## 6.1.1.) Non-Degenerate Perturbation Theory

$E_n^0$ is non-degenerate, $g_n^0 = 1$. Thus the label k in the eigenstates $|\varphi_{n,k}\rangle$ is not necessary, so we drop it.

Thus $H_0|\varphi_n\rangle = E_n^0|\varphi_n\rangle$ and we have that $|\psi_n^{(0)}\rangle = |\varphi_n\rangle$ with $\epsilon_n^{(0)} = E_n^0$. Further we assume that $\lambda$ is small enough so that for $\lambda \neq 0$ the eigenvalue remains non-degenerate. We denote this energy eigenvalue of $H = H(\lambda)$ by $E_n(\lambda) = E_n \xrightarrow[\lambda\to 0]{} E_n^0$. Thus the unique eigenvector corresponding to $E_n(\lambda)$ is $|\psi_n(\lambda)\rangle = |\psi_n\rangle$. It also approaches $|\varphi_n\rangle$ as $\lambda \to 0$.

Next we consider the $\lambda^1$ term in the Schrödinger equation expansion

$$(H_0 - \epsilon_n^{(0)})|\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(0)}\rangle = 0$$

This becomes

$$\boxed{(H_0 - E_n^0)|\psi_n^{(1)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\varphi_n\rangle = 0}$$

First we determine $\epsilon_n^{(1)}$:
project this equation onto $\langle\varphi_n|$

$$0 = \underbrace{\langle\varphi_n| H_0 - E_n^0}_{=0} |\psi_n^{(1)}\rangle + \langle\varphi_n|\hat{H}' - \epsilon_n^{(1)}|\varphi_n\rangle$$

$$\Rightarrow \quad \boxed{\epsilon_n^{(1)} = \langle\varphi_n|\hat{H}'|\varphi_n\rangle}$$

and to first order in $\lambda$

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

$$= E_n^0 + \lambda\langle\varphi_n|\hat{H}'|\varphi_n\rangle + O(\lambda^2)$$

$$\boxed{E_n = E_n^0 + \langle\varphi_n|H'|\varphi_n\rangle + O(\lambda^2)}$$

$$= \langle\varphi_n|H_0 + H'|\varphi_n\rangle + O(\lambda^2)$$

$$= \langle\varphi_n|H|\varphi_n\rangle + O(\lambda^2).$$

Next we determine $|\psi_n^{(1)}\rangle$:

We project the $\lambda'$ equation onto the unperturbed basis vectors orthogonal to $|\varphi_n\rangle$ that is $\langle\varphi_{m,\ell}|$ $m \neq n$ $\Rightarrow$

$$0 = \langle\varphi_{m,\ell}|H_0 - E_n^0|\psi_n^{(1)}\rangle + \langle\varphi_{m,\ell}|\hat{H}' - \epsilon_n^{(1)}|\varphi_n\rangle$$

Since

$$\langle\varphi_{m,\ell}|H_0 = E_m^0\langle\varphi_{m,\ell}|$$

and

$$\langle\varphi_{m,\ell}|\epsilon_n^{(1)}|\varphi_n\rangle = \epsilon_n^{(1)}\langle\varphi_{m,\ell}|\varphi_n\rangle = 0$$

for $m \neq n$

we have

$$(E_m^0 - E_n^0)\langle\varphi_{m,\ell}|\psi_n^{(1)}\rangle + \langle\varphi_{m,\ell}|\hat{H}'|\varphi_n\rangle = 0$$

Since $m \neq n$ we can divide by $E_m^0 - E_n^0$ $\Rightarrow$

$$\boxed{\langle\varphi_{m,\ell}|\psi_n^{(1)}\rangle = \frac{1}{E_n^0 - E_m^0}\langle\varphi_{m,\ell}|\hat{H}'|\varphi_n\rangle}$$

Now $\{|\varphi_{m,\ell}\rangle\}$ are a complete set
So
$$|\psi_n^{(1)}\rangle = \sum_m \sum_{\ell=1}^{g_m^0} |\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|\psi_n^{(1)}\rangle$$

$$= \sum_{m\neq n} \sum_{\ell=1}^{g_m^0} |\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|\psi_n^{(1)}\rangle$$

$$+ |\varphi_n\rangle \underbrace{\langle\varphi_n|\psi_n^{(1)}\rangle}_{\substack{=\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle \\ =0 \text{ from the norm} \\ \text{\& phase convention} \\ \text{(page -118-)}}}$$

Thus we have

$$\boxed{|\psi_n^{(1)}\rangle = \sum_{m\neq n} \sum_{\ell=1}^{g_m^0} \frac{|\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}|\hat{H}'|\varphi_n\rangle}{E_n^0 - E_m^0}}$$

Hence to order $\lambda$ we have for the eigenvector

$$\boxed{\begin{aligned} |\psi_n\rangle &= |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + O(\lambda^2) \\ &= |\varphi_n\rangle + \sum_{m\neq n} \sum_{\ell=1}^{g_m^0} |\varphi_{m,\ell}\rangle \frac{\langle\varphi_{m,\ell}|H'|\varphi_n\rangle}{E_n^0 - E_m^0} + O(\lambda^2) \end{aligned}}$$

Note: 1) $H'$ is said to "mix" the unperturbed state $|\varphi_n\rangle$ with all the other eigenstates of $H_o$. In general the closer $E_m^o$ is to $E_n^o$ the stronger the mixing of the $|\varphi_{m,\ell}\rangle$ states with $|\varphi_n\rangle$ (assuming the matrix element $\langle\varphi_{m,\ell}|H'|\varphi_n\rangle$ is not arbitrarily small)

2) For the perturbation expansion to be consistent it is necessary that

$$\left|\frac{\langle\varphi_{m,\ell}|H'|\varphi_n\rangle}{E_n^o - E_m^o}\right| \ll 1 \quad , m \neq n .$$

That is the non-diagonal matrix elements of $H'$ must be smaller than the unperturbed energy differences.

3) Example: Ground State of He atom
Consider an atom with nuclear electric charge $Ze$ and only 2 electrons (it is $(Z-2)$ times ionized). The nucleus is much heavier than the electrons so we can consider the Hamiltonian to be given by the electrons moving in the nuclear

Coulomb attractive potential plus the e-e repulsive Coulomb potential

$$H = \frac{1}{2m}\vec{P}_1^{\,2} + \frac{1}{2m}\vec{P}_2^{\,2} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_1|} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_2|}$$

$$+ \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} .$$

The unperturbed Hamiltonian $H_0$ is taken as the Nuclear Coulomb attractive terms

$$H_0 = \frac{\vec{P}_1^{\,2} + \vec{P}_2^{\,2}}{2m} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_1|} - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_2|}$$

While the perturbation is the e-e repulsion term

$$H' = \frac{e^2}{4\pi\epsilon_0|\vec{r}_1 - \vec{r}_2|} ,$$

and $H = H_0 + H'$.

The ground state of $H_0$ corresponds to both electrons in the hydrogen-like 1s ground state. The energy is just the sum of H-ground state energies

$$E_n^0 = -2Z^2 E_H$$

$n = 1s$

$$E_H = 13.6\,eV = \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2}$$

The wavefunction for the 1S ground state of hydrogen, recall, is simply $\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$ with

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{me^2} = 0.53\ \mathring{A} = \text{Bohr radius}$$

For a nucleus with charge $Ze$ this becomes

$$\frac{1}{\sqrt{\pi a^3}} e^{-r/a} \quad ; \quad a = \frac{a_0}{Z}$$

. Thus the unperturbed ground state wavefunction for He is

$$\langle \vec{r}_1, \vec{r}_2 | \varphi_n \rangle = \frac{1}{\pi a^3} e^{-\frac{(r_1+r_2)}{a}}$$

$\uparrow$ 2(1S-state $e^-$)

where $r_{1,2} = |\vec{r}_{1,2}|$.

The first order correction to the ground state energy is given by

$$\lambda \epsilon_n^{(1)} = \langle \varphi_n | H' | \varphi_n \rangle .$$ Thus

$$\lambda \epsilon_n^{(1)} = \langle \varphi_n | H' | \varphi_n \rangle$$

$$= \int d^3r_1 d^3r_2 d^3r_1' d^3r_2' \langle \varphi_n | \vec{r}_1 \vec{r}_2 \rangle \times$$

$$\times \underbrace{\langle \vec{r}_1, \vec{r}_2 | H' | \vec{r}_1', \vec{r}_2' \rangle}_{= \delta^3(\vec{r}_1 - \vec{r}_1') \delta^3(\vec{r}_2 - \vec{r}_2') \times \frac{e^2/4\pi\epsilon_0}{|\vec{r}_1 - \vec{r}_2|}} \langle \vec{r}_1', \vec{r}_2' | \varphi_n \rangle$$

$$= \int d^3r_1 d^3r_2 \langle \varphi_n | \vec{r}_1, \vec{r}_2 \rangle \frac{e^2/4\pi\epsilon_0}{|\vec{r}_1 - \vec{r}_2|} \langle \vec{r}_1, \vec{r}_2 | \varphi_n \rangle$$

$$= \frac{e^2/4\pi\epsilon_0}{\pi^2 a^6} \int d^3r_1 d^3r_2 \frac{e^{-2(r_1+r_2)/a}}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{\rho_1(r_1)\rho_2(r_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$\rho_i(r_i) \equiv \frac{e^{-2r_i/a}}{\pi a^3}$$ , this is just the Coulomb energy of two spherical charge distributions [$-e\rho(r)$].

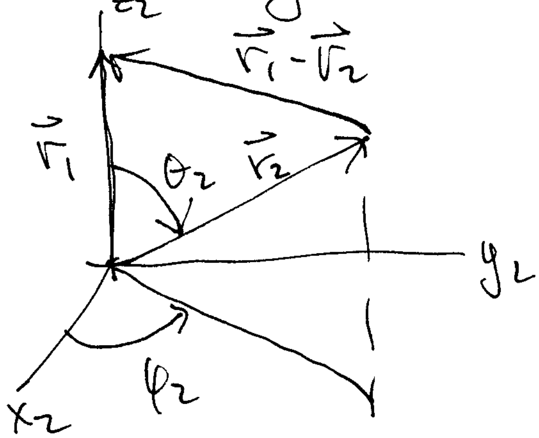
$$\rho_i(r_i) = \frac{e^{-2r_i/a}}{\pi a^3}$$



So we have to evaluate

$$I = \int d^3r_1\, d^3r_2 \; \frac{\rho_1(r_1)\rho_2(r_2)}{|\vec r_1 - \vec r_2|}$$

Let's do the $\vec r_2$ integral first with $\vec r_1$ fixed. Choose our coordinate system so that $\vec r_1$ is along the $z_2$ axis (the polar axis)




So
$$|\vec r_1 - \vec r_2| = \sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}$$

Then $= 2\pi$

$$\int_{-1}^{+1} d\xi_2 \qquad \xi_2 = \cos\theta_2$$

$$I_2 = \int d^3r_2 \; \frac{\rho_2(r_2)}{|\vec r_1 - \vec r_2|} = \underbrace{\int_{\varphi_2=0}^{2\pi} d\varphi_2}_{2\pi} \underbrace{\int_{\theta_2=0}^{\pi} d\theta_2 \sin\theta_2}_{} \int_{r_2=0}^{\infty} r_2^2\, dr_2 \;\times$$

$$\times \frac{1}{\pi a^3}\; \frac{e^{-2r_2/a}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta_2}}$$

$$= \frac{2}{a^3}\int_0^\infty dr_2\, r_2^2\, e^{-\frac{2r_2}{a}} \underbrace{\int_{-1}^{+1} d\xi_2 \; \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\xi_2}}}$$

$$= \left. \frac{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\xi_2}}{-r_1r_2} \right|_{\xi_2=-1}^{+1}$$

$$I_2 = \frac{2}{a^3}\int_0^\infty dr_2 \frac{r_2^2 e^{-\frac{2r_2}{a}}}{r_1 r_2}\left[\sqrt{r_1^2+r_2^2+2r_1r_2} - \sqrt{r_1^2+r_2^2-2r_1r_2}\right]$$

$$= \frac{2}{a^3 r_1}\int_0^\infty dr_2\, r_2\, e^{-\frac{2r_2}{a}}\left[\sqrt{(r_1+r_2)^2} - \sqrt{(r_1-r_2)^2}\right]$$

$$= \frac{2}{a^3 r_1}\int_0^\infty dr_2\, r_2\, e^{-\frac{2r_2}{a}}\underbrace{\Big((r_1+r_2) - |r_1-r_2|\Big)}_{= \begin{cases} r_1+r_2-(r_1-r_2) \text{ if } r_1>r_2 \\ \quad = 2r_2 \\ r_1+r_2-(r_2-r_1) \text{ if } r_2>r_1 \\ \quad = 2r_1 \end{cases}}$$

$$= \frac{2}{a^3 r_1}\left\{\int_0^{r_1} dr_2\, 2r_2\, r_2\, e^{-\frac{2r_2}{a}} + \int_{r_1}^\infty dr_2\, 2r_1\, r_2\, e^{-\frac{2r_2}{a}}\right\}$$

$$= \frac{4}{a^3 r_1}\int_0^{r_1} dr_2\, r_2^2\, e^{-\frac{2r_2}{a}} + \frac{4}{a^3}\int_{r_1}^\infty dr_2\, r_2\, e^{-\frac{2r_2}{a}}$$

Now $\int dr\, r^n e^{-2r/a} = \int dr\, r^n e^{-\beta r}$

$$(\beta \equiv \tfrac{2}{a}) \qquad = \left(-\frac{\partial}{\partial\beta}\right)^n \int dr\, e^{-\beta r}$$

$$= \left(-\frac{\partial}{\partial\beta}\right)^n \left(-\frac{1}{\beta} e^{-\beta r}\right)$$

So $$\int_{r_1}^{\infty} dr_2\, r_2 \rho_2(r_2) = \frac{1}{\pi a^3}\left(-\frac{\partial}{\partial\beta}\right)\left(-\frac{1}{\beta} e^{-\beta r_2}\right)\Bigg|_{r_1}^{\infty}$$

$$= \frac{-1}{\pi a^3}\frac{\partial}{\partial\beta}\left(\frac{1}{\beta} e^{-\beta r_1}\right)$$

$$= -\frac{1}{\pi a^3}\left[-\frac{1}{\beta^2} e^{-\beta r_1} - \frac{r_1}{\beta} e^{-\beta r_1}\right]$$

$$= \frac{1}{\pi a^3}\left[\frac{a^2}{4} e^{-\frac{2r_1}{a}} + \frac{a r_1}{2} e^{-\frac{2r_1}{a}}\right]$$

and $$\int_0^{r_1} dr_2\, r_2^2 \rho_2(r_2) = \frac{\partial^2}{\partial\beta^2}\left(-\frac{1}{\beta} e^{-\beta r_1} + \frac{1}{\beta}\right)\frac{1}{\pi a^3}$$

$$= \frac{\partial}{\partial\beta}\left[\frac{1}{\beta^2} e^{-\beta r_1} + \frac{r_1}{\beta} e^{-\beta r_1} - \frac{1}{\beta^2}\right]\frac{1}{\pi a^3}$$

$$= \left[-\frac{2}{\beta^3} e^{-\beta r_1} - \frac{r_1}{\beta^2} e^{-\beta r_1} - \frac{r_1}{\beta^2} e^{-\beta r_1} - \frac{r_1^2}{\beta} e^{-\beta r_1} + \frac{2}{\beta^3}\right]\frac{1}{\pi a^3}$$

Now $$\int_0^{r_1} dr_2\, r_2^2\, \rho_2(r_2) = \frac{1}{\pi a^3}\left[\frac{a^3}{4} - \frac{a^3}{4} e^{-2r_1/a} - \frac{a^2 r_1}{2} e^{-2r_1/a} - \frac{r_1^2 a}{2} e^{-2r_1/a}\right]$$

So combining these terms ⟹

$$I_2 = \frac{4}{a^3}\left[\frac{a^2}{4} e^{-\frac{2r_1}{a}} + \cancel{\frac{a r_1}{2} e^{-2r_1/a}} + \frac{a^3}{4r_1} - \frac{a^3}{4r_1} e^{-2r_1/a} - \frac{a^2 r_1}{2r_1} e^{-2r_1/a} - \cancel{\frac{r_1^2 a}{2r_1} e^{-2r_1/a}}\right]$$

$$\boxed{I_2 = \frac{4}{a^3}\left[\frac{a^3}{4r_1}\left(1 - e^{-2r_1/a}\right) - \frac{a^2}{4} e^{-2r_1/a}\right]}$$

$$\boxed{= \frac{1}{r_1}\left(1 - e^{-2r_1/a}\right) - \frac{1}{a} e^{-2r_1/a}}$$

Finally

$$I = \int d^3 r_1\, \rho_1(r_1)\, I_2$$

$$= \underbrace{\int_0^{2\pi} d\varphi_1 \int_{-1}^{+1} d\mu_1}_{=4\pi} \int_0^{\infty} dr_1\, r_1^2\, \frac{e^{-2r_1/a}}{\pi a^3}\, I_2(r_1)$$

So

$$I = \frac{4}{a^3}\int_0^\infty dr_1\, r_1^2 \left[\frac{1}{r_1}\left(e^{-2r_1/a} - e^{-4r_1/a}\right) - \frac{1}{a} e^{-4r_1/a}\right]$$

$$= \frac{4}{a^3}\int_0^\infty dr_1 \left[r_1 e^{-2r_1/a} - r_1 e^{-4r_1/a} - \frac{r_1^2}{a} e^{-4r_1/a}\right]$$

$$= \frac{4}{a^3}\left[ \frac{-\partial}{\partial\beta}\left(-\frac{1}{\beta}e^{-\beta r_1}\right)\Bigg|_{\substack{r_1=0 \\ \beta=2/a}}^{\infty} - \frac{-\partial}{\partial\beta}\left(-\frac{1}{\beta}e^{-\beta r_1}\right)\Bigg|_{\substack{r_1=0 \\ \beta=4/a}}^{\infty} - \frac{1}{a}\left(\frac{-\partial}{\partial\beta}\right)^2\left(-\frac{1}{\beta}e^{-\beta r_1}\right)\Bigg|_{\substack{r_1=0 \\ \beta=4/a}}^{\infty}\right]$$

$$= \frac{4}{a^3}\left[\left(-\frac{1}{\beta^2}e^{-\beta r_1} - \frac{r_1}{\beta}e^{-\beta r_1}\right)\Bigg|_{\substack{r_1=0 \\ \beta=2/a}}^{\infty} - \left(\frac{-1}{\beta^2}e^{-\beta r_1} - e^{-\beta r_1}\frac{r_1}{\beta}\right)\Bigg|_{\substack{r_1=0 \\ \beta=4/a}}^{\infty} - \frac{1}{a}\left(\frac{-2}{\beta^3}e^{-\beta r_1} - \frac{r_1}{\beta^2}e^{-\beta r_1} - \frac{r_1}{\beta^2}e^{-\beta r_1} - \frac{r_1^2}{\beta}e^{-\beta r_1}\right)\Bigg|_{\substack{r_1=0 \\ \beta=4/a}}^{\infty}\right]$$

So all $r_1 \to \infty$ terms vanish & all powers of $r_1$ at $r_1 \to 0$ vanish $\Rightarrow$

$$I = \frac{4}{a^3}\left[\frac{a^2}{4} - \frac{a^2}{16} - \frac{1}{a}\frac{2a^3}{4\cdot 16}\right]$$

$$= \frac{4}{a^3}\left[\frac{a^2}{4} - \frac{a^2}{16} - \frac{a^2}{32}\right] = \frac{4}{a}\left[\underbrace{\frac{1}{4} - \frac{1}{16} - \frac{1}{32}}_{=5/32}\right]$$

$$\boxed{I = \frac{5}{8}\frac{1}{a}}$$

Thus $I = \frac{5}{8}\frac{1}{a}$ implies

$$\lambda \epsilon_n^{(1)} = \frac{5}{8}\frac{e^2}{4\pi\epsilon_0 a} = \frac{5}{8}\frac{Z e^2}{4\pi\epsilon_0 a_0}$$

$n =$ ground state

$$= \frac{5}{8} Z \underbrace{\frac{m e^4}{(4\pi\epsilon_0)^2 \hbar^2}}_{= 2 E_H}$$

$$\boxed{\lambda \epsilon_n^{(1)} = \frac{5}{4} Z E_H}$$

gd. st. of He like atom

So we find the first order correction to the ground state energy

$$\boxed{\lambda \epsilon_n^{(1)} = \frac{5}{4} Z E_H}$$

Recall the unperturbed energy was given by

$$\boxed{\epsilon_n^{(0)} = E_n^0 = -2Z^2 E_H}$$

Hence to first order the ground state energy for Helium-like atoms is

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

$$\boxed{E_n = -2ZE_H \left(Z - \frac{5}{8}\right)}$$

Table

| | $Z$ | $E_n^0$ (eV) | $\lambda \epsilon_n^{(1)}$ (eV) | $E_n = \epsilon_n^{(0)} + \lambda \epsilon_n^{(1)}$ (eV) | $E_n^{exp.}$ (eV) |
|---|---|---|---|---|---|
| He | 2 | −108 | 34 | −74 | −78.6 |
| $Li^+$ | 3 | −243.5 | 50.5 | −193 | −197.1 |
| $Be^{++}$ | 4 | −433 | 67.5 | −365.5 | −370.0 |

6.1.2) Next we consider the higher order corrections to the energy eigenvalue

Recall the $\lambda^2$ term in the Schrödinger equation is

$$(H_0 - \epsilon_n^{(0)})|\psi_n^{(2)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(1)}\rangle - \epsilon_n^{(2)}|\psi_n^{(0)}\rangle = 0$$

That is

$$(H_0 - E_n^0)|\psi_n^{(2)}\rangle + (\hat{H}' - \epsilon_n^{(1)})|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}|\varphi_n\rangle$$

So projecting onto the $\langle\varphi_n|$ state again

$$\underbrace{\langle\varphi_n|H_0 - E_n^0}_{=0}|\psi_n^{(2)}\rangle + \langle\varphi_n|\hat{H}' - \epsilon_n^{(1)}|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\underbrace{\langle\varphi_n|\varphi_n\rangle}_{=1}$$

and using the normalization conditions

$$\langle\varphi_n|\psi_n^{(1)}\rangle = \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$$

we have

$$\epsilon_n^{(2)} = \langle \varphi_n | \hat{H}' | \psi_n^{(1)} \rangle$$

substituting for $|\psi_n^{(1)}\rangle$ yields (page -125-)

$$\epsilon_n^{(2)} = \sum_{m \neq n}' \sum_{l=1}^{g_m^0} \frac{\langle \varphi_n | \hat{H}' | \varphi_{m,l} \rangle \langle \varphi_{m,l} | \hat{H}' | \varphi_n \rangle}{E_n^0 - E_m^0}$$

$$\boxed{\epsilon_n^{(2)} = \sum_{m \neq n}' \sum_{l=1}^{g_m^0} \frac{|\langle \varphi_n | \hat{H}' | \varphi_{m,l} \rangle|^2}{E_n^0 - E_m^0}}$$

The energy of the full Hamiltonian to this order is given by

$$E_n = E_n^0 + \lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)} + O(\lambda^3)$$

$$= \langle \varphi_n | H_0 | \varphi_n \rangle + \langle \varphi_n | \lambda \hat{H}' | \varphi_n \rangle + \sum_{m \neq n}' \sum_{l=1}^{g_m^0} \frac{|\langle \varphi_n | \lambda \hat{H}' | \varphi_{m,l} \rangle|^2}{E_n^0 - E_m^0} + O(\lambda^3)$$

Thus with $H = H_0 + H' = H_0 + \lambda \hat{H}'$ we have

$$\boxed{E_n = \langle \varphi_n | H | \varphi_n \rangle + {\sum_{m\neq n}}' \sum_{l=1}^{g_m^0} \frac{|\langle \varphi_n | H' | \varphi_{m,l}\rangle|^2}{E_n^0 - E_m^0} + O(\lambda^3)}$$

---

Example: Consider a SHO in one-dimension

$$H_0 = \hbar\omega(a^\dagger a + \tfrac{1}{2}) = \frac{1}{2m}P^2 + \frac{1}{2}m\omega^2 X^2$$

with a perturbing $X^3$ potential $\left(X = \sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger)\right)$

(i.e. $V = \frac{1}{2}m\omega^2 x^2 + \lambda\hbar\omega\left(\frac{m\omega}{\hbar}\right)^{3/2} x^3$

)

$$H' = \lambda\hbar\omega\left(\frac{m\omega}{\hbar}\right)^{3/2} X^3$$

$$= \frac{\lambda\hbar\omega}{2^{3/2}}(a+a^\dagger)^3$$

$$= \frac{\lambda\hbar\omega}{2^{3/2}}\left[a^{\dagger 3} + a^3 + 3Na^\dagger + 3(N+1)a\right]$$

where $N \equiv a^\dagger a$.

The full Hamiltonian is given by $H = H_0 + H'$

The eigenvalues of $H_0$ are $E_n^0 = (n + \frac{1}{2})\hbar\omega$

$n = 0, 1, 2, \ldots$ and are non-degenerate

The unique, complete set of unperturbed energy eigenstates are

$$|\varphi_n\rangle \equiv \frac{1}{\sqrt{n!}}(a^\dagger)^n|\varphi_0\rangle$$

where $|\varphi_0\rangle = |0\rangle$ is defined by

$$a|\varphi_0\rangle = 0.$$

Now the only non-zero matrix elements of $H'$ are

$$\langle\varphi_{n+3}|H'|\varphi_n\rangle = \lambda\left[\frac{(n+3)(n+2)(n+1)}{8}\right]^{1/2}\hbar\omega$$

$$\langle\varphi_{n-3}|H'|\varphi_n\rangle = \lambda\left[\frac{n(n-1)(n-2)}{8}\right]^{1/2}\hbar\omega$$

$$\langle\varphi_{n+1}|H'|\varphi_n\rangle = 3\lambda\left(\frac{n+1}{2}\right)^{3/2}\hbar\omega$$

$$\langle\varphi_{n-1}|H'|\varphi_n\rangle = 3\lambda\left(\frac{n}{2}\right)^{3/2}\hbar\omega$$

Hence the 1st order correction to the energy corresponding to unperturbed energy $E_n^0$, $E_n$ vanishes. Recall

$$H|\Psi_n\rangle = E_n|\Psi_n\rangle$$

now with the second order formula

$$E_n = \langle\varphi_n|H|\varphi_n\rangle$$

$$+\sum_{m\neq n}\sum_{l=1}^{g_m^0} \frac{|\langle\varphi_n|H'|\varphi_{m,l}\rangle|^2}{E_n^0 - E_m^0} + O(\lambda^3)$$

since $g_m^0 = 1$ and

$$\langle\varphi_n|H|\varphi_n\rangle = \langle\varphi_n|H_0|\varphi_n\rangle + \cancelto{0}{\langle\varphi_n|H'|\varphi_n\rangle}$$

$$= E_n^0 = (n+\tfrac{1}{2})\hbar\omega$$

This reduces to

$$E_n = (n+\tfrac{1}{2})\hbar\omega + \frac{|\langle\varphi_n|H'|\varphi_{n+3}\rangle|^2}{E_n^0 - E_{n+3}^0}$$

$$+\frac{|\langle\varphi_n|H'|\varphi_{n-3}\rangle|^2}{E_n^0 - E_{n-3}^0} + \frac{|\langle\varphi_n|H'|\varphi_{n+1}\rangle|^2}{E_n^0 - E_{n+1}^0}$$

$$+\frac{|\langle\varphi_n|H'|\varphi_{n-1}\rangle|^2}{E_n^0 - E_{n-1}^0} + O(\lambda^3)$$

Now $E_n^0 - E_{n\pm 3}^0 = \mp 3\hbar\omega$

$$E_n^0 - E_{n\pm 1}^0 = \mp 1\hbar\omega$$

Thus we find using the above matrix elements of $H'$

$$E_n = (n+\tfrac{1}{2})\hbar\omega + \lambda^2\hbar\omega\Big\{\frac{n(n-1)(n-2)}{24} - \frac{(n+3)(n+2)(n+1)}{24} + 9\left(\frac{n}{2}\right)^3 - 9\left(\frac{n+1}{2}\right)^3\Big\} + O(\lambda^3)$$

$$= (n+\tfrac{1}{2})\hbar\omega - \lambda^2\hbar\omega\Big\{\frac{1}{8}(3n^2+3n+2) + \frac{9}{8}(3n^2+3n+1)\Big\} + O(\lambda^3)$$

$$= (n+\tfrac{1}{2})\hbar\omega - \lambda^2\hbar\omega\,\frac{5}{4}(3n^2+3n+\tfrac{3}{4}) - \lambda^2\hbar\omega\left(\frac{11}{8} - \frac{15}{16}\right) + O(\lambda^3)$$

$$\boxed{E_n = (n+\tfrac{1}{2})\hbar\omega - \lambda^2\hbar\omega\,\frac{15}{4}(n+\tfrac{1}{2})^2 - \frac{7}{16}\lambda^2\hbar\omega + O(\lambda^3)}$$

The $H'$ lowers the energy levels for any sign $\lambda$, further the larger $n$, the greater the energy shift:

$$E_n - E_{n-1} = \hbar\omega\left[1 - \tfrac{15}{2}\lambda^2 n\right].$$

---

## 6. 2. Degenerate Perturbation Theory

Suppose now that $E_n^0$ is degenerate, $g_n^0 > 1$. Then

$$H_0 |\psi_n^{(0)}\rangle = \epsilon_n^{(0)} |\psi_n^{(0)}\rangle$$

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

is not sufficient to determine $|\psi_n^{(0)}\rangle$. Indeed, $|\psi_n^{(0)}\rangle$ can be any linear combination of the $|\varphi_{n,l}\rangle$, $l = 1, \ldots, g_n^0$. Since

$H_0 |\varphi_{n,l}\rangle = E_n^0 |\varphi_{n,l}\rangle$; such a linear combination will have energy $E_n^0$. Thus

$$|\psi_n^{(0)}\rangle = \sum_{l=1}^{g_n^0} \psi_{nl} |\varphi_{n,l}\rangle$$

and

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