PH 585 AMO

Solutions of HW #2

Problem #1 1.15 of B & J

$H_\alpha \Rightarrow n=3 \rightarrow n=2$ transition

$$\bar{\nu}_{ab} = R\left(\frac{1}{n_a^2} - \frac{1}{n_b^2}\right) = \frac{1}{\lambda_{ab}}$$

$\bar{\nu}_{ab}$: wave numbers; R: Rydberg const

For $H_\alpha \Rightarrow \nu_{3\to2} = R\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{5}{36}R \Rightarrow$

$\lambda = \frac{36}{5R} \Rightarrow$

Difference in λ for H (hydrogen) & D (deuterium) $\Rightarrow$

$$\Delta\lambda = \lambda_H - \lambda_D = \frac{36}{5}\left(\frac{1}{R_H} - \frac{1}{R_D}\right) = 1{,}7718 \cdot 10^{-8}\,\text{cm}$$

Table 1.2: $R_H = 109677{,}58\ \text{cm}^{-1}$, $R_D = 109707{,}19\ \text{cm}^{-1}$

$\approx 0{,}177$ nm

PRL 1974 experiment: $\Delta\nu = \nu_{H_\alpha} - \nu_{D_\alpha} = 4{,}145\ \text{cm}^{-1}$ ($\nu_{H_\alpha} = 15233{,}07\ \text{cm}^{-1}$, $\nu_{D_\alpha} = 15237{,}215\ \text{cm}^{-1}$)

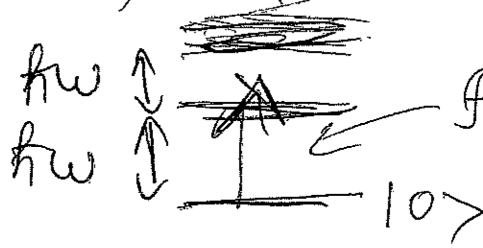
So $\Delta\lambda = \frac{1}{15233{,}07} - \frac{1}{15237{,}215} = (6{,}565 - 6{,}563)\cdot 10^{-5}\,\text{cm}$

$\approx 0{,}2$ nm $\rightarrow$ match well!

Problem #2   2.22 of B&J

$$H' = -qx\,\mathcal{E}(t), \qquad \mathcal{E}(t) = \mathcal{E}_0\, e^{-t/\tau}$$

$$H = H_0 + H'$$



Probability of $|0\rangle \to |n\rangle = ?$

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \leftarrow \text{harmonic oscillator}$$

Recall (2.343b in B&J) from time-dependent perturbation theory: $P_{ba}^{(1)} = |c_b^{(1)}(t)|^2 =$

$$= \frac{1}{\hbar^2}\left|\int_0^t \underbrace{H'_{ba}}(t')\, e^{i\omega_{ba} t'}\, dt'\right|^2$$

$$\langle b|H'|a\rangle = -q\mathcal{E}_0 e^{-t/\tau}\langle b|x|a\rangle$$

$|a\rangle = |0\rangle \leftarrow$ ground state $\Rightarrow$

$$\langle b|x|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle b|a + a^+|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}$$

$\neq 0$ only for $\boxed{b = 1}$

$a|0\rangle = 0$

$a^+|0\rangle = |1\rangle$

need P of transition at $t \to \infty \Rightarrow$

③

Then, $\int_0^{t \to \infty} H'_{10}(t')\, e^{i \overbrace{\omega_{10}}^{=\omega} t'} dt' =$

$$= -q\mathcal{E}_0 \sqrt{\frac{\hbar}{2m\omega}} \int_0^{\infty} e^{t'(i\omega - \frac{1}{\tau})} dt' =$$

$$= -q\mathcal{E}_0 \sqrt{\frac{\hbar}{2m\omega}} \frac{-1}{i\omega - \frac{1}{\tau}} \Rightarrow$$

$$\mathcal{P}_{|0\rangle \Rightarrow |1\rangle} = \frac{(q\mathcal{E}_0)^2}{\hbar^2} \frac{\hbar}{2m\omega} \frac{1}{\omega^2 + \frac{1}{\tau^2}} =$$

$$= \frac{(q\mathcal{E}_0)^2}{2m\hbar\omega} \frac{1}{\omega^2 + \frac{1}{\tau^2}}$$

Problem #3 B & J 4.8

④

$$\bar{f}_{n'l',nl} = \frac{1}{2l+1} \sum_{m'=-l}^{l} \sum_{m=-l}^{l} f_{n'l'm',nlm}$$

Show $\sum_k f_{ka} = 1$ applies to ↩

$n'l'$ $n'l'$ nl

Recall

$$f_{n'l'm',nlm} = f^x_{n'l'm',nlm} + f^y_{n'l'm',nlm} + f^z_{n'l'm',nlm} =$$

$$= \frac{2m\omega_{n'n}}{3\hbar} \underbrace{\left(|x_{n'l'm',nlm}|^2 + |y_{\ldots}|^2 + |z_{\ldots}|^2\right)}_{|\vec{r}_{n'l'm',nlm}|^2}$$

Then, pp. 213-214
(4.138 - 4.140c in B & J) ⇒

$$f^x_{n'l'm',nlm} = \frac{i}{3\hbar} \{ \langle nlm|p_x|n'l'm'\rangle\langle n'l'm'| x|nlm\rangle - \langle nlm|x|n'l'm'\rangle\langle n'l'm'|p_x|nlm\rangle \}$$

$$\Rightarrow \frac{1}{2l+1} \sum_{m'} \sum_{m} f^x_{n'l'm',nlm} = $$

$$= \frac{1}{2l+1} \sum_{m',m} \frac{i}{3\hbar} \{ \langle nlm | p_x | n'l'm' \rangle \langle n'l'm' | x | nlm \rangle - \langle nlm | x | n'l'm' \rangle \langle n'l'm' | p_x | nlm \rangle \}$$ (5)

Same for $\frac{1}{2l+1} \sum_{m',m} f^{y,z}_{n'l'm',nlm}$ ($x \to y$ or z, $p_x \to p_y$ or p_z)

Now

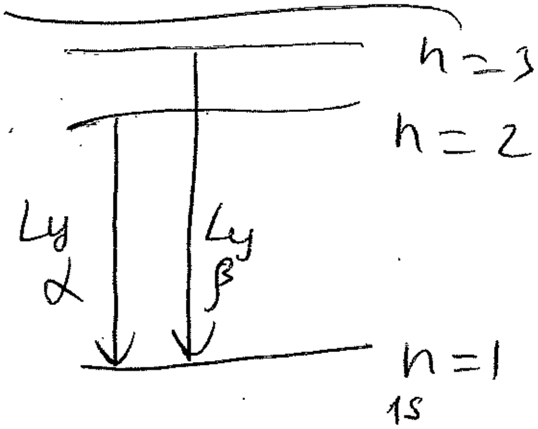
$$\sum_{n',l'} f_{n'l',nl} = \frac{1}{2l+1} \sum_{n'l'} \sum_{m',m} \frac{i}{3\hbar} \{ \langle nlm | p_x | n'l'm' \rangle \langle n'l'm' | \cancel{x} | nlm \rangle - \langle nlm | x | n'l'm' \rangle \cdot \langle n'l'm' | p_x | nlm \rangle + \text{same with } y + \text{same with } z \} =$$

$$= \frac{1}{2l+1} \sum_m \frac{i}{3\hbar} \{ \langle nlm | \underbrace{p_x x - x p_x}_{-i\hbar} | nlm \rangle + \text{same for } y + \text{same for } z \} =$$

$$\uparrow \quad \sum_{n'l'm'} | n'l'm' \rangle \langle n'l'm' | = 1$$

$$= \frac{1}{2l+1} \sum_{m=-l}^{l} \frac{i}{\cancel{3\hbar}} \cdot (-i\cancel{\hbar}) \underbrace{\langle nlm | nlm \rangle}_{1} \cdot \cancel{3} = \frac{1}{2l+1} \cdot \sum_{m=-l}^{l} 1 = \frac{1}{2l+1} (2l+1) = 1$$

Problem # 2   Ly α & β



Need: $\dfrac{W^{s,D}_{2\to1}}{W^{s,D}_{3\to1}} = \dfrac{\omega_{21}^2 f_{21}}{\omega_{31}^2 f_{31}} =$

$$= \frac{\omega_{21}^3}{\omega_{31}^3}\frac{|\vec{r}_{21}|^2}{|\vec{r}_{31}|^2}\,; \quad \frac{I_{2\to1}}{I_{3\to1}} = \frac{\hbar\omega_{21}W^{s,D}_{2\to1}}{\hbar\omega_{31}W^{s,D}_{3\to1}}$$

(In some other definitions of "line intensity" may see relative intensity $= \dfrac{|\vec{r}_{21}|^2}{|\vec{r}_{31}|^2}$ or $\dfrac{f_{21}}{f_{31}}$, i.e. without the frequency factors)

Calculate $|\vec{r}_{\substack{21\\31}}|^2 \Rightarrow \psi_{2lm} = R_{2l}(r)\,Y_{lm}(\theta,\varphi)$, $l = 0, 1$

$\vec{r}_{\substack{21\\31}} = \langle \psi_{1s} | \vec{r} | \psi_{\substack{2lm\\3lm}} \rangle$ $\psi_{3lm} = R_{3l}(r)\,Y_{lm}(\theta,\varphi)$, $l = 0,1,2$

Allowed transitions: $2p \to 1s$
(in electric dipole approx.) $3p \to 1s$

$$|\vec{r}_{\substack{21\\3}}|^2 = \frac{1}{3}\sum_{m=-1}^{1} |\underbrace{r}_{\substack{21m\\3}}{}_{\substack{21\\3}}{}^{\nwarrow 100}|^2 = \frac{1}{3}\sum_m \Big(\frac{1}{2}\underbrace{|x_{\substack{21\\3}} + i y_{\substack{21\\3}}|^2}_{(r\sin\theta e^{i\varphi})_{\substack{21\\31}}} + \frac{1}{2}\underbrace{|x_{\substack{21\\3}} - i y_{\substack{21\\3}}|^2}_{(r\sin\theta e^{-i\varphi})_{\substack{21\\31}}} +$$

$$+ \underbrace{|z_{\substack{21\\3}}|^2}_{(r\cos\theta)_{\substack{21\\31}}} \Big)$$

$$\text{Then,}\quad x_{\substack{21\\31}} + i y_{\substack{21\\31}} = \langle 1\,0\,0 | r \underbrace{\sin\theta\, e^{i\varphi}}_{=-Y_{11}\cdot\sqrt{\frac{8\pi}{3}}} | n\,1\,m \rangle =$$

(2023)

$$= -\frac{1}{\sqrt{\pi a_0^3}} \frac{\sqrt{8\pi}}{\sqrt{3}} \int_0^\infty e^{-r/a_0} R_{n1}(r)\, r^3 dr \underbrace{\int Y_{11} Y_{1m}\, d\Omega}_{=\delta_{m,1}}$$

$$x_{n1} - i y_{n1} = \frac{2\sqrt{2}}{\sqrt{3a_0^3}} \int_0^\infty e^{-r/a_0} R_{n1}(r)\, r^3 dr\ \delta_{m,+1}$$

$$z_{n1} = \frac{2}{\sqrt{3a_0^3}} \int_0^\infty e^{-r/a_0} R_{n1}(r)\, r^3 dr\ \delta_{m0}$$

For $2p \to 1s$ transitions, we already worked through this calculation (see pp. 200–201 of B & J)
Lecture #4

For $3p \to 1s$:

$$\int_0^\infty e^{-r/a_0} \underbrace{R_{31}(r)}_{=\frac{4\sqrt{2}}{9(3a_0)^{3/2}}\left(1-\frac{r}{6a_0}\right)\frac{r}{a_0} e^{-\frac{r}{3a_0}}} r^3 dr = \frac{4\sqrt{2}}{9(3a_0)^{3/2}} \left[\frac{1}{a_0} \underbrace{\int_0^\infty r^4 e^{-\frac{4}{3}\frac{r}{a_0}} dr}_{=\left(\frac{3a_0}{4}\right)^5 \Gamma(5)} - \right.$$

$\Gamma(5) = 4!$

$$\left. - \frac{1}{6a_0^2} \underbrace{\int_0^\infty r^5 e^{-\frac{4}{3}\frac{r}{a_0}} dr}_{=\left(\frac{3a_0}{4}\right)^6 \Gamma(6)} \right] = \frac{4\sqrt{2}\, a_0^4}{9(3a_0)^{3/2}} \underbrace{\left[\frac{3^5}{4^5} 4! - \frac{3^6}{4^6 \cdot 6} 5! \right]}_{=\frac{3^5}{4^5}\left(4! - \frac{3}{4\cdot 6} 5!\right)} =$$

$\Gamma(6) = 5!$

$$\frac{3^5}{4^5}\left(4! - \frac{3}{4\cdot 6} 5!\right) = = \frac{3^5}{4^4} \cdot 6 \left(1 - \frac{15}{24}\right) = \frac{3^7}{4^5}$$

$$= \frac{4\sqrt{2}\, a_0^4}{9\,(3a_0)^{3/2}} \cdot \frac{3^7}{4^5} = \frac{3^4}{4^4}\sqrt{\frac{2}{3}}\, a_0^{5/2}$$

Then, $$x_{31} \pm i y_{31} = \mp \frac{2\sqrt{2}}{\sqrt{3a_0^3}} \cdot \frac{3^4}{4^4} \sqrt{\frac{2}{3}}\, a_0^{5/2}\, \delta_{m,\pm 1} =$$

$$= \mp \frac{3^3}{4^3}\, a_0\, \delta_{m,\pm 1}$$

$$z_{31} = \frac{2\sqrt{2}}{4^4}\, 3^3\, a_0\, \delta_{m,0}$$

$$|\vec{r}_{31}|^2 = \frac{1}{3}\sum_m \left(\frac{1}{2}\cdot \frac{3^6}{4^6} a_0^2\, \delta_{m,1} + \frac{1}{2}\, \frac{3^6}{4^6} a_0^2\, \delta_{m,-1} + \frac{2^3\cdot 3^6}{4^8} a_0^2\, \delta_{m,0} \right) = \frac{1}{3}\left(\frac{3^6}{4^6} a_0^2 + \frac{2^3\cdot 3^6}{4^8} a_0^2 \right) = a_0^2 \cdot \frac{3^{\cancel{7}\,6}}{2^{13}} \cdot \cancel{\frac{1}{3}}$$

So, $$\frac{|r_{21}|^2}{|r_{31}|^2} = \frac{\frac{2^{15}}{3^{10}} \cancel{a_0^2}}{\frac{3^6}{2^{13}} \cancel{a_0^2}} = \frac{2^{28}}{3^{16}} \simeq 6{,}23$$

$$\omega_{21} = E_I \cdot \frac{3}{4}\,; \quad \omega_{31} = E_I \cdot \frac{8}{9}$$

Lyα

$$\frac{I_{2\to 1}}{I_{3\to 1}} = 6.23 \left(\frac{3/4}{8/9} \right)^4 = 6.23 \left(\frac{27}{32} \right)^4 \simeq 3.16$$

Lyβ