on left by <1|

$$\downarrow$$

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

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

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

if the diagonal elements are 0

$$a_2 H_{12}^{(1)}(t) e^{-i\omega t} = i\hbar \dot{a}_1$$
$$a_1 H_{21}^{(1)}(t) e^{+i\omega t} = i\hbar \dot{a}_2$$

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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

$$H_{12}^{(1)}(t) = \hbar V$$
$$H_{21}^{(1)}(t) = \hbar V^*$$

$$\dot{a}_1 = \frac{1}{i\hbar} a_2 \hbar V e^{-i\omega t}$$
$$\dot{a}_2 = \frac{1}{i\hbar} a_1 \hbar V^* e^{+i\omega t}$$

$$\dot{a}_1 = -i a_2 V e^{-i\omega t}$$
$$\dot{a}_2 = -i a_1 V^* e^{+i\omega t}$$

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

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

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

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

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

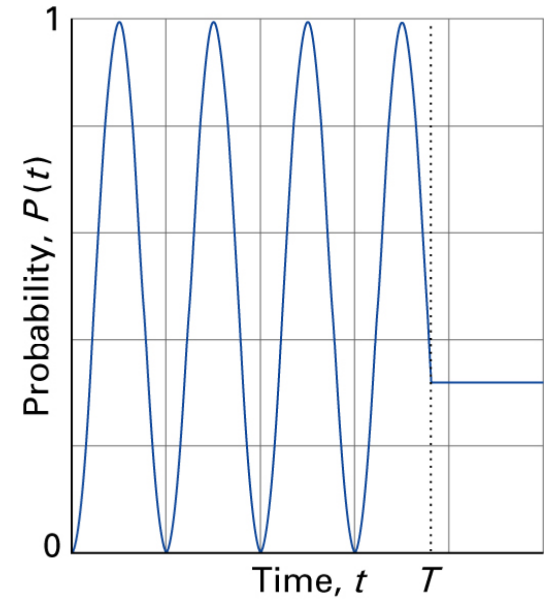
$$a_2(t) = -\frac{i|V|}{\Omega} [\sin\Omega t] e^{i\omega t/2}$$

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

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

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

Rabi formula



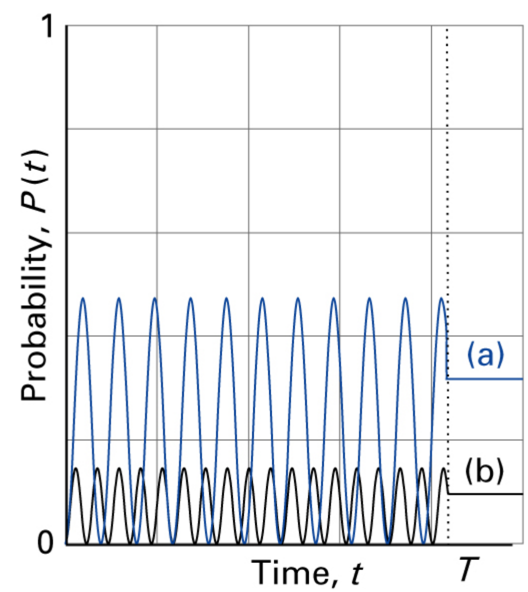
if the two states are degenerate

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

System simply oscillates between the two states

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

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



small probability that the perturbation will drive system into |2>

Skip sections 6.13, 6.14, 6.15, 6.16

Einstein transition probabilities

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

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

W = rate

$$B_{if} = B_{fi} = \frac{\left|\mu_{fi}\right|^2}{6\varepsilon_0\hbar^2}$$

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

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

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

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

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

The two equations Inconsistent

Sorted out by Einstein – need to consider spontaneous emission

Lifetime + energy

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

$$|\Psi|^2 = |\psi|^2,$$ Independent of *t*

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

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

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

exponentially decaying state ⇔ complex energy (the energy has a width)

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

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

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

The shorter the lifetime, the greater the width

"uncertainty-like" principle