

$$H = H_0 + \lambda H_1$$

$$H_0 |n\rangle = E_n^{(0)} |n\rangle$$

$$H |\psi_n\rangle = E_n |\psi_n\rangle$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}$$

$$\uparrow$$

$$E_n^{(1)} = \langle n | H | n \rangle$$

① $E_n^{(1)}$ b/c sometimes $E_n^{(1)} = 0$
 ② how to deal degenerate eigenvalues

Example:

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 + \lambda H_1$$

i) $\lambda H_1 = \lambda x^3$

$$E_n^{(1)} = \langle n | \lambda x^3 | n \rangle$$

$$= \int_{-\infty}^{+\infty} |\psi_n(x)|^2 x^3 dx = 0$$

\uparrow even \uparrow odd \nearrow

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger)$$

$$\langle n | (a + a^\dagger)^3 | n \rangle$$

$$\langle n | a^3 + a^2 a^\dagger + a a^\dagger a + a^\dagger a^2 | n \rangle = 0$$

ii) $\lambda H_1 = \lambda x^4$

$$E_n^{(1)} = \langle n | x^4 | n \rangle = \left(\frac{\hbar}{2m\omega}\right)^2 \langle n | (a + a^\dagger)^4 | n \rangle$$

16 terms \rightarrow only 6 terms where num of a^\dagger = num of a

$$E_n^{(1)} = \frac{3\hbar^2}{4m^2\omega^2} (1 + 2n + 2n^2)$$

$$\langle n | a a a^\dagger a^\dagger + a a^\dagger a a^\dagger + a^\dagger a a a^\dagger + a^\dagger a a^\dagger a + a^\dagger a^\dagger a a + a a^\dagger a^\dagger a | n \rangle$$

using $a | n \rangle = \sqrt{n} | n-1 \rangle$

$$\dagger a^\dagger | n \rangle = \sqrt{n+1} | n+1 \rangle$$

iii) $\lambda H_1 = \lambda x^2$

$$\frac{1}{2} m \omega^2 x^2 + \lambda x^2 = \frac{1}{2} m \omega'^2 x^2$$

$$\omega' = \omega^2 + \frac{2\lambda}{m}$$

$$E_n = \frac{1}{2} \hbar \omega' (n + \frac{1}{2}) = \omega (1 + \frac{\lambda}{m\omega} + O(\lambda^2))$$

Atomic Systems often degenerate when we study the
 1^{st} order degenerate perturbation theory

$$H_0 |n\rangle = E_n^{(0)} |n\rangle$$

\uparrow
 d_n states of energy $E_n^{(0)}$

$$|n_i\rangle \quad i=1, \dots, d_n$$

give each degenerate state
 a specific α_i value or β_j value

$$H_0 |n, i\rangle = E_n^{(0)} |n, i\rangle$$

$$|\Psi_n(\lambda)\rangle = N(\lambda) \left[\sum_{i=1}^{d_n} \alpha_i |n, i\rangle + \sum_{k \neq n} \sum_{j=1}^{d_k} \beta_j C_{n,k}^{(0)} |k, j\rangle \right]$$

put into $(H_0 + \lambda H_1) |\Psi_n(\lambda)\rangle = (E_n^{(0)} + \lambda E_n^{(1)} + \dots) |\Psi_n(\lambda)\rangle$

to $O(\lambda)$ is $\lambda H_1 \sum \alpha_i |n_i\rangle + \text{stuff ortho. to } |n_j\rangle$

rhs has $\lambda E_n^{(1)} \sum \alpha_i |n, i\rangle + \text{stuff ortho to } |n, i\rangle$

$$\langle n, i | k, j \rangle = 0$$

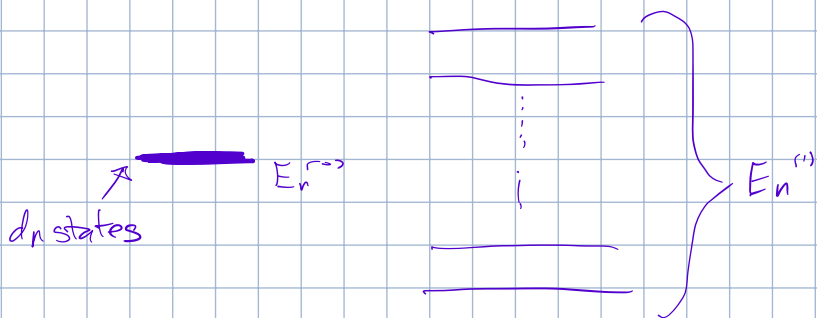
$$\langle n, j | \lambda H_1 \sum \alpha_i |n, i\rangle + 0 = \lambda E_n^{(1)} \langle n, j | \sum \alpha_i |n, i\rangle + 0$$

$$\sum_i \langle n, j | \lambda H_1 |n, i\rangle \alpha_i = \lambda E_n^{(1)} \alpha_j$$

$$\sum_i (\lambda H_1)_{ji}^{(n)} \alpha_i = \lambda E_n^{(1)} \alpha_j$$

$$(\lambda H_1) \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_{d_n} \end{pmatrix} = \lambda E_n^{(1)} \begin{pmatrix} \alpha_1 \\ \vdots \\ \alpha_{d_n} \end{pmatrix}$$

1^{st} order corrections to the energy
 of a d_n -fold deg. energy
 eigenstate are the eigenvalues of
 the perturbation in the
 degenerate space



Helium - using pert. theory for
ground state | $1s^2$ order pert. theory
| $1s^1$ excited states deg | $1s^2$ order

"derive" Hund's rules regarding spin

$$H = \underbrace{\frac{\vec{p}_1^2}{2m_e} - \frac{ze^2}{|\vec{r}_1|} + \frac{\vec{p}_2^2}{2m_e} - \frac{ze^2}{|\vec{r}_2|}}_{H_0} + \underbrace{\frac{\vec{p}_1 \cdot \vec{p}_2}{m_e}}_{\lambda H_1}$$