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problem-one

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H atom. Consider only $n=1,2$. (TDPT)

states: ψ_{nlm} : ie 5. recall: $l = 0,\dots,n-1$

$m = -l,\dots,l$

	n	l	m	
s	1	0	0	o
	2	0	0	O
p	2	1	-1	∞
	2	1	0	8
	2	1	1	∞

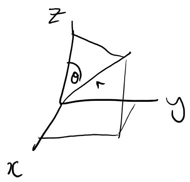
} g.s.

(degenerate) 1^{st} exc. st.

pert^{n}

$$H(t) = H_0 + H'(t) \qquad H'(t) = -eE(t)z \qquad \left(\underline{E} = E(t)\,\hat{\underline{z}}\right)$$

$z = r\cos\theta$ $\qquad r = \frac{z}{\cos\theta}$



$$Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$\Rightarrow \quad z = \sqrt{\frac{4\pi}{3}}\, r\, Y_{1,0}$$

— (*)

$$H'_{ij} = \langle \psi_i | H' | \psi_j \rangle$$

b) <u>Show $\langle H'_{ii} \rangle = 0 \quad \forall$ states</u>

$$H'_{ii} = \langle \psi_{nlm} | -eEz | \psi_{nlm} \rangle$$

$$= -eE \int dx \int dy \int dz \; \underbrace{z}_{\text{odd}} \; \underbrace{|\psi_{nlm}(x,y,z)|^2}_{\text{we know this is even in } z} = 0 \quad \forall \text{ states}$$

: odd×even = odd

& $\int dz\, f(z) = 0$ for odd f

↓ ie. $\psi_{nlm} = R_{nl} Y_{lm}$

$$\psi_{100} = R_{10} Y_{00} = \frac{2}{\sqrt{a^3}} \frac{1}{\sqrt{4\pi}} e^{-r/a} \Rightarrow |\psi_{100}|^2 = \frac{e^{-2r/a}}{2\pi a^3}$$

$$\psi_{200} = R_{20} Y_{00} = \frac{\frac{1}{\sqrt{2a^3}}\left(1-\frac{r}{2a}\right)}{\sqrt{4\pi}} e^{-r/2a} \;\ldots$$

a) i) $\langle \psi_{100} | H' | \psi_{200} \rangle = 0$ $\quad$ $\parallel$ly.

ii, iii) $$\langle \psi_{100} | H' | \psi_{21\pm1} \rangle = \int dV \; \frac{2}{\sqrt{a^3 4\pi}} e^{-r/a} \; \frac{1}{2\sqrt{6a^3}} \frac{r}{a} e^{-r/2a} (\mp 1) \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi}$$

$$\sim \int_0^{2\pi} d\phi \; e^{\pm i\phi} \ldots = 0 \quad \text{since osc.}$$

i.e. $\int d\phi \left(\cos\phi \pm i \sin\phi\right) = 0$

iv) $$\langle \psi_{100} | H' | \psi_{210} \rangle = \int dV \; R_{10} Y_{00} \; (-eEz) \; R_{21} Y_{10}$$

(*)

$$= -eE \int dr\, r^2 R_{10} R_{21} \int d\Omega \; \underbrace{Y_{00}}_{\frac{1}{\sqrt{4\pi}}} Y_{10} \; \sqrt{\frac{4\pi}{3}}\, r\, Y_{1,0}$$

$$= \frac{-eE}{\sqrt{3}} \int dr\, r^3 \frac{1}{\sqrt{6a^3}} \frac{r}{a} e^{-\frac{3r}{2a}} \qquad \underbrace{\int d\Omega \; |Y_{10}|^2}_{=1}$$

$\in \mathbb{R}$

$18 = 2.9$

$$= \frac{-eE}{a^4 3\sqrt{2}} \underbrace{\int dr\, r^4 e^{-\frac{3r}{2a}}}$$

$$\int dr\, r^4 e^{-\alpha r} = \frac{4!}{\left(\frac{3}{2a}\right)^5} = \frac{2^5 a^5 \, 3 \, 2^3}{3^5} = \frac{2^8 a^5}{3^4}$$

$24 = 3.2^3$

$$= \frac{-eE\sqrt{2}}{a^4 \; 2.3} \; \frac{2^8 a^5}{3^4}$$

$$= \frac{-eE\sqrt{2}\; 2^7 a}{3^5} \qquad \left(= -0.745\, eEa \right)$$

problem-two

Tuesday, 6 November, 2018 12:10

$T = 300K$ – room temperature

spontaneous emission rate:

$$A = \frac{\omega^3 |P|^2}{3\pi \varepsilon_0 \hbar c^3}$$

thermally stimulated emission rate:

$$R = \frac{\pi}{3\varepsilon_0 \hbar^2} |P|^2 \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1}$$

$$\Rightarrow R = \frac{|P|^2 \omega^3}{3\varepsilon_0 \hbar c^3 \pi} \frac{1}{e^{\hbar\omega/k_BT} - 1}$$

$$\begin{cases} \hbar = 1.05 \times 10^{-34} \text{ Js} \\ k_B = 1.38 \times 10^{-23} \text{ JK}^{-1} \end{cases}$$

ratio $\frac{\text{spontaneous}}{\text{thermal}}$

$$\boxed{r = A/R = e^{\frac{\hbar\omega}{k_BT}} - 1}$$

- "middle point": ω_0

$$\omega_0 = 5 \times 10^{12} \text{ Hz} \Rightarrow r \sim e^{\frac{10^{-34}\omega}{10^{-23} 10^2}} - 1 = e^{\omega \cdot 10^{-13}} - 1$$

- well below: ($\sim$ 100 less): $\omega_\downarrow$

$$\omega_\downarrow = 10^{10} \text{ Hz} \Rightarrow r \sim e^{10^{-3}} - 1 \sim 10^{-3} \Rightarrow R \text{ dominates}$$

- well above ($\sim$ 100 more): $\omega_\uparrow$

$$\omega_\uparrow = 10^{14} \text{ Hz} \Rightarrow r \sim e^{10} - 1 \sim 10^4 \Rightarrow A \text{ dominates}$$

- visible light: $\omega \sim 10^2\ THz = 10^{14}\ Hz \Rightarrow$

$\rightarrow$ 430-770 THz (ie $\gg \omega_0$)

problem-three

Tuesday, 6 November, 2018 12:22

will need this

$$P = \langle \psi_f | \underbrace{q\, \underline{r}}_{\text{dipole moment}} | \psi_i \rangle \qquad q = e$$

matrix element

Spontaneous emission:

want this for $\psi_{2\ell m}$ $\rightarrow$ $A = \dfrac{\omega_0^3 |P|^2}{3\pi \varepsilon_0 \hbar c^3}$

$$\omega = \frac{E}{\hbar} \qquad \text{H atom: } E_n = \frac{E_1}{n^2}$$

want: $\left.\begin{matrix}\psi_{200}\\ \psi_{210}\\ \psi_{21\pm1}\end{matrix}\right\} \rightarrow \psi_{100}$

$$E_{n=1} = -\frac{\hbar^2}{2ma^2}$$

this is the $\Delta\omega$ for

$$\omega_0 = \frac{E_2 - E_1}{\hbar} = \frac{E_1\left(\frac{1}{4} - 1\right)}{\hbar}$$

$$= -\frac{3}{4}\frac{E_1}{\hbar} = \frac{\hbar^2}{2ma^2}\frac{3}{4}\frac{1}{\hbar}$$

$$= \frac{3}{2^3}\frac{\hbar}{ma^2}$$

$$\Rightarrow A = \frac{|P|^2}{3\pi\varepsilon_0 \hbar c^3}\,\frac{3^3}{2^9}\,\frac{\hbar^3}{m^3 a^6} = \frac{|P|^2\, 3^2\, \hbar^2}{\pi \varepsilon_0 c^3\, 2^9\, m^3 a^6}$$

remains to find P.

$$P = \langle \psi_{100} | e\, \underline{r} | \psi_{2\ell m} \rangle = er\Big[\underbrace{\langle \psi_{100} | \cos\theta | \psi_{2\ell m} \rangle \hat{\underline{z}}}_{①}$$

$$+ \underbrace{\langle \psi_{100} | \sin\theta\cos\phi\, \hat{\underline{x}} + \sin\theta\sin\phi\, \hat{\underline{y}} | \psi_{2\ell m} \rangle}_{②} \Big] \quad -(\dagger)$$

$$\underline{r} = x\underline{x} + y\underline{y} + z\underline{z}$$

$$\equiv \begin{pmatrix} x \\ y \\ z \end{pmatrix} = r \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

① $\hat{z}$: from Q1, know only non-zero for ψ_{210}

$$\Rightarrow \quad p_z = \frac{e\sqrt{2}\, 2^7 a}{3^5} \qquad \text{(from Q1)}$$

Ⓐ

② $\hat{x}, \hat{y}$-plane: know $\int dV\, x\, f_1(x) = \int dV\, y\, f_2(y) = 0$

if f_1 even in x & f_2 even in y.

ie. $\int dV\, xy\, f_1(x) f_2(y) = 0$

but $f_i = f_i(r, \theta, \phi)$

what is $f_i(x,y)$ sym.?

✓ $\psi_{100} \sim e^{-r/a}$

✓ $\psi_{200} \sim \left(1 - \frac{r}{2a}\right) e^{-r}$

✓ $\psi_{210} \sim r e^{-r} \cos\theta$

$r = \sqrt{x^2 + y^2 + z^2}$

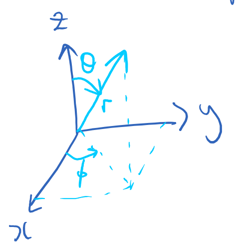
so $x, y \to -x, y$

$\Rightarrow r \to r$

$\left\{ \begin{matrix} x \to -x \\ y \to -y \end{matrix} \right\} : \theta \to \theta$

$\Rightarrow$ even in x, y

recall that θ is the polar angle, so doesn't depend on (x, y)



"doubly"

x

so we have $\int dV\, xy\, f(x,y) \overset{\text{"doubly"}}{=} 0$ with $f(x,y)$ sym. in x & y.

Thus $\langle \psi_{100} | a | \psi_{2l0} \rangle = 0$ for $l = 0,1$ & $a = x, y$. —— B

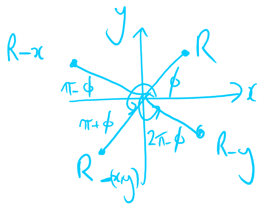
Can also see this as:

$$x \pm iy = r \sin\theta\, e^{\pm i\phi} = \mp r \sqrt{\frac{8\pi}{3}}\, Y_{1,\pm 1} \quad (**)$$

$$\langle 100 | x \pm iy | 200 \rangle = \langle 100 | x \pm iy | 210 \rangle = 0$$

because you get a $\int d\phi\, e^{\pm i\phi} = 0$

only remaining non-zero part of (†):



$$P = er \sum_{m \in \{-1,+1\}} \langle \psi_{100} | \sin\theta\cos\phi\, \hat{x} + \sin\theta\sin\phi\, \hat{y} | \psi_{2,1,m} \rangle$$

Now, eg. $\psi_{211} \ni Y_{11} \propto \sin\theta\, e^{i\phi} \xrightarrow{(x,y)\to-(x,y)} \sin\theta\, e^{i(\pi-\phi)} = \sin\theta\, e^{-i\phi} \propto Y_{1,-1}$

$\Rightarrow \psi_{2,1,\pm1}$ neither odd nor even, so can't exploit sym. $\to 0$.

but we have $Y_{11} \xrightarrow{-(x,y)} Y_{1,-1}$

so for $\langle 100 | \ldots | 21, \pm 1 \rangle$, we'll use a trick:

First, return to Cartesians:

$$P = e \sum_{m\in\{-1,+1\}} \langle \psi_{100} | \; x \; \hat{x} + \; y \; \hat{y} | \psi_{2,1,m} \rangle$$

n.b.

$$x \pm iy = r(\sin\theta\cos\phi \pm i \sin\theta\sin\phi)$$
$$= r\sin\theta(\cos\phi \pm i \sin\phi)$$
$$= r\sin\theta \; e^{\pm i\phi}$$
$$= \mp r\sqrt{\frac{8\pi}{3}} \, Y_{1,\pm 1}(\theta,\phi) \quad - \text{recall} \quad (**)$$

$$\left[Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}} \sin\theta \, e^{\pm i\phi} \right]$$

so Consider that:

$$\langle 100 | (x \pm iy) | 211 \rangle = \mp \frac{\cancel{2}}{\sqrt{a^3}} \frac{1}{\cancel{2}\sqrt{6a^3}} \frac{1}{\sqrt{4\cancel{\pi}}} \int r^2 dr \, e^{-r/a} \frac{r}{a} e^{-r/2a} \underbrace{\int d\Omega}_{} \; r\sqrt{\frac{8\cancel{\pi}}{3}} \underbrace{Y_{1,\pm1} Y_{1,1}}_{\text{orthonormal}}$$

$$\Rightarrow \begin{cases} + \neq 0 \\ - = 0 \end{cases}$$

$$= \begin{cases} -\dfrac{1}{a^4}\sqrt{\dfrac{\cancel{8}}{\cancel{6}\cdot\cancel{4}\cdot 3^2}} \underbrace{\displaystyle\int dr \; r^4 e^{-\left(\frac{3}{2a}\right)r}}_{= \frac{2^8 a^5}{3^4} \text{ (from Q1)}} & \text{for } + \\ 0 & \text{for } - \end{cases}$$

$$\stackrel{+}{=} -\frac{1}{3a^4}\frac{2^8 a^5}{3^4} = -\frac{2^8 a}{3^5}$$

So we have: $\begin{cases} \langle 100 | x+iy | 211\rangle = -\dfrac{2^8 a}{3^5} \\ \langle 100 | x-iy | 211\rangle = 0 \end{cases}$

$+ \ \& \ -$

$$\Rightarrow \begin{cases} \langle 100 | x | 211\rangle = -\dfrac{2^7 a}{3^5} \\ \langle 100 | y | 211\rangle = \dfrac{i\,2^7 a}{3^5} \end{cases}$$

$''$ly, $\langle 1,0,0 | x \pm iy | 2,1,-1\rangle = \begin{cases} \dfrac{2^8 a}{3^5} & \text{for } - \\ 0 & \text{for } + \end{cases}$ i.e. swap

$$\Rightarrow \begin{cases} \langle 100 | x | 21-1\rangle = \dfrac{2^7 a}{3^5} \\ \langle 100 | y | 21-1\rangle = -\dfrac{i\,2^7 a}{3^5} \end{cases}$$

which together gives:

$$\begin{cases} \langle 100 | x | 2,1,\pm 1\rangle = \mp \dfrac{2^7 a}{3^5} \\ \langle 100 | y | 2,1,\pm 1\rangle = \pm \dfrac{i\,2^7 a}{3^5} \end{cases} \qquad \text{C}$$

Thus, $\langle 100 | e\underline{r} | 200\rangle = e\Big[\underbrace{\langle 100 | x | 2,0,0\rangle \hat{x} + \langle 100 | y | 2,0,0\rangle \hat{y}}_{=0 \text{ by B}}$

$+ \underbrace{\langle 100 | z | 200\rangle \hat{z}}_{=0 \text{ by A}}\Big]$

$= 0$

$''$ly $\langle 100 | e\underline{r} | 210\rangle = \dfrac{e\sqrt{2}\,2^7 a}{3^5}\hat{z}$ — by A, B

$$\langle 100|e\underline{r}|21\pm1\rangle = e\left[\langle 100|x|2,1,\pm1\rangle\hat{\underline{x}} + \langle 100|y|2,1,\pm1\rangle\hat{\underline{y}}\right]$$

$$= \mp\frac{e\,2^7 a}{3^5}\hat{\underline{x}} \pm \frac{i\,2^7 a}{3^5}\hat{\underline{y}} \quad \text{— by (c)}$$

$$= \mp\frac{e a\,2^7}{3^5}\left(\hat{\underline{x}} - i\hat{\underline{y}}\right)$$

Then

$$|\langle 100|e\underline{r}|210\rangle|^2 = \frac{2^{15}}{3^{10}}(ea)^2$$

&

$$|\langle 100|e\underline{r}|2,1,\pm1\rangle|^2 = (ea)^2\frac{2^{14}}{3^{10}}\underbrace{\left(|\hat{\underline{x}}|^2 + |\hat{\underline{y}}|^2 + \cancel{i\hat{\underline{x}}\hat{\underline{y}}} - \cancel{i\hat{\underline{y}}\hat{\underline{x}}}\right)}_{=2}$$

$$= (ea)^2\frac{2^{15}}{3^{10}}$$

So

$$|P_{200\to100}|^2 = 0 \quad \longrightarrow A = 0$$

$$|P_{210\to100}|^2 = \frac{(ea)2^{15}}{3^{10}}$$

$$|P_{21\pm1\to100}|^2 = \uparrow$$

for these

Then,

$$A = \frac{|P|^2\,3^2\hbar^2}{\pi\varepsilon_0 c^3 2^9 m^3 a^6} = \frac{3^2\hbar^2}{\pi\varepsilon_0 c^3 2^9 m^3 a^6}\frac{ea\,2^{15}}{3^{10}}$$

$$= \frac{\hbar^2\,2^6}{\quad}$$

$$= \frac{\hbar^2 \, 2^6}{\pi \varepsilon_0 c^3 m^3 a^5 \, 3^8}$$

$$\& \quad \tau = 1/A = \frac{\pi \varepsilon_0 c^3 m^3 a^5 \, 3^8}{\hbar^2 2^6}$$

problem-four

Tuesday, November 5, 2019 1:04 PM

$$H = \frac{1}{2m}\left[\vec{p} - q\vec{A}(\vec{r})\right]^2 \qquad [\vec{p}, \vec{A}(\vec{r})] = \vec{p}\cdot\vec{A}(\vec{r}) - \vec{A}(\vec{r})\cdot\vec{p}$$

a) Consider action on test function:

$$[\vec{p}, \vec{A}]\psi = \vec{p}(\vec{A}\psi) - \vec{A}(\vec{p}\psi) \qquad ; \quad \vec{p} = -i\hbar\vec{\nabla}$$

$$= -i\hbar\left(\underbrace{\vec{\nabla}(\vec{A}\psi) - \vec{A}(\vec{\nabla}\psi)}_{= (\vec{\nabla}\cdot\vec{A})\psi + \cancel{\vec{A}\cdot(\vec{\nabla}\psi)} - \cancel{\vec{A}\cdot(\vec{\nabla}\psi)}}\right)$$

$$= -i\hbar(\vec{\nabla}\cdot\vec{A})\psi$$

n.b. only $\vec{p}$ is an operator

b)
$$H\psi = \frac{1}{2m}\left[\vec{p} - q\vec{A}(\vec{r})\right]\left[\vec{p} - q\vec{A}(\vec{r})\right]\psi$$

$$= \frac{1}{2m}\left[|\vec{p}|^2 - q\vec{p}\cdot\vec{A} - q\vec{A}\cdot\vec{p} + q^2|\vec{A}|^2\right]\psi$$

$$= \frac{1}{2m}\left[p^2\psi - q\,\vec{p}\cdot\vec{A}\psi - q\vec{A}\cdot\vec{p}\psi + q^2A^2\psi\right]$$

need chain rule on $\vec{p}$

$$= \frac{1}{2m}\left(p^2\psi - q(\vec{p}\cdot\vec{A})\psi - q(\vec{p}\psi)\cdot A - q\vec{A}\cdot(\vec{p}\psi) + q^2A^2\psi\right)$$

$$= \frac{1}{2m}\left[p^2\psi + q^2A^2\psi - q\left(\vec{p}\cdot\vec{A}\right)\psi - 2q\,\vec{A}\cdot\left(\vec{p}\,\psi\right)\right]$$

div A

$$= \frac{1}{2m}\left\{\left[-\hbar^2\nabla^2 + q^2A^2 - 2qi\hbar\,\vec{A}\cdot\vec{\nabla}\right]\psi - qi\hbar\,\psi\left(\vec{\nabla}\cdot\vec{A}\right)\right\}$$