

## Selection rules

As we derived in the previous lectures, the probability of transition between states is proportional to the absolute square of  $\langle \psi_f | \hat{H}' | \psi_i \rangle$  (we assume that  $H'(\vec{r}, t) = \hat{H}'(\vec{r}) f(t)$  is separable). Typically, whether an atom/molecule emits or absorbs the radiation, the wavelength of that radiation is much longer than the size of the system (for an atom that would be  $a_0$  - the Bohr radius). Indeed, optical/ultraviolet/infrared transitions typically have  $\lambda \approx 100 - 1000 \text{ nm}$ , whereas  $a_0 \approx 0.05 \text{ nm}$ . Hence the spatial profile of the field is essentially uniform. The potential, which corresponds to a uniform field is

$$\hat{H}'(\vec{r}) = e\vec{E} \cdot \vec{r}$$

With such  $\hat{H}'$  the transition probability is proportional to  $|\langle \psi_f | \hat{H}' | \psi_i \rangle|^2$ , or, more generally to  $|\langle \psi_f | \vec{r} | \psi_i \rangle|^2$ . Oftentimes, these quantities are zero. It is helpful to know in advance when this is going to happen. Selection rules that constrain the possible transitions have been derived precisely for that purpose. In molecules the selection rules have been derived for electronic, vibrational, and rotational transitions. Below we will consider selection rules for the electronic transitions on the example of the hydrogen atom, or any system with a spherically symmetric hamiltonian.

We will be looking at the matrix elements of this kind:

$$\langle n' l' m' | \vec{r} | n l m \rangle$$

where  $n, l, m$  are the usual quantum numbers

Selection rules for  $m$  and  $m'$ :

Consider commutators

$$[L_z, x] = iy \quad [L_z, y] = -ix \quad [L_z, z] = 0$$

$$\begin{aligned} 0 &= \langle n' l' m' | [L_z, z] | n l m \rangle = \langle n' l' m' | L_z z - z L_z | n l m \rangle \\ &= \langle n' l' m' | (m' \hbar z - z m \hbar) | n l m \rangle = (m' - m) \hbar \langle n' l' m' | z | n l m \rangle \end{aligned}$$

Therefore either  $m' = m$  or else  $\langle n' l' m' | z | n l m \rangle = 0$

Similarly,

$$\begin{aligned} \langle n' l' m' | [L_z, x] | n l m \rangle &= \langle n' l' m' | L_z x - x L_z | n l m \rangle = \\ &= (m' - m) \hbar \langle n' l' m' | x | n l m \rangle = i \hbar \langle n' l' m' | y | n l m \rangle \end{aligned}$$

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

Finally,

$$\begin{aligned} \langle n' l' m' | [L_z, y] | n l m \rangle &= \langle n' l' m' | L_z y - y L_z | n l m \rangle = \\ &= (m' - m) \hbar \langle n' l' m' | y | n l m \rangle = -i \hbar \langle n' l' m' | x | n l m \rangle \quad (**) \end{aligned}$$

Combining (\*) and (\*\*) we get

$$(m' - m)^2 \langle n' l' m' | x | n l m \rangle = i (m' - m) \langle n' l' m' | y | n l m \rangle = \langle n' l' m' | x | n l m \rangle$$

Hence

$$\text{either } (m' - m)^2 = 1 \quad \text{or} \quad \langle n' l' m' | x | n l m \rangle = \langle n' l' m' | y | n l m \rangle = 0$$

The conclusion is such that no transition occurs unless

$$\Delta m = \pm 1, 0$$

This rule constitutes the conservation of the  $z$ -component of the ang. mom. of the total (atom + photon) system

Selection rules for  $l$  and  $l'$

First let us derive the following commutator:

$$[L^2, [L^2, \vec{r}]]$$

To do so we start with simpler relations

$$\vec{L} = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \vec{e}_x - i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \vec{e}_y - i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \vec{e}_z$$

$$[L_x, x] = 0$$

$$[L_x, y] = -i\hbar \left[ \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) y - y \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] =$$

$$= i\hbar z$$

$$[L_x, z] = -i\hbar \left[ \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) z - z \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right] =$$

$$= -i\hbar y$$

$$[L_y, x] = -i\hbar \left[ \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) x - x \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right] = -i\hbar z$$

$$[L_y, y] = 0$$

$$[L_y, z] = i\hbar x$$

$$[L_z, x] = i\hbar y$$

$$[L_z, y] = -i\hbar x$$

$$[L_z, z] = 0$$

recall $[\frac{\partial}{\partial x}, x] = 1$ and $\frac{\partial}{\partial x} x = x \frac{\partial}{\partial x} + 1$
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Next

$$[L_x^2, x] = 0$$

$$[L_x^2, y] = L_x(L_x y) - y L_x^2 = L_x(y L_x + i\hbar z) - y L_x^2 = (L_x y) L_x + i\hbar(L_x z) - y L_x^2 =$$

$$= (y L_x + i\hbar z) L_x + i\hbar L_x z - y L_x^2 = i\hbar(z L_x + L_x z) = i\hbar(z L_x + z L_x - i\hbar y) = 2i\hbar z L_x + \hbar^2 y$$

$$[L_x^2, z] = L_x(L_x z) - z L_x^2 = L_x(z L_x - i\hbar y) - z L_x^2 = (L_x z) L_x - i\hbar(L_x y) - z L_x^2 =$$

$$= (z L_x - i\hbar y) L_x - i\hbar(y L_x + i\hbar z) - z L_x^2 = -i\hbar y L_x - i\hbar y L_x + \hbar^2 z = -2i\hbar y L_x + \hbar^2 z$$

$$[L_y^2, x] = L_y(L_y x) - x L_y^2 = L_y(x L_y - i\hbar z) - x L_y^2 = (L_y x) L_y - i\hbar(L_y z) - x L_y^2 =$$

$$= (x L_y - i\hbar z) L_y - i\hbar(z L_y + i\hbar x) - x L_y^2 = -i\hbar z L_y - i\hbar z L_y + \hbar^2 x = -2i\hbar z L_y + \hbar^2 x$$

$$[L_y^2, y] = 0$$

$$[L_y^2, z] = L_y(L_y z) - z L_y^2 = L_y(z L_y + i\hbar x) - z L_y^2 = (L_y z) L_y + i\hbar(L_y x) - z L_y^2 =$$

$$= (z L_y + i\hbar x) L_y + i\hbar(x L_y - i\hbar z) - z L_y^2 = i\hbar x L_y + i\hbar x L_y + \hbar^2 z = 2i\hbar x L_y + \hbar^2 z$$

$$[L_z^2, x] = 2i\hbar y L_z + \hbar^2 x$$

$$[L_z^2, y] = -2i\hbar x L_z + \hbar^2 y$$

Next

$$[L^2, x] = 0 - 2i\hbar z L_y + \hbar^2 x + 2i\hbar y L_z + \hbar^2 x = 2\hbar^2 x + 2i\hbar(y L_z - z L_y)$$

$$= 2i\hbar(y L_z - z L_y - i\hbar x)$$

$$[L^2, y] = 2i\hbar(z L_x - x L_z - i\hbar y)$$

$$[L^2, z] = 2i\hbar(x L_y - y L_x - i\hbar z)$$

Now

$$[L^2, [L^2, x]] = 2i\hbar [L^2, y L_z - z L_y - i\hbar x] =$$

$$= 2i\hbar (L^2 y L_z - y L_z L^2 - L^2 z L_y + z L_y L^2 - i\hbar \{L^2 x - x L^2\}) =$$

$$= 2i\hbar ( \underbrace{[L^2, y] L_z + y [L^2, L_z]}_0 - \underbrace{[L^2, z] L_y + z [L^2, L_y]}_0 - i\hbar \{L^2 x - x L^2\} ) =$$

$$= 2i\hbar \left( 2i\hbar (zL_x - xL_z - ity)L_z - 2i\hbar (xL_y - yL_x - itz)L_y - i\hbar (L^2x - xL^2) \right)$$

$$= -2\hbar^2 \left( 2zL_xL_z - 2xL_z^2 - 2ityL_z - 2xL_y^2 + 2yL_xL_y + 2itizL_y - i\hbar (L^2x - xL^2) \right)$$

Now  $2xL_z^2 + 2xL_y^2 = 2x(L_x^2 + L_y^2 + L_z^2) - 2xL_x^2 = 2xL^2 - 2xL_x^2$

So

$$[L^2, [L^2, x]] = -2\hbar^2 \left( 2zL_xL_z - 2ityL_z - 2xL^2 + 2xL_x^2 + 2yL_xL_y + 2itizL_y - L_x^2 + xL^2 \right)$$

$$= 2\hbar^2 (xL^2 + L^2x) - 4\hbar^2 \left( \underbrace{(zL_x - ity)L_z}_{L_x z} + \underbrace{(yL_x + itz)L_y}_{L_x y} + \underbrace{xL_xL_x}_{L_x \times L_x} \right)$$

$$= 2\hbar^2 (xL^2 + L^2x) - 4\hbar^2 \left( \underbrace{L_x zL_z + L_x yL_y + L_x \times L_x}_{L_x (\vec{r} \cdot \vec{L})} \right);$$

So  $[L^2, [L^2, x]] = 2\hbar^2 (xL^2 + L^2x)$

and, more generally,

$$[L^2, [L^2, \vec{r}]] = 2\hbar^2 (\vec{r}L^2 + L^2\vec{r})$$

Now we use the above commutator and place it between  $\langle n' e' m' |$  and  $| n e m \rangle$

$$\begin{aligned} \langle n' e' m' | [L^2, [L^2, \vec{r}]] | n e m \rangle &= 2\hbar^2 \langle n' e' m' | (\vec{r}^2 L^2 + L^2 \vec{r}^2) | n e m \rangle = \\ &= 2\hbar^4 (e'(e'+1) + e'(e'+1)) \langle n' e' m' | \vec{r}^2 | n e m \rangle = \langle n' e' m' | (L^2 [L^2, \vec{r}] - [L^2, \vec{r}] L^2) | n e m \rangle \\ &= \hbar^2 (e'(e'+1) - e(e+1)) \langle n' e' m' | [L^2, \vec{r}^2] | n e m \rangle = \\ &= \hbar^2 (e'(e'+1) - e(e+1)) \langle n' e' m' | (L^2 \vec{r}^2 - \vec{r}^2 L^2) | n e m \rangle = \\ &= \hbar^4 (e'(e'+1) - e(e+1))^2 \langle n' e' m' | \vec{r}^2 | n e m \rangle \end{aligned}$$

From where we can conclude that

either  $2(e'(e'+1) + e'(e'+1)) = (e'(e'+1) - e(e+1))^2$   
 otherwise  $\langle n' e' m' | \vec{r}^2 | n e m \rangle = 0$

However,

$$\begin{aligned} (e'(e'+1) - e(e+1)) &= (e'+e+1)(e'-e) \\ (e'(e'+1) - e(e+1))^2 &= (e'+e+1)^2 (e'-e)^2 \end{aligned}$$

and

$$2(e'(e'+1) + e'(e'+1)) = (e'+e+1)^2 + (e'-e)^2 - 1$$

Then we have  $(e'+e+1)^2 (e'-e)^2 - ((e'+e+1)^2 + (e'-e)^2 - 1) = 0$

or  $((e'+e+1)^2 - 1)((e'-e)^2 - 1) = 0$

otherwise  $\langle n' e' m' | \vec{r}^2 | n e m \rangle = 0$

The first factor  $((e'+e+1)^2 - 1)$  cannot be zero (unless  $e' = e = 0$ ) so the condition simplifies to  $e' = e \pm 1$ , or

$$\Delta l = \pm 1$$

This result can also be interpreted as the conservation of angular momentum of a combined atom-photon system.