

# Hydrogen selection rules

Verify the following selection rules by computing spontaneous emission rates.

$$|\Delta l| = 1, \quad |\Delta m| \leq 1$$

The spontaneous emission rate is

$$A_{i \rightarrow f} = \frac{4\alpha\omega_{i \rightarrow f}^3 |R_{i \rightarrow f}|^2}{3c^2}$$

where

$$\omega_{i \rightarrow f} = \frac{E_f - E_i}{\hbar}, \quad E_n = -\frac{\alpha\hbar c}{2n^2 a_0}$$

$$|R_{i \rightarrow f}|^2 = |x_{i \rightarrow f}|^2 + |y_{i \rightarrow f}|^2 + |z_{i \rightarrow f}|^2$$

$$x_{i \rightarrow f} = \int_0^\infty \int_0^\pi \int_0^{2\pi} x \psi_f^* \psi_i dV, \quad y_{i \rightarrow f} = \int_0^\infty \int_0^\pi \int_0^{2\pi} y \psi_f^* \psi_i dV, \quad z_{i \rightarrow f} = \int_0^\infty \int_0^\pi \int_0^{2\pi} z \psi_f^* \psi_i dV$$

and

$$x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi, \quad z = r \cos \theta$$

$$dV = r^2 \sin \theta dr d\theta d\phi$$

The wave function for hydrogen is

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

where

$$R_{nl}(r) = \frac{2}{n^2} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left( \frac{2r}{na_0} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2r}{na_0} \right) \exp \left( -\frac{r}{na_0} \right) a_0^{-3/2}$$

$$L_n^m(x) = (n+m)! \sum_{k=0}^n \frac{(-x)^k}{(n-k)!(m+k)!k!}$$

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos \theta) \exp(im\phi)$$

$$P_l^m(\cos \theta) = \begin{cases} \left( \frac{\sin \theta}{2} \right)^m \sum_{k=0}^{l-m} (-1)^k \frac{(l+m+k)!}{(l-m-k)!(m+k)!k!} \left( \frac{1-\cos \theta}{2} \right)^k, & m \geq 0 \\ (-1)^m \frac{(l+m)!}{(l-m)!} P_l^{|m|}(\cos \theta), & m < 0 \end{cases}$$