

PH410 LECTURE 25

From Wednesday: $\hat{H} = \hat{H}_0 + \hat{H}'$ H_0 solutions known, \hat{H}' small.

$$\text{If } |n\rangle = |n^{(0)}\rangle + |n^{(1)}\rangle + |n^{(2)}\rangle + \dots$$

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

Can calculate by perturbation equation:

$$\hat{H}_0 |n^{(k)}\rangle + \hat{H}' |n^{(k-1)}\rangle = E_n^{(0)} |n^{(k)}\rangle + E_n^{(1)} |n^{(k-1)}\rangle + \dots + E_n^{(k)} |n^{(0)}\rangle$$

So one starts by solving for $E_n^{(1)}$, then $|n^{(1)}\rangle$, then $E_n^{(2)}$, then $|n^{(2)}\rangle$.

To get $E_n^{(k)}$ take inner product with $|n^{(0)}\rangle$:

$$\langle n^{(0)} | \hat{H}_0 |n^{(k)}\rangle + \langle n^{(0)} | \hat{H}' |n^{(k-1)}\rangle = \sum_{j=0}^k E_n^{(j)} \langle n^{(0)} | n^{(k-j)} \rangle = S_{kj}$$

$$E_n^{(0)} \langle n^{(0)} | n^{(k)} \rangle + \langle n^{(0)} | \hat{H}' |n^{(k-1)}\rangle = E_n^{(k)}$$

$\searrow \delta_{k0}$

$$\text{so } E_n^{(k)} = \langle n^{(0)} | \hat{H}' |n^{(k-1)}\rangle \text{ for } k > 0.$$

First order very easy: $E_n^{(1)} = \langle n^{(0)} | \hat{H}' |n^{(0)}\rangle$ ← just expectation value of \hat{H}' for $|n^{(0)}\rangle$.

For second order energy correction, need to find $|n^{(1)}\rangle$, in the H_0 basis. Project the perturbation equation with $\langle m^{(0)} |$ in n , remembering $\langle m^{(0)} | \hat{H}_0 = E_m^{(0)} \langle m^{(0)} |$.

$$\langle m^{(0)} | \hat{H}_0 |n^{(1)}\rangle + \langle m^{(0)} | \hat{H}' |n^{(0)}\rangle = E_n^{(0)} \langle m^{(0)} | n^{(1)}\rangle + E_n^{(1)} \langle m^{(0)} | n^{(0)}\rangle$$

$$E_m^{(0)} \langle m^{(0)} | n^{(1)}\rangle + \langle m^{(0)} | \hat{H}' |n^{(0)}\rangle = E_n^{(0)} \langle m^{(0)} | n^{(1)}\rangle$$

$$\langle m^{(0)} | n^{(1)} \rangle = \frac{\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n$$

so to first order

$$|n\rangle \approx |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

Now we can calculate $E^{(2)}$:

$$\begin{aligned} E^{(2)} &= \langle n^{(0)} | \hat{H}' | n^{(1)} \rangle \\ &= \sum_{m \neq n} \langle n^{(0)} | \hat{H}' | m^{(0)} \rangle \frac{\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \\ &= \sum_{m \neq n} \frac{|\langle n^{(0)} | \hat{H}' | m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}} \end{aligned}$$

So to 2nd order

$$E_n \approx E_n^{(0)} + \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle + \sum_{m \neq n} \frac{|\langle n^{(0)} | \hat{H}' | m^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

So ~~by~~ by "calculate" these corrections we mean "express entirely in \hat{H}^0 eigenstates & eigenvalues." In general, start with 1st order and stop when corrections are small enough that you are satisfied with the accuracy. (or the ~~series~~ corrections start to grow — a sign of a diverging series).

Easy example: anharmonic oscillator: $\hat{H}_0 = \frac{1}{2} p^2 + \frac{1}{2} x^2 + \epsilon x^4$
($\hbar = m = \omega = 1$). Treat ϵx^4 as perturbation \hat{H}' , $\epsilon \ll 1$.

$$E_n = E_n^{(0)} + e \langle n^{(0)} | \hat{X}^4 | n^{(0)} \rangle$$

$$\text{where } \hat{X}^4 = \frac{1}{2} (\hat{a} + \hat{a}^\dagger)^4$$

$$\text{so } \hat{X}^4 | n^{(0)} \rangle$$

$$= \frac{1}{2} (\hat{a} + \hat{a}^\dagger) (\hat{a} + \hat{a}^\dagger) (\hat{a} + \hat{a}^\dagger) (\hat{a} + \hat{a}^\dagger) | n^{(0)} \rangle$$

only terms proportional to $\hat{a}^k \hat{a}^{\dagger k}$ or $\hat{a}^{\dagger k} \hat{a}^k$ will yield ~~non-zero~~ a state non-orthogonal to $|n^{(0)}\rangle$!

$$\text{Answer turns out to be } E_n^{(1)} = e \frac{3}{4} (2n^2 + 2n + 1) -$$

Helium ground state: Coulomb repulsion of electrons.

$$\hat{H}_0 = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - Ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right), \quad \hat{H}' = \frac{e^2}{r_{12}}$$

Use product of 2 "hydrogenic" ground states as $\langle \vec{r}_1, \vec{r}_2 | 0^{(0)} \rangle$:

$$\psi^{(0)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\pi a^3} e^{-(r_1+r_2)/a} \left(\frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \right) \quad \alpha = \frac{a_0}{Z}$$

Zeroth order energy is $E^{(0)} = -2Z^2 R_y$ where $1 R_y = 13.6 \text{ eV}$.

$$E^{(1)} = \langle 0^{(0)} | \hat{H}' | 0^{(0)} \rangle = \int d^3r_1 d^3r_2 |\psi^{(0)}|^2 \frac{e^2}{r_{12}} = e^2 \int d^3r_1 \int d^3r_2 \frac{\rho(r_1)\rho(r_2)}{r_{12}}$$

where $\rho(r) = e^{-2r/a}$ prob. density.

Hard to evaluate: $r_{12} = |\vec{r}_1 - \vec{r}_2|$.

Can do with an expansion trick:

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \frac{r_l^l}{r_l^{l+1}} P_l(\cos \theta) \quad \text{where } r_l = \min(r_1, r_2) \quad r_s = \max(r_1, r_2)$$

angle between \vec{r}_1, \vec{r}_2

$$\cos \theta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 r_2}$$

Don't worry about that math trick — won't be used again.

To handle integrals, take fixed \vec{r}_1 : for r_2 integration write

$$d\vec{r}_2 = r_2^2 dr_2 d\phi_2 d\cos\theta \quad \text{where } \cos\theta = \frac{\vec{r}_1 \cdot \vec{r}_2}{r_1 r_2}, \text{ i.e. the}$$

$\cos\theta$ in the $\frac{1}{r_{12}}$ expansion. Now: use orthogonality of the Legendre polynomials $\int_{-1}^1 d\cos\theta P_l(\cos\theta) = 2\delta_{l0}$.

Now the big angular integration vanishes except for $l=0$ term in the expansion! So

$$E^{(1)} = 16\pi^2 e^2 \int_0^\infty dr_1 r_1^2 \rho(r_1) \left[\int_0^{r_1} r_2^2 dr_2 \rho(r_2) \frac{1}{r_1} + \int_{r_1}^\infty r_2^2 dr_2 \rho(r_2) \frac{1}{r_2} \right]$$

The integrals are straightforward but tedious.

$$E^{(1)} = \frac{5}{4} Z R_y.$$

Look at this vs. experiment: For Helium, $Z=2$.

$$E^{(0)} = -8 R_y = -108 \text{ eV}$$

$$E^{(1)} = \frac{5}{2} R_y = +34 \text{ eV}$$

so to first order $E \approx -74 \text{ eV}$. Experimentally, it's -78.6 eV .

Pretty close!

For beryllium Be^{++} with 2 electrons, $E^{(0)} = -2(4^2) R_y = -32 R_y = -433 \text{ eV}$.

$$E^{(1)} = 5 R_y = +67 \text{ eV} \Rightarrow E \approx -366 \text{ eV}$$

Experimentally, $E = -370 \text{ eV} \rightarrow \sim 1\% \text{ off!}$ Note that the perturbation scales as Z but $E^{(0)}$ as Z^2 — so the corrections shrink at higher Z .

Note that our corrected energy $(E^{(0)} + E^{(1)})$ is always above the true ground state energy. This is not a coincidence!

Recall that $E_0^{(0)} + E_0^{(1)} = \langle 0^{(0)} | \hat{H}^0 | 0^{(0)} \rangle + \langle 0^{(0)} | \hat{H}' | 0^{(0)} \rangle$
 $= \langle 0^{(0)} | \hat{H} | 0^{(0)} \rangle$

So if $|0^{(0)}\rangle$ is the true ground state, then $E_0^{(0)} + E_0^{(1)}$ is the true ground state energy (actually $|0^{(1)}\rangle = 0$). If not, then the variational principle says $\langle 0^{(0)} | \hat{H} | 0^{(0)} \rangle \geq \text{true } E_0$.

Degenerate perturbation theory.

Recall that $|n\rangle \approx |n^{(0)}\rangle + \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$

which obviously is not valid when $E_n^{(0)} = E_m^{(0)}$ — i.e. if \hat{H}^0 has degenerate eigenvalues.

Could get around this problem if we can make the numerator vanish whenever the denominator does. Since the denominator only vanishes for degenerate eigenvalues, we only have to modify our procedures for those subspaces. Concentrate on each degenerate eigenvalue separately:

Note that the numerator $\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle$ ~~is~~ is independent of diagonal matrix element since it only appears in an $m \neq n$ sum. So the solution is to diagonalize the perturbing Hamiltonian in the degenerate subspace.

Given an \hat{H}^0 with a q -fold degeneracy, the subspace of the Hilbert space corresponding to states with that eigenvalue $E_n^{(0)}$ is a q -dimensional subspace. — the degenerate subspace.

i.e. an $n=2$ hydrogen atom has an 8-fold degeneracy spanned by $|n=2, l, m_l, m_s\rangle$. Now, the operator \hat{H}' actually commutes with \hat{H}^0 in this degenerate subspace. (So do all operators, actually!).

So we must find a basis where \hat{H}' is diagonal in this subspace.