07/21/2019 3. Quantum Mechanics (Fall 2005)

An electron in the n = 3, l = 0, m = 0 state of hydrogen decays by a sequence of electric dipole transitions to the ground state.

(a) What decay routes are possible? Specify them by listing the sequence of states |nlm| in each possible route.

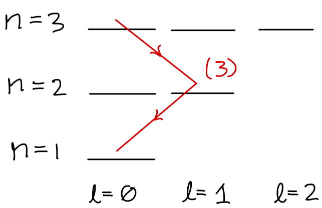
(b) If you had a large number of atoms in this state |300>, what fraction of them would decay via each route? Give an explicit justification for your answer from the expression for the matrix element of the relevant operator.

Hint: You may want to use some of the following: $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ $\quad Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$ $\quad Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}$

This is griffiths QM prob. 9.14 parts (a) and (b).

Solution:

Part a: Electric dipole transitions are governed by the l-selection rule: $\Delta l = \pm 1$.
This is because emitted photons carry-away $\pm\hbar$ in angular momentum.
The m-selection rule is $\Delta m = 0, \pm 1$, depending on the polarization of the incident light.



The allowed paths:
(1) $|300\rangle \to |210\rangle \to |100\rangle$.
(2) $|300\rangle \to |211\rangle \to |100\rangle$
(3) $|300\rangle \to |21{-1}\rangle \to |100\rangle$.

Part b: Here we are asked to compute the probabilities of each path starting with an initial $|300\rangle$ population, going to $|100\rangle$, treating the intermediate trans. as independent events.
c.f. Sakurai eq. 5.7.7 and 5.6.40

For harmonic perturbations,
$$C_n^{(1)} = \frac{-i}{\hbar}\int_0^t dt'\left(\mathcal{V}_{ni}e^{i\omega t'} + \mathcal{V}_{ni}^{+}e^{-i\omega t'}\right)e^{i\omega_{ni}t'} \qquad \text{then } P(|i\rangle \to |n\rangle) \sim |C_n^{(1)}|^2.$$
Where the matrix elements, $\mathcal{V}_{ni}$ are of primary concern.
They are computed, for a harmonic EM field,
$$\mathcal{V}_{ni}^{+} \propto \langle n|\, e^{i(\omega/c)(\hat{n}\cdot\vec{x})}\,\hat{\varepsilon}\cdot\vec{p}\,|i\rangle \qquad \text{with } \hat{n}\text{: propogation direction. } \hat{\varepsilon}\text{: polarization dir.}$$
The electric dipole approx. is to take, $e^{i(\omega/c)(\hat{n}\cdot\vec{x})} \sim 1 + i\frac{\omega}{c}\hat{n}\cdot\vec{x}$. and keep only the 1.

Therefore,
$$\mathcal{V}_{ni}^{+} \propto \langle n|\hat{\varepsilon}\cdot\vec{p}|i\rangle = \hat{\varepsilon}\cdot\langle n|\vec{p}|i\rangle$$
Now use Sakurai eq. 2.2.26 to write, $[\vec{x}, H] = \frac{i\hbar}{m}\vec{p} \to \vec{p} = \frac{m}{i\hbar}[\vec{x}, H]$.
$$\begin{aligned}\mathcal{V}_{ni}^{+} &\approx \frac{m}{i\hbar}\hat{\varepsilon}\cdot\langle n|[\vec{x}, H]|i\rangle \\ &= m/i\hbar\ \hat{\varepsilon}\cdot(\langle n|\vec{x}H|i\rangle - \langle n|H\vec{x}|i\rangle) \\ &= m/i\hbar\ \hat{\varepsilon}\cdot(E_i\langle n|\vec{x}|i\rangle - E_n\langle n|\vec{x}|i\rangle) \\ \mathcal{V}_{ni}^{+} &= im\omega_{ni}\,\hat{\varepsilon}\cdot\underline{\langle n|\vec{x}|i\rangle}.\end{aligned}$$
↳ Wigner-Eckhart tells us that if $\hat{\varepsilon}$ is along the x-axis or y-axis then $\Delta m = \pm 1$. But if $\hat{\varepsilon}$ is along $\hat{z}$, then $\Delta m = 0$.

! We are not told which axis to select, in general all axes should be considered s.t. all possible transitions are allowed from part (a).

(1) $|300\rangle \to |210\rangle$: since $\Delta m = 0$ we need only compute: $\langle 210|z|300\rangle\hat{z}$

(2,3) $|300\rangle \to |21{\pm}1\rangle$: with $\Delta m = \pm 1$ we compute: $\langle 21{\pm}1|x|300\rangle\hat{x} + \langle 21{\pm}1|y|300\rangle\hat{y}$.

Now, Griffiths QM eq. 9.70 tells us how to relate the x and y matrix elements. Specifically,

$$(m'-m)\langle n'l'm'|x|nlm\rangle = i\langle n'l'm'|y|nlm\rangle .$$

so for $m=\pm1$, $m'=0$ we find,

$$\mp\langle 21\pm1|x|300\rangle = i\langle 21\pm1|y|300\rangle .$$

And so,

$$(1): \langle 210|z|300\rangle \hat{z}$$

$$(2,3): \langle 21\pm1|x|300\rangle\hat{x} + \mp\frac{1}{i}\langle 21\pm1|x|300\rangle\hat{y} = \langle 21\pm1|x|300\rangle(\hat{x}\pm i\hat{y}).$$

We have reduced the problem to only 2 matrix elements we need to compute.

1:

$$\langle 210|z|300\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2\sin\theta\, dr\,d\theta\,d\phi \left[R_{21}(r)Y_1^0(\theta,\phi)\right]^\dagger r\cos\theta\left[R_{30}(r)Y_0^0(\theta,\phi)\right].$$

$$= I\int_0^\pi\int_0^{2\pi}\sin\theta\cos\theta\, Y_1^0(\theta,\phi)^* Y_0^0(\theta,\phi)\,d\phi\,d\theta$$

$$= I\sqrt{\frac{1}{4\pi}}\sqrt{\frac{3}{4\pi}}\cdot 2\pi\int_0^\pi \sin\theta\cos^2\theta\,d\theta$$

$$= I\,\sqrt{3}/2\left[2/3\right] = \underline{I/\sqrt{3}}$$

* since we are not given the normalized radial wavefunctions I'll just assume they don't matter in the end and absorb them into a constant "I".

and,

2:

$$\langle 21\pm1|x|300\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} r^2\sin\theta\,dr\,d\theta\,d\phi\left[R_{21}(r)Y_1^{\pm1}(\theta,\phi)\right]^\dagger r\cos\phi\sin\theta\left[R_{30}(r)Y_0^0(\theta,\phi)\right].$$

$$= I\int_0^\pi\int_0^{2\pi}\cos\phi\sin^2\theta\, Y_1^{\pm1}(\theta,\phi)^* Y_0^0(\theta,\phi)\,d\phi\,d\theta$$

$$= I\left(\mp\sqrt{\frac{3}{8\pi}}\right)\left(\frac{1}{\sqrt{4\pi}}\right)\int_0^\pi\int_0^{2\pi}\sin^3\theta\cos\phi\, e^{\mp i\phi}\,d\phi\,d\theta$$

$$= I\left(\mp\sqrt{\frac{3}{8\pi}}\right)\left(\frac{1}{\sqrt{4\pi}}\right)\cdot\left(\frac{4}{3}\right)\int_0^{2\pi}d\phi\cdot\cos\phi\, e^{\mp i\phi}$$

$$= \mp I\sqrt{\frac{3}{2}}\,\frac{1}{\cancel{4\pi}}\left(\frac{\cancel{4}}{3}\right)\cdot\cancel{\pi} = \mp I\sqrt{\frac{3}{2}}\cdot\frac{1}{3} = \underline{\mp I\,1/\sqrt{6}}.$$

Now, each path will have probability proportional to the modulus-squared of each matrix element.

Thus,

$$(1): P(|300\rangle\rightarrow|210\rangle) \propto |\langle 210|z|300\rangle|^2 = \underline{I^2/3}.$$

and

$$(2)\; P(|300\rangle\rightarrow|21\pm1\rangle) \propto |\langle 21\pm1|x|300\rangle(\hat{x}\pm i\hat{y})|^2$$

$$= I^2/6\,(\hat{x}\pm i\hat{y})(\hat{x}\mp i\hat{y})$$

$$= I^2/6\,(2)$$

$$= \underline{I^2/3}.$$

→ All 3 paths out of $|300\rangle$ have equal weighting.... So we expect all equal populations.