VI.) Approximation Methods For Bound States

There are very few situations in which we can solve Schrödinger's equation exactly. Hence approximation techniques form an important tool in analyzing physical systems. The general idea of these approximations is that the bulk of the properties of a system we can determine precisely, it is the small deviations from this major behaviour that perturbation theory will calculate. There are two types of problems for which we will develop approximation techniques. Time dependent and time independent Hamiltonian operators. We first consider time independent Hamiltonian operators. We will determine the approximate stationary states and energy eigenvalues for this case. Needless to say there are many approaches to this problem we first consider the approach of Rayleigh and Schrödinger.

6.1. Rayleigh-Schrödinger Stationary State Perturbation Theory

Consider the case where the Hamiltonian is time independent. The Schrödinger equation becomes the energy eigenvalue equation for the stationary states $|\psi_n\rangle$

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

where for convenience we label the energy eigenvalues with a discrete index n, they could in principle be continuous as well. Of course, these eigenvalues can be degenerate and we can include an additional label $k = 1, \ldots, g_n$ for the needed commuting operators A, $|\psi_{n,k}\rangle$.

In general we cannot solve this problem but must find approximate solutions to the stationary states. In particular, suppose

$$H = H_0 + H' = H_0 + \lambda \hat{H}', \quad \lambda \in \mathbb{R},$$

where $|\lambda| \ll 1$ and $H_0, H', \hat{H}'$ are time independent and we can

solve the unperturbed eigenvalue problem exactly. That is

$$H_0 |\varphi_{m,\ell}\rangle = E^0_m |\varphi_{m,\ell}\rangle$$

where E^0_m, $(|\varphi_{m,\ell}\rangle)$ are the known eigenvalues (eigenstates) of H_0. Again we label the energies E^0_m with a discrete index m, in general it could also be continuous. ℓ labels the possible unperturbed energy degenerate states. It could happen that the set of energies E_n, which are considered smooth functions of λ, have a different number of elements than the set E^0_m; i.e. 2 different $E_n(\lambda)$ approach the same E^0_m at $\lambda = 0$. As well, the degeneracies may be different i.e. $\ell \in 1, \ldots, g^0_m$ while $k = 1, \ldots, g_n$.

Further we assume that the states $|\varphi_{m,\ell}\rangle$ are orthonormal

$$\langle \varphi_{m',\ell'} | \varphi_{m,\ell} \rangle = \delta_{m'm} \delta_{\ell'\ell}$$

and complete $\quad \underline{1} = \sum_m \sum_{\ell=0}^{g^0_m} |\varphi_{m,\ell}\rangle\langle\varphi_{m,\ell}| .$

The idea of the perturbation expansion is that when the perturbation is off, $\lambda = 0$, we have the energies E_m^0 and eigenstates $|\phi_{m,\ell}\rangle$. Assuming the full energies and eigenstates vary smoothly with the perturbation strength λ, we determine, for a given initial energy E_m^0, the full energies E_n and states $|\psi_n\rangle$ as power series in λ.

Thus we assume that the energy eigensolutions to the full problem

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

have Taylor series in the small (to be defined) perturbing interaction parameter λ:

$$E_n = \sum_{i=0}^{\infty} \lambda^i E_n^{(i)} = \epsilon_n^{(0)} + \lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)} + \cdots$$

$$|\psi_n\rangle = \sum_{i=0}^{\infty} \lambda^i |\psi_n^{(i)}\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots$$

with $\epsilon_n^{(i)}$ and $|\psi_n^{(i)}\rangle$ independent of λ.

Before determining the $E_n^{(i)}$ and $|\psi_n^{(i)}\rangle$ by using the Schrödinger equation, we consider the normalization constraints on $|\psi_n\rangle$. As we know, the Schrödinger equation determines $|\psi_n\rangle$ only up to an overall normalization constant (a complex number). We will fix the normalization by the following convention:

1) norm: $\langle\psi_n|\psi_n\rangle \equiv 1$

2) phase: $\langle\psi_n^{(0)}|\psi_n\rangle$ = Real number

These normalization conventions imply certain constraints on the $|\psi_n^{(i)}\rangle$'s.

$$1 = \langle\psi_n|\psi_n\rangle$$

$$= \left[\langle\psi_n^{(0)}| + \lambda\langle\psi_n^{(1)}| + \lambda^2\langle\psi_n^{(2)}| + \cdots\right] \times$$

$$\times \left[|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots\right]$$

$$1 = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$
$$+ \lambda \left[\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \right]$$
$$+ \lambda^2 \left[\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle \right]$$
$$+ O(\lambda^3) .$$

Since λ is considered an independent parameter we set equal powers of λ equal to each other

$\Rightarrow$

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

λ^1 : $0 = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(0)} \rangle$

λ^2 : $0 = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle$

$\vdots$

λ^i : $0 = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(i-1)} | \psi_n^{(1)} \rangle + \cdots + \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle$

$\vdots$

From the phase normalization $\langle \psi_n^{(0)} | \psi_n \rangle = \text{Real}$ we find

$$\langle \psi_n^{(0)} | \psi_n \rangle = \langle \psi_n^{(0)} | \left(|\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \cdots \right)$$

$$= \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \lambda \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle + \lambda^2 \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \cdots$$

$$\equiv \text{real number}.$$

Again equating equal powers of λ

λ^0 : $\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = \text{real}$ ($=1$ from above already)

λ^1 : $\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(1)} \rangle^*$

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

λ^2 : $\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle^*$

$$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle$$

λ^i : $\langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \text{real} = \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle^*$

$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle$

Combining this with the $\langle \psi_n | \psi_n \rangle = 1$ normalization implies

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

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

λ^2 : $0 = 2\langle \psi_n^{(0)} | \psi_n^{(2)} \rangle + \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle$

$\Rightarrow \langle \psi_n^{(0)} | \psi_n^{(2)} \rangle = \langle \psi_n^{(2)} | \psi_n^{(0)} \rangle$

$= -\frac{1}{2} \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle$

λ^i : $\langle \psi_n^{(0)} | \psi_n^{(i)} \rangle = \langle \psi_n^{(i)} | \psi_n^{(0)} \rangle$

$= -\frac{1}{2} \left[\langle \psi_n^{(i-1)} | \psi_n^{(1)} \rangle + \cdots + \langle \psi_n^{(1)} | \psi_n^{(i-1)} \rangle \right]$

We can next substitute the power series for H, E_n, $|\psi_n\rangle$ into the Schrödinger equation to determine the corresponding energy coefficients and states.

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

becomes

$$(H_0+\lambda\hat{H}')\sum_{i=0}^{\infty}\lambda^i|\psi_n^{(i)}\rangle$$

$$=\left(\sum_{j=0}^{\infty}\lambda^j\epsilon_n^{(j)}\right)\left(\sum_{i=0}^{\infty}\lambda^i|\psi_n^{(i)}\rangle\right),$$

That is

$$(H_0+\lambda\hat{H}')\left(|\psi_n^{(0)}\rangle+\lambda|\psi_n^{(1)}\rangle+\lambda^2|\psi_n^{(2)}\rangle+\cdots\right)$$

$$=\left(\epsilon_n^{(0)}+\lambda\epsilon_n^{(1)}+\lambda^2\epsilon_n^{(2)}+\cdots\right)\times$$

$$\times\left(|\psi_n^{(0)}\rangle+\lambda|\psi_n^{(1)}\rangle+\cdots\right).$$

Once again equating the same powers of λ we find

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

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

$\Rightarrow$

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

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

$\Rightarrow$

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

$\vdots$

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

$\Rightarrow$

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

$\vdots$

The λ^0 term $\Rightarrow$

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

Thus $|\psi_n^{(0)}\rangle$ is an eigenvector of H_0 with eigenvalue $\epsilon_n^{(0)}$. Thus $\epsilon_n^{(0)}$ belongs to the spectrum of H_0. This is expected since we assumed that each eigenvalue of H approached, as $\lambda \to 0$, one of the eigenvalues of $H|_{\lambda=0} = H_0$, an unperturbed energy.

So we choose a particular value for $\epsilon_n^{(0)}$; say

$$\epsilon_n^{(0)} = E_n^0 .$$

It could be that several energies $E = E(\lambda)$ approach E_n^0 as $\lambda \to 0$, the eigenstates of these $E(\lambda) \xrightarrow[\lambda \to 0]{} E_n^0$ span a vector subspace whose dimension is the degeneracy of E_n^0, g_n^0. If E_n^0 is non-degenerate, it can evolve only into one $E(\lambda)$ and this energy is non-degenerate.

For simplicity we consider first the case where E_n^0 is <u>non-degenerate</u>

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 λ is small enough so that for $\lambda \neq 0$ the eigenvalue remains non-degenerate. We denote this energy eigenvalue of $H = H(\lambda)$ by $E_n(\lambda) \xrightarrow[\lambda \to 0]{} E_n^0$. 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 λ^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 $\langle\varphi_n|$

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

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

and to first order in λ

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

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

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

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

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

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

We project the λ' equation into the unperturbed basis vectors orthogonal to $|\psi_n\rangle$ that is $\langle\psi_{m,\ell}|$ $m \neq n \Rightarrow$

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

Since

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

and

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

for $m \neq n$

we have

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

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

$\Rightarrow$

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

Now $\{|\varphi_{m,\ell}\rangle\}$ are a complete set so

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

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

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

Thus we have

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

from the norm & phase convention (page -847-)

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

Hence to order λ we have for the eigenvectors

$$\boxed{|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + O(\lambda^2)}$$

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

Note: 1) H' is said to "mix" the unperturbed state $|\varphi_n\rangle$ with all the other eigenstates of H_0. In general the closer E_m^0 is to E_n^0 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

$$\left|\frac{\langle\varphi_{m,\ell}|H'|\varphi_n\rangle}{E_n^0 - E_m^0}\right| << 1 \quad , \; m \neq n$$

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

attractive
Coulomb potential plus the e-e repulsive Coulomb potential

$$H = \frac{1}{2m}\vec{P}_1^2 + \frac{1}{2m}\vec{P}_2^2 - \frac{Ze^2}{|\vec{r}_1|} - \frac{Ze^2}{|\vec{r}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} .$$

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

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

While the perturbation is the e-e repulsion term

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

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

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

$n = 1s$

$$E_H = 13.6\ eV = \frac{me^4}{2\hbar^2}$$

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

$$a_0 = \frac{\hbar^2}{me^2} = 0.53\,\text{Å} = \text{Bohr radius}$$

For a nucleus with charge Ze this becomes $\frac{1}{\sqrt{\pi a^3}} e^{-r/a}$; $a = \frac{a_0}{Z}$. Thus the unperturbed ground state wavefunction for He is

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

(φ_n: 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

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

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

$$\times \underbrace{\langle \vec{r}_1, \vec{r}_2 | H' | \vec{r}_1', \vec{r}_2' \rangle} \langle \vec{r}_1', \vec{r}_2' | \varphi_n \rangle$$

$$= \delta^3(\vec{r}_1 - \vec{r}_1') \delta^3(\vec{r}_2 - \vec{r}_2') \times \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

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

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

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

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

Using $\dfrac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{k=0}^{\infty} \dfrac{r_<^k}{r_>^{k+1}} P_k(\cos\alpha)$

with $\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 \cos\alpha$ & $r_<$ = smaller of r_1, r_2
$r_>$ = larger of r_1, r_2

we find

$$I \equiv \int d^3r_1 d^3r_2 \frac{\rho_1(r_1)\rho_2(r_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \int_0^{2\pi} d\varphi_1 d\varphi_2 \int_0^{\pi} d\theta_1 d\theta_2 \int_0^{\infty} dr_1 dr_2 \, r_1^2 \sin\theta_1 \sin\theta_2 \times r_2^2$$

$$\times \rho_1(r_1)\rho_2(r_2) \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \frac{4\pi}{2k+1} \sum_{m=-k}^{+k} Y_k^{m*}(\theta_1,\varphi_1) \, Y_k^m(\theta_2,\varphi_2)$$

$$= P_k(\cos\alpha)$$

(addition theorem for spherical Harmonics)

but $(4\pi)^{-1/2} = Y_0^0(\theta,\varphi)$ so we can write the angular integrals as

$$\int d\Omega_2 \, Y_0^{0*}(\theta_2,\varphi_2) \, Y_k^m(\theta_2,\varphi_2) = \delta_{m0}\delta_{k0}$$

$$\int d\Omega_1 \, Y_k^{*m}(\theta_1,\varphi_1) \, Y_0^0(\theta,\varphi) = \delta_{m0}\delta_{k0}$$

hence we find

$$I = \int_0^{\infty} dr_1 dr_2 \, \rho_1(r_1)\rho_2(r_2) \frac{r_1^2 r_2^2}{r_>} (4\pi)^2$$

$$= 16\pi^2 \int_0^{\infty} dr_1 \, r_1 \rho_1(r_1) \left[\int_0^{r_1} dr_2 \, r_2^2 \rho_2(r_2) + r_1 \int_{r_1}^{\infty} dr_2 \, r_2 \rho_2 \right.$$

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

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

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

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

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

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

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

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

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

$= \left[-\frac{2}{\beta^3} e^{-\beta r_1} - \frac{r_1}{\beta^2} e^{-\beta r_1} - \frac{r_1}{\beta^2} e^{-\beta r_1}\right.$

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

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

$\left. - \frac{a^2 r_1}{2}e^{-2r_1/a} - \frac{r_1^2 a}{2}e^{-2r_1/a}\right]$

Combining these we find

$$I = \frac{16\pi^2}{\pi a^3}\int_0^\infty dr_1 \rho_1(r_1)\left\{\frac{r_1 a^3}{4}\right.$$

$$\left. - \frac{a^3 r_1}{4}e^{-2r_1/a} - \frac{a^2 r_1^2}{4}e^{-2r_1/a}\right\}$$

$$= \frac{4\pi^2}{\pi^2 a^6}\int_0^\infty dr\left[a^3 r - (a^3 r + a^2 r^2)e^{-2r/a}\right]e^{-2r/a}$$

$$= \frac{4}{a^6}\left\{\frac{a^5}{4} - \frac{a^5}{16} - \frac{a^5}{32}\right\}$$

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

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

$$= \frac{5}{4}Z E_H$$

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

Next we consider the higher order corrections to the energy eigenvalues

Recall the λ^2 term in the Schrödinger equation is

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

That is

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

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

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

and using the normalization conditions

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

we have

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

substituting for $|\psi_n^{(1)}\rangle$ yields (page -854-)

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

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

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

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

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

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

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

Example: Consider a SHO in one-dimension

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

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

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

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

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

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 <u>non-degenerate</u>

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

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

Since $g_m = 1$ and

$$\langle\psi_n|H|\psi_n\rangle = \langle\psi_n|H_0|\psi_n\rangle + \cancel{\langle\psi_n|H'|\psi_n\rangle}^{\to 0}$$

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

This reduces to

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

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

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

Now $E_n^0 - E_{n\pm3}^0 = \mp 3\hbar\omega$

$E_n^0 - E_{n\pm1}^0 = \mp 1\hbar\omega$

Thus we find using the above matrix elements of H'

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

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

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

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

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

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

6.1.2. 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 $|\varphi_{n,\ell}\rangle$, $\ell = 1, \ldots, g_n$. Since

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

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

and

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

below superscript 0 is dropped

When $\lambda \neq 0$, H' will act, in general to remove the degeneracy, part or all, of the E_n^0 eigenvalue. We can then use the first order Schrödinger equation to find $|\psi_n^{(0)}\rangle$. Recall this equation

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

with $\epsilon_n^{(0)} = E_n^0$ this is

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

Again, projecting this onto the $|\varphi_{n,\ell}\rangle$ state gives

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

$$\Rightarrow \langle\varphi_{n,\ell}|\hat{H}'|\psi_n^{(0)}\rangle = \epsilon_n^{(1)}\langle\varphi_{n,\ell}|\psi_n^{(0)}\rangle$$

Substituting the expansion for $|\psi_n^{(0)}\rangle$

$$|\psi_n^{(0)}\rangle = \sum_{\ell=1}^{g_n} a_{n\ell}|\varphi_{n,\ell}\rangle$$

with

$$a_{n\ell} = \langle\varphi_{n,\ell}|\psi_n^{(0)}\rangle$$

we have

$$\sum_{k=1}^{g_n} \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle \, 4_{nk} = \epsilon_n^{(1)} \, 4_{nl}$$

Defining the matrix elements of $\hat{H}'$ in this g_n-dimensional subspace as

$$\hat{H}'_{lk} \equiv \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle$$

we see this becomes of <u>matrix</u> eigenvalue equation

$$\boxed{\sum_{k=1}^{g_n} \hat{H}'_{lk} \, 4_{nk} = \epsilon_n^{(1)} \, 4_{nl}}$$

$(\hat{H}')_{lk}$ is a $g_n \times g_n$ matrix and the $(4_n)_l$ are components of a g_n-dimensional column vector, the eigenvectors of the matrix $(\hat{H}')_{lk}$ with eigenvalues $\epsilon_n^{(1)}$.

The eigenvalues $\epsilon_n^{(1)}$ of $(\hat{H}')_{lk}$ will give the $O(\lambda)$ energy shifts

for the n^{th} level. Hence we see that to determine the zeroth order eigenstates $|\psi_n^{(0)}\rangle$, i.e. $(\psi_n)_k$, and the first order energy shifts, i.e. $\epsilon_n^{(1)}$, we must solve the $g_n \times g_n$-matrix eigenvalue problem. Thus we need only to diagonalize the H' operator on the degenerate subspace spanned by the E_n^0 degenerate eigenvectors $|\psi_{n,\ell}\rangle$ in this order. We do not have to worry about mixing to the whole Hilbert space, only this degenerate subspace.

From a practical point of view we can most easily diagonalize H' restricted to this subspace by choosing a convenient set of basis vectors of H_0; $\{|\psi_{n,\ell}\rangle\}$. For instance if there is a Hermitian operator A that commutes with H_0 and H'

$$[H_0, A] = 0 = [H', A],$$

then the $|\psi_{n,k}\rangle$ should also be

chosen to be its eigenstates (since $[A, H_0] = 0$ this is allowed)

$$A|\varphi_{n,l}\rangle = a_l |\varphi_{n,l}\rangle .$$

Since $[A, H'] = 0 \Rightarrow$

$$\langle \varphi_{n,l} | [A, \hat{H}'] | \varphi_{n,k} \rangle = 0$$

$$= (a_l - a_k) \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle$$

$$\Rightarrow \quad (\hat{H}')_{lk} = \langle \varphi_{n,l} | \hat{H}' | \varphi_{n,k} \rangle = 0$$

unless $l = k$, that is $(\hat{H}')_{lk}$ is automatically diagonal in this basis. Of course, often the case is not this, but that $[A, H'] \neq 0$ and we must work to diagonalize $(H')_{lk}$.

If the energy shift eigenvalues $E_n^{(1)}$ are all different, the degenerate energy level E_n^0 has been completely split by H' at first order.

The $|\psi_n^{(0)}\rangle$, i.e. ψ_{nl}, are completely determined (up to normalization). We can now use the non-degenerate perturbation theory techniques to calculate all the higher order effects.

On the other hand, it could be that not all of the g_n-fold degeneracy of E_n^0 is removed. It could be that some or even all of the g_n eigenvalues $\epsilon_n^{(1)}$ are the same. We can label the different eigenvalues $\epsilon_n^{(1)}$ by $\epsilon_{nj}^{(1)}$ with $j = 1, \ldots, f_n^{(1)}$ where $f_n^{(1)} \leq g_n$. If $f_n^{(1)} = g_n$ we have g_n distinct energy shifts — the degeneracy is completely removed. If $f_n^{(1)} < g_n$, the degeneracy, to first order, is only partially removed (if $f_n^{(1)} = 1$, the degeneracy is not removed at all).

So again we now choose a particular $\epsilon_{nj}^{(1)}$. If $\epsilon_{nj}^{(1)}$ is non-degenerate then corresponding

eigenvector ψ_{nk} ($|\psi_n^{(0)}\rangle$) is uniquely determined and we proceed to higher orders via non-degenerate perturbation theory.

If $\epsilon_{nj}^{(1)}$ is g_{nj}-fold degenerate we now must consider diagonalizing the g_{nj}-dimensional problem. That is $|\psi_n^{(0)}\rangle$ now belongs to a g_{nj}-dimensional subspace of the original g_n-dimensional subspace and we must proceed to 2nd order perturbation theory to determine the $|\psi_n^{(0)}\rangle$ in terms of the $|\psi_{n,k}\rangle$.

To be specific, let's consider the case where $f_{nj}^{(1)} = 1$, that is H' in first order does not remove any of the g_n-fold degeneracy of E_n^0. Thus $\langle\psi_{n,k}|H'|\psi_{n,l}\rangle$ has only one eigenvalue $\epsilon_n^{(1)}$ and it occurs g_n times. As is often the case and to simplify the ensuing notation we can realize this by assuming that H' vanishes between the g_n - E_n^0 eigenstates.

Let $$\langle\psi_{n,k}|H'|\psi_{n,l}\rangle = 0.$$

So the eigenvalue $\epsilon_n^{(1)} = 0$ and the $|\psi_{nk}\rangle$ are undetermined in 1st order.

This being the case consider the λ^2 Schrödinger equation

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

As usual we project this onto the g_n-dimensional subspace spanned by $\{|\varphi_{n,k}\rangle \; k = 1, \ldots, g_n\}$

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

$$\Rightarrow \boxed{\langle\varphi_{n,k}|\hat{H}'|\psi_n^{(1)}\rangle = \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle}$$

Inserting a complete set of states on the LHS

$$1 = \sum_{k=1}^{g_n} |\varphi_{n,k}\rangle\langle\varphi_{n,k}| + \sum_{m\neq n}\sum_{k=1}^{g_m} |\varphi_{m,k}\rangle\langle\varphi_{m,k}|$$

we find

$$\sum_{l=1}^{g_n} \langle \varphi_{n,k} | \hat{H}' | \varphi_{n,l} \rangle \langle \varphi_{n,l} | \psi_n^{(1)} \rangle$$

$$+ \sum_{m \neq n} \sum_{l=1}^{g_m} \langle \varphi_{n,k} | \hat{H}' | \varphi_{m,l} \rangle \langle \varphi_{m,l} | \psi_n^{(1)} \rangle$$

$$= \epsilon_n^{(2)} \langle \varphi_{n,k} | \psi_n^{(0)} \rangle$$

but $\langle \varphi_{n,k} | \hat{H}' | \varphi_{n,l} \rangle = 0$ by assumption,

Thus

$$\boxed{\sum_{m \neq n} \sum_{l=1}^{g_m} \langle \varphi_{n,k} | \hat{H}' | \varphi_{m,l} \rangle \langle \varphi_{m,l} | \psi_n^{(1)} \rangle = \epsilon_n^{(2)} \langle \varphi_{n,k} | \psi_n^{(0)} \rangle}$$

To continue further we need the components of $|\psi_n^{(1)}\rangle$ in the space orthogonal to the g_n dimensional subspace. As usual this can be determined from the λ^1 equation projected onto this complementary space spanned by the $\{|\varphi_{m,l}\rangle ; m \neq n\}$. The λ^1 Schrödinger equation is

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

Projecting onto $|\varphi_{m,\ell}\rangle$

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

Since $E_m^0 \neq E_n^0$ we find

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

Thus we obtain an eigenvalue equation

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

$$= \epsilon_n^{(2)}\langle\varphi_{n,k}|\psi_n^{(0)}\rangle$$

Recalling that $|\psi_n^{(0)}\rangle = \sum_{j=1}^{g_n} a_{nj}|\varphi_{nj}\rangle$

we finally secure the matrix eigenvalue equation

$$\sum_{j=1}^{g_n} \underbrace{\left\{ \sum_{m\neq n}^{} \sum_{l=1}^{g_m} \frac{\langle \varphi_{n,k} | \hat{H}' | \varphi_{m,l} \rangle \langle \varphi_{m,l} | \hat{H}' | \varphi_{n,j} \rangle}{E_n^0 - E_m^0} \right\}}_{\equiv \left(\hat{H}'_{(2)}\right)_{kj}} \psi_{nj} = \epsilon_n^{(2)} \psi_{nk}$$

Thus

$$\sum_{j=1}^{g_n} \left(\hat{H}'_{(2)}\right)_{kj} \psi_{nj} = \epsilon_n^{(2)} \psi_{nk}$$

we obtain a $g_n \times g_n$ matrix eigenvalue equation for the second order energy shifts $\epsilon_n^{(2)}$ and zeroth order eigenstate ψ_{nk}. In secondorder we see that $\left(\hat{H}'_{(2)}\right)_{kj}$ now has in it information about the matrix elements of $\hat{H}'$ between the complementary subspaces $m \neq n$.

In first order, we only had $\hat{H}'$ connecting states in the g_n-dimensional degenerate subspace. Clearly, this gets complicated rapidly.

As previously, the eigenvalues $E_n^{(2)}$ are the second order energy shifts. If we have g_n different eigenvalues, then the E_n^0 degeneracy is completely broken in 2nd order. If some of the $E_n^{(2)}$ eigenvalues remain degenerate, we must proceed to third order perturbation theory to try to remove it. For the non-degenerate $E_n^{(2)}$ eigenvalues, we can proceed to higher order calculations using the non-degenerate perturbation theory techniques.

All degenerate energies or close to them (i.e. where $(E_n^0 - E_m^0)^{-1}$ gets very large) the Rayleigh-Schrödinger perturbation scheme is quite complicated. As well, higher order expressions for the energy levels and eigenstates become cumbersome. So we would like to introduce a new scheme, that of Brillouin and Wigner that, first, will generalize to higher order more simply than the R-S scheme.

Second the R-S scheme is

messy near or at degenerate energy levels, the B-W scheme will handle these cases more simply.

6.2. Brillouin-Wigner Stationary State Perturbation Theory

As we saw above, the unperturbed energy differences in denominators led to a breakdown of the non-degenerate R-S perturbation theory at or close to degenerate energy levels. In general then we would like to avoid such denominators. At the same time, we would like to develop a general expression for the eigenvalue equations, applicable even in the degenerate case. Recall in that case we must determine which vectors the $|\psi_n\rangle$ go into at $\lambda = 0$.

Thus we can first consider an expansion not in $\frac{1}{E_n^0 - E_m^0}$ but $\frac{1}{E_n - E_n^0}$, which does not blow up at degenerate values, since we assume $E_n \neq E_n^0$.