and using $\int_0^\pi \sin\theta\cos^2\theta\,d\theta = \int_{-1}^{1} x^2 dx = \frac{2}{3}$, we have

$$\begin{aligned}\langle 210 \mid z \mid 100\rangle &= \int_0^\infty r^3 R_{21}^*(r) R_{10}(r) dr \int_0^\pi \sin\theta\cos^2\theta\,d\theta \int_0^{2\pi} d\phi \\ &= \frac{4\pi}{3}\frac{1}{4\pi a_0^4\sqrt{2}}\int_0^\infty r^4 e^{-3r/2a_0} dr = \frac{2^8 a_0}{3^5\sqrt{2}}. \end{aligned} \tag{10.210}$$

Inserting (10.208) and (10.210) into (10.207) we have

$$P_{1\text{s}\to 2\text{p}} = \frac{2^{15} e^2 E_0^2 \tau^2 a_0^2}{3^{10}\hbar^2}\left|\int_{-\infty}^{+\infty}\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}dt\right|^2. \tag{10.211}$$

We may calculate this integral using the method of residues by closing the contour in the upper half of the t-plane. Since the infinite semicircle has no contribution to the integral, the pole at $t = i\tau$ gives

$$\begin{aligned}\int_{-\infty}^{+\infty}\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}dt &= 2\pi i\,\text{Res}\left[\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}\right]_{t=i\tau} = 2\pi i \lim_{t\to i\tau}\left[\frac{e^{i\omega_{fi}t}}{\tau^2+t^2}\times(t-i\tau)\right] \\ &= 2\pi i \lim_{t\to i\tau}\left[\frac{e^{i\omega_{fi}t}(t-i\tau)}{(t+i\tau)(t-i\tau)}\right] = \frac{\pi}{\tau}e^{-\omega_{fi}\tau}, \end{aligned} \tag{10.212}$$

where

$$\omega_{fi} = \frac{1}{\hbar}(E_f - E_i) = \frac{1}{\hbar}\left(E_{2\text{p}} - E_{1\text{s}}\right) = \frac{1}{\hbar}\left(\frac{1}{4}E_{1\text{s}} - E_{1\text{s}}\right) = -\frac{3}{4\hbar}E_{1\text{s}} = \frac{3R_y}{4\hbar}, \tag{10.213}$$

where R_y is the Rydberg constant: $R_y = 13.6\,\text{eV}$. Inserting (10.212) into (10.211), we obtain the transition probability

$$P_{1\text{s}\to 2\text{p}} = \frac{2^{15}e^2\pi^2E_0^2a_0^2}{3^{10}\hbar^2}\exp\left(-2\omega_{fi}\tau\right) = \frac{2^{15}e^2\pi^2E_0^2a_0^2}{3^{10}\hbar^2}\exp\left(-\frac{3R_y}{2\hbar}\tau\right). \tag{10.214}$$

Problem 10.9

A hydrogen atom is in its excited 2p state. Calculate the transition rate associated with the 2p $\to$ 1s transitions (Lyman) and the lifetime of the 2p state.

Solution

The first expression of the total transition rate is given by (10.141):

$$W_{2\text{p}\to 1\text{s}} = \frac{4\omega_{2\text{p}\to 1\text{s}}^3}{3\hbar c^3}\left|\vec{d}_{2\text{p}\to 1\text{s}}\right|^2, \tag{10.215}$$

where

$$|\vec{d}_{2\text{p}\to 1\text{s}}|^2 = e^2|\langle 2\text{p} \mid \vec{\varepsilon}\cdot\vec{r} \mid 1\text{s}\rangle|^2 = e^2\left|\int_0^\infty r^3 R_{21}^* R_{10}(r)\,dr\int d\Omega\, Y_{1m}^*\vec{\varepsilon}\cdot\hat{r}\,Y_{00}\right|^2. \tag{10.216}$$

First, we need to calculate $\langle 2\text{p} \mid \vec{\varepsilon} \cdot \vec{r} \mid 1\text{s}\rangle$. The radial integral is given by

$$\int_0^\infty r^3 R_{21}^*(r) R_{10}(r)\, dr = \frac{1}{a_0^4\sqrt{6}} \int_0^\infty r^4 e^{-3r/2a_0} dr = \frac{2^8 a_0}{3^4\sqrt{6}}. \tag{10.217}$$

The angular part can be calculated from (10.127) as follows:

$$\begin{aligned}\int d\Omega Y_{1m}^*(\Omega)\vec{\varepsilon}.\hat{r} Y_{00}(\Omega) &= \sqrt{\frac{4\pi}{3}} \int Y_{1m}^* \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} + \epsilon_z Y_{10}\right) Y_{00} d\Omega \\ &= \frac{1}{\sqrt{3}} \int Y_{1m}^* \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{11} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1-1} + \epsilon_z Y_{10}\right) d\Omega \\ &= \frac{1}{\sqrt{3}} \left(\frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m,1} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} \delta_{m,-1} + \epsilon_z \delta_{m,0}\right),\end{aligned} \tag{10.218}$$

since $\int Y_{1m}^*(\theta, \phi) Y_{l_i m_i}(\theta, \phi)\, d\Omega = \delta_{l_i,1}\delta_{m,m_i}$. An insertion of (10.217) and (10.218) into (10.216) leads to

$$|\vec{d}_{2\text{p}\to 1\text{s}}|^2 = 32 \left(\frac{2}{3}\right)^{10} e^2 a_0^2 \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0}\right], \tag{10.219}$$

which, when inserted into (10.215), leads to the total transition rate corresponding to a certain value of the azimuthal quantum number m:

$$W_{2\text{p}\to 1\text{s}} = \frac{4\omega_{2\text{p}\to 1\text{s}}^3}{3\hbar c^3} |\vec{d}_{fi}|^2 = \frac{128 e^2 a_0^2 \omega^3}{3\hbar c^3} \left(\frac{2}{3}\right)^{10} \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0}\right]. \tag{10.220}$$

Summing over the three possible m-states, $m = -1, 0, 1$,

$$\sum_{m=-1}^{1} \left[\frac{1}{2}(\epsilon_x^2 + \epsilon_y^2)(\delta_{m,-1} + \delta_{m,1}) + \epsilon_z^2 \delta_{m,0}\right] = \epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2 = 1, \tag{10.221}$$

and since, as shown in (10.213), $\omega_{2\text{p}\to 1\text{s}} = (E_{2\text{p}} - E_{1\text{s}})/\hbar = 3R_y/(4\hbar) = 3e^2/(8\hbar a_0)$ (because the Rydberg constant R_y is equal to $e^2/(2\hbar a_0)$), we can reduce (10.220) to

$$W_{2\text{p}\to 1\text{s}} = \frac{128}{3\hbar c^3} \left(\frac{2}{3}\right)^{10} e^2 a_0^2 \omega_{2\text{p}\to 1\text{s}}^3 = \left(\frac{2}{3}\right)^8 \left(\frac{e^2}{\hbar c}\right)^4 \frac{c}{a_0} = \left(\frac{2}{3}\right)^8 \frac{c\alpha^4}{a_0}, \tag{10.222}$$

where $\alpha = e^2/(\hbar c) = 1/137$ is the fine structure constant and $a_0 = 0.529 \times 10^{-10}$ m is the Bohr radius. The numerical value of the transition rate is

$$W_{2\text{p}\to 1\text{s}} = \left(\frac{2}{3}\right)^8 \frac{c\alpha^4}{a_0} \simeq \left(\frac{2}{3}\right)^8 \frac{3 \times 10^8\,\text{m}\,\text{s}^{-1}}{137^4 \times 0.529 \times 10^{-10}\,\text{m}} = 0.628 \times 10^9\,\text{s}^{-1}. \tag{10.223}$$

The lifetime of the 2p state is then given by

$$\tau = \frac{1}{W_{2\text{p}\to 1\text{s}}} = \left(\frac{3}{2}\right)^8 \frac{a_0}{c\alpha^4} = \frac{1.5^8 \times 137^4 \times 0.529 \times 10^{-10}\,\text{m}}{3 \times 10^8\,\text{m}\,\text{s}^{-1}} = 1.6 \times 10^{-9}\,\text{s}. \tag{10.224}$$

This value is in very good agreement with experimental data.

Remark
Another way of obtaining (10.222) is to use the relation

$$W_{2p\to 1s} = \frac{4e^2\omega^3_{2p\to 1s}}{3\hbar c^3}\frac{1}{3}\sum_{m=-1}^{1}|\langle 21m \mid \vec{r} \mid 100\rangle|^2$$
$$= \frac{4e^2\omega^3_{2p\to 1s}}{9\hbar c^3}\sum_{m=-1}^{1}\left[|\langle 21m \mid \hat{x} \mid 100\rangle|^2 + |\langle 21m \mid \hat{y} \mid 100\rangle|^2 + |\langle 21m \mid \hat{z} \mid 100\rangle|^2\right], \tag{10.225}$$

where we have averaged over the various transitions. Using the relations $x = r\sin\theta\cos\phi = -\sqrt{2\pi/3}\,r(Y_{11} - Y_{1-1})$, $y = r\sin\theta\sin\phi = i\sqrt{2\pi/3}\,r(Y_{11} + Y_{1-1})$, and $z = r\cos\theta = \sqrt{4\pi/3}\,rY_{10}$, we can show that

$$\langle 21m \mid \hat{x} \mid 100\rangle = -\frac{1}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R^*_{21}(r)R_{10}(r)dr\int Y^*_{1m}(\Omega)\,(Y_{11} - Y_{1-1})\,d\Omega$$
$$= -\frac{1}{\sqrt{6}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right](\delta_{m,1} - \delta_{m,-1}), \tag{10.226}$$

$$\langle 21m \mid \hat{y} \mid 100\rangle = \frac{i}{\sqrt{4\pi}}\sqrt{\frac{2\pi}{3}}\int_0^\infty r^3 R^*_{21}(r)R_{10}(r)dr\int Y^*_{1m}(Y_{11} + Y_{1-1})d\Omega$$
$$= \frac{i}{\sqrt{6}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right](\delta_{m,1} + \delta_{m,-1}), \tag{10.227}$$

$$\langle 21m \mid \hat{z} \mid 100\rangle = \frac{1}{\sqrt{4\pi}}\sqrt{\frac{4\pi}{3}}\int_0^\infty r^3 R^*_{21}(r)R_{10}(r)dr\int Y^*_{1m}Y_{10}d\Omega$$
$$= \frac{1}{\sqrt{3}}\left[\frac{24}{\sqrt{6}}\left(\frac{2}{3}\right)^5 a_0\right]\delta_{m,0}. \tag{10.228}$$

A combination of the previous three relations leads to

$$\sum_{m=-1}^{1}|\langle 21m \mid \vec{r} \mid 100\rangle|^2 = 96a_0^2\left(\frac{2}{3}\right)^{10}\sum_m\left[\frac{1}{6}(\delta_{m,1} - \delta_{m,-1})^2 + \frac{1}{6}(\delta_{m,1} + \delta_{m,-1})^2 + \frac{1}{3}\delta^2_{m,0}\right]$$
$$= 96a_0^2\left(\frac{2}{3}\right)^{10}\sum_m\left[\frac{1}{6}(\delta_{m,1} + \delta_{m,-1}) + \frac{1}{6}(\delta_{m,1} + \delta_{m,-1}) + \frac{1}{3}\delta_{m,0}\right]$$
$$= \frac{96a_0^2}{3}\left(\frac{2}{3}\right)^{10}\sum_{m=-1}^{1}(\delta_{m,-1} + \delta_{m,1} + \delta_{m,0}) = 96\left(\frac{2}{3}\right)^{10}a_0^2. \tag{10.229}$$

Finally, substituting (10.229) into (10.225) and using $\omega_{2p\to 1s} = 3e^2/(8\hbar a_0)$, we obtain

$$W_{2p\to 1s} = \frac{128e^2a_0^2}{3\hbar c^3}\omega^3\left(\frac{2}{3}\right)^{10} = \left(\frac{2}{3}\right)^8\left(\frac{e^2}{\hbar c}\right)^4\frac{c}{a_0} = \left(\frac{2}{3}\right)^8\frac{c\alpha^4}{a_0}. \tag{10.230}$$