SELECTION RULES FOR SPONTANEOUS EMISSION OF RADIATION

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 9.12.

In calculating emission rates (either stimulated or spontaneous) of radiation from an atom, we are confronted with calculating the matrix elements of the dipole moment

$$\mathfrak{p} = q\left\langle \psi_b \left| \mathbf{r} \right| \psi_a \right\rangle \tag{1}$$

Although the calculation of these elements is, in general, quite a complicated affair, in the case where the hamiltonian is spherically symmetric (as in the case of the hydrogen atom) then we can solve the Schrödinger equation by separation of variables, giving a wave function that is the product of a radial function and a spherical harmonic. Since spherical harmonics are eigenfunctions of angular momentum, we can use the commutation relations between the angular momentum operators and the position coordinates to derive some selection rules for radiative transitions. The relevant commutation relations are

$$\begin{aligned} [L_z, x] &= i\hbar y && (2)\\ [L_z, y] &= -i\hbar x && (3)\\ [L_z, z] &= 0 && (4) \end{aligned}$$

Using the last relation, we have

$$\left\langle n'l'm' \left| L_z z - z L_z \right| nlm \right\rangle = 0 \tag{5}$$

Since $|nlm\rangle$ is an eigenstate of L_z with eigenvalue $m\hbar$ and L_z is hermitian, we have

$$\left\langle L_z n'l'm' \left| z \right| nlm \right\rangle - m\hbar\left\langle n'l'm' \left| z \right| nlm \right\rangle = m'\hbar\left\langle n'l'm' \left| z \right| nlm \right\rangle - m\hbar\left\langle n'l'm' \left| z \right| nlm \right\rangle \tag{6}$$

$$= \left(m' - m\right)\hbar\left\langle n'l'm' \left| z \right| nlm \right\rangle \tag{7}$$

$$= 0 \tag{8}$$

Thus either $m' = m$ or $\langle n'l'm'|z|nlm\rangle = 0$, so only elements where $m' = m$ can possibly be non-zero.

Using the other two commutation relations (done in Griffiths, section 9.3.3) gives us the selection rule that only transitions where $\Delta m = \pm 1, 0$ can occur.

To get selection rules involving the l quantum number, we need a more complex commutation relation. We start with the identity:

$$\left[A^2, B\right] = A[A,B] + [A,B]A \tag{9}$$

Applying this to $\left[L^2, z\right]$ we get

$$\begin{aligned}\left[L^2, z\right] &= \left[L_x^2, z\right] + \left[L_y^2, z\right] + \left[L_z^2, z\right] &(10)\\ &= L_x[L_x, z] + [L_x, z]L_x + L_y[L_y, z] + [L_y, z]L_y + 0 &(11)\end{aligned}$$

since $[L_z, z] = 0$.

To get the other commutators, we can use the 3-D version of the identity

$$[x, p_x] = [y, p_y] = [z, p_z] = i\hbar \tag{12}$$

We get

$$\begin{aligned}[L_x, z] &= [yp_z - zp_y, z] &(13)\\ &= -i\hbar y &(14)\\ [L_y, z] &= [zp_x - xp_z, z] &(15)\\ &= i\hbar x &(16)\end{aligned}$$

Going back to 11 we get

$$\left[L^2, z\right] = -i\hbar(L_x y + yL_x) + i\hbar(L_y x + xL_y) \tag{17}$$

We now need a couple more commutators

$$\begin{aligned}[L_x, y] &= [yp_z - zp_y, y] &(18)\\ &= i\hbar z &(19)\\ L_x y &= yL_x + i\hbar z &(20)\\ [L_y, x] &= [zp_x - xp_z, x] &(21)\\ &= -i\hbar z &(22)\\ L_y x &= xL_y - i\hbar z &(23)\end{aligned}$$

Therefore, 17 becomes

$$\begin{aligned}\left[L^2, z\right] &= -i\hbar\left(2yL_x + i\hbar z\right) + i\hbar\left(2xL_y - i\hbar z\right) &(24)\\ &= 2i\hbar\left(xL_y - yL_x - i\hbar z\right) &(25)\end{aligned}$$

We can cyclically permute x, y and z to get

$$\begin{aligned}\left[L^2, x\right] &= 2i\hbar\left(yL_z - zL_y - i\hbar x\right) &(26)\\ \left[L^2, y\right] &= 2i\hbar\left(zL_x - xL_z - i\hbar y\right) &(27)\end{aligned}$$

We now form the compound commutator

$$\left[L^2, \left[L^2, z\right]\right] = 2i\hbar\left[L^2, xL_y - yL_x - i\hbar z\right] \qquad (28)$$

Looking at the first term on the RHS:

$$\begin{aligned}\left[L^2, xL_y\right] &= \left[L^2, x\right]L_y + x\left[L^2, L_y\right] &(29)\\ &= 2i\hbar\left(yL_z - zL_y - i\hbar x\right)L_y &(30)\\ &= 2i\hbar\left(yL_z - i\hbar x\right)L_y - zL_y^2 &(31)\\ &= 2i\hbar\left(L_z yL_y - zL_y^2\right) &(32)\end{aligned}$$

where the second line uses $\left[L^2, L_y\right] = 0$ and the fourth line uses 3. Using similar arguments, the second term in 28 is

$$\begin{aligned}-\left[L^2, yL_x\right] &= -\left[L^2, y\right]L_x - y\left[L^2, L_x\right] &(33)\\ &= -2i\hbar\left(zL_x - xL_z - i\hbar y\right)L_x &(34)\\ &= 2i\hbar\left(-zL_x^2 + xL_zL_x + i\hbar yL_x\right) &(35)\\ &= 2i\hbar\left(-zL_x^2 + L_z xL_x\right) &(36)\end{aligned}$$

where the last line uses 2. Now adding 32 and 36 we get

$$\begin{aligned}\left[L^2, xL_y\right] - \left[L^2, yL_x\right] &= 2i\hbar\left(L_z xL_x + L_z yL_y - z\left(L_x^2 + L_y^2\right)\right) &(37)\\ &= 2i\hbar\left(L_z\mathbf{r}\cdot\mathbf{L} - zL_z^2 - zL^2 + zL_z^2\right) &(38)\\ &= -2i\hbar zL^2 &(39)\end{aligned}$$

To get the last line, we used $\mathbf{r}\cdot\mathbf{L} = \mathbf{r}\cdot(\mathbf{r}\times\mathbf{p}) = 0$.
The final term on the RHS of 28 is

$$-i\hbar\left[L^2, z\right] = -i\hbar\left(L^2 z - zL^2\right) \qquad (40)$$

so combining the last two formulas, we get

$$\begin{aligned} \left[L^2,\left[L^2,z\right]\right] &= 2i\hbar\left(-2i\hbar zL^2 - i\hbar\left(L^2z - zL^2\right)\right) && (41)\\ &= 2\hbar^2\left(L^2z + zL^2\right) && (42) \end{aligned}$$

The same formula applies to the other two coordinates, so we get

$$\left[L^2,\left[L^2,\mathbf{r}\right]\right] = 2\hbar^2\left(L^2\mathbf{r} + \mathbf{r}L^2\right) \tag{43}$$

By inserting this commutator in a matrix element, we can work out

$$\left\langle n'l'm'\left|\left[L^2,\left[L^2,\mathbf{r}\right]\right]\right|nlm\right\rangle = 2\hbar^2\left\langle n'l'm'\left|\left(L^2\mathbf{r} + \mathbf{r}L^2\right)\right|nlm\right\rangle \tag{44}$$

After some algebra (done by Griffiths), we get the condition that either

$$\left\langle n'l'm'\left|\mathbf{r}\right|nlm\right\rangle = 0 \tag{45}$$

or

$$\left[\left(l'+l+1\right)^2 - 1\right]\left[\left(l'-l\right)^2 - 1\right] = 0 \tag{46}$$

The latter condition requires that either $l' = l = 0$ or $l' = l \pm 1$. In the next post, we'll see that $l' = l = 0$ also gives a zero matrix element, so the only allowed transitions are ones for which $\Delta l = \pm 1$.

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