

Hydrogen selection rules

By computing transition elements, verify the following selection rules.

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

The transition element $|R_{i \rightarrow f}|^2$ for spontaneous emission is

$$|R_{i \rightarrow f}|^2 = |\langle \psi_f | \hat{x} | \psi_i \rangle|^2 + |\langle \psi_f | \hat{y} | \psi_i \rangle|^2 + |\langle \psi_f | \hat{z} | \psi_i \rangle|^2$$

where

$$\langle \psi_f | \hat{x} | \psi_i \rangle = \int_V \psi_f^* \hat{x} \psi_i dV, \quad \langle \psi_f | \hat{y} | \psi_i \rangle = \int_V \psi_f^* \hat{y} \psi_i dV, \quad \langle \psi_f | \hat{z} | \psi_i \rangle = \int_V \psi_f^* \hat{z} \psi_i dV$$

For the dipole approximation the operators are

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

In spherical coordinates the measure is

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

The wave function for hydrogen is

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

where

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

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

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

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