Phys 522

Lectures 11-13

Stationary perturbation theory

Structure $\uparrow$ Bound states – eigenfunctions, eigenvalues $\uparrow$ Approximate methods $\rightarrow$ Dynamics

$$H = \underset{\substack{\uparrow \\ \text{easy}}}{H_0} + \underset{\substack{\uparrow \\ \text{"small"}}}{W} \longrightarrow H_0 + \lambda \hat{W}$$

λ → bookkeeping device

$H_0 |\varphi_{pi}\rangle = E_p^{(0)} |\varphi_{pi}\rangle$

i → degeneracy parameter

$\langle \varphi_{p'i'} | \varphi_{pi} \rangle = \delta_{pp'} \delta_{ii'}$

$\sum_{p,i} |\varphi_{pi}\rangle\langle\varphi_{pi}| = 1$

$H(\lambda) = H_0 + \lambda \hat{W}$

$H(\lambda) |\psi(\lambda)\rangle = E(\lambda) |\psi(\lambda)\rangle$

Behavior of $E(\lambda)$ and $|\psi(\lambda)\rangle$ — nondeg, deg, level crossings

Matrix rep

Unperturbed problem:

$$H_0 |\varphi_{pi}\rangle = E_p^{(0)} |\varphi_{pi}\rangle$$

i → deg index

$\langle \varphi_{pi} | \varphi_{p'i'} \rangle = \delta_{pp'} \delta_{ii'}$

$\underline{1} = \sum_{p,i} |\varphi_{pi}\rangle\langle\varphi_{pi}| = \sum_p P_p$

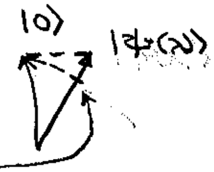
$H_0 = \sum_{p,i} E_p^{(0)} |\varphi_{pi}\rangle\langle\varphi_{pi}| = \sum_p E_p^{(0)} P_p$

$$E(\lambda) = \epsilon_0 + \lambda\epsilon_1 + \dots = \sum_{q=0}^{\infty} \lambda^q \epsilon_q$$

general behavior of $E(\lambda)$ – degeneracies, level crossings

convergence?

$$|\psi(\lambda)\rangle = |0\rangle + \lambda|1\rangle + \dots = \sum_{q=0}^{\infty} \lambda^q |q\rangle$$



$$(H_0 + \lambda\hat{W})\left(\sum_q \lambda^q |q\rangle\right) = \left(\sum_q \lambda^q \epsilon_q\right)\left(\sum_{q'} \lambda^{q'} |q'\rangle\right)$$

$$\sum_{q=0}^{\infty} \lambda^q \left(H_0|q\rangle + \hat{W}|q-1\rangle\right) = \sum_{q=0}^{\infty} \lambda^q \left(\sum_{r=0}^{q} \epsilon_{q-r}|r\rangle\right)$$

BC: $\langle 0|\psi(\lambda)\rangle = 1$

Scale this by a λ-dep constant

normalize at each order if desired

C-T BC: $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$

$$\Longrightarrow \boxed{(H_0 - \epsilon_0)|q\rangle + (\hat{W} - \epsilon_1)|q-1\rangle - \sum_{r=0}^{q-2} \epsilon_{q-r}|r\rangle = 0}$$

$q=0$: $(H_0 - \epsilon_0)|0\rangle = 0 \longrightarrow$ $|0\rangle$ and ϵ_0 are eigenstate and eigenvalue of

$q=1$: $(H_0 - \epsilon_0)|1\rangle + (\hat{W} - \epsilon_1)|0\rangle = 0$

$q=2$: $(H_0 - \epsilon_0)|2\rangle + (\hat{W} - \epsilon_1)|1\rangle - \epsilon_2|0\rangle = 0$

$\vdots$

Nondegenerate unperturbed state:

BC: $1 = \langle 0|\psi(\lambda)\rangle = \langle\varphi_n|\varphi_n\rangle + \sum_{q=1}^{\infty}\lambda^q \underbrace{\langle\varphi_n|q\rangle}_{=0}$

$\Longrightarrow \langle\varphi_n|q\rangle = 0, \quad q \geq 1$

$q=0$: $(H_0 - \epsilon_0)|0\rangle = 0$

$|0\rangle = |\varphi_n\rangle \; ; \quad \epsilon_0 = E_n^{(0)}$

$q=1$: $(H_0 - E_n^{(0)})|1\rangle + (\hat{W} - \epsilon_1)|\varphi_n\rangle = 0$

ⓐ Project onto $|\varphi_n\rangle$: $\boxed{\epsilon_1 = \langle\varphi_n|\hat{W}|\varphi_n\rangle}$

ⓑ Project onto $|\varphi_{pi}\rangle$, $p \neq n$:

$$(E_p^{(0)} - E_n^{(0)})\langle\varphi_{pi}|1\rangle + \langle\varphi_{pi}|\hat{W}|\varphi_n\rangle = 0$$

$$\Longrightarrow \langle\varphi_{pi}|1\rangle = \frac{\langle\varphi_{pi}|\hat{W}|\varphi_n\rangle}{E_n^{(0)} - E_p^{(0)}}, \quad p \neq n$$

$$|1\rangle = \sum_{p,i}|\varphi_{pi}\rangle\langle\varphi_{pi}|1\rangle$$

$$\boxed{|1\rangle = \sum_{p\neq n, i}|\varphi_{pi}\rangle\frac{\langle\varphi_{pi}|\hat{W}|\varphi_n\rangle}{E_n^{(0)} - E_p^{(0)}} = \frac{1}{E_n^{(0)} - H_0}(1 - P_n)\hat{W}|\varphi_n\rangle}$$

$$\boxed{\frac{1 - P_n}{E_n^{(0)} - H_0} = \sum_{p\neq n, i}\frac{|\varphi_{pi}\rangle\langle\varphi_{pi}|}{E_n^{(0)} - E_p^{(0)}}}$$

Gather results to 1st order:

$$E_n = E_n^{(0)} + \lambda\langle\varphi_n|\hat{W}|\varphi_n\rangle = E_n^{(0)} + \langle\varphi_n|W|\varphi_n\rangle$$

$$|\psi_n\rangle = |\varphi_n\rangle + \lambda|1\rangle \cdot |\varphi_n\rangle + \sum_{p\neq n, i}|\varphi_{pi}\rangle\frac{\langle\varphi_{pi}|W|\varphi_n\rangle}{E_n^{(0)} - E_p^{(0)}}$$

Normalization: $\langle\psi_n|\psi_n\rangle = 1 + O(\lambda^2)$

Convergence: what's small $\dfrac{\text{matrix elements}}{\Delta E}$

Role of matrix elements:

$q \geq 2$: Why it works iteratively

ⓐ Project onto $|\varphi_n\rangle$: $\epsilon_q = \langle \varphi_n | \hat{W} | q-1 \rangle$ Get ϵ_q in terms of $|q-1\rangle$

ⓑ Project onto $|\varphi_{pi}\rangle$, $p \neq n$:

$$(E_p^{(0)} - E_n^{(0)}) \langle \varphi_{pi} | q \rangle + \langle \varphi_{pi} | (\hat{W} - \epsilon_1) | q-1 \rangle - \sum_{r=1}^{q-2} \epsilon_{q-r} \langle \varphi_{pi} | r \rangle = 0$$

Get $\langle \varphi_{pi} | q \rangle$ in terms of $|1\rangle, \ldots, |q-1\rangle$ $r=0$ term vanishes.

$q=2$: $\epsilon_2 = \langle \varphi_n | \hat{W} | 1 \rangle$

$$= \langle \varphi_n | \hat{W} (1 - P_n) | 1 \rangle$$

$$\boxed{\begin{aligned} \epsilon_2 &= \langle \varphi_n | \hat{W} \frac{1-P_n}{E_n^{(0)} - H_0} \hat{W} | \varphi_n \rangle \\ &= \sum_{p \neq n, i} \frac{|\langle \varphi_n | \hat{W} | \varphi_{pi} \rangle|^2}{E_n^{(0)} - E_p^{(0)}} \end{aligned}}$$

$$(E_p^{(0)} - E_n^{(0)}) \langle \varphi_{pi} | 2 \rangle = - \langle \varphi_{pi} | (\hat{W} - \epsilon_1) | 1 \rangle$$

$$|2\rangle = \sum_{\substack{p \neq n, i \\ p' \neq n, i'}} |\varphi_{pi}\rangle \frac{\langle \varphi_{pi} | (\hat{W} - \langle \varphi_n | \hat{W} | \varphi_n \rangle) | \varphi_{p'i'} \rangle \langle \varphi_{p'i'} | \hat{W} | \varphi_n \rangle}{(E_n^{(0)} - E_p^{(0)})(E_n^{(0)} - E_{p'}^{(0)})}$$

$$= \sum_{p \neq n, i} |\varphi_{pi}\rangle \left(\sum_{p' \neq n, i'} \frac{\langle \varphi_{pi} | \hat{W} | \varphi_{p'i'} \rangle \langle \varphi_{p'i'} | \hat{W} | \varphi_n \rangle}{(E_n^{(0)} - E_p^{(0)})(E_n^{(0)} - E_{p'}^{(0)})} - \frac{\langle \varphi_n | \hat{W} | \varphi_n \rangle \langle \varphi_{pi} | \hat{W} | \varphi_n \rangle}{(E_n^{(0)} - E_p^{(0)})^2} \right)$$

What happens to λ?

Degenerate unperturbed states

$q=0$: $(H_0 - \epsilon_0)|0\rangle = 0$

$\epsilon_0 = E_n^{(0)}$

$|0\rangle$ is a unit vector in the degenerate subspace n with projector $P_n = \sum_i |\varphi_{ni}\rangle\langle\varphi_{ni}|$

$q=1$: $(H_0 - E_n^{(0)})|1\rangle + (\hat{W} - \epsilon_1)|0\rangle = 0$

ⓐ Project onto degenerate subspace

$$\epsilon_1 |0\rangle = P_n \hat{W} |0\rangle = \underbrace{P_n \hat{W} P_n}_{\hat{W}^{(n)}} |0\rangle$$

$\hat{W}^{(n)} \longrightarrow$ W restricted to degenerate subspace matrix rep.

$$\hat{W}^{(n)} |0\rangle = \epsilon_1 |0\rangle \qquad \begin{cases} W^{(n)} |\varphi_{ni\alpha}\rangle = \epsilon_{ni} |\varphi_{ni\alpha}\rangle \\ \epsilon_{ni} = \langle \varphi_{ni} | \hat{W} | \varphi_{ni} \rangle \end{cases}$$

α → additional degeneracy index

ϵ_{ni} → 1st order energy correction

Eigenvalue problem in the degenerate subspace.

Proceed by letting unperturbed state $|0\rangle$ stay undetermined till the perturbation theory determines it.

$|0\rangle$ is a unit vector in degenerate subspace ni with projector $P_{ni} = \sum_\alpha |\varphi_{ni\alpha}\rangle\langle\varphi_{ni\alpha}|$

$$E_{ni} = E_n^{(0)} + \lambda \epsilon_{ni} = E_n^{(0)} + \langle \varphi_{ni\alpha} | W | \varphi_{ni\alpha} \rangle \quad \begin{pmatrix} \text{any} \\ \alpha \end{pmatrix}$$

ⓑ Project $\perp$ to degenerate subspace

$$p \neq n: \quad (E_p^{(0)} - E_n^{(0)}) \langle \varphi_{pj} | 1 \rangle + \langle \varphi_{pj} | \hat{W} | 0 \rangle = 0$$

$$\langle \varphi_{pj} | 1 \rangle = \frac{\langle \varphi_{pj} | \hat{W} | 0 \rangle}{E_n^{(0)} - E_p^{(0)}}$$

This is the same as for nondegenerate states

$$(1 - P_n)|1\rangle = \sum_{p \neq n, j} |\varphi_{pj}\rangle\langle\varphi_{pj}|1\rangle = \sum_{p \neq n, j} |\varphi_{pj}\rangle \frac{\langle \varphi_{pj} | \hat{W} | 0 \rangle}{E_n^{(0)} - E_p^{(0)}} = \frac{1 - P_n}{E_n^{(0)} - H_0} \hat{W} |0\rangle$$

Still don't know $|1\rangle$, because don't know $\langle \varphi_{nj} | 1 \rangle$, i.e., $P_n |1\rangle$, so we have to go to

$$q=2: \quad (H_0 - E_n^{(0)})|2\rangle + (\hat{W} - \epsilon_{ni})|1\rangle - \epsilon_2 |\varphi\rangle = 0$$

① ϵ_{ni} nondegenerate: $|0\rangle = |\varphi_{ni}\rangle$ $\quad (P_{ni} = |\varphi_{ni}\rangle\langle\varphi_{ni}|)$

ⓐ Project onto $|\varphi_{ni}\rangle$

$$\epsilon_2 = \langle \varphi_{ni} | (\hat{W} - \epsilon_{ni}) | 1 \rangle = \underbrace{\langle \varphi_{ni} | (\hat{W} P_n - \epsilon_{ni}) | 1 \rangle}_{=0} + \langle \varphi_{ni} | \hat{W} (1 - P_n) | 1 \rangle$$

$$\boxed{\epsilon_2 = \langle \varphi_{ni} | \hat{W} \frac{1 - P_n}{E_n^{(0)} - H_0} \hat{W} | \varphi_{ni} \rangle = \sum_{p \neq n, j} \frac{|\langle \varphi_{ni} | \hat{W} | \varphi_{pj} \rangle|^2}{E_n^{(0)} - E_p^{(0)}}}$$

ⓑ Project onto $|\varphi_{nj}\rangle$, $j \neq i$

$$0 = \langle \varphi_{nj} | (\hat{W} - \epsilon_{ni}) | 1 \rangle = \underbrace{\langle \varphi_{nj} | (\hat{W} P_n - \epsilon_{ni}) | 1 \rangle}_{(\epsilon_{nj} - \epsilon_{ni}) \langle \varphi_{nj} | 1 \rangle} + \underbrace{\langle \varphi_{nj} | \hat{W} (1 - P_n) | 1 \rangle}_{\sum_{p \neq n, k} \frac{\langle \varphi_{nj} | \hat{W} | \varphi_{pk} \rangle \langle \varphi_{pk} | \hat{W} | \varphi_{ni} \rangle}{E_n^{(0)} - E_p^{(0)}}}$$

$$\langle \varphi_{nj} | 1 \rangle = \sum_{p \neq n, k} \frac{\langle \varphi_{nj} | \hat{W} | \varphi_{pk} \rangle \langle \varphi_{pk} | \hat{W} | \varphi_{ni} \rangle}{(\epsilon_{nj} - \epsilon_{ni})(E_n^{(0)} - E_p^{(0)})}$$

Gather 1st order results: $\qquad$ 1st order correction

$$E_{ni} = E_n^{(0)} + \langle \varphi_{ni} | \hat{W} | \varphi_{ni} \rangle$$

$$|\psi_n^i\rangle = |\varphi_{ni}\rangle + \sum_{j \neq i} |\varphi_{nj}\rangle \frac{\langle \varphi_{nj} | \hat{W} | \varphi_{pk} \rangle \langle \varphi_{pk} | W | \varphi_{ni} \rangle}{(\epsilon_{nj} - \epsilon_{ni})(E_n^{(0)} - E_p^{(0)})}$$

$$+ \sum_{p \neq n, j} |\varphi_{pj}\rangle \frac{\langle \varphi_{pj} | \hat{W} | \varphi_{ni} \rangle}{E_n^{(0)} - E_p^{(0)}}$$

ⓒ Project orthogonal to degenerate subspace to get $|2\rangle$.

② ϵ_{ni} degenerate (still don't know what $|0\rangle$ is, except that it is in degenerate subspace ni)

ⓐ Project onto $P_{ni} = \sum_\alpha |\varphi_{ni\alpha}\rangle\langle\varphi_{ni\alpha}|$

$$P_{ni}(\hat{W} - \epsilon_{ni})|1\rangle = \epsilon_2|0\rangle$$

$$P_{ni}\hat{W} = \underbrace{P_{ni}\hat{W}P_n} + P_{ni}\hat{W}(1-P_n)$$

$$P_{ni}P_n\hat{W}P_n = P_{ni}\sum_j \epsilon_{nj}P_{nj} = \epsilon_{ni}P_{ni}$$

$$P_{ni}\hat{W}\underbrace{(1-P_n)|1\rangle} = \epsilon_2|0\rangle$$

$$\frac{1-P_n}{E_n^{(0)}-H_0}\hat{W}|0\rangle = \frac{1-P_n}{E_n^{(0)}-H_0}\hat{W}P_{ni}|0\rangle$$

$$P_{ni}\hat{W}\frac{1-P_n}{E_n^{(0)}-H_0}\hat{W}P_{ni}|0\rangle = \epsilon_2|0\rangle$$

Eigenvalue problem that determines ϵ_2 and, if no degeneracies left, $|0\rangle = |\varphi_{ni\alpha}\rangle$.

ⓑ Project $\perp$ to P_{ni} — get $|1\rangle$ and $|2\rangle$

Degeneracies to all orders: Suppose A such that

$[A, H_0] = 0 \qquad A|\varphi_{pi}\rangle = \lambda_i|\varphi_{pi}\rangle$

$[W, A] = 0 \implies 0 = \langle\varphi_{pi}|[W, A]|\varphi_{p'i'}\rangle$

$= (\lambda_{i'} - \lambda_i)\langle\varphi_{pi}|W|\varphi_{p'i'}\rangle$

$\implies \langle\varphi_{pi}|W|\varphi_{p'i'}\rangle = 0$ if $i \neq i'$

Perturbation doesn't couple degenerate levels

W is block-diagonal wrt i, so can apply nd theory to each value of i

Stark effect: Physics of perturbation theory

1- electron atom : $W = e\vec{R}\cdot\vec{E}$ ← evaluated at nucleus $\quad (\vec{F} = -\nabla W = -e\vec{E})$

↑ external electric field

Assume nondegenerate perturbation theory

$$E_n = E_n^{(0)} + \langle\varphi_n|W|\varphi_n\rangle + \sum_{p\neq n}\frac{|\langle\varphi_p|W|\varphi_n\rangle|^2}{E_n^{(0)}-E_p^{(0)}}$$

$$\langle\varphi_p|W|\varphi_n\rangle = e\underbrace{\langle\varphi_p|\vec{R}|\varphi_n\rangle}_{\vec{R}_{pn}}\cdot\vec{E} = e\vec{R}_{pn}\cdot\vec{E}$$

$$E_n = E_n^{(0)} + e\vec{R}_{nn}\cdot\vec{E} + e^2\sum_{p\neq n}\frac{|\vec{R}_{pn}\cdot\vec{E}|^2}{E_n^{(0)}-E_p^{(0)}}$$

$$\vec{p} = \begin{pmatrix}\text{dipole}\\ \text{moment}\end{pmatrix} = \int d^3r\, -e|\psi_n(\vec{r})|^2\vec{r} = -e\langle\psi_n|\vec{R}|\psi_n\rangle$$

$$|\psi_n\rangle = |\varphi_n\rangle + \sum_{p\neq n}|\varphi_p\rangle\frac{\langle\varphi_p|W|\varphi_n\rangle}{E_n^{(0)}-E_p^{(0)}} + \cdots$$

all $\perp$ to $|\varphi_n\rangle$

Normalization? $\quad = |\varphi_n\rangle + e\sum_{p\neq n}|\varphi_p\rangle\frac{\vec{R}_{pn}\cdot\vec{E}}{E_n^{(0)}-E_p^{(0)}} + \cdots$

$$\vec{p} = \underbrace{-e\langle\varphi_n|\vec{R}|\varphi_n\rangle}_{\vec{p}_0 = \begin{pmatrix}\text{permanent}\\ \text{dipole}\\ \text{moment}\end{pmatrix}} - \underbrace{e^2\sum_{p\neq n}\frac{\vec{R}_{np}(\vec{R}_{pn}\cdot\vec{E}) + \vec{R}_{pn}(\vec{R}_{np}\cdot\vec{E})}{E_n^{(0)}-E_p^{(0)}}}$$

$$\underbrace{-e^2\sum_{p\neq n}\frac{\vec{R}_{np}\otimes\vec{R}_{pn} + \vec{R}_{pn}\otimes\vec{R}_{np}}{E_n^{(0)}-E_p^{(0)}}}_{\overleftrightarrow{\alpha} = \begin{pmatrix}\text{polarizability}\\ \text{tensor}\end{pmatrix}}\cdot\vec{E}$$

real, symmetric

$$\boxed{\vec{p} = \vec{p}_0 + \overleftrightarrow{\alpha}\cdot\vec{E}}$$

$$-\vec{p}\cdot\vec{E} = + \langle \psi_n^{(0)} | W | \psi_n^{(0)} \rangle$$

$$= + \underbrace{\langle \varphi_n | W | \varphi_n \rangle}_{-\vec{p}_0\cdot\vec{E}} + 2\underbrace{\sum_{p\neq n} \frac{|\langle \varphi_p | W | \varphi_n \rangle|^2}{E_n^{(0)} - E_p^{(0)}}}_{-\vec{E}\cdot\overleftrightarrow{\alpha}\cdot\vec{E}}$$

$$= -\vec{p}_0\cdot\vec{E} - \vec{E}\cdot\overleftrightarrow{\alpha}\cdot\vec{E}$$

$$E_n = E_n^{(0)} - \vec{p}_0\cdot\vec{E} - \frac{1}{2}\vec{E}\cdot\overleftrightarrow{\alpha}\cdot\vec{E} + \ldots$$

Why this 1/2?

$$\vec{F} = -\nabla E_n = \vec{p}_0\cdot\nabla\vec{E} + \vec{E}\cdot\overleftrightarrow{\alpha}\cdot\nabla\vec{E}$$

$$= \vec{p}\cdot\nabla\vec{E}$$ ⟵ This is true for permanent or induced dipole

$$\vec{F} = \int \rho\, d^3x\, \vec{E}$$

$$= \int \rho\, d^3x\, (\vec{E}_0 + \vec{E}_{,j}|_0\, x_j)$$

$$= Q\vec{E}_0 + \vec{e}_k\, p_j \underbrace{E_{k,j}|_0}_{E_{j,k}|_0 + \cancel{E_{[k,j]}}|_0 \,\to\, 0}$$

$$= Q\vec{E}_0 + \vec{p}\cdot\nabla\vec{E}|_0$$

$$\vec{p}_0 = -e\vec{R}_{nn} = 0$$

↑ parity eigenstates

if energy eigenstates are nond, they must be parity eigenstates

$$\vec{E} = E_0\vec{e}_z \qquad [Z, J_z] = 0,$$ so Z doesn't couple different m

Quadratic Stark effect

AC Stark effect

Linear Stark effect in H: $|n\ell m\rangle$ Degenerate perturbation theory

$|21,\pm1\rangle$ display quadratic Stark effect

$|200\rangle$ and $|210\rangle$ are mixed by perturbation

$$W \to eE_0 \begin{pmatrix} \overbrace{\langle 200|z|200\rangle}^{0} & \overbrace{\langle 200|z|210\rangle}^{\mu} \\ \underbrace{\langle 210|z|200\rangle}_{\mu} & \underbrace{\langle 210|z|210\rangle}_{0} \end{pmatrix}$$

$$\mu = \langle 210|z|200\rangle = \int d^3r\, \psi_{210}\, z\, \psi_{200}$$

$$\psi_{200} = \frac{1}{\sqrt{4\pi}}\left(\frac{1}{2a}\right)^{3/2}\left(2-\frac{r}{a}\right)e^{-r/2a}$$

$$\psi_{210} = \frac{1}{\sqrt{4\pi}}\left(\frac{1}{2a}\right)^{3/2}\frac{r}{a}e^{-r/2a}\cos\theta$$

$$= \frac{1}{4\pi}\left(\frac{1}{2a}\right)^3 2\pi \int_0^\infty r^2 dr \left(2-\frac{r}{a}\right)\frac{r}{a}e^{-r/a}\, r$$

$$\times \underbrace{\int_0^\pi \sin\theta\, d\theta\, \cos^2\theta}_{\frac{2}{3}}$$

$$= \frac{1}{3}\,\frac{1}{8}\,a \underbrace{\int_0^\infty du\, u^4 (2-u)e^{-u}}_{2\times 4! - 5! = -3(4!)}$$

$$= -\frac{4!}{8}a$$

$$= -3a$$

$$W \longrightarrow -3aeE_0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\Delta E = \mp 3aE_0 \qquad \begin{matrix} \frac{1}{\sqrt{2}}(|200\rangle + |210\rangle) \\ \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle) \end{matrix}$$