

Lecture 1

Time independent perturbation theory.

The essence of the method: split Hamiltonian into 2 parts = $H_0 + H_1$,

where H_0 is large and exactly solvable \equiv unperturbed part

and $H_1 \equiv$ perturbation. Changes in eigen states and eigenvalues is treated as a power series in the perturbation parameter

Let's develop this calculation scheme for non degenerate and degenerate case separately.

A. Non-degenerate case: or 1 eigenstate has one eigenvalue.

$H(\lambda) = H^{(0)} + H^{(1)}\lambda$, we solve $H\Phi_n = E_n\Phi_n$
 $(H^{(0)} + H^{(1)}\lambda)\Phi_n = E_n\Phi_n$, if $\lambda=0$ $H^{(0)}\Phi_n^{(0)} = E_n^{(0)}\Phi_n^{(0)}$

We assume we do know $\langle \Phi_n^{(0)} |$ and $E_n^{(0)}$

Our goal is to express the complete solution as:

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

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

For simplicity let's work out it for $(E_n^{(1)}, \Phi_n^{(1)})$ (1st and 2^d order perturbations)

$H\psi = E\psi$

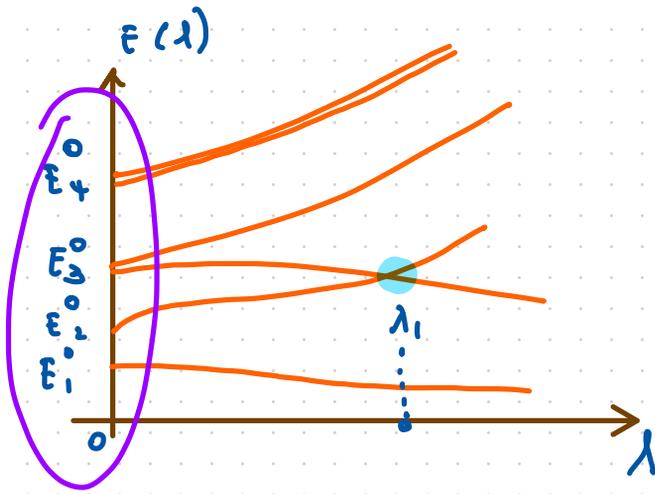
$$[H^{(0)} + \lambda H^{(1)}] [\Phi_n^{(0)} + \lambda \Phi_n^{(1)} + \lambda^2 \Phi_n^{(2)} + \dots] = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (\Phi_n^{(0)} + \lambda \Phi_n^{(1)} + \lambda^2 \Phi_n^{(2)} + \dots)$$

All the terms with equal power in λ should be set to 0.

λ^0 : $H^{(0)}\Phi_n^{(0)} = E_n^{(0)}\Phi_n^{(0)}$

λ^1 : $H^{(0)}\Phi_n^{(1)} + H^{(1)}\Phi_n^{(0)} = E_n^{(0)}\Phi_n^{(1)} + E_n^{(1)}\Phi_n^{(0)}$

λ^2 : $H^{(0)}\Phi_n^{(2)} + H^{(1)}\Phi_n^{(1)} = E_n^{(0)}\Phi_n^{(2)} + E_n^{(1)}\Phi_n^{(1)} + E_n^{(2)}\Phi_n^{(0)}$

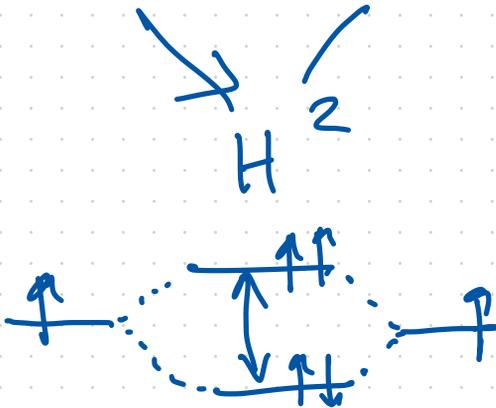


for $H(\lambda) = H_0 + \lambda H_1$
 $\lambda \ll 1$

Application of perturbation usually removes DEGENERACY but it may introduce accidental new degeneracies (e.g. at $\lambda = \lambda_1$)

$$E_0 \frac{H}{+}$$

$$\frac{H}{+} E_0$$



We assume we know the exact solution of the unperturbed case i.e.

$$H^{(0)} \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)}$$

Lets solve for $\psi^{(1)}$, for this purpose we select the basis vectors $|\phi_m^{(0)}\rangle \equiv \phi_m^{(0)}$ and as such

$$\phi_n^{(1)} = \sum_m C_m^{(1)} \phi_m^{(0)}$$

We can do this

since the basis vectors $\phi_m^{(0)}$ are known and they are good (orthogonal etc.) unit like

order

$$\sum C_m^{(1)} H^{(0)} \phi_m^{(0)} + H^{(1)} \phi_n^{(0)} = E_n^{(0)} \sum C_m^{(1)} \phi_m^{(0)} + E_n^{(1)} \phi_n^{(0)} \Rightarrow$$

$$\int \phi_r^{(0)*} \left[\sum C_m^{(1)} (E_m^{(0)} - E_n^{(0)}) \phi_m^{(0)} \right] = (E_n^{(1)} - H^{(1)}) \phi_n^{(0)}$$

$$\int \phi_r^{(0)*} \sum_m C_m^{(1)} (E_m^{(0)} - E_n^{(0)}) \phi_r^{(0)} \phi_m^{(0)} = \int \phi_r^{(0)*} (E_n^{(1)} - H^{(1)}) \phi_n^{(0)}$$

$$C_r^{(1)} (E_r^{(0)} - E_n^{(0)}) = E_n^{(1)} \delta_{rn} - H_{rn}^{(1)}$$

here $H_{rn}^{(1)} = \int_{-\infty}^{\infty} \phi_r^{(0)*} H^{(1)} \phi_n^{(0)} dV$

and $\int_{-\infty}^{\infty} \phi_r^{(0)*} \phi_m^{(0)} dV = \delta_{rm}$

To determine $E_n^{(1)}$ set $r=n$

$$C_n^{(1)} (E_n^{(0)} - E_n^{(0)}) = E_n^{(1)} = \langle \phi_n^{(0)} | H^{(1)} | \phi_n^{(0)} \rangle \Rightarrow$$

$$E_n^{(1)} = \langle \phi_n^{(0)} | H^{(1)} | \phi_n^{(0)} \rangle \equiv H_{nn}^{(1)}$$

And for eigenstates: $C_m^{(1)}$ if $r \neq n$

$$C_r^{(1)} = \frac{E_n^{(1)} \delta_{rn} - H_{rn}^{(1)}}{E_r^{(0)} - E_n^{(0)}} = \frac{H_{nr}^{(1)} \delta_{rn} - H_{rn}^{(1)}}{E_r^{(0)} - E_n^{(0)}} = 0$$

$r \neq n$

$$C_r^{(1)} = \frac{-H_{rn}^{(1)}}{E_r^{(0)} - E_n^{(0)}} = \frac{H_{nr}^{(1)}}{E_n^{(0)} - E_r^{(0)}} = \frac{\langle \phi_r^{(0)} | H^{(1)} | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_r^{(0)}}$$

Notice that we can write down

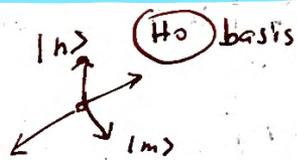
$$\Phi_n^{(s)} = \Phi_n^{(s)} + \Phi_n^{(0)} \quad \text{since } \Phi_n^{(0)} \text{ are orthogonal}$$

So all our equations for $E_n^{(1)}$ and $C_r^{(1)}$ remain the same.

Recall that: $\Phi_n = \Phi_n^{(0)} + \lambda \Phi_n^{(1)} + \lambda^2 \Phi_n^{(2)} + \dots$

$$\begin{cases} \Phi_n \approx \Phi_n^{(0)} + \lambda \Phi_n^{(1)} = \Phi_n^{(0)} + \lambda \sum_{m \neq n} \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \Phi_m^{(0)} \\ E_n \approx E_n^{(0)} + \lambda H_{nn}^{(1)} \leftarrow \langle n | H^{(1)} | n \rangle \text{ ground state} \\ \text{with } \lambda H_{mn}^{(1)} \ll |E_n^{(0)} - E_m^{(0)}| \end{cases}$$

$$|\Phi_n\rangle \approx |\Phi_n^{(0)}\rangle + \lambda \sum_{m \neq n} \frac{\langle \Phi_m^{(0)} | H^{(1)} | \Phi_n \rangle}{E_n^{(0)} - E_m^{(0)}}$$



$\langle m | H^{(1)} | n \rangle$ between the basis states of $H^{(0)}$

In other words the change in the energy caused by $H^{(1)}$ should be much smaller than the distance between levels $|E_n^{(0)} - E_m^{(0)}|$

So the perturbation doesn't have to be small itself, it needs

to be much smaller than spacing between the states of the unperturbed (ground state) hamiltonian

$$E = E_0 + E^{(1)} + E^{(2)} + \dots$$

For the second order we get

$$E_n^{(2)} = \sum_{n \neq m} C_m^{(1)} H_{nm}^{(1)} = \sum_{n \neq m} \frac{|H_{nm}^{(1)}|^2}{(E_n^{(0)} - E_m^{(0)})}$$

This will be a part of your 1st home work.

NOTICE

1. The ground state is lowered in the 2nd order. since $\frac{1}{E_n^{(0)} - E_m^{(0)}} < 0$
2. Energies are pushed apart in the 2nd order.
3. Blc of $\frac{1}{E_n^{(0)} - E_m^{(0)}}$ if $E_n^{(0)} \approx E_m^{(0)}$ the change is huge

One of the problems with $n=2$ and up is that we need to do summation over the infinite series. Enter the Dalgarno and Lewis method.

Read pp. 336-337 of the textbook.

Here I just quote the final result:

if $H^{(1)}$ contains no differential operator:

$$E_n^{(2)} = \langle n | H^{(1)} \cdot F_n | n \rangle - E_n^{(1)} \langle n | F_n | n \rangle$$

$$E_n^{(3)} = \langle n | F_n H^{(1)} \cdot F_n | n \rangle - 2 E_n^{(2)} \langle n | F_n | n \rangle - E_n^{(1)} \langle n | F_n | n \rangle$$

$$\langle m | F_n | n \rangle = \frac{H_{mn}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \quad m \neq n$$

By looking at $E_n^{(2)}$ we see we need only calculate 2 integrals instead of ∞ !

i.e. $\langle n | H^{(1)} F_n | n \rangle$ and $\langle n | F_n | n \rangle$

see pp. 336-337

Q: The question is what to do with F_n ?

A: This method works superbly well if

$H^{(1)}$ the perturbation has no differential term(s). In this case

$$F_n(x) = \int_x \frac{1}{|\psi_n^{(0)}|^2} \left\{ \frac{2n}{\hbar} \int_a^x (H^{(1)} - E_n^{(1)}) \cdot (\psi_n^{(0)})^2 dx \right\} dx$$

Let's work out the problem of particle in the box $H = H^{(0)} + H^{(1)}$ where

$$H^{(0)} = \frac{p^2}{2m} + V(x) = \begin{cases} 0 & |x| \leq \frac{\pi}{2} \\ \infty & |x| > \frac{\pi}{2} \end{cases}$$



a is where $\psi_n^{(0)}(a) = 0$
some value

and we will apply a perturbation

$$H^{(1)} = \begin{cases} \alpha x & |x| \leq \pi/2 \\ 0 & |x| > \pi/2 \end{cases}$$

The gradient field

LI

Recall from your QM the unperturbed states are:

$\psi \phi_0^{(0)} = \sqrt{\frac{2}{\pi}} \cos x$ $\psi \phi_1^{(0)} = \sqrt{\frac{2}{\pi}} \sin 2x$
 $\psi \phi_3^{(0)} = \sqrt{\frac{2}{\pi}} \sin 4x$ $\psi E_n^{(0)} = (n+1)^2 \frac{\hbar^2}{2m}$

Lets apply the D-L method: For the ground state \rightarrow

$\rightarrow F_0(x) = \frac{2m\alpha}{\hbar^2} \int_a^x \frac{1}{\cos^2 \xi} \left(\int_a^\xi \cos^2 \zeta d\zeta \right) dx =$
 $= \frac{\alpha m}{\hbar^2} \int_x \sec^2 x \left[\frac{\xi^2}{2} + \frac{1}{4} (2\xi \sin 2\xi + \cos 2\xi) \right]_a^x dx$ *↑ integration by parts*
 $= \frac{\alpha m}{2\hbar^2} \int_x \left[x^2 \sec^2 x + 2x \tan x + 1 - \frac{1}{2} \sec^2 x - \sec^2 x \left(a^2 + a \sin 2a + \frac{1}{2} \cos 2a \right) \right] dx$

$\phi_0^{(0)}(a) = 0 \Rightarrow \sqrt{\frac{2}{\pi}} \cos(a) = 0 \Rightarrow a = \pm \pi/2$

$F_0^{a=\pi/2}(x) = F_0^{a=-\pi/2}(x) = \frac{\alpha m}{2\hbar^2} \left[\left(x^2 - \frac{\pi^2}{4} \right) \tan x + x \right]$

↑ proof this!

Direct calculation:
 $E_0^{(2)} = \frac{\langle 0 | H^{(1)} | 0 \rangle \langle 1 | H^{(1)} | 0 \rangle}{E_0^{(0)} - E_1^{(0)}} + \frac{\langle 0 | H^{(1)} | 2 \rangle \langle 2 | H^{(1)} | 0 \rangle}{E_0^{(0)} - E_2^{(0)}} + \dots$

$= \frac{\langle 0 | H^{(1)} | 1 \rangle}{E_0^{(0)} - E_1^{(0)}} = \frac{\int_{-\pi/2}^{\pi/2} \sqrt{\frac{2}{\pi}} \cos x \cdot \alpha x \cdot \sqrt{\frac{2}{\pi}} \sin 2x dx}{\left(\frac{\hbar^2}{2m} - \frac{4\hbar^2}{2m} \right)}$

$= \frac{\int_{-\pi/2}^{\pi/2} \sqrt{\frac{2}{\pi}} \sin 2x dx}{-3\hbar^2/2m} = -\frac{32\alpha}{27\pi}$; Finally

$E_0^{(2)} = \frac{\langle 0 | H^{(1)} | 1 \rangle \langle 1 | H^{(1)} | 0 \rangle}{E_0^{(0)} - E_1^{(0)}} + \dots = \frac{2^9 \alpha^2 m}{3^5 \pi^2 \hbar^2} + \dots$

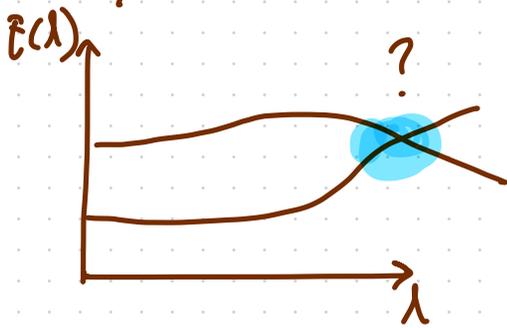
Next $\langle 0 | F_0 | 2 \rangle = 0$ and $\langle 0 | F_0 | 3 \rangle = 2^6 \alpha m \pi / 3^5 \hbar^2$

$E_0^{(2)} = -\frac{2^9 \alpha^2 m}{3^5 \pi^2 \hbar^2} - \frac{2^6 \alpha^2 m}{3^5 \pi^2 \hbar^2} \approx -\frac{2.1097 \alpha^2 m}{\hbar^2 \pi^2}$ (D-L Method)

Exact correction: $E_0^{(2)} = \frac{\alpha^2 m}{\hbar^2 \pi^2} \int_{-\pi/2}^{\pi/2} x \left[\left(x^2 - \frac{\pi^2}{4} \right) \tan x + x \right] \cos^2 x dx = -\frac{(15-\pi^2) \pi^2 \alpha^2 m}{24 \hbar^2 \pi^2}$

Perturbation theory for 2-level systems.

Some very interesting situations arise when we consider what happens when $H^{(1)}$ drives the system to the case:



- Is it possible that levels will cross?
- and when/if they do

what happens to the system? Let's look at the solution of the Schrödinger eqn:

$$(H_0 + H^1) \psi = E \psi$$

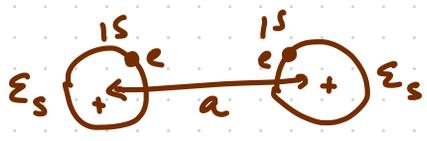
in the form of a superposition of states with 2 adjacent levels:

THEORY OF SMALL MOLECULES

$$\sum_{\alpha} \langle n | H | n \rangle U_{\alpha} - E U_{\alpha} = 0 \rightarrow \det(H_{nn} - E \delta_{nn}) = 0$$

↑
 $\langle n | H | n \rangle$

For a 2-state problem $|1\rangle$ and $|2\rangle$
e.g. Hydrogen 1s state



interaction

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0$$

Let's call total energy of atom 1 = ϵ_s
2 = ϵ_s

$$\begin{pmatrix} \epsilon_s - E & V_2 \\ -V_2 & \epsilon_s - E \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0 \Rightarrow \det() = 0$$

Some definitions

$$E = \frac{H_{11} + H_{22} \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}H_{21}}}{2}$$

COVALENT ENERGY

$$V_2 \equiv -H_{12} = -H_{21} > 0$$

if $H_{11} - H_{22} \gg H_{12}$
 $\epsilon_b \approx H_{11} + \frac{H_{12}H_{21}}{H_{11} - H_{22}}$

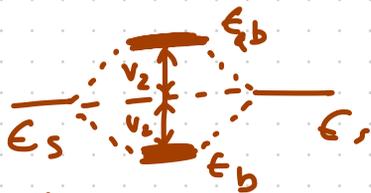
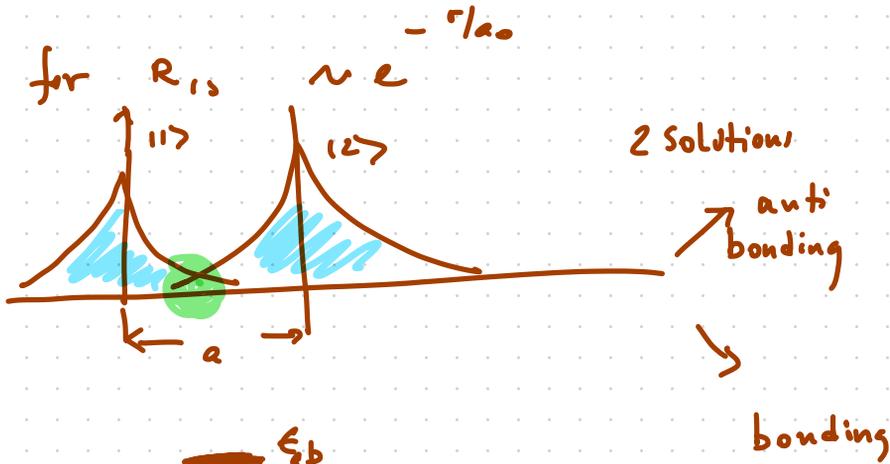
bonding energy = $\epsilon_b = \epsilon_s - V_2$

anti-bonding energy = $\epsilon_{ab} = \epsilon_s + V_2$

$$E = \begin{cases} \epsilon_s - V_2 \\ \epsilon_s + V_2 \end{cases} \quad \text{and}$$

$$\begin{aligned} (U_1, U_2) &= (2)^{-1/2} \\ (U_1, -U_2) &= (2)^{1/2} \end{aligned}$$

What's physical meaning?



↳ Homopolar molecule formation.

What happens for NaCl?
or HETEROPOLAR MOLECULE

$$\begin{pmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0$$

$$\begin{aligned} \text{Na} &\equiv \epsilon_s^1 \\ \text{Cl} &\equiv \epsilon_s^2 \end{aligned}$$

$$\begin{pmatrix} \epsilon_s^1 - E & v_2 \\ -v_2 & \epsilon_s^2 - E \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = 0 \Rightarrow$$

let's introduce

$$v_3 = \frac{\epsilon_s^2 - \epsilon_s^1}{2}$$

POLAR ENERGY

and average cation-anion energy $\bar{\epsilon} = \frac{\epsilon_s^1 + \epsilon_s^2}{2}$

we get

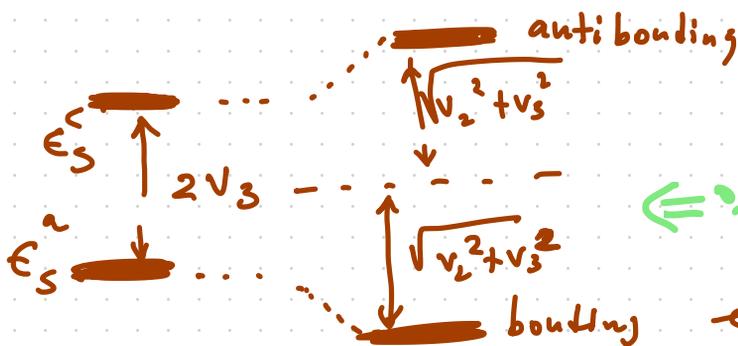
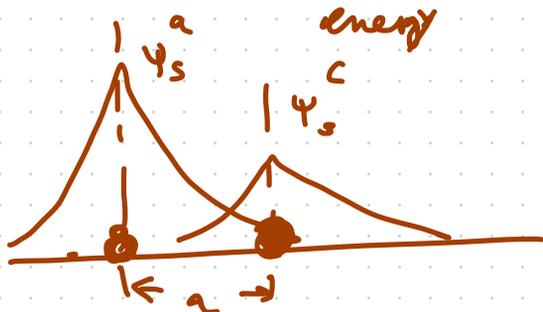
$$\begin{pmatrix} \bar{E} - V_3 - E & V_2 \\ -V_2 & \bar{E} + V_3 - E \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0$$

det = 0

=>

$$E_{a,b} = \bar{E} \pm \sqrt{V_2^2 + V_3^2}$$

\uparrow average energy \uparrow covalency \uparrow energy difference = polar energy



HW.

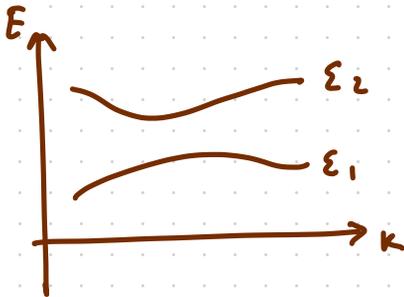
Determine eigenstates!
 of the polar molecule

express your

$$\alpha_p = \frac{V_3}{\sqrt{V_2^2 + V_3^2}}$$

Answer in terms of polarity and covalency $\alpha_c = V_2 / \sqrt{V_2^2 + V_3^2}$

THE STARK EFFECT in the CASE OF ADJACENT LEVELS: [degeneracy removal]



and now we apply an electric field
 $V(x) = -\mathcal{E}x$

Let's find out how this

energy changes in the field:

First: $\langle \psi | V(x) | \psi \rangle$ for any ψ

with a definitive parity = 0

$$V(r \rightarrow -r) = -V \quad \text{and}$$

$$d_x = \int \psi^*(r) x \psi(r) dr \quad r \rightarrow -r \quad d_x \rightarrow -d_x$$

$$\Rightarrow d_x = 0$$

From the previous discussion the 2-level system will have the energy change

$$E_{1,2} = \frac{\mathcal{E}_1 + \mathcal{E}_2}{2} \pm \sqrt{\frac{(\mathcal{E}_1 - \mathcal{E}_2)^2}{4} + |V_{12}|^2}$$

Consider e.g. $2S_{1/2}$ and $2P_{1/2}$

in H atom are degenerate

but there is a splitting effect:

$$E_{2P_{1/2}} - E_{2S_{1/2}} = 2|V_{12}|$$

We can estimate this effect:

$$R_{2s1/2} = \left(\frac{1}{4\pi}\right)^{1/2} R_{20}(r)$$

$$R_{2p1/2} = \left(\frac{3}{4\pi}\right)^{1/2} R_{21}(r) \cos \theta$$

R_{nl} are the Coulomb radial functions

$$\Rightarrow V_{12} = -E \langle R_{20} | r | R_{21} \rangle \frac{\sqrt{3}}{4\pi} \int \cos \theta d\Omega$$
$$= V_{21} = -\frac{E}{\sqrt{3}} \langle R_{20} | r | R_{21} \rangle$$

$$\int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\phi$$

i.e.
$$\begin{cases} R_{2,0} = \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \\ R_{2,1} = \frac{1}{\sqrt{24}} a_0^{-3/2} \frac{r}{a_0} e^{-r/2a_0} \end{cases}$$

From sympy: $\langle R_{20} | r | R_{21} \rangle = 3\sqrt{3}$

$$\Rightarrow |V_{12}| = -\frac{E}{\sqrt{3}} \cdot 3\sqrt{3} = -3E$$

From this $E_{2p1/2} - E_{2s1/2} = -3.2E = \underline{\underline{6E}}$

in atomic units

Also this result is unique

because for all other atoms

$$E = E_0 + \frac{\alpha}{2} E^2$$

the reason is that for different l 's the levels are not degenerate

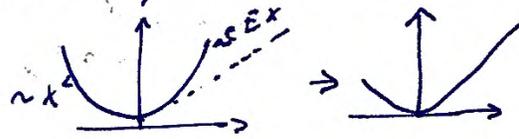
Before switching to the applications we need to recap the second quantisation:

(SEE LECTURE LO* posted on-line)

Perturbed linear harmonic oscillator.

What will happen when we apply an external electric field to our crystal with ions bound to the harmonic potential?

$$V(x) = \frac{m\omega^2 x^2}{2} - eEx$$



in other words

$$H = H^{(0)} + H^{(1)} \lambda \quad \text{where}$$

$$H^{(0)} = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 x^2 \quad \text{and} \quad H^{(1)} = -eEx$$

for $\lambda = 0$ we get $E_n = (n + \frac{1}{2})\hbar\omega \quad n = 0, 1, 2, \dots$

$$\psi_n = N_n H_n(\xi) e^{-\xi^2/2}$$

$$N_n = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} \quad \text{and}$$

$H_n(\xi)$ are Hermite polyn.

This problem is nice b/c the exact solution for $H = H^{(0)} + \lambda H^{(1)}$ is also well known.

1) Exact way: $H = \frac{1}{2m} p_x^2 + \frac{1}{2} m\omega^2 x^2 - \lambda eEx$

new variable $x \equiv y + \alpha \Rightarrow$

$$H = \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 (y^2 + 2\alpha y + \alpha^2) - \lambda eE (y + \alpha)$$

$$= \frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 (y^2 + \alpha^2) - \lambda eE \alpha + \underbrace{\left(\frac{1}{2} m\omega^2 \cdot 2\alpha - \lambda eE \right)}_{\downarrow 0} y$$

$$\frac{1}{2} m\omega^2 \cdot 2\alpha - \lambda eE = 0 \Rightarrow \alpha = \lambda eE / m\omega^2$$

hence $H = \underbrace{\frac{p_x^2}{2m} + \frac{1}{2} m\omega^2 y^2}_{\text{harmonic oscillator}} - \frac{\lambda^2 e^2 E^2}{2m\omega^2} \leftarrow \text{constant shift in energy}$

$$\Rightarrow E_n(\text{exact}) = (n + \frac{1}{2})\hbar\omega - \frac{\lambda^2 e^2 E^2}{2m\omega^2}$$

the change in the energy is the 2^d order process.

2) Apply the perturbation theory:

$$E_n^{(1)} = \langle n | H^{(1)} | n \rangle \equiv H_{nn}^{(1)} = \int_{-\infty}^{\infty} \phi_n^{(0)*} x H^{(1)} \phi_n^{(0)} dx$$

The solution is much easier if we move to a and a^\dagger

$$x = \sqrt{\frac{\hbar}{2m\omega}} (a + a^\dagger) \quad \text{and} \quad \left. \begin{aligned} a |n\rangle &= \sqrt{n} |n-1\rangle \\ a^\dagger |n\rangle &= \sqrt{n+1} |n+1\rangle \end{aligned} \right\}$$

and $\langle n | n \rangle = \delta_{n'n}$

for $E_n^{(1)} = \langle n | H^{(1)} | n \rangle = -eE \left(\frac{\hbar}{2m\omega} \right)^{1/2} \left[\sqrt{n} \langle n | n-1 \rangle + \sqrt{n+1} \langle n | n+1 \rangle \right] = 0!$

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle n | H^{(1)} | m \rangle|^2}{E_n^{(0)} - E_m^{(0)}} =$$

$$= \frac{e^2 E^2}{2m\omega^2} \sum_{m \neq n} \frac{|\sqrt{m} \delta_{n, m-1} + \sqrt{m+1} \delta_{n, m+1}|^2}{(n + \frac{1}{2}) - (m + \frac{1}{2})} =$$

$$= \frac{e^2 E^2}{2m\omega^2} \left(\frac{m^2 \delta_{n, m-1}^2 + (m+1)^2 \delta_{n, m+1}^2 + \sqrt{m} \cdot \sqrt{m+1} \delta_{n, m-1} \cdot \delta_{n, m+1}}{n - m} \right)$$

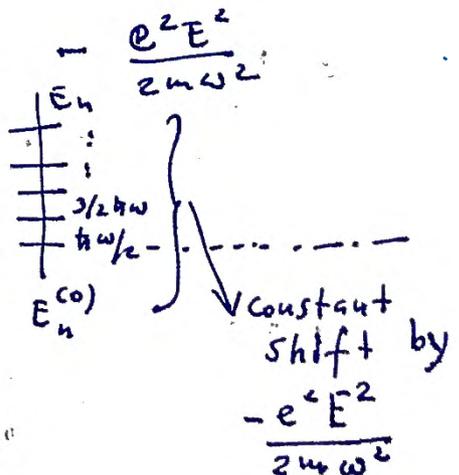
↑ this is mass!

→ e.g. $\left[\frac{n^2}{n-1} + \frac{(n+1)^2}{n+1} \right] = -\frac{e^2 E^2}{2m\omega^2}$

and thus $E_n = E_n^{(0)} \text{ (exact)} - \frac{e^2 E^2}{2m\omega^2}$

So the results coincide

$n = m - 1$

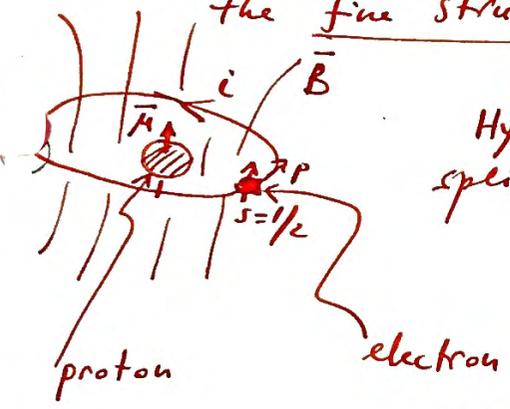


Hyperfine splitting in hydrogen atom

Start this section by reading FLP VIII p. 12-1 Ch. 12.

The short cut version will be presented in-class.

Splitting of energy due to the extra interaction of the electron orbital current \leftrightarrow a magnetic field B with the nuclear magnetic dipole is called the fine structure.



Hyperfine splitting is very small splitting of the spectral lines of H.

From electrodynamics the magnetic field of the magnetic dipole at the center of a sphere is:

$$B(r) = \frac{\mu_0}{4\pi r^3} [3(m \cdot r)r - m] + \frac{2}{3} \mu_0 m \delta^3(r)$$

The energy of the dipole in the magnetic field B is $H = -m \cdot B$

Now we have two magnetic dipoles m_1 and m_2

$$H = -\frac{\mu_0}{4\pi r^3} [3(m_1 \cdot r_1)(m_2 \cdot r_2) - m_1 \cdot m_2] - \frac{2}{3} \mu_0 m_1 \cdot m_2 \delta^3(r)$$



From the perturbation theory:

$$E_0^{(1)} = \langle u | H^{(1)} | u \rangle \equiv H_{uu}^{(1)} = \int \phi_0^* H \phi_0 dV$$

where $\phi_0 = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$ where $a_0 = a_{Bohr}$ radius

since ϕ_0 is spherically symmetric \equiv s-state! we can conclude $E_0^{(1)} = \int_{-\infty}^{\infty} \dots$ w.r.t $\theta = 0$

$$E_0^{(1)} = -\frac{2}{3} \mu_0 \langle m_1 \cdot m_2 \rangle \int \phi_0^2 \delta^3(r) dV = -\frac{2}{3} \frac{\mu_0}{\pi a_0^3} \langle m_1 \cdot m_2 \rangle$$

↑ nucleus
↑ electron

$$\bar{m}_1 = \gamma_p \bar{S}_p \quad m_2 = -\gamma_e S_e \quad \text{or}$$

$$E' = \frac{2}{3} \frac{\mu_0}{4\pi a_0^3} \gamma_p \gamma_e \langle S_e \cdot S_p \rangle$$

$$\gamma_e = \frac{e g_e \hbar}{2m} \quad \gamma_p = \frac{e g_p \hbar}{2m}$$

2.0023 5.5857

The good quantum number is $j = S_1 + S_2$ or

$$j^2 = S_1^2 + S_2^2 + 2S_1 \cdot S_2 \Rightarrow \frac{j^2 - S_1^2 - S_2^2}{2} = \bar{S}_1 \cdot \bar{S}_2$$

~~A~~ $j = 1$ or $j = 0$
 triplet singlet

$$S_1^2 = S_1(S_1+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}\hbar^2$$

$$S_2^2 = S_2(S_2+1) = \frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}\hbar^2$$

$$\text{or } \langle S_e \cdot S_p \rangle = \begin{cases} 1 - \frac{3}{4} = \frac{1}{4}\hbar^2 \\ 0 - \frac{3}{4} = -\frac{3}{4}\hbar^2 \end{cases}$$

Singlet is better since



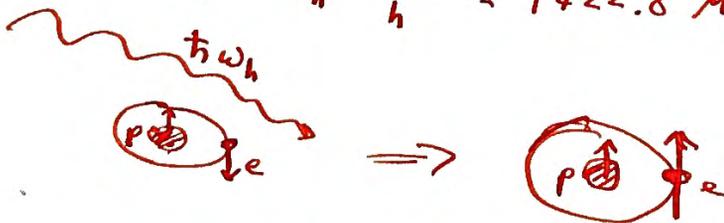
The energy gap between the singlet and triplet:

$$\Delta E = \frac{2\mu_0 \hbar^2}{3\pi a_0^3} \gamma_p \gamma_e \sim 5.884 \cdot 10^{-6} \text{ eV}$$

$\sim 5.8 \mu\text{eV}$

and if we pump it from singlet to triplet we need to use a laser with

$$\omega_h = \frac{\Delta E}{\hbar} = 1422.8 \text{ MHz}$$



Looks like the perturbation term works very well since the energy ΔE is indeed very small w.t. electron energy of $\sim 10 \text{ eV}$.

Theory for degenerate levels

If the levels are degenerate s.o.e., $E_n^{(0)} = E_m^{(0)}$
 all the perturbation terms becomes problematic
 since $\sim \frac{1}{E_n^{(0)} - E_m^{(0)}}$. So we need to develop
 a special case for the degenerate levels.

Recall degeneracy of the ground states stems
 from the symmetry of a Hamiltonian.

→ If the perturbation breaks the symmetry
 it will remove the degeneracy and our
 non-degenerate case is OK.

Let's start assuming that eigenvalues of
 the unperturbed Hamiltonian are m -fold degenerate.
 i.e. we have m linearly independent

$\phi_1^{(0)}, \phi_2^{(0)}, \dots, \phi_m^{(0)}$ corresponding to
 the same $E_1^{(0)} = E_2^{(0)} = \dots = E_m^{(0)} = E^{(0)}$

Since $H^{(0)}$ cannot select the "correct" ground
 state or eigenstate we form

$$\phi^{(0)} = \sum_{i=1}^m c_i \phi_i^{(0)} \quad \text{and expect that}$$

$H^{(1)}$ will "select" the proper ground state

Recall for the non-degenerate case

$$\begin{cases} \phi = \phi^{(0)} + \lambda \phi^{(1)} + \lambda^2 \phi^{(2)} + \dots \\ E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \end{cases}$$

$$H \phi = E \phi \Rightarrow [H^{(0)} + \lambda H^{(1)}] \phi = E \phi$$

$$\begin{pmatrix} H^{(0)} + \lambda H^{(1)} \\ (\phi^{(0)} + \lambda \phi^{(1)} + \dots) \end{pmatrix} = \begin{pmatrix} E^{(0)} + \lambda E^{(1)} + \dots \\ (\phi^{(0)} + \lambda \phi^{(1)} + \dots) \end{pmatrix}$$

$$\lambda^0: H^{(0)} \phi^{(0)} = E^{(0)} \phi^{(0)}$$

$$\lambda^1: H^{(0)} \phi^{(1)} + H^{(1)} \phi^{(0)} = E^{(0)} \phi^{(1)} + E^{(1)} \phi^{(0)}$$

$\phi^{(0)} = \sum_{i=1}^m c_i \phi_i^{(0)}$

since we don't know anything about the perturbations (no constraint) we can make the solution in the following form:

$$\phi^{(1)} = \sum_i a_i \phi_i^{(0)}$$

$$\int d\tau \phi_r^* \left| \sum_i (E_i^{(0)} - E^{(0)}) a_i \phi_i^{(0)} = (E^{(1)} - H^{(1)}) \sum_i c_i \phi_i^{(0)} \right.$$

$$a_r (E_r^{(0)} - E^{(0)}) = E^{(1)} c_r - \sum_{i=1}^m H_{ri}^{(1)} c_i$$

for $r \leq m$ $E_r^{(0)} = E^{(0)}$ (since the levels are degenerate)

$$0 = E^{(1)} c_r - \sum_{i=1}^m H_{ri}^{(1)} c_i \quad \text{or}$$

$$\sum_{i=1}^m (H_{ri}^{(1)} - E^{(1)} \delta_{ri}) c_i = 0 \quad r=0,1,2,\dots$$

This means we have m equations for c_i

As usual for a non-trivial case:

$$\begin{vmatrix} H_{11}^{(1)} - E^{(1)} & \dots & H_{1m}^{(1)} \\ \vdots & \ddots & \vdots \\ H_{m1}^{(1)} & \dots & H_{mm}^{(1)} - E^{(1)} \end{vmatrix} = 0 \Rightarrow \text{get a set of } E^{(1)} \text{ for } i \leq m$$

if all $E_1^{(1)}, \dots, E_m^{(1)}$ are distinct
the perturbations remove degeneracy completely

Otherwise we have the case of partial removal.

The eigenfunction can be found by setting $c_r = 0$ for $r > m$ or :

$$a_r = \frac{\sum_{i=1}^m H_{ri}^{(1)} c_i}{E^{(0)} - E_r^{(0)}} \quad \text{for } r > m$$

To make it clear we use $r \leq m$ equations to compute $E^{(1)}$ and the remaining $r > m$ states to compute the coeff. a_r for the $\phi^{(1)}$ eigenvector.

Thus we have $r > m$ eqn. Therefore we can set $a_r = 0$ for $r \leq m$:

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

$$\phi_k = \phi_k^{(0)} + \lambda \sum_{r > m} \frac{\sum_{i=1}^m H_{ri}^{(1)} c_i}{(E^{(0)} - E_r^{(0)})} \phi_r^{(0)}$$

First, read the Stark effect in H

Example :

2D Harmonic oscillator:

$$H^{(0)} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{k}{2} (x^2 + y^2) \quad \text{with eigenstates } |n_x n_y\rangle$$

Lets perturb the oscillator with a static potential: $H^{(1)} = \lambda xy$ for the two-fold degenerate state $|01\rangle$ and $|10\rangle$.

To simplify the calculation we introduce a, a^\dagger and b, b^\dagger for x , and y like this:

$$\begin{cases} a = \frac{1}{\sqrt{2}} \left(\alpha x + \frac{1}{\alpha} \frac{d}{dx} \right) & a^\dagger = \frac{1}{\sqrt{2}} \left(\alpha x - \frac{1}{\alpha} \frac{d}{dx} \right) \\ b = \frac{1}{\sqrt{2}} \left(\alpha y + \frac{1}{\alpha} \frac{d}{dy} \right) & b^\dagger = \frac{1}{\sqrt{2}} \left(\alpha y - \frac{1}{\alpha} \frac{d}{dy} \right) \end{cases}$$

$$x = \frac{1}{\sqrt{2}\alpha} (a + a^\dagger) \quad y = \frac{1}{\sqrt{2}\alpha} (b + b^\dagger), \quad \alpha \equiv \frac{m\omega}{\hbar}$$

$$p_x = -\frac{i\hbar\alpha}{\sqrt{2}} (a - a^\dagger) \quad p_y = \frac{i\hbar\alpha}{\sqrt{2}} (b - b^\dagger) \quad \frac{m\omega^2}{4\alpha^2}$$

$$H^{(0)} = \frac{\hbar^2 \alpha^2}{2} \cdot \frac{1}{2m} (a - a^\dagger)^2 + \frac{\hbar^2 \alpha^2}{2} (-1) (b - b^\dagger)^2 + \frac{k}{2} \left(\frac{1}{2\alpha} (a + a^\dagger)^2 + \frac{1}{2\alpha} (b + b^\dagger)^2 \right) =$$

Consider the coefficients in front of the brackets:

$$-\frac{\hbar^2 \alpha}{2} \cdot \frac{1}{2m} = -\frac{\hbar^2}{4m} \left(\frac{m\omega}{\hbar}\right)^2 = -\frac{\hbar\omega}{4}$$

$$\frac{k}{2} \cdot \frac{1}{2\alpha} = \left(\frac{k}{m} = \omega^2\right) = \frac{m\omega^2}{4} \cdot \frac{1}{\alpha} = \frac{m\omega^2}{4} \cdot \frac{1}{\frac{m\omega}{\hbar}} = \frac{\hbar\omega}{4}$$

so now we have:

$$\begin{aligned} H_x^{(0)} &= -\frac{\hbar\omega}{4} (a^\dagger - a)^2 + \frac{\hbar\omega}{4} (a^\dagger + a)^2 \\ &= \frac{\hbar\omega}{4} \left((a^\dagger + a)^2 - (a^\dagger - a)^2 \right) = \\ &= \frac{\hbar\omega}{4} \left(\cancel{a^\dagger a^\dagger} + \cancel{aa} + (a^\dagger a + a a^\dagger) - \cancel{a^\dagger a^\dagger} - \cancel{aa} \right. \\ &\quad \left. + (a^\dagger a + a a^\dagger) \right) = \frac{\hbar\omega}{2} (a^\dagger a + a a^\dagger) \\ &= \frac{\hbar\omega}{2} (2a^\dagger a + 1) = \hbar\omega \left(n_x + \frac{1}{2} \right) \end{aligned}$$

the same for $H_y^{(0)} = \hbar\omega \left(n_y + \frac{1}{2} \right)$ or

$$E_{n_x, n_y} = \hbar\omega \left(n_x + n_y + \frac{1}{2} + \frac{1}{2} \right) = \hbar\omega (n_x + n_y + 1)$$

The eigenstates are given by $|n_x\rangle |n_y\rangle \equiv |n_x n_y\rangle$

Note E_{n_x, n_y} is $(n_x + n_y + 1)$ fold degenerate

e.g. $|01\rangle$ and $|10\rangle$ will have the same energy of $2\hbar\omega$

Lets go to the perturbation term $H^{(1)} = \lambda xy$
the secular matrix is:

$$\begin{vmatrix} \langle 10 | \lambda xy | 10 \rangle - E^{(1)} & \langle 10 | \lambda xy | 01 \rangle \\ \langle 01 | \lambda xy | 10 \rangle & \langle 01 | \lambda xy | 01 \rangle - E^{(1)} \end{vmatrix} = 0$$

consider $\langle 10 | \lambda xy | 10 \rangle = \lambda \langle 1x | 1 \rangle \langle 0y | 10 \rangle = 0$

sin e.g. $x \sim a + a^\dagger \rightarrow \langle 1 | a + a^\dagger | 1 \rangle =$

$$\langle 1 | a | 1 \rangle + \langle 1 | a^\dagger | 1 \rangle = \langle 1 | 0 \rangle + \langle 1 | 2 \rangle = 0 + 0 = 0$$

Now off diagonal terms:

$$\langle 10 | \lambda xy | 01 \rangle = \lambda \langle 11x | 10 \rangle \langle 01y | 11 \rangle = \\ = \lambda \cdot \frac{1}{\sqrt{2}} \alpha \cdot \frac{1}{\sqrt{2}} \cdot \frac{1}{\alpha} = \frac{\lambda}{2\alpha^2} \quad \text{so we get}$$

$$\begin{vmatrix} 0 - E^{(1)} & \frac{\lambda}{2\alpha^2} \\ \frac{\lambda}{2\alpha^2} & 0 - E^{(1)} \end{vmatrix} = 0 \Rightarrow E^{(1)} = \pm \frac{\lambda}{2\alpha^2}$$

So after applying this perturbation term we will lift the degeneracy of the states $|10\rangle$ and $|01\rangle$

$$2\hbar\omega_0 |10\rangle = |110\rangle \begin{cases} \nearrow 2\hbar\omega_0 + \lambda/2\alpha^2 \\ \searrow 2\hbar\omega_0 - \lambda/2\alpha^2 \end{cases}$$

The corresponding new eigenvectors

$$\begin{pmatrix} -E^{(1)} & \lambda/2\alpha^2 \\ \lambda/2\alpha^2 & -E^{(1)} \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0 \quad \text{where } E_{1,2}^{(1)} = \pm \frac{\lambda}{2\alpha^2}$$

$$\text{for } \begin{pmatrix} -\lambda/2\alpha^2 & \lambda/2\alpha^2 \\ \lambda/2\alpha^2 & -\lambda/2\alpha^2 \end{pmatrix} \begin{pmatrix} U_1 \\ U_2 \end{pmatrix} = 0 \Rightarrow U_1 = U_2$$

$$\text{so } \phi_1 = \frac{1}{\sqrt{2}} (|10\rangle + |01\rangle) \quad \text{and for}$$

$$E_2^{(1)} = -\lambda/2\alpha^2 \quad \text{we get } U_1 = -U_2 \quad \text{so } \phi_2 = \frac{1}{\sqrt{2}} (|10\rangle - |01\rangle)$$

Perturbation removes degeneracy AND mixes up the eigenstates of the system.

END OF L1 !



REQUIRED READING: pp 345-350. Ch 13.5

1st ORDER STARK EFFECT IN HYDROGEN ATOM.

~~show: pp 110-121, 144-149~~