

Selection Rules

Calculation of transition probability for absorption, stimulated emission and spontaneous emission has been reduced to the evaluation of the transition dipole moment.

$$\mu_{kn} = \langle \Psi_k | \mu | \Psi_n \rangle \rightarrow (1)$$

Where $\mu = -er$. Transition between all the states are not allowed. The selection rule's specify the transition that may occur on the basis of dipole approximation. Transitions for which the transition dipole moment is nonzero are **allowed transitions** and those for which it is zero are **forbidden transitions**. The transition dipole moment can be considered as a measure of the imbalance created in the electromagnetic field when the electron makes a transitions between states.

We have already seen that the parity of an atomic orbital with quantum number l is $(-1)^l$. The S and d - orbitals have even parity whereas p and f orbitals have odd parity. The parity of the integrand of the transition dipole moment μ_{kn} is

$$(-1)^{l_k}(-1)(-1)^{l_n} = (-1)^{l_k+l_n+1} \rightarrow (2)$$

Which is even, if the two orbitals have opposite parity and odd if they have the same parity. Group theoretical considerations suggests that a transition dipole moment will be finite only when the integrand is totally symmetric under symmetry operation system. Therefore, the only allowed electric dipole transitions are those involving a change in parity. This is called the **Laporte selection rule**.

For hydrogenic atoms, we may specify the states by the usual quantum numbers n, l, m . For a transition to be allowed, the dipole moment matrix element $\langle n'l'm' | r | nlm \rangle$ Must be finite. On the basis of the **Laporte selection rule**, this matrix element will be finite only when.

$$l' - l = \Delta l = \pm 1 \rightarrow (3)$$

To obtain the selection rule on quantum number m , we may write matrix element as $\langle n'l'm' | r | nlm \rangle = \hat{i} \langle n'l'm' | x | nlm \rangle + \hat{j} \langle n'l'm' | y | nlm \rangle + \hat{k} \langle n'l'm' | z | nlm \rangle \rightarrow (4)$

If the radiations is plane polarized with electric field in z- direction, the z- component of the dipole moment is the only relevant quantity which is given by $\langle n'l'm' | r \cos \theta | nlm \rangle$.

The ϕ - part of this integral

$$\int_0^{2\pi} \exp [i(m - m')\phi] d\phi = \text{finite}$$

$$\text{Only when } m = m' \quad \text{or } \Delta m = 0$$

If the radiation is polarized in the xy- plane, we have to calculate the matrix elements of x and y. However, it is found convenient to evaluate the matrix element of $x \pm iy$ since it is always possible to get the corresponding values of x and y by the relations

$$X = \frac{1}{2} [(x+iy) + (x-iy)]$$

And

$$Y = \frac{1}{2i} [(x+iy) - (x-iy)]$$

In polar coordinates

$$x \pm iy = r \sin \theta \cos \phi \pm ir \sin \theta \exp (\pm i\phi)$$

Now the matrix element of $x \pm iy$ is

$$\langle n'l'm' | r \sin \theta \exp (\pm i\phi) | nlm \rangle = f(r, \theta) \int_0^{2\pi} \exp [i(m - m' \pm 1)\phi] d\phi$$

The ϕ part is nonvanishing only when

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

Therefore , for arbitrary polarization, the general selection rule is

The radial part of the integral $\langle n'l'm' | r | nlm \rangle$ is nonvanishing whatever be the values of n' , l' , n and l . Any value of Δn is therefore allowed when transitions are in conformity with the other selection rules. Thus , the selection rules for hydrogenic atoms are

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

The origin of the selection rule $\Delta l = \pm 1$ may be linked to spin angular momentum of photon which is equal to 1. When a photon is emitted or absorbed, to conserve the total angular momentum, the original angular momentum of the electron depending on the orientation of the electron's angular momentum with the angular momentum of photon.