Single electron atom in time-independent background electric and magnetic field :

$$\Delta H \longrightarrow \text{non-degenerate Perturbation Theory ?}$$

$$\longrightarrow \text{degenerate Perturbation Theory ?}$$

- Question of energy scales $\longrightarrow$ Relativistic corrections

$\downarrow$

shifts due to ΔH

- Example : 2-state system

$$H = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

$$\Delta H = \begin{pmatrix} (\Delta H)_{11} & (\Delta H)_{12} \\ (\Delta H)_{21} & (\Delta H)_{22} \\ = (\Delta H)_{12} & \end{pmatrix}$$

Full Hamiltonian

$$\begin{pmatrix} E_1 + (\Delta H)_{11} & (\Delta H)_{12} \\ (\Delta H)_{12} & E_2 + (\Delta H)_{22} \end{pmatrix}$$

$\Rightarrow$ Characteristic equation

$$(\lambda - E_1 - (\Delta H)_{11})(\lambda - E_2 - (\Delta H)_{22}) = (\Delta H)_{12}^2$$

$$\Rightarrow \lambda = \left(E_1 + E_2 + (\Delta H)_{11} + (\Delta H)_{22} \pm \sqrt{\left(E_1 - E_2 + (\Delta H)_{11} - (\Delta H)_{22}\right)^2 + 4(\Delta H_{12})^2}\right) \Big/ 2$$

Consider the case $|E_1 - E_2| >> |(\Delta H)_{ij}|$

$$\lambda \simeq \frac{1}{2}\Big\{ E_1 + E_2 + (\Delta H)_{11} + (\Delta H)_{22} \pm \big(E_1 - E_2 + (\Delta H)_{11} - (\Delta H)_{22} + O(\Delta H_{ij})^2\big) \Big\}$$

$$\simeq E_1 + (\Delta H)_{11} \quad \underline{\text{OR}} \quad E_2 + (\Delta H)_{22}$$

$\Rightarrow$ A result of non-degenerate perturbation theory.

If $|E_1 - E_2| << |\Delta H_{ij}|$, then

(any $\Delta H_{ij} \rightarrow$ important)

$$\lambda \simeq \frac{1}{2}\Big(\underbrace{E_1 + E_2}_{\text{unperturbed}} + (\Delta H)_{11} + (\Delta H)_{22} \pm \sqrt{(\Delta H_{11} - \Delta H_{22})^2 + 4(\Delta H_{12})^2}\,.\Big)$$

(everything upto leading order)

- This is the answer given by degenerate perturbation theory.

Static, uniform magnetic fields

(The Zeeman effect)

$$\Delta H = \frac{e}{2m}\vec{B}\cdot(\vec{L} + 2\vec{S}) \quad \text{(previous analysis)}$$

along z-direction

$$\frac{e}{2m} B (L_z + 2S_z) \longrightarrow \boxed{\Delta H}$$

(upto linear order in $\vec{B}$.)

- Good enough approximation.

Weak $\vec{B}$

Basis : $|n, l, s, j, m_j\rangle$

(Take into account fine-structure splitting)

$j = \frac{1}{2}, \frac{3}{2}, \ldots \; n - \frac{1}{2}$

0 1 - -

$l \longrightarrow$ degeneracy

$m_j \longrightarrow$ ''

$$\left[\begin{array}{l} l = (j - \frac{1}{2}) \text{ or } (j + \frac{1}{2}) \\ \text{except for } j = n - \frac{1}{2}, \quad l = n - 1 \end{array}\right]$$

$m_j \longrightarrow J_z$ eigenvalue

$$\langle n\, l\, s\, j\, m_j | S_z | n\, l'\, s\, j\, m_j' \rangle$$

$\longrightarrow$ Diagonal $\boxed{m_j = m_j'}$

$\underline{\underline{l = l'}}$ $\quad [S_z, J_z] = 0 = [S_z, L^2]$

- Diagonal perturbation.

Need $\langle n\, l\, s\, j\, m_j | S_z | n\, l\, s\, j\, m_j \rangle$

$$= C^{j\;1\;j}_{m_j\;0\;m_j} \langle n, l, s, j \| S \| n, l, s, j \rangle$$

$$\Downarrow$$

$$\frac{\langle n, l, s, j, m_j | J_z | n, l, s, j, m_j \rangle}{\langle n\, l\, s\, j \| J \| n\, l\, s\, j \rangle}$$

So, $$= m_j \frac{\langle n\, l\, s\, j \| S \| n\, l\, s\, j \rangle}{\langle n\, l\, s\, j \| J \| n\, l\, s\, j \rangle}$$

$$\frac{1}{j(j+1)} \langle n, l, s, j, m_j | \vec{J} \cdot \vec{S} | s\, j\, m_j\, n\, l \rangle$$

$$\vec{J}\cdot\vec{S} = \frac{-1}{2}\left\{ \underbrace{(\vec{J}-\vec{S})^2}_{\vec{L}^2} - \vec{S}^2 - \vec{J}^2 \right\}$$

$$= -\frac{1}{2}\left(l(l+1) - \frac{3}{4} - j(j+1) \right)$$

$$\Delta E_{n l s j m_j} = \frac{eB}{2m}\left[1 + \left\{ \frac{1}{2} j(j+1) - l(l+1) + 3/4 \right\} / j(j+1) \right.$$

Scale of energy

$$\left. \cancel{j(j+1)} \right]$$

$$\left[\begin{array}{lll} \text{For} & l = \left(j + \frac{1}{2}\right), & -\frac{1}{(2l+1)} \\ & l = \left(j - \frac{1}{2}\right) & \frac{1}{(2l+1)} \end{array} \right]$$

Strong magnetic field

$$\frac{eB}{2m}\left(L_z + 2S_z \right) \qquad |n, l, m_l, S, m_s\rangle$$

$$\text{gives} \longrightarrow \frac{eB}{2m}\left(m_l + 2m_s \right)$$

- Effect of fine-structure splitting (Relativistic corrections)

- A different approach

(Bransden & Joachain)

Read

Appendix 7

* Start with Dirac Hamiltonian.

* Take the non-relativistic limit.

* Keep the first correction $(o(1/c).)$ (in the Hamiltonian)

Time-independent electric field (Stark effect)

• Strong $\vec{E}$ field

Ignore the effect of fine structure splitting

$\vec{E} = E\hat{z}$ (uniform field along z-direction)

$$\Delta H = eE\hat{z} \quad (e > 0).$$

Basis : $|n, l, m_l, s, m_s\rangle$

$$\begin{bmatrix} l = 0, 1, \cdots (n-1) \\ m_l = -l, \cdots, l \\ m_s = \pm\frac{1}{2} \end{bmatrix}$$

All degenerate

$[S_z, z] = 0$

$[L_z, z] = 0$

$[L^2, z] \neq 0$.

$$\begin{bmatrix} l' = l+1 \text{ or } \\ l-1 \end{bmatrix}$$
(parity)

$m_s' = m_s$

$m_l' = m_l$

$n = \cancel{0}1$

$l=0$: $\boxed{\Delta E = 0}$

$\underline{n=2}$: $l = 0, 1$ $m_s = \pm\frac{1}{2}$

$m_l = 0 \quad 0, \pm 1$

mix

$$(\Delta H)_{\text{matrix}} = \begin{pmatrix} 0 & \langle n=2, l=1, m_l=0, s, m_s | eEz | n=2, l=0, m_l=0, s, m_s\rangle \\ \langle\ \rangle^* & 0 \end{pmatrix}$$

$\langle\quad\rangle = ?$ (PTO)

$$eE \; \frac{\int \cancel{d^3r}\, r^2\,dr \left(R_{20}(r)\right) r \left(R_{21}(r)\right)}{\sqrt{\int r^2\,dr \left(R_{20}(r)\right)^2}\sqrt{\int r'^2\,dr' \; R_{21}(r')^2}}$$

$$\times \; \frac{\int \sin\theta\, d\theta\, d\phi \;\; Y_{10}(\theta,\phi) \cos\theta \; Y_{00}(\theta,\phi)}{\sqrt{\int \sin\theta\, d\theta\, d\phi \; \left(Y_{10}(\theta,\phi)\right)^2}\sqrt{\int \sin\theta'\, d\theta'\, d\phi' \, Y_{00}(\theta',\phi')^2}}$$

Exercise $= -\dfrac{3eE}{Ze^2 m}$

$n = 3$

$l = 0, \; 1, \; 2$

$m_l = 0 \quad m_l = 1, 0, -1 \quad m_l = 2, 1, 0, -1, -2$

$$\begin{pmatrix} 0 & a & 0 \\ a & 0 & b \\ 0 & b & 0 \end{pmatrix} \quad 3\times 3$$

for $m_l = 0$

For $m_l = \pm 1$

$\Rightarrow$ diagonalize (2×2) matrix

$m_l = \pm 2 \longrightarrow$ lone states

- Ionization $\longrightarrow$ Rate
- Approximate Bound states

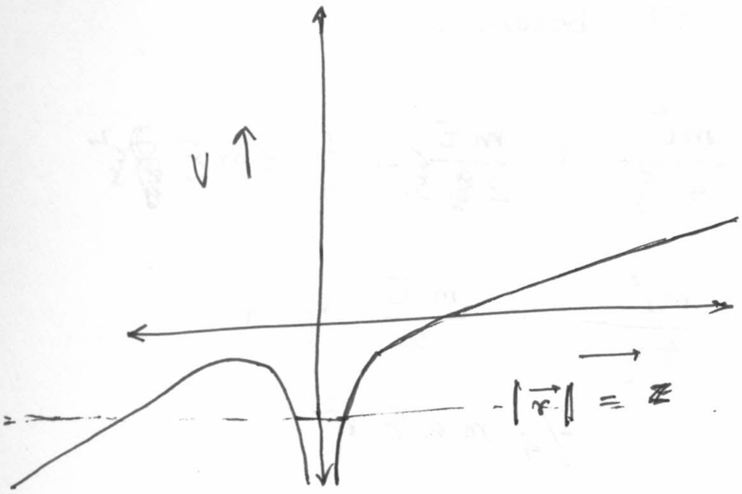
24.01.2013

(5)

Ionization of a single electron atom by uniform electric field:

$$V(r) = -\frac{Ze^2}{r} + e\mathcal{E}z$$

$x = y = 0$



System is unstable

① First reduce this to a one-dimensional problem.

② Calculate the tunneling rate using WKB approx.

- Rotational symmetry is not preserved.
- Use parabolic coordinates. $\{\xi, \eta, \phi\}$ $\downarrow$ usual azimuthal angle

$0 \leq \xi, \eta < \infty$.

- $$\left\{ \begin{aligned} x &= \sqrt{\xi\eta}\cos\phi \\ y &= \sqrt{\xi\eta}\sin\phi \\ z &= \frac{1}{2}(\xi - \eta) \end{aligned} \right\} \Rightarrow r = \frac{1}{2}(\xi + \eta)$$ (work out!)

- Exercise : $$\nabla^2\psi \equiv \frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial\psi}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial\psi}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\phi^2}\psi$$

$$V = -\frac{2Ze^2}{\xi+\eta} + \frac{1}{2}e\mathcal{E}(\xi - \eta)$$

SE : $$-\frac{1}{2m}\nabla^2\psi + V\psi = E\psi$$

Look for solutions of the form :

$$\psi = f(\xi)\, g(\eta)\, e^{i m_l \phi}$$

- Tip : Convert from spherical polar coordinates.

Exercise : Check that SE becomes —

$$\frac{1}{f}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial f}{\partial \xi}\right) - \frac{m_l^2}{4\xi} + \frac{mE}{2}\xi - \frac{1}{4} em\mathcal{E}\xi^2$$

$$+ \frac{1}{g}\frac{\partial}{\partial \eta}\left(\eta \frac{\partial g}{\partial \eta}\right) - \frac{m_l^2}{4\eta} + \frac{mE}{2}\eta + 1/4\, me\mathcal{E}\eta^2$$

$$+ Zme^2 = 0 .$$

- All derivatives are actually total derivatives.
- SE separates in $\{\xi, \eta\}$ variables.

$$\therefore \frac{1}{f}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial f}{\partial \xi}\right) - \frac{m_l^2}{4\xi} + \frac{mE}{2}\xi + \nu_1 - 1/4\, em\mathcal{E}\xi^2 = 0$$

$$\frac{1}{g}\frac{\partial}{\partial \eta}\left(\eta \frac{\partial f}{\partial \eta}\right) - \frac{m_l^2}{4\eta} + \frac{mE}{2}\eta + \nu_2 + \frac{1}{4} me\mathcal{E}\eta^2 = 0 .$$

$$\boxed{\nu_1 + \nu_2 = Zme^2}$$

- Set $\mathcal{E} = 0 \Rightarrow$ see how unperturbed results match
- Try to remove the linear ξ term.

Define
$$\left[\begin{array}{l} \beta = (-2mE)^{1/2} \\ \rho = \beta\xi \end{array}\right] \quad \text{Rescaling}$$

Equation becomes —

$$\frac{d}{d\rho}\left(\rho \frac{df}{d\rho}\right) - \frac{m_l^2}{4\rho} f - \frac{\rho}{4} f + \lambda_1 f = 0$$

$$\lambda_1 = \nu_1/\beta$$

- Try for series solutions

- Check, that as $\rho \to 0$, $f \sim \rho^{|m_\ell|/2}$

  As $\rho \to \infty$, $f \sim e^{-\rho/2}$.

$\Rightarrow$ Look for solutions of the form –

$$\rho^{|m_\ell|/2} e^{-\rho/2} \sum_{n=0}^{\infty} a_n \rho^n .$$

- Exercise : $\lambda_1 = \frac{1}{2}(|m_\ell| + 1) + n_1$

  n_1 can take values $0, 1, 2, \ldots$

Similarly, $\lambda_2 = \frac{1}{2}(|m_\ell| + 1) + n_2$

n_2 can take values $0, 1, 2, \ldots$

$$Z m e^2 = \nu_1 + \nu_2$$
$$= \beta (\lambda_1 + \lambda_2)$$
$$= \sqrt{-2mE}\,(|m_\ell| + 1 + n_1 + n_2)$$

$$\boxed{E = \frac{Z^2 m e^4}{-2(\underbrace{|m_\ell| + 1 + n_1 + n_2}_{})^2}}$$

$$E = -\frac{Z^2 m e^4}{2n^2}$$

$n = n_r + l$

(previously)

Degeneracy $= n^2$ (for given n)

$\boxed{\text{Identify as } n}$

- Ground state : $|m_\ell| = 0 = n_1 = n_2$.

$$E_g = -\frac{Z^2 m e^4}{2}.$$

$$\beta = (-2mE)^{1/2} = Zme^2.$$

$$f(\xi)\Big|_{\text{ground state}} \propto e^{-\beta\xi/2}.$$

$$g(\xi)\Big|_{\text{ground state}} \propto e^{-\beta\eta/2}.$$

(We can normalize.)

<u>Measure of normalization</u>

<u>Exercise</u> Calculate measure in $\{\xi, \eta, \phi\}$ coordinates and normalize.

Go back to the perturbed equations —

$$\frac{1}{f}\frac{\partial}{\partial\xi}\left(\xi\frac{\partial f}{\partial\xi}\right) - \frac{m_\ell^2}{4\xi} + \frac{mE}{2}\xi + \nu_1 - \frac{1}{4}em\mathcal{E}\xi^2 = 0$$

$$\frac{1}{g}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial f}{\partial\eta}\right) - \frac{m_\ell^2}{4\eta} + \frac{mE}{2}\eta + \nu_2 + \frac{1}{4}em\mathcal{E}\eta^2 = 0$$

Define $\left\{\begin{array}{l} f = \xi^{-1/2}F \\ g = \eta^{-1/2}G \end{array}\right\}$

<u>Check F & G satisfy</u>

$$\frac{d^2F}{d\xi^2} - \frac{m_\ell^2-1}{4\xi^2}F + \frac{mE}{2}F + \frac{\nu_1}{\xi}F - \frac{1}{4}em\mathcal{E}\xi F = 0.$$

$$\frac{d^2G}{d\eta^2} - \frac{(m_\ell^2-1)}{4\eta^2}G + \frac{mE}{2}G + \frac{\nu_2}{\eta}G + \frac{1}{4}em\mathcal{E}\eta G = 0.$$

$$-\frac{1}{2m}\frac{d^2F}{d\xi^2} + \frac{1}{2m}\underbrace{\left\{\frac{m_\ell^2-1}{4\xi^2} - \frac{\nu_1}{\xi} + \frac{1}{4}em\mathcal{E}\xi\right\}}_{V_1(\xi)} F = E/4\, F$$

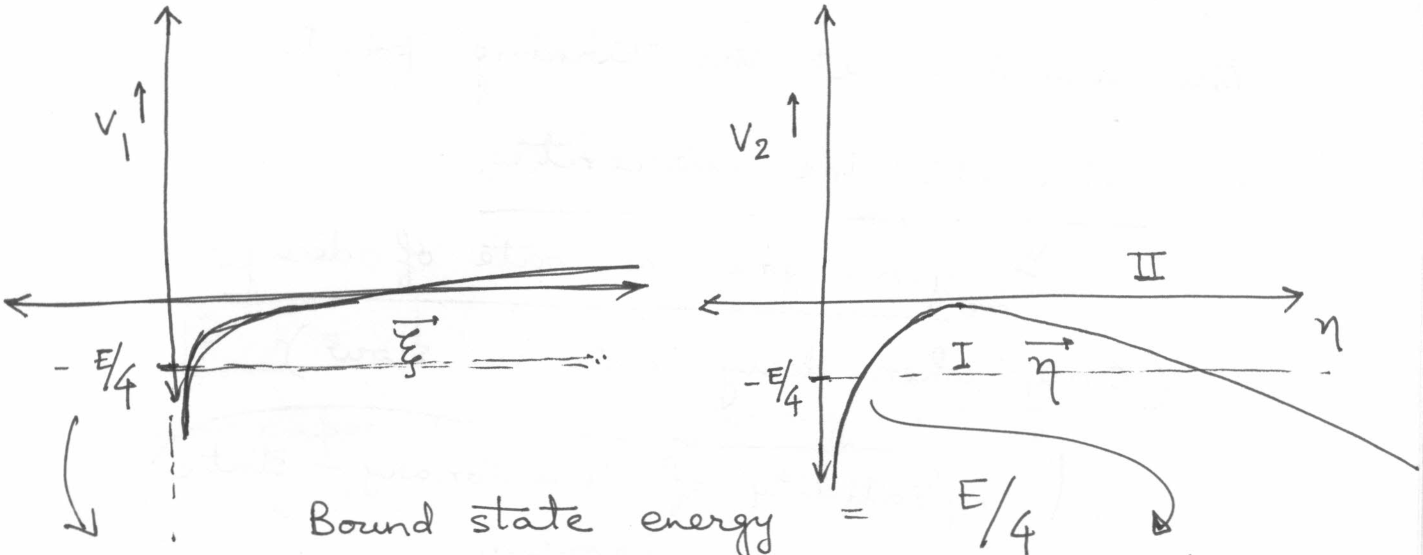
$$-\frac{1}{2m}\frac{d^2G}{d\eta^2} + \frac{1}{2m}\underbrace{\left\{\frac{m_\ell^2-1}{4\eta^2} - \frac{\nu_2}{\eta} - \frac{1}{4}em\mathcal{E}\eta\right\}}_{V_2(\eta)} G = E/4\, G.$$

(Two independent Schrödinger problems)

- Let's examine the effective potentials — (set $m_\ell = 0$)

$\boxed{\text{Ground state}}$

$$m_\ell = 0,\ \nu_1 = \nu_2 = \frac{\beta}{2} = \frac{1}{2}Zme^2.$$



genuine bound state

Bound state energy $= E/4$

not a genuine bound state

- How to calculate the tunneling probability?

<u>WKB approximation</u>

$$\mathrm{I}: \quad G(\eta) = B_+ \left(q(\eta)\right)^{-1/2} \exp\left(\int_{\eta_0}^{\eta} q(\eta')\,d\eta'\right)$$

$$+ B_- \left(q(\eta)\right)^{-1/2} \exp\left(-\int_{\eta_0}^{\eta} q(\eta')\,d\eta'\right)$$

$$q(\eta) = \sqrt{2m\left(V_2(\eta) - E/4\right)} \qquad q > 0$$

$\boxed{B_+ = 0}$. B_- should be determined by matching the Normalization.

In region II, the solution will be –

$$G(\eta) = A_+ \left(p(\eta)\right)^{-1/2} \exp\left(i \int_{\tilde{\eta}_0}^{\eta} p(\eta')\, d\eta'\right)$$
$$+ A_- \left(p(\eta)\right)^{-1/2} \exp\left(i \int_{\tilde{\eta}_0}^{\eta} p(\eta')\, d\eta'\right)$$

$$p(\eta) = \sqrt{\left(E/4 - V_2(\eta)\right) 2m} \;.$$

- Now, calculate A_+ and A_- by matching the solutions at the turning points.
- Calculate the current.

⇓ gives you the rate of decay.

(Only when decay rate is slow)

⇓

- Validity of stationary-state problem

- Answer : Decay rate $\sim e^{-c/E}$.

$c \longrightarrow$ constant you'll calculate !!!

Next Friday $\longrightarrow$ $\boxed{\text{TUTORIAL}}$

~~Calculate~~

30.01.2013

Lecture - 06 :

- Single electron atom in electromagnetic wave

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \quad ; \quad A_0 = -\phi$$

$$\vec{B} = \vec{\nabla} \times \vec{A} .$$ In free space,

$$\vec{\nabla} \cdot \vec{E} = 0$$

In Coulomb gauge,

$$\vec{\nabla} \times \vec{B} = + \frac{\partial \vec{E}}{\partial t} \qquad \vec{\nabla} \cdot \vec{A} = 0 .$$

$$\therefore \quad \vec{\nabla}^2 \phi = 0 . \qquad \vec{\nabla} \times (\vec{\nabla} \times \vec{A}) = \frac{\partial \vec{E}}{\partial t}$$

$$\boxed{\phi = 0}$$

$$\Rightarrow \quad \epsilon_{ijk} \partial_j (\epsilon_{klm} \partial_l A_m) = \frac{\partial E_i}{\partial t}$$

$$\Rightarrow (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}) \partial_j \partial_l A_m = \frac{\partial E_i}{\partial t}$$

$$\Rightarrow \left(\partial^2/\partial t^2 - \vec{\nabla}^2 \right) A_i = 0 .$$

$$\Rightarrow \vec{A} = a(\omega)\, \hat{\epsilon} \cos (\vec{k} \cdot \vec{r} - \omega t + \delta)$$

$$\omega = |\vec{k}|$$

$$\vec{\nabla} \cdot \vec{A} = 0$$

$$\Rightarrow \boxed{\hat{\epsilon} \cdot \vec{k} = 0}$$ (Transversality condition)

- Take superposition of waves propagating along the same direction with different energies.

$$\vec{A}(\vec{r}, t) = \int d\omega\, a(\omega)\, \hat{\epsilon} \cos (\vec{k} \cdot \vec{r} - \omega t + \delta_\omega)$$

Exercise : $\vec{A}(\vec{r}, t) = \int d^3k\, a(\vec{k})\, \hat{\epsilon}(\vec{k}) \cos (\vec{k} \cdot \vec{r} - \omega t + \delta_{\vec{k}})$

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = \cancel{\int d^3k} - \int d\omega\, a(\omega)\, \omega\, \hat{\epsilon} \cancel{(\vec{k})} \sin (\vec{k} \cdot \vec{r} - \omega t + \delta_\omega)$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$= -\int d\omega\, a(\omega)\, \omega\, (\hat{k} \times \hat{\epsilon}) \sin (\vec{k} \cdot \vec{r} - \omega t + \delta_\omega) .$$

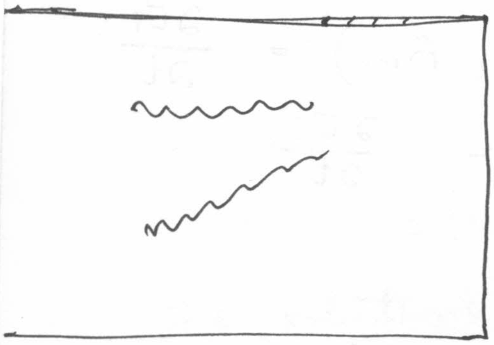
$$\text{Energy} = \frac{1}{8\pi}\int d^3r \left(\vec{E}^2 + \vec{B}^2\right)$$

$$= \frac{1}{8\pi}\int d^3r \int d\omega\, d\omega'\, a(\omega)\, a(\omega') \times$$

$$\sin\left(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega\right) \sin\left(\vec{k}'\cdot\vec{r} - \omega' t + \delta_{\omega'}\right)$$

$$\times\ 2\,\omega\,\omega'$$

- <u>Use incoherent approximation</u>
  - δ_ω & $\delta_{\omega'}$ are <u>random</u> & depend on time
  - "Random Phases"



$$\left\langle\!\left\langle e^{i\delta_\omega}\, e^{i\delta_{\omega'}} \right\rangle\!\right\rangle = 0.$$

$$\left\langle\!\left\langle e^{i\delta_\omega}\, e^{-i\delta_{\omega'}} \right\rangle\!\right\rangle = c\,\delta(\omega-\omega')$$

Some constant

So, $\text{energy} = \frac{1}{4\pi} \times \frac{1}{4} \times 2\,c \int d^3r\, d\omega\, \omega^2 |a(\omega)|^2$

$= \int d^3r \int d\omega\, \rho(\omega)$ where

$$\boxed{\rho(\omega) = \frac{c}{8\pi}\,\omega^2\,|a(\omega)|^2}$$

[energy density / unit frequency interval

(Measurable qty.)

- Take a single-electron atom in this field.

$H = H_0 + H_1$

unperturbed (time-independent)

perturbation

$= -e\phi + \frac{e}{m}\vec{A}\cdot(-i\vec{\nabla})$

(In Coulomb Gauge, $\phi = 0$)

$$H_1 = \frac{e}{m} \int d\omega\, a(\omega) \cos(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)\, \hat{\epsilon}\cdot(-i\vec{\nabla})$$

$$= \left\{ \frac{e}{2m} \int d\omega\, a(\omega)\, e^{i(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)}\, \hat{\epsilon}\cdot(-i\vec{\nabla}) + \frac{e}{2m} \int d\omega\, a(\omega)\, e^{-i(\vec{k}\cdot\vec{r} - \omega t + \delta_\omega)}\, \hat{\epsilon}\cdot(-i\vec{\nabla}) \right\}$$

$$= e^{-i\omega t} e^{i\delta_\omega} H_1^{+} + e^{i\omega t} e^{-i\delta_\omega} H_1^{-}$$

- Perturbation parameter $\longrightarrow$ $a(\omega)$ / ρ
- Study the effect of this perturbation on the original spectrum (due to H_0)

Time-dependent perturbation theory

$\{u_k(\vec{r})\}$: Eigenfunctions of H_0 with E.V. E_k

1. Start with $\psi = u_a(\vec{r})$ at $t=0$.
2. switch on the perturbation ~~at~~ for time T.
3. Calculate $\frac{1}{T} \times$ prob. of finding the particle in state $u_b(\vec{r})$.

Procedure : Take $\psi(\vec{r}, t) = \sum_k c_k(t)\, u_k(\vec{r})\, e^{-iE_k t}$

Initial condition : $c_k(t=0) = \delta_{ka}$

Schrödinger Equation tells us that –

$$\dot{c}_b = -i \sum_k \langle b | H_1 | k \rangle\, c_k(t)\, e^{i\omega_{bk} t}.$$

(QM 1 Course)

$$\approx -i \langle b | H_1 | a \rangle\, e^{i\omega_{ba} t}$$

$$\left(c_k(t) \xrightarrow{\sim} c_k(0) = \delta_{ka} \right)$$

P.T.O.

$$\therefore \quad \dot{c}_b = -i \int d\omega \left[e^{-i\omega t} e^{i\delta_\omega} \langle b | H_1^+ | a \rangle + e^{i\omega t} e^{-i\delta_\omega} \langle b | H_1^- | a \rangle \right] e^{i\omega_{ba} t}$$

Integrate this from 0 to T.

$$\Rightarrow \quad c_b(T) = -i \int d\omega \left[e^{i\delta_\omega} \langle b | H_1^+ | a \rangle \times \frac{e^{i(\omega_{ba}-\omega)T} - 1}{i(\omega_{ba}-\omega)} + e^{i\delta_\omega} \langle b | H_1^- | a \rangle \times \frac{e^{i(\omega_{ba}+\omega)T} - 1}{i(\omega_{ba}+\omega)} \right]$$

$\sum_{\delta\omega}$

$$|c_b(T)|^2$$

$$= \int d\omega \, C \left[|\langle b | H_1^+ | a \rangle|^2 \cdot 4 \frac{\sin^2\left(\frac{(\omega_{ba}-\omega)T}{2}\right)}{(\omega_{ba}-\omega)^2} + |\langle b | H_1^- | a \rangle|^2 \, 4 \frac{\sin^2\left(\frac{(\omega_{ba}+\omega)T}{2}\right)}{(\omega_{ba}+\omega)^2} \right]$$

$$H_1^\pm = \frac{e}{2m} a(\omega) \, e^{\pm i \vec{k}\cdot\vec{x}} \, \hat{\epsilon}\cdot(-i\vec{\nabla})$$

We wish to calculate $\dfrac{|C_b(T)|^2}{T}$ (transition rate) for $T \to \infty$ (formally)

$$\left\{ \begin{array}{l} \omega_{ba} \longrightarrow \omega \\ \omega_{ba} \longrightarrow -\omega \end{array} \right\}$$

$\omega_{ba} = E_b - E_a$

$\omega_{ba} > 0 \rightarrow$ first term contributes

$\omega_{ba} < 0 \rightarrow$ second term contributes.

<u>Let's take $\omega_{ba} > 0$.</u>

$$\frac{1}{T}\left|c_b(T)\right|^2 = c\,\frac{e^2}{4m^2}\left|a(\omega_{ba})\right|^2 \left|\langle b|\,M^+|\,a\rangle\right|^2_{\omega=\omega_{ba}}$$

$$\times\ 4\int d\omega\ \frac{\sin^2\left(\frac{(\omega_{ba}-\omega)T}{2}\right)}{(\omega_{ba}-\omega)^2\,T}$$

$$M^\pm = e^{\pm i\vec{k}\cdot\vec{r}}\ \hat{\epsilon}\,(-i\vec{\nabla})$$

Make a change of variable $\rightarrow$ $\boxed{x = \frac{(\omega_{ba}-\omega)T}{2}}$

$$\text{Integral} = \int_{-\infty}^{\infty} \frac{2}{T}\,dx\ \frac{\sin^2 x}{\left(\frac{2x}{T}\right)^2 T}$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}\,dx = \frac{\pi}{2}\ \checkmark$$

So, transition rate

$$= \frac{|c_b(T)|^2}{T} = \frac{e^2}{4m^2}\,c\left|a(\omega_{ba})\right|^2\left|\langle b|M^+|a\rangle\right|^2 \times (2\pi)$$

$$= \frac{\pi e^2}{2m^2}\,c\left|a(\omega_{ba})\right|^2\left|\langle b|M^+|a\rangle\right|^2$$

We had derived, $\boxed{\rho(\omega) = \frac{c}{8\pi}\,\omega^2\left(a(\omega)\right)^2}$

So, transition rate

$$= \frac{e^2}{\cancel{2}m^2}\,\pi\,\frac{\overset{4\pi}{\cancel{8\pi}}\,\rho(\omega_{ba})}{(\omega_{ba})^2}\left|\langle b|M^+|a\rangle\right|^2$$

$$= \frac{4\pi^2 e^2}{m^2}\,\frac{\rho(\omega_{ba})}{(\omega_{ba})^2}\left|\langle b|M^+|a\rangle\right|^2.$$

If $\underline{\underline{E_b < E_a}}$,

$$\frac{|c_b(T)|^2}{T} = \frac{4\pi^2 e^2}{m^2}\,\frac{\rho(-\omega_{ba})}{(\omega_{ba})^2}\left|\langle b|M^-|a\rangle\right|^2.$$

31.01.2013

Lecture - 07 :

$$|a\rangle \longrightarrow |b\rangle$$

(1) $E_b > E_a$: $W_{ba} = \frac{e^2}{m^2} 4\pi^2 \frac{\rho(\omega_{ba})}{(\omega_{ba})^2} |\mathcal{M}^+_{ba}|^2$

$$= \rho(\omega_{ba}) B_{ba}$$

$$\mathcal{M}^+_{ba} = \langle b| e^{i\vec{k}\cdot\vec{r}} \hat{\epsilon}\cdot(-i\vec{\nabla})|a\rangle \Big|_{\omega = \omega_{ba}}$$

(We'll consider angular averages)

$B_{ba} \rightarrow$ property of the atom

Here $\omega_{ba} = E_b - E_a$

$\rho(\omega)\, d\omega$ = energy density in the range $(\omega, \omega + d\omega)$

(2) $E_b < E_a$: $W_{ba} = \frac{e^2}{m^2} \cdot 4\pi^2 \frac{\rho(-\omega_{ba})}{\omega_{ba}^2} |\mathcal{M}^-_{ba}|^2$

$$\boxed{\mathcal{M}^-_{ba} = \langle b| e^{-i\vec{k}\cdot\vec{r}} \hat{\epsilon}\cdot(-i\vec{\nabla})|a\rangle} = \rho(-\omega_{ba})\, B_{ba}$$

same notation

Consider a two-level system

$E_2 > E_1$

———— 2

———— 1

We'll calculate the transition rates $1 \longrightarrow 2$ & $2 \longrightarrow 1$.

$$W_{21} = \rho(\omega_{21})\, B_{21}$$

$$B_{21} = \frac{4\pi^2 e^2}{m^2} \frac{1}{\omega_{21}^2} |\mathcal{M}^+_{21}|^2$$

$$W_{12} = \rho(\omega_{12})\, B_{12}$$

$$B_{12} = \frac{4\pi^2 e^2}{m^2} \frac{1}{\omega_{21}^2} |\mathcal{M}^-_{12}|^2.$$

- Observe that $\left(\mathcal{M}^{+}_{21}\right)^{*} = \mathcal{M}^{-}_{12}$

Proof: $\langle 2 | e^{i\vec{k}\cdot\vec{r}} \, \hat{\epsilon}\cdot(-i\vec{\nabla}) | 1 \rangle^{*}$

$$= \langle 1 | \underbrace{\hat{\epsilon}\cdot(-i\vec{\nabla}) \, e^{-i\vec{k}\cdot\vec{r}}}_{\text{~~How?~~} \Rightarrow \, \| \quad (\hat{\epsilon}\cdot\vec{k} = 0.)} | 2 \rangle$$

$$= \langle 1 | e^{-i\vec{k}\cdot\vec{r}} \, \hat{\epsilon}\cdot(-i\vec{\nabla}) | 2 \rangle .$$

$\Rightarrow B_{12} = B_{21}.$

- Consider a situation where

N_1 = no. of atoms in level 1.

N_2 = " " " " 2.

$$N_2 = N_1 \, e^{-\omega_{21}/k_B T} \quad \text{(Statistical Mechanics)}$$

(Dilute gas of atoms)

Rate of transitions $1 \longrightarrow 2$: $W_{21} \times N_1$.

Rate of transitions $2 \longrightarrow 1$: $W_{12} \times N_2$.

- Seems that there's some inconsistency!
- <u>Spontaneous emission</u> (Quantize Maxwell Field ?)
- $\exists$ a bypass route!
- Let's call the spontaneous emission rate from $2 \longrightarrow 1$ as A_{12}.

$$\therefore \; W_{21} N_1 = W_{12} N_2 + A_{12} N_2$$

$$\Rightarrow \rho(\omega_{21}) \frac{N_1}{N_2} B_{21} = \rho(\omega_{21}) B_{12} + A_{12}$$

$$\Rightarrow \rho(\omega_{21}) \, e^{\omega_{21}/k_B T} B_{21} = \rho(\omega_{21}) B_{12} + A_{12}$$

$$\Rightarrow \quad A_{12} = \rho(\omega_{21}) \left\{ B_{21}\, e^{\omega_{21}/k_B T} - B_{12} \right\}$$

$\longleftrightarrow$ Quantum Stat.

information Mech.

$$\rho(\omega_{12}) = \frac{\omega_{21}^3}{\pi^2} \frac{1}{e^{\omega_{21}/k_B T} - 1}.$$

- A_{12} can't have any dependence on T.

$\longrightarrow \quad B_{12} = B_{21}$ (comes from consistency check!)

- Incoherent superposition of spontaneous & induced emission. (✓)

- $$A_{12} = \frac{\omega_{21}^3}{\pi^2} B_{\cancel{21}\,12}$$

$$\Rightarrow \quad A_{12} = \frac{\omega_{21}^3}{\cancel{\pi^2}} \cdot 4\cancel{\pi^2} \frac{e^2}{m^2} \left|\mathcal{M}^+_{21}\right|^2 \times 1/\omega_{21}^2$$

$$= \omega_{21}\, 4 \frac{e^2}{m^2} \left|\mathcal{M}^+_{21}\right|^2$$

$\Rightarrow$ <u>Calculation of matrix elements</u>

$$\mathcal{M}^+_{21} = \langle 2 |\, e^{i\vec{k}\cdot\vec{r}}\, \hat{\epsilon}\cdot(-i\vec{\nabla})\, | 1 \rangle$$

$$|\vec{k}| = \omega_{ba} \sim 1/\lambda_{ba}$$

$$\vec{k}\cdot\vec{r} \sim 0 \quad \text{for} \quad r \sim a_0$$

$$\approx \langle 2 |\, \hat{\epsilon}\cdot(-i\vec{\nabla})\, | 1 \rangle$$

(The Dipole Approximation)

$$H_0 = \frac{\vec{p}^{\,2}}{2m} + V(r) + \text{corrections}$$

(fine structure / hyperfine / ---)

$$[H_0, \vec{r}] = -\frac{i\vec{p}}{m}.$$

$$\mathcal{M}^+_{21} = im \langle 2 | [H_0, \vec{r}\cdot\hat{\epsilon}] | 1 \rangle$$

$$= im (E_2 - E_1) \langle 2 | \vec{r}\cdot\hat{\epsilon} | 1 \rangle$$

$$= im\, \omega_{\cancel{12}21} \hat{\epsilon}\cdot\vec{r}_{21}$$

$$\left(\vec{r}_{21} = \langle 2 | \vec{r} | 1 \rangle \right).$$

$$A_{12} = 4\, e^2/\cancel{m^2}\, \omega_{21} \times \cancel{m^2}\, \omega_{21}^2 \left(\hat{\epsilon}\cdot\vec{r}_{21}\right)^2$$

$$= 4\, \omega_{21}^3 e^2 \left(\hat{\epsilon}\cdot\vec{r}_{\cancel{12}21}\right)^2 \longrightarrow \text{ordinary vector}$$

$$\underline{e\vec{r} = \vec{D}} \longrightarrow \text{Dipole operator}$$

$$= 4\,\omega_{21}^3 \cancel{e^2} \left(\hat{\epsilon}\cdot\vec{D}_{21}^{\,2}\right)$$

$$\underline{\vec{D}_{12} = \langle 1 | \vec{D} | 2 \rangle}.$$

- Now, we've to average over $\hat{\epsilon}$'s.
- Take θ as the angle between $\hat{\epsilon}$ & $\vec{r}_{21}$.

$$|\hat{\epsilon}\cdot\vec{r}_{21}|^2 = \vec{r}_{21}^{\,2} \cos^2\theta$$

$$\langle \cos^2\theta \rangle = \frac{\int_0^{\pi} d\theta \int_0^{2\pi} d\phi\, \cancel{\cos}\, \sin\theta \cos^2\theta\, d\theta}{\int_0^{\pi} d\theta \int_0^{2\pi} d\phi\, \sin\theta\, \cancel{d\theta}}$$

$$= 1/3.$$

• Detailed Balance

(After $\hat{\epsilon}$ averaging)

For B's, one doesn't need averaging as such.

$$A_{12} = \frac{4}{3}\,\omega_{21}^3\; e^2 \left(\vec{r}_{21}\right)^2$$

$$= \frac{4}{3}\,\omega_{21}^3\; \vec{D}_{21}^{\,2}\,.$$

* Derive selection rules

- What conditions do 1 & 2 have to satisfy?

(1) $l_2 - l_1 = 0, \pm 1$ Angular momentum

But, there is parity. (0 is not allowed)

$$\therefore\; l_2 - l_1 = \pm 1$$

$$\Delta m_l = 0, \pm 1.$$

(2) $\Delta m_s = 0$ $\quad [S_z, (\vec{D}_{21})] = 0$

$\vec{B}\cdot\vec{S}$ term $\longrightarrow$ we've ignored !!!

No change of our result

($\omega_{21} = 0$)

- Hyperfine, ... $\longrightarrow$ $\vec{B}\cdot\vec{S}$ has some effect
- Intensity of spontaneous emission can also be calculated.

Line width : • Role of the uncertainty principle

E_2 $\qquad \left(\sum_{i,\; E_i < E_2} A_{i2}\right) N_2$

in vacuo

$$0 \qquad \frac{dN_2}{dt} = -\left(\sum_i A_{i2}\right) N_2$$

$$\Rightarrow\quad N_2 = N_2^0 \exp\left(-\left(\sum_i A_{i2}\right) t\right)$$

$$N_2^0 = N_2(t=0)$$

$\therefore$ State E_2 has lifetime $\sim \dfrac{1}{\sum_i A_{i2}}$.

- Energy uncertainty in E_2 is of order $\sim \sum_i A_{i2}$.
- Similar result is true for E_1 also.
- Uncertainty of the difference $\sim$ larger of the two uncertainties
- Dominant effect near $T \to 0$.
- $\exists$ Doppler type effects also.

06/02/2013

Lecture - 08 :

Two - electron atoms :

* Ignore the effect of nuclear mass
* Ignore magnetic & electric moments of nucleus
* Ignore relativistic corrections

- Here e-e interaction is far more important than these effects.

$$H = -\frac{1}{2m}\left(\vec{\nabla}_1^2 + \vec{\nabla}_2^2\right) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

- First, ignore $\dfrac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ term.

$$\psi(\vec{r}_1, \vec{r}_2) = u_{n_1 l_1 m_{l_1}}(\vec{r}_1)\, u_{n_2 l_2 m_{l_2}}(\vec{r}_2) \times |m_{s_1}\rangle_1 \otimes |m_{s_2}\rangle_2 .$$

- Identical Fermions.

- Antisymmetrize basis states

$$\frac{1}{\sqrt{2}}\Big(u_{n_1 l_1 m_1}(\vec{r}_1)\, u_{n_2 l_2 m_2}(\vec{r}_2)\, |m_{s_1}\rangle_1 \otimes |m_{s_2}\rangle_2$$

$$- u_{n_2 l_2 m_2}(\vec{r}_1)\, u_{n_1 l_1 m_1}(\vec{r}_2)\, |m_{s_2}\rangle_1 \otimes |m_{s_1}\rangle_2\Big)$$

(This is a possibility.)

- Convenient choice of basis

$$\frac{1}{2}\Big(u_{n_1 l_1 m_1}(\vec{r}_1)\, u_{n_2 l_2 m_2}(\vec{r}_2) \pm u_{n_2 l_2 m_2}(\vec{r}_1)\, u_{n_1 l_1 m_1}(\vec{r}_2)\Big)$$

$$\Big(|m_{s_1}\rangle_1 |m_{s_2}\rangle_2 \mp |m_{s_2}\rangle_1 |m_{s_1}\rangle_2\Big)$$

(Take antisymmetric combinations of explicitly symmetrized / antisymmetrized space/spin parts).

spin part :

$$\frac{1}{\sqrt{2}}\Big(|\tfrac{1}{2}\rangle_1 \otimes |-\tfrac{1}{2}\rangle_2 - |-\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}\rangle_2\Big)$$

unique antisymmetric combination

Symmetric $\longrightarrow$ 3 possibilities

3 states

$$\begin{cases} |\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}\rangle_1 \;;\; |-\tfrac{1}{2}\rangle_1 \otimes |-\tfrac{1}{2}\rangle_2 \;; \\ \frac{1}{\sqrt{2}}\Big(|\tfrac{1}{2}\rangle_1 \otimes |-\tfrac{1}{2}\rangle_2 + |-\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}\rangle_2\Big) \end{cases}$$

It's not difficult to show that these states are eigenstates of total spin operator $\vec{S}$.

$$\begin{cases} \vec{S} = \vec{S}_1 + \vec{S}_2 \\ [S_i, S_j] = i\,\epsilon_{ijk}\, S_k \end{cases}$$

$\vec{S}^2 \equiv s(s+1)$ eigenvalue

$s = 0, \; 1$

$0 \to$ antisymmetric, $1 \to$ symmetric

$[H, s_i] = 0$. $\left\{ \begin{array}{l} S=0 \Rightarrow \text{para-helium} \\ S=1 \Rightarrow \text{ortho-helium} \end{array} \right\}$

$\left\{ \begin{array}{l} S=0 \ \& \ S=1 \text{ sectors} \\ \text{don't mix.} \end{array} \right\}$

Define $\vec{L} = \vec{L}_1 + \vec{L}_2$.

$[\vec{L}, H] = 0$. (even with $\dfrac{e^2}{|\vec{r}_1 - \vec{r}_2|}$ present)

- Label eigenstates with $\vec{S}^2$, S_z, $\vec{L}^2$, L_z eigenvalues.
- E is independent of m_S and m_L.

$\left\{ \begin{array}{l} [H, L^{\pm}] = 0 \\ [H, S^{\pm}] = 0 \end{array} \right\}$ ← Reason.

$\underset{S=0/1}{{}^{(2S+1)}} L \longrightarrow$ symbol

L: 0, 1, 2, 3

S P D F (capital letters)

write principal quantum no. to the left

$(n_1 + n_2 - 1)\ {}^{2S+1} L$

Ground State

(ignoring last term)

Single electron result

$$E_g = -\frac{Z^2 e^4 m}{2n^2}$$

$1\,{}^1S \longrightarrow$ understand

para

excited states

- 1st excited state —

$\left\{ \begin{array}{l} n_1 = 1 \Rightarrow l_1 = 0 \\ n_2 = 2 \Rightarrow l_2 = 0, 1 \end{array} \right.$

$$\underbrace{2\,{}^1S,\ 2\,{}^3S}_{3 \text{ states}} \oplus \underbrace{2\,{}^1P}_{3 \text{ states}} \oplus \underbrace{2\,{}^3P}_{9 \text{ states}}$$

$=$ 16 states (in total)

$2 \times 1^2 \times 2 \times 2^2 = 16.$

Had the electrons not been identical, we should have got 32 states.

$$E_{n_1,n_2} = -\frac{Z^2 e^4 m}{2}\left(1/n_1^2 + 1/n_2^2\right).$$

Ionization energy : $n_1 = 1, \quad n_2 = \infty$.

$$E_{\text{ionization}} = -\frac{Z^2 e^4 m}{2}$$

Is $E_{n_1,n_2} > E_{\text{ionization}}$?

If $1/n_1^2 + 1/n_2^2 < 1 \rightarrow$ then (n_1, n_2) is not a true bound state.

- Only way to have a bound state is that at least one of $\{n_1, n_2\}$ is 1.

$E_{\text{ionization}}$ (defined in this way) doesn't depend on $e^2/|\vec{r}_1 - \vec{r}_2|$. The inclusion of this term makes "bound" state condition even more stringent. (doesn't help)

- One can't solve the problem exactly.

Perturbation Theory

- Should be good for large Z
- Calculate shift in the ground state energy

$$\Delta E_0 = \int d^3r_1\, d^3r_2\, \Psi_{\underset{n\,l\,m_l}{100}}(\vec{r}_1)^* \Psi^*_{100}(\vec{r}_2) \times H_1 \Psi_{100}(\vec{r}_1)\Psi_{100}(\vec{r}_2)$$

$$H_1 = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}.$$

$$\Psi_{100} = \frac{N}{\sqrt{4\pi}} e^{-Zme^2 r}$$

$$\int \Psi^*_{100}(\vec{r})\, \Psi_{100}(\vec{r})\, d^3 r = 1$$

$$\Rightarrow \quad N = 2(me^2 Z)^{3/2}$$

(exercise)

$$\Delta E_0 = \frac{N^4}{16\pi^2}$$

$$\times \int r_1^2 \sin\theta_1 \, d\theta_1 \, d\phi_1 \, dr_1$$

$$\times \int r_2^2 \sin\theta_2 \, d\theta_2 \, d\phi_2 \, dr_2 \; e^{-2mZe^2(r_1+r_2)}$$

$$\times \frac{e^2}{r_{12}} \qquad r_{12} = |\vec{r}_1 - \vec{r}_2|$$

- Choose coordinates for $\vec{r}_2$ depending on $\vec{r}_1$.
- Take $\vec{r}_1$ as the z-axis of coordinates chosen for $\vec{r}_2$.

$$e^2/r_{12} = \frac{e^2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}$$

$\underline{\theta_2, \phi_2 \text{ integral}}$

$$2\pi \times \frac{1}{r_1 r_2} \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2} \Bigg|_0^{\theta_2 = \pi}$$

$$= 2\pi \frac{1}{r_1 r_2} \big(\underbrace{r_1 + r_2 - |r_1 - r_2|} \big)$$

$r_{\lessgtr}$

$= 2r_2$ if $r_1 > r_2$

$= 2r_1$ if $r_2 > r_1$

$\frac{4\pi}{r_1}$ if $r_1 > r_2$ or $\frac{4\pi}{r_2}$ if $r_1 < r_2$

$$\Delta E_0 = \frac{N^4}{16\pi^2} \times 4\pi \times 4\pi \times e^2$$

θ_1, ϕ_1 integral

$$\int_0^\infty r_1^2 \, dr_1 \, e^{-2Zme^2 r_1} \int_0^\infty r_2^2 \, dr_2 \, e^{-2Zme^2 r_2}$$

$$\times \begin{cases} 1/r_1 & (\text{if } r_1 > r_2) \\ 1/r_2 & (\text{if } r_2 > r_1) \end{cases}$$

$$= 2\int_0^\infty \frac{dr_1}{r_1} r_1^2 e^{-2Zme^2 r_1} \int_0^{r_1} r_2^2 \, dr_2 \, e^{-2Zme^2 r_2} \times e^2$$

(Understand the logic!)

Write $\begin{Bmatrix} \rho_1 = 2Zme^2 r_1 \\ \rho_2 = 2Zme^2 r_2 \end{Bmatrix}$

$$\Delta E_0 = N^4 \times 2 \times (2Zme^2)^{-5} \times \cancel{\int_0^\infty dr_1 r_1^2 e^{-2Zme^2}}$$

$$\times \underbrace{\int_0^\infty d\rho_1 \, \rho_1 e^{-\rho_1} \int_0^{\rho_1} d\rho_2 \, \rho_2^2 e^{-\rho_2} \times e^2}_{\boxed{\text{exercise}}} = 5/8$$

$$\Delta E_0 = \frac{5}{8} \times \cancel{16} \times (Zme^2)^6 \times \cancel{2} \times \frac{1}{\cancel{32}} \times (Zme^2)^{-5}$$

$$= \frac{5}{8}(Zme^2) \times e^2 = \boxed{5/8 \; Zme^4}.$$

$$\therefore \quad E = -Z^2 me^4 + 5/8 \; Zme^4$$

(upto first order perturbation theory)

$$= -Z^2 me^4 \left(1 - 5/8Z\right)$$

The variational method:

- Take a trial wavefunction.

Take $\psi = N^2 e^{-C(r_1 + r_2)}$

C → parameter

$N \longrightarrow$ fixed in terms of C by normalization.

$$\int |\psi|^2 \, r_1^2 dr_1 \sin\theta_1 d\phi_1 d\theta_1 \times r_2^2 dr_2 \sin\theta_2 d\phi_2 d\theta_2 = 1$$

Ex: c^3/π

$\langle \psi | H | \psi \rangle$

exercise $= \dfrac{1}{2m}(c^2 + c^2) - Ze^2 (c + c) + \dfrac{5}{8} e^2 c$

- Extremize wrt c . . . $\partial/\partial c \langle \psi | H | \psi \rangle = 0$

$\Rightarrow c = + \left(Ze^2 - 5/16\, e^2 \right) m.$

Substitute c in $\langle \psi | H | \psi \rangle$

$$E_{ground} = - Z^2 e^4 m \left\{ 1 - 5/16 Z \right\}^2.$$

- Better variational wavefunctions . . .

<u>07/02/2013</u> <u>Lecture - 09</u> :

Excited states of 2-electron atom

- First, we'll discuss Perturbation Theory.

$$\frac{1}{\sqrt{2}} \left(\psi_{100}(\vec{r}_1) \psi_{n l m_l}(\vec{r}_2) \pm \psi_{n l m_l}(\vec{r}_1) \psi_{100}(\vec{r}_2) \right)$$

$\times$ spin part

$$\begin{cases} S = 0 \Rightarrow \text{para} \\ S = 1 \Rightarrow \text{ortho} \end{cases} \quad l = 0, 1, \ldots, n-1 \quad E = E_1 + E_n$$

$$m_l = -l, -l+1, \ldots, l$$

$$E = -\frac{Z^2 e^4 m}{2} \left(1 + 1/n^2 \right)$$

- Degenerate Perturbation Theory ? $\rightarrow$ NO.

<u>Why?</u> $[\vec{L}, H] = 0 \Rightarrow$ different $(\underset{l}{\overset{\shortparallel}{L}}, \underset{m_l}{\overset{\shortparallel}{m_L}})$ values don't mix. (other part is $\overline{100}$)

$\Rightarrow$ Different l, m_l values don't mix.

$[\vec{S}, \vec{H}] = 0 \Rightarrow$ different (S, m_S) values don't mix.

- We'll use non-degenerate Perturbation Theory.

$$\psi^{(0)}_{n l m_l} = \frac{1}{\sqrt{2}} \left(\psi_{100}(\vec{r}_1)\, \psi_{n l m_l}(\vec{r}_2) \pm \psi_{n l m_l}(\vec{r}_1)\, \psi_{100}(\vec{r}_2) \right)$$

$$H_1 = \text{Perturbing Hamiltonian} = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$\int d^3 r_1\, d^3 r_2\, \psi^{(0)}_{n l m_l}(\vec{r}_1, \vec{r}_2)^*\, H_1\, \psi^{(0)}_{n l m_l}(\vec{r}_1, \vec{r}_2)$$

$$= J_{nl} \pm K_{nl}.$$

$$J_{nl} = e^2 \int_0^\infty r_1^2\, dr_1\, \sin\theta_1\, d\theta_1\, d\phi_1 \times \left(\psi_{n l m_l}(\vec{r}_1)\right)^2 \times$$

$$\int_0^\infty r_2^2\, dr_2\, \sin\theta_2\, d\theta_2\, d\phi_2 \left(\psi_{100}(\vec{r}_2)\right)^2 \times$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

- Choose axes for $\vec{r}_2$ coordinates. (Why can we do this always?) ✓

$$1/r_{12} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}.$$

$$\psi_{n l m_l}(\vec{r}_1) = R_{nl}(r_1)\, Y_{l m_l}(\theta_1, \phi_1)$$

$$\int \sin\theta_1\, d\theta_1\, d\phi_1 \left(Y_{l m_l}(\theta_1, \phi_1)\right)^2 = 1.$$

Final result: $J_{nl} = e^2 \int_0^\infty r_1^2\, dr_1 \left(R_{nl}(r_1)\right)^2 \times$

$$\int_0^\infty r_2^2\, dr_2 \left(R_{10}(r_2)\right)^2 \frac{1}{r_>} \longrightarrow \begin{array}{l} r_1 \text{ if } r_1 > r_2 \\ r_2 \text{ if } r_1 < r_2 \end{array}$$

(Exercise)

$$J_{nl} = e^2 \int_0^\infty dr_1\, r_1^2 \left(R_{nl}(r_1)\right)^2 1/r_1$$

$$\times \int_0^{r_1} dr_2\, r_2^2 \left(R_{10}(r_2)\right)^2 +$$

$$e^2 \int_0^\infty dr_1\, r_1^2 \left(R_{nl}(r_1)\right)^2 \int_{r_1}^{\infty} dr_2\, r_2 \left(R_{10}(r_2)\right)^2 .$$

This can be calculated. (For given (n, l))

Next part $\longrightarrow$ evaluation of K_{nl}.

$$K_{nl} = e^2 \int_0^\infty dr_1\, r_1^2 \left(R_{nl}(r_1)\, R_{10}(r_1)\right) \int_0^\infty r_2^2\, dr_2 \times$$

$$\left(R_{nl}(r_2)\; R_{10}(r_2)\right) \times \int \sin\theta_1\, d\theta_1\, d\phi_1 \times \int \sin\theta_2\, d\theta_2\, d\phi_2$$

$$\times\; Y^*_{lm_l}(\theta_1, \phi_1)\; Y_{00}(\theta_1, \phi_1)\; Y_{lm_l}(\theta_2, \phi_2)\; Y_{00}(\theta_2, \phi_2)$$

$$1/\sqrt{4\pi} \qquad \times \frac{1}{|\vec{r}_1 - \vec{r}_2|} \qquad 1/\sqrt{4\pi}$$

Identity: (Found in standard textbooks)

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l'=0}^{\infty} \sum_{m_l'=-l'}^{l'} \frac{4\pi}{2l'+1} \frac{(r_<)^{l'}}{(r_>)^{l'+1}}\, Y_{l'm'}(\theta_1, \phi_1)\, Y_{l'm'}(\theta_2, \phi_2)^*$$

(Ref: Jackson)

$r_<$: smaller of (r_1, r_2)

$r_>$: larger " "

- Use orthonormality of Y_{lm}'s.

$$K_{nl} = \frac{e^2}{(2l+1)} \int_0^\infty r_1^2\, dr_1\, R_{nl}(r_1)\, R_{10}(r_1) \int_0^\infty r_2^2\, dr_2 \times R_{nl}(r_2)\, R_{10}(r_2)\, \frac{(r_<)^l}{(r_>)^{l+1}} .$$

$$= \frac{e^2}{2l+1} \int_0^\infty dr_1\, R_{nl}(r_1)\, R_{10}(r_1)$$

suppose $r_2 < r_1$

$$\Big\{ r_1^{-l+1} \int_0^{r_1} dr_2\, R_{nl}(r_2)\, R_{10}(r_2)\, r_2^{l+2}$$

$$+\; r_1^{l+2} \int_{r_1}^\infty dr_2\, R_{nl}(r_2)\, R_{10}(r_2)\, r_2^{-l+1} \Big\}$$

{This is the answer!}

$$E_{n l m_l} = -\frac{Z^2 e^4 m}{2}\left(1 + 1/n^2\right) + J_{nl} \pm K_{nl}$$

+ sign : $S = 0$ (para)

− sign : $S = 1$ (ortho)

$$\left[\begin{array}{l} \vec{S}^2 = 0 \text{ for para} \\ \quad = 2 \text{ for ortho} \end{array}\right]$$

$$(\vec{S}^2 - 1) = \begin{cases} -1 & \text{for para} \\ 1 & \text{" ortho} \end{cases}$$

We can rewrite

$$E_{n l m_l} = -\frac{Z^2 e^4 m}{2}\left(1 + 1/n^2\right) + J_{nl} - (\vec{S}^2 - 1) K_{nl}$$

(effect of statistics !!)

$(\vec{S}^2 - 1) K_{nl}$

$\longrightarrow$ exchange interaction

- $K_{nl} > 0$. (easy to see for $l = n-1$)

  $\Downarrow$

  ?

  ($R_{n\,n-1}$ has no nodes !!)

- Therefore, $S = 0$ has higher energy compared to $S = 1$. (Physical interpretation ??)

Variational Methods

- States carrying different (L, S) values don't mix. (Role of symmetry)

Ground state : $\left\{\begin{array}{l} L = 0 \\ S = 0 \end{array}\right\} \longrightarrow$ antisymmetric

$\underline{1^1 S}$. $\boxed{\text{LABEL}}$

- 1st excited state

$\left\{ \checkmark \to \text{good choices} \right\}$ (for variational method)

2^1S, 2^1P ✓, 2^3S ✓, 2^3P ✓.

(unperturbed wavefunctions)

$2^3S \longrightarrow \boxed{l_1 = 0, \; l_2 = 0}$

unperturbed

$$\left(R_{10}(r_1)\, R_{20}(r_2) - R_{20}(r_1)\, R_{10}(r_2)\right)$$

$$R_{10}(r_1) = \mathcal{N} e^{-Ze^2 m r_1}$$

$$R_{20}(r_2) = \tilde{\mathcal{N}} e^{-Ze^2 m/2 \, r_2} \left(1 - \frac{Ze^2 m}{2} r_2\right)$$ (one node

- Screening $\mathcal{N}\left\{ e^{-Cr_1}(1 - Br_2)\, e^{-Br_2} - e^{-Br_1}(1 - Br_1)\, e^{-Cr_2} \right\}$

⊛ Use B & C as Variational parameters.

Good choice of wavefunction

- Do the variation and find out E_{opt}.

(~~Part~~ Homework Problem 3).

2^1P : $\boxed{S = 0 \; ; \; L = 1}$

$$\left\{ R_{10}(r_1)\, R_{21}(r_2)\, Y_{1m}(\theta_2, \phi_2) + R_{21}(r_1)\, Y_{10}(\theta_1, \phi_1)\, R_{10}(r_2) \right\}$$

$$\downarrow$$

$$r_1 \exp\left(-\frac{Ze^2 m}{2} r_1\right)$$

Trial wavefunction

$$\mathcal{N}\left\{ \exp(-Cr_1)\, r_2 \exp(-Br_2)\, Y_{10}(\theta_2, \phi_2) \pm e^{-Cr_2}\, r_1\, e^{-Br_1}\, Y_{10}(\theta_1, \phi_1) \right\}$$

Fate of doubly excited states:

$$E = -\frac{Z^2 e^4 m}{2}\left(1/n_1^2 + 1/n_2^2 \right) > -\frac{Z^2 e^4 m}{2}$$

$\{$ for $n_1 \geq 2$, $n_2 \geq 2$ $\}$

- The state can decay into a single electron atom + a free electron of momentum $\vec{k}$.
- The momentum can also be calculated.

$$\vec{k}^2/2m \; - \; \frac{Z^2 e^4 m}{2\, n^2} \qquad \text{(energy conservation)}$$

$$= - \frac{Z^2 e^4 m}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right)$$

$$\Rightarrow \quad \vec{k}^2/2m = \frac{Z^2 e^4 m}{2} \left(1 - 1/n_1^2 - 1/n_2^2 \right)$$

$$\Gamma = \frac{2\pi}{\hbar} \left| \langle \Psi(E) \,|\, H_1 \,|\, \Psi_0^{(0)} \rangle \right|^2 \rho(E)$$

(very crude) density of states

$$\Psi_0^{(0)} = \frac{1}{\sqrt{2}} \Big(\Psi_{n_1 l_1 m_{l_1}}(\vec{r}_1)\, \Psi_{n_2 l_2 m_{l_2}}(\vec{r}_2) \pm \Psi_{n_2 l_2 m_{l_2}}(\vec{r}_1)\, \Psi_{n_1 l_1 m_{l_1}}(\vec{r}_2) \Big)$$

$$\Psi(E) = \frac{1}{\sqrt{L^3}} \frac{1}{\sqrt{2}} \left(e^{i\vec{k}\cdot\vec{r}_1} \Psi_{100}(\vec{r}_2) \pm e^{i\vec{k}\cdot\vec{r}_2} \Psi_{100}(\vec{r}_1) \right)$$

$$\rho(E) = \sin\theta \, d\theta \, d\phi \times \frac{L^3}{8\pi^3} \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{2} E^{1/2}.$$

$$\vec{k} = |\vec{k}| \left(\sin\theta\cos\phi, \; \sin\theta \sin\phi, \; \cos\theta \right)$$

$$\Delta E \sim 1/\Gamma \qquad \text{(Time - energy uncertainty)}$$

Expt. connection $\longleftrightarrow$ $\boxed{\text{ABSORPTION LINES}}$

Photon absorption spectrum