tydrogen 2s-1s transition

In non-relativistic QM, this transition is forbidden to all multipole orders or single photon emission. It turns out to be allowed in Dirac theory, however the first non-zero moment is the M1 (magnetic ~~multipole~~ dipole):

transition current $\vec{j}_{fi} = \phi_f^* \vec{\sigma} \chi_i + \chi_f^* \vec{\sigma} \phi_i$ recall Dirac spinor $\psi = \begin{pmatrix} \phi \\ \chi \end{pmatrix}$

"magnetic moment" $\vec{\mu}_{fi} = \frac{1}{2} e \int \vec{r} \times \vec{j}_{fi} \, d^3x$

transition probability $w = \dfrac{4\omega^3}{3\hbar c^3} |\vec{\mu}_{fi}|^2$ ω = transition frequency.

he Dirac spinors for the 2s and 1s states of Hydrogen are known. If they re plugged in and the calculation carried through we get:

$$w = \frac{2^5 \alpha^5 \hbar^2 \omega^3}{3^6 m^2 c^4} = \frac{mc^2 \alpha^{11}}{2^4 3^3 \hbar} = 5.6 \times 10^{-6} \; s^{-1}$$ i.e. ~ once every 2 days

his process is very slow and, as we will see, is dominated by the second-order two photon emission. With two photons, the electric ipole E1 transition is allowed, and we have, up to some constant factors,

$$\text{I} \quad dw = \frac{e^4 \omega'^3 \omega''^3}{\hbar^2 c^6} \left[\left| \sum_n \left(\frac{\langle 1s|\vec{r}\cdot\hat{\epsilon}'|n\rangle\langle n|\vec{r}\cdot\hat{\epsilon}''|2s\rangle}{\omega_{n2} + \omega''} + \frac{\langle 1s|\vec{r}\cdot\hat{\epsilon}''|n\rangle\langle n|\vec{r}\cdot\hat{\epsilon}'|2s\rangle}{\omega_{n2} + \omega'} \right) \right|^2 \right]_{avg} d\omega'$$

bove, ω', ω'', $\hat{\epsilon}'$, and $\hat{\epsilon}''$ are the frequencies and polarizations of the two emitted otons. By conservation of energy we have $\omega' + \omega'' = \omega_{21}$. The averaging is one over all emission directions and polarizations independently. The sum is er all intermediate states (including unbound states).

The only allowed intermediate bound states are the p states which, neglecting fine structure, are triply degenerate. For each n we can then define x-, y-, and z-type orbitals ξ, η, and ζ such that:

$$\langle 1s|\vec{r}\cdot\hat{\epsilon}'|np\rangle\langle np|\vec{r}\cdot\hat{\epsilon}''|2s\rangle = \langle 1s|x\epsilon_x'|n\xi\rangle\langle n\xi|x\epsilon_x''|2s\rangle + \langle 1s|y\epsilon_y'|n\eta\rangle\langle n\eta|y\epsilon_y''|2s\rangle$$
$$+ \langle 1s|z\epsilon_z'|n\zeta\rangle\langle n\zeta|z\epsilon_z''|2s\rangle$$

$$= \cancel{\langle 1s|z\epsilon_z} \; \langle 1s|z|n\zeta\rangle\langle n\zeta|z|2s\rangle\left(\epsilon_x'\epsilon_x''+\epsilon_y'\epsilon_y''+\epsilon_z'\epsilon_z''\right)$$

since $\langle 1s|x|n\xi\rangle\langle n\xi|x|2s\rangle = \langle 1s|y|n\eta\rangle\langle n\eta|y|2s\rangle = \langle 1s|z|n\zeta\rangle\langle n\zeta|z|2s\rangle$

and $\langle 1s|x|n\eta\rangle = \langle 1s|x|n\zeta\rangle = \ldots = 0$ by symmetry.

he sum in (I) for the bound states is then:

$$\hat{\epsilon}'\cdot\hat{\epsilon}'' \sum_{n=2}^{\infty}\left(\frac{1}{\omega_{n2}+\omega''}+\frac{1}{\omega_{n2}+\omega'}\right)\overbrace{\langle 1s|z|n\zeta\rangle\langle n\zeta|z|2s\rangle}^{\text{denote } z_{1n}z_{n2}}$$

The average over polarizations is $(\hat{\epsilon}'\cdot\hat{\epsilon}'')^2_{avg} = \frac{1}{3}$, so (I) becomes.

$$\text{(II)} \quad dw = \frac{e^4\omega'^3\omega''^3}{3\hbar^2c^6}\left|\sum_{n=2}^{\infty}\left(\frac{1}{\omega_{n2}+\omega''}+\frac{1}{\omega_{n2}+\omega'}\right)z_{1n}z_{n2} + \begin{matrix}\text{unbound state}\\ \text{contribution}\end{matrix}\right|^2 d\omega'$$

$$\frac{\omega_{m2}}{\omega_{21}} = \frac{\frac{1}{4}-\frac{1}{m^2}}{\frac{3}{4}}$$

le next relate $z_{1n}z_{n2}$ to the known radial wave functions of Hydrogen by

$$\omega_{21} = \frac{3e^2}{8a_0\hbar}$$

$$z_{1n}z_{n2} = \frac{1}{3}\left(\int_0^\infty r^3 R_{1s}(r)R_{np}(r)dr\right)\left(\int_0^\infty r^3 R_{np}(r)R_{2s}(r)dr\right) \equiv \frac{1}{3}R_{np}^{1s}R_{np}^{2s}$$

$\omega' \to y\omega_{21}$

$\omega'' \to (1-y)\omega_{21}$

nd we define $y \equiv \frac{\omega'}{\omega_{21}}$. The sum inside the brackets then becomes:

$$S = \frac{8a_0^3\hbar}{9e^2}\left[\sum_{m=2}^{\infty}R_{mp}^{1s}R_{mp}^{2s}\left(\frac{1}{\frac{1}{3}-\frac{4}{3m^2}+y}+\frac{1}{\frac{4}{3}-\frac{4}{3m^2}-y}\right) + \int_0^\infty C_{1s}C_{2s}\left(\frac{1}{\frac{1}{3}+\frac{4}{3}x^2+y}+\frac{1}{\frac{4}{3}+\frac{4}{3}x^2-y}\right)dx\right] \quad *$$

he continuous variable x is related to the unbound energy by $E = \frac{e^2x^2}{2a_0}$.

$_{1s}$ and C_{2s} are ~~some~~ (known) functions of x which encode transition information.

This expression would then be squared, multiplied by the factor at front, and integrated over $y \in (0,1)$ to obtain the total decay rate. This can be done numerically, but it is a little simpler to find bounds for w by noting that S is maximized at $y = \frac{1}{2}$ and minimized at $y=0$ or $y=1$.

Keeping the dominant m=2 term and substituting $y=\frac{1}{2}$ or $y=0$ for the others gives upper and lower bounds on S:

$$S_{min} = \frac{2a_0^3 h}{3e^2}\left[\frac{\frac{4}{3}R_{2p}^{1s}R_{2p}^{2s}}{y(1-y)} + \overbrace{\sum_{m=3}^{\infty}\frac{2R_{mp}^{1s}R_{mp}^{2s}}{\frac{5}{8}-\frac{1}{m^2}} + \int_0^{\infty}\frac{2C_{1s}C_{2s}}{\frac{5}{8}+x^2}dx}^{b_1}\right]$$

$$S_{max} = \frac{2a_0^3 h}{3e^2}\left[\frac{\frac{4}{3}R_{2p}^{1s}R_{2p}^{2s}}{y(1-y)} + \overbrace{\sum_{m=3}^{\infty}R_{mp}^{1s}R_{mp}^{2s}\left(\frac{1}{\frac{1}{4}-\frac{1}{m^2}}+\frac{1}{1-\frac{1}{m^2}}\right) + \int_0^{\infty}C_{1s}C_{2s}\left(\frac{1}{\frac{1}{4}+x^2}+\frac{1}{1+x^2}\right)dx}^{b_2}\right]$$

The bounds on w are then:

$$W_{min/max} = \frac{3^4}{8^5}\cdot\alpha^6\cdot\frac{e^2}{2a_0 h}\left[\frac{a^2}{6}-\frac{ab_{1/2}}{15}+\frac{b_{1/2}^2}{140}\right]s^{-1} \qquad a \equiv \frac{4}{3}R_{2p}^{1s}R_{2p}^{2s}$$

$$= 1.22\left[\frac{a^2}{6}-\frac{ab_{1/2}}{15}+\frac{b_{1/2}^2}{140}\right]s^{-1}$$

$$\Rightarrow 4.4\ s^{-1} \leq w \leq 8.7\ s^{-1}$$

The exact value is known to be around $7\ s^{-1}$, or once every .15s. This is much faster than the single photon M1 transition and so is the dominant mode of decay. This is of particular interest since this process has a continuous emission spectrum, as opposed to the discrete line emissions of single photon decays. Any large collection of 2s Hydrogen atoms in vacuum (such as in a nebula) would thus emit a band of radiation near the Lyman α-line.

* From Breit and Teller:

$$C_{1s} = 4^2 \frac{e^{-\left(\frac{2}{x}\right)\tan^{-1}x}}{\sqrt{1-e^{-2\pi/x}}} \cdot \frac{\sqrt{x}}{(1+x^2)^{5/2}}$$

$$C_{2s} = 2^{\frac{17}{2}} \frac{e^{-\left(\frac{2}{x}\right)\tan^{-1}2x}}{\sqrt{1-e^{-2\pi/x}}} \frac{\sqrt{x(1+x^2)}}{(1+4x^2)^3}$$