Selection rule for electric dipole transition

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Electric dipole transition is the dominant effect of an interaction of an electron in an atom with the electromagnetic field. The transition dipole moment or transition moment, usually denoted $\langle l', m'|\hat{\boldsymbol{r}}|l, m\rangle$ for a transition between an initial state, $|l, m\rangle$, and a final state, $|l, m\rangle$, is the electric dipole moment associated with the transition between the two states. The emission of photon occurs as a result of the transition. The polarization of the photon (linearly polarized photon, the right-hand circularly polarized photon, and the left-hand circularly polarized photon) is dependent on the detail of the transitions. The angular momentum of the photon can be derived from the conservation of the total angular momentum.

Here we discuss the selection rule of the electric dipole transition. We need to discuss first the properties of the commutation relations for the angular momentum (the orbital angular momentum $\hat{\boldsymbol{L}}$, the spin angular momentum $\hat{\boldsymbol{S}}$, the total angular momentum $\hat{\boldsymbol{J}}$) for the electrons in an atom.

1. Orbital angular momentum of electron

The orbital angular momentum $\hat{\boldsymbol{L}}$ of the electron is defined as

$$\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}},$$

or

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x,$$

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y,$$

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z.$$

The following commutation relations are valid:

$$\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}} = i\hbar\hat{\boldsymbol{L}},$$

or

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x , \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y , \qquad [\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z .$$

We also have the commutation relations,

$$[\hat{L}_z, \hat{z}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{z}] = 0 ,$$

$$[\hat{L}_z, \hat{x}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = -[\hat{y}\hat{p}_x, \hat{x}] = -\hat{y}[\hat{p}_x, \hat{x}] = i\hbar\hat{y} ,$$

$$[\hat{L}_z, \hat{y}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}] = [\hat{x}\hat{p}_y, \hat{y}] = -i\hbar\hat{x} ,$$

or

$$[\hat{L}_z, \hat{x} + i\hat{y}] = [\hat{L}_z \hat{x}] + i[\hat{L}_z, \hat{y}] = i\hbar\hat{y} + i(-i\hbar\hat{x}) = \hbar(\hat{x} + i\hat{y}) ,$$

$$[\hat{L}_z, \hat{x} - i\hat{y}] = [\hat{L}_z \hat{x}] - i[\hat{L}_z, \hat{y}] = i\hbar\hat{y} - i(-i\hbar\hat{x}) = -\hbar(\hat{x} - i\hat{y}) .$$

We also note that

$$[\hat{\boldsymbol{L}}^2, [\hat{\boldsymbol{L}}^2, \hat{x}]] = 2\hbar^2 \{\hat{x}, \hat{\boldsymbol{L}}^2\} , \qquad (1)$$

where

$$\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A} , \qquad \text{(anti-commutation)}$$

and

$$\hat{\boldsymbol{L}}^2 = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_x{}^2 + \hat{L}_z{}^2 .$$

((**Mathematica**))
The proof of the above commutation relation of the orbital angular momentum (Eq.(1)) is given by Mathematica.

(**Proof**)

```
Clear["Global`"];

ux = {1, 0, 0}; uy = {0, 1, 0}; uz = {0, 0, 1};
r = {x, y, z};

Lx := (ħ ux.(-i Cross[r, Grad[#, {x, y, z}]]) &) // Simplify
Ly := (ħ uy.(-i Cross[r, Grad[#, {x, y, z}]]) &) // Simplify
Lz := (ħ uz.(-i Cross[r, Grad[#, {x, y, z}]]) &) // Simplify
Lsq := (Lx[Lx[#]] + Ly[Ly[#]] + Lz[Lz[#]] &);

eq2 = Lsq[Lsq[x ψ[x, y, z]]] - Lsq[x Lsq[ψ[x, y, z]]] -
    Lsq[x Lsq[ψ[x, y, z]]] + x Lsq[Lsq[ψ[x, y, z]]] //
   FullSimplify;

eq3 = 2 ħ^2 (x Lsq[ψ[x, y, z]] + Lsq[x ψ[x, y, z]]) //
   FullSimplify;

eq2 - eq3 // Simplify

0
```

2. Eigenkets of orbital angular momentum for electron

$|l,m\rangle$ is the simultaneous eigenstate of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$, where

$$[\hat{\boldsymbol{L}}^2, \hat{L}_z] = 0$$

where

$$\hat{\boldsymbol{L}}^2 |l,m\rangle = \hbar^2 l(l+1)|l,m\rangle ,$$

$$\hat{L}_z |l,m\rangle = \hbar m |l,m\rangle ,$$

where l is an integer (l = 0, 1, 2, 3…), $m = l$, l-1, l-2,…, -l. We note that

$$\hat{L}_+|l,m\rangle = \hbar\sqrt{(l-m)(l+m+1)}|l,m+1\rangle,$$

$$\hat{L}_-|l,m\rangle = \hbar\sqrt{(l+m)(l-m+1)}|l,m-1\rangle,$$

where

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y, \qquad \hat{L}_- = \hat{L}_x - i\hat{L}_y.$$

3. Selection rule-I

Using the relation

$$\hat{L}_z|l,m\rangle = \hbar m|l,m\rangle,$$

we have

$$\langle l',m'|[\hat{L}_z,\hat{z}]|l,m\rangle = 0,$$

or

$$\langle l',m'|\hat{L}_z\hat{z} - \hat{z}\hat{L}_z|l,m\rangle = 0,$$

or

$$(m'-m)\langle l',m'|\hat{z}|l,m\rangle = 0.$$

$\langle l',m'|\hat{z}|l,m\rangle \neq 0$, only if $m' = m$.

4. Selection rule-II

Using the relation

$$\hat{L}_z|l,m\rangle = \hbar m|l,m\rangle,$$

we have

$$\langle l',m'|[\hat{L}_z,\hat{x}+i\hat{y}]|l,m\rangle = \hbar\langle l',m'|\hat{x}+i\hat{y}|l,m\rangle,$$

or

$$\langle l', m'|\hat{L}_z(\hat{x} + i\hat{y}) - (\hat{x} + i\hat{y})\hat{L}_z|l, m\rangle = \hbar\langle l', m'|\hat{x} + i\hat{y}|l, m\rangle ,$$

or

$$(m' - m - 1)\langle l', m'|\hat{x} + i\hat{y}|l, m\rangle = 0 .$$

or

$$\langle l', m'|\hat{x} + i\hat{y}|l, m\rangle \neq 0 , \qquad \text{only if } m' = m + 1 .$$

5. Selection rule-III

Using the relation

$$\hat{L}_z|l, m\rangle = \hbar m|l, m\rangle ,$$

we have

$$\langle l', m'|[\hat{L}_z, \hat{x} - i\hat{y}]|l, m\rangle = -\hbar\langle l', m'|\hat{x} - i\hat{y}|l, m\rangle ,$$

or

$$\langle l', m'|\hat{L}_z(\hat{x} - i\hat{y}) - (\hat{x} - i\hat{y})\hat{L}_z|l, m\rangle = -\hbar\langle l', m'|\hat{x} - i\hat{y}|l, m\rangle ,$$

or

$$(m' - m + 1)\langle l', m'|\hat{x} - i\hat{y}|l, m\rangle = 0 .$$

or

$$\langle l', m'|\hat{x} - i\hat{y}|l, m\rangle \neq 0 , \text{ only if } m' = m - 1 .$$

6. Selection rule-IV

Using the commutation relation

$$[\hat{\boldsymbol{L}}^2, [\hat{\boldsymbol{L}}^2, \hat{x}]] = 2\hbar^2\{\hat{x}, \hat{\boldsymbol{L}}^2\} ,$$

we get the following equation,

$$\langle l',m'|[\hat{\boldsymbol{L}}^2,[\hat{\boldsymbol{L}}^2,\hat{x}]]|l,m\rangle = 2\hbar^2\langle l',m'|\{\hat{x},\hat{\boldsymbol{L}}^2\}|l,m\rangle,$$

or

$$\langle l',m'|\hat{\boldsymbol{L}}^2\hat{\boldsymbol{L}}^2\hat{x} - 2\hat{\boldsymbol{L}}^2\hat{x}\hat{\boldsymbol{L}}^2 + \hat{x}\hat{\boldsymbol{L}}^2\hat{\boldsymbol{L}}^2|l,m\rangle = 2\hbar^2\langle l',m'|\hat{x}\hat{\boldsymbol{L}}^2 + \hat{\boldsymbol{L}}^2\hat{x}|l,m\rangle.$$

Here we use the relation

$$\hat{\boldsymbol{L}}^2|l,m\rangle = \hbar^2 l(l+1)|l,m\rangle, \qquad \text{and} \qquad \langle l,m|\hat{\boldsymbol{L}}^2 = \hbar^2 l(l+1)\langle l,m|.$$

Then we have

$$\hbar^4[l'^2(l'+1)^2 - 2l'(l'+1)l(l+1) + l^2(l+1)^2 - 2l'(l'+1) - 2l(l+1)]\langle l',m'|\hat{x}|l,m\rangle = 0,$$

or

$$(l'-l-1)(l'-l+1)(l'+l)(l'+l+2)\langle l',m'|\hat{x}|l,m\rangle = 0,$$

The last factor yields the selection rule

$$l' = l \pm 1.$$

This means that no transition occurs if $l' = l$.

((**Mathemtica**))
Proof of the identity:

$$[l'^2(l'+1)^2 - 2l'(l'+1)l(l+1) + l^2(l+1)^2 - 2l'(l'+1) - 2l(l+1)]$$
$$= (l'-l-1)(l'-l+1)(l'+l)(l'+l+2)$$

```
g1 = a^2 (a + 1)^2 - 2 a (a + 1) b (b + 1) + b^2 (b + 1)^2 -
    2 a (a + 1) - 2 b (b + 1) // Factor
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(-1 + a - b) (1 + a - b) (a + b) (2 + a + b)
```

Since l' and l are both non-negative, the $(l'+l+2)$ term cannot vanish, and the $(l'+l)$ term can only vanish for $l' = l = 0$. However, this selection rule cannot be satisfied, since the states with $l' = l = 0$ are independent of direction, and therefore these matrix elements of $\hat{x}$ vanish. Formally, one easily shows this

$$\langle l=0, m=0|\hat{x}|l=0, m=0\rangle = 0,$$

using the property of the parity operator $\hat{\pi}$.

((**Proof**))

$$\hat{\pi}\hat{x}\hat{\pi} = -\hat{x}, \qquad \text{(property of } \hat{\pi}\text{)}$$

where the parity operator satisfies the relations,

$$\hat{\pi}^{+} = \hat{\pi}, \qquad \hat{\pi}^{2} = \hat{1},$$

$$\langle 0,0|\hat{\pi}\hat{x}\hat{\pi}|0,0\rangle = -\langle 0,0|\hat{x}|0,0\rangle, \tag{1}$$

We note that

$$\hat{\pi}|l,m\rangle = (-1)^{l}|l,m\rangle,$$

In other words, $|0,0\rangle$ has the even parity,

$$\hat{\pi}|0,0\rangle = |0,0\rangle,$$

$$\langle 0,0|\hat{\pi} = \langle 0,0|.$$

Then we get

$$\langle 0,0|\hat{\pi}\hat{x}\hat{\pi}|0,0\rangle = \langle 0,0|\hat{x}|0,0\rangle. \tag{2}$$

From Eqs.(1) and (2), we get

$$\langle 0,0|\hat{x}|0,0\rangle = 0.$$

7. Dipole selection rule

The dipole radiation is emitted if

$$M = \langle f|\boldsymbol{\varepsilon}\cdot\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{\varepsilon}\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle = \boldsymbol{\varepsilon}\cdot\boldsymbol{D}_{fi},$$

does not vanish, where $\boldsymbol{\varepsilon}$ is the electric field (the polarization vector), and

$$\boldsymbol{D}_{fi} = \langle f|\hat{\boldsymbol{r}}|i\rangle = \langle f|\hat{x}|i\rangle\boldsymbol{e}_x + \langle f|\hat{y}|i\rangle\boldsymbol{e}_y + \langle f|\hat{z}|i\rangle\boldsymbol{e}_z .$$

We assume that the initial state $|i\rangle = |l,m\rangle$ and the final state $|f\rangle = |l',m'\rangle$. Then we have

$$\boldsymbol{D}_{fi} = \langle l',m'|\hat{x}|l,m\rangle\boldsymbol{e}_x + \langle l',m'|\hat{y}|l,m\rangle\boldsymbol{e}_y + \langle l',m'|\hat{z}|l,m\rangle\boldsymbol{e}_z .$$

or

$$\begin{aligned}
\boldsymbol{D}_{fi} &= \langle l',m'|\hat{x}\boldsymbol{e}_x + \hat{y}\boldsymbol{e}_y + \hat{z}\boldsymbol{e}_z|l,m\rangle \\
&= \langle l',m'|\hat{x}\boldsymbol{e}_x + \hat{y}\boldsymbol{e}_y|l,m\rangle + \langle l',m'|\hat{z}|l,m\rangle\boldsymbol{e}_z \\
&= \langle l',m'|\hat{r}_+\boldsymbol{e}_- + \hat{r}_-\boldsymbol{e}_+|l,m\rangle + \langle l',m'|\hat{z}|l,m\rangle\boldsymbol{e}_z \\
&= \boldsymbol{e}_-\cdot\langle l',m'|\hat{r}_+|l,m\rangle + \boldsymbol{e}_+\cdot\langle l',m'|\hat{r}_-|l,m\rangle + \langle l',m'|\hat{z}|l,m\rangle\boldsymbol{e}_z
\end{aligned}$$

where

$$\boldsymbol{e}_+ = \frac{\boldsymbol{e}_x + i\boldsymbol{e}_y}{\sqrt{2}}, \qquad \boldsymbol{e}_- = \frac{\boldsymbol{e}_x - i\boldsymbol{e}_y}{\sqrt{2}}. \qquad \text{(Jones vector notation)}$$

or

$$\boldsymbol{e}_x = \frac{1}{\sqrt{2}}(\boldsymbol{e}_+ + \boldsymbol{e}_-), \qquad \boldsymbol{e}_y = \frac{1}{\sqrt{2}i}(\boldsymbol{e}_+ - \boldsymbol{e}_-).$$

and

$$\hat{x}\boldsymbol{e}_x + \hat{y}\boldsymbol{e}_y = \hat{r}_+\boldsymbol{e}_- + \hat{r}_-\boldsymbol{e}_+ .$$

Note that

$$\boldsymbol{e}_+ \cdot \boldsymbol{e}_+ = 0. \qquad \boldsymbol{e}_- \cdot \boldsymbol{e}_- = 0,$$

$$\boldsymbol{e}_+ \cdot \boldsymbol{e}_- = 1. \qquad \boldsymbol{e}_- \cdot \boldsymbol{e}_+ = 1.$$

(i) For $m' = m$, $l' = l \pm 1$

$$\langle l', m' | \hat{z} | l, m \rangle \neq 0, \qquad \langle l', m' | \hat{r}_+ | l, m \rangle = 0, \qquad \langle l', m' | \hat{r}_- | l, m \rangle = 0$$

So we have

$$\boldsymbol{D}_{fi} = \langle l', m' | \hat{z} | l, m \rangle \boldsymbol{e}_z$$

$\boldsymbol{D}_{fi}$ is directed along the z axis.

(a) Suppose that the wavevector $\boldsymbol{k}$ of the emitted photon is along the z axis. There is no radiation in the z-direction since the polarization vector $\boldsymbol{\varepsilon}$ is perpendicular to $\boldsymbol{D}_{fi}$ (the z axis).

(b) For example, we consider light going in the x direction. It can have two directions of polarization, either in the z or in the y direction. A transition in which $\Delta m = 0$, can produce only light which is linearly polarized in the z direction.

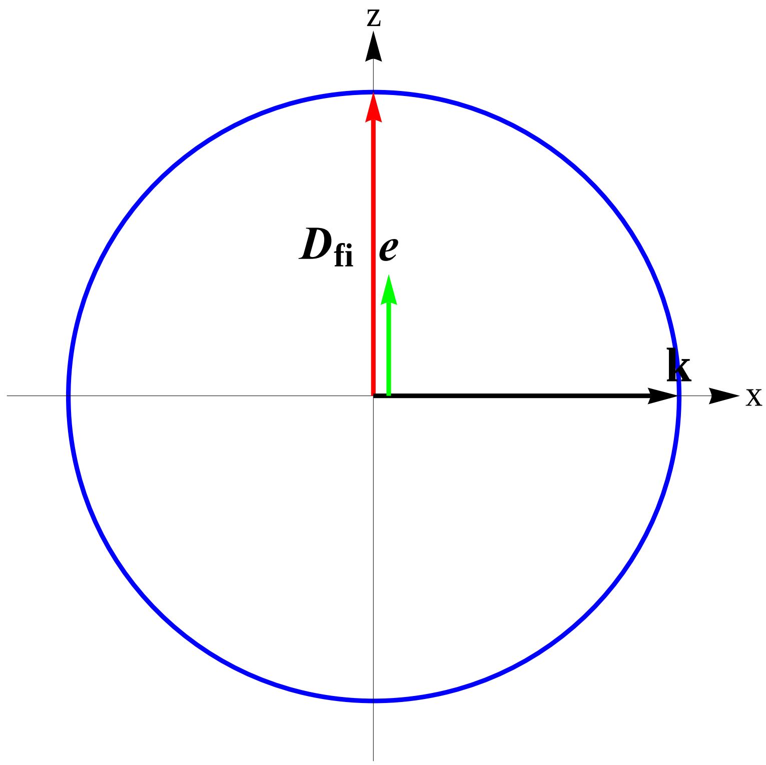

Fig. $m' = m$. $D_{fi} // z$. The light propagating along the x direction. It is a linearly polarized wave (along the z axis).

We now consider the matrix element with $m' = m \pm 1$.

(ii) For $m' = m + 1$, and $l' = l \pm 1$

$$\langle l', m' | \hat{r}_+ | l, m \rangle \neq 0, \qquad \langle l', m' | \hat{r}_- | l, m \rangle = 0, \qquad \langle l', m' | \hat{z} | l, m \rangle = 0.$$

$$\boldsymbol{D}_{fi} = \langle l', m' | \hat{x}\boldsymbol{e}_x + \hat{y}\boldsymbol{e}_y | l, m \rangle = \boldsymbol{e}_- \langle l', m' | \hat{r}_+ | l, m \rangle$$

has the same direction of the left circularly polarization vector ($\boldsymbol{e}_-$). Then the emitted photon which is right circularly polarized ($\boldsymbol{e}_+$), can propagate along the z axis, since $M = \boldsymbol{\varepsilon} \cdot \boldsymbol{D}_{fi}$ and $\boldsymbol{e}_+ \cdot \boldsymbol{e}_- = 1$. A photon with right-hand circular polarization carries a spin $+\hbar$ in the z direction (the propagation direction).

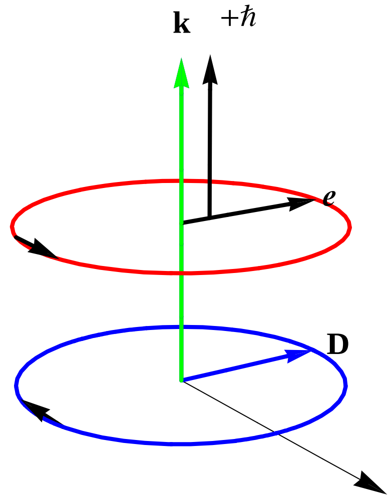

Fig. The case of $m' = m + 1$ (right circularly polarization, σ^+). A right circularly polarized photon ($\boldsymbol{e}_+$) propagates with a wavevector $\boldsymbol{k}$ in the z direction. Note that the electric field is denoted by $\cos(kz - \omega t)\boldsymbol{e}_x + \sin(kz - \omega t)\boldsymbol{e}_y$. This electric field rotates in clock-wise sense with time t, and rotates in counter clock-wise sense with z (as the wave propagates forward). The corresponding spin of the photon is directed in the positive z direction ($\hbar$). $\boldsymbol{D}_{fi}(\approx \boldsymbol{e}_-)$. $\boldsymbol{\varepsilon}(\approx \boldsymbol{e}_+)$. ($\boldsymbol{e}_+ \cdot \boldsymbol{e}_- = 1, \boldsymbol{e}_- \cdot \boldsymbol{e}_- = 0$).

(iii) For $m' = m - 1$ and $l' = l \pm 1$

$$\langle l', m' | \hat{r}_- | l, m \rangle \neq 0, \qquad \langle l', m' | \hat{r}_+ | l, m \rangle = 0 \qquad \langle l', m' | \hat{z} | l, m \rangle = 0.$$

$$\boldsymbol{D}_{fi} = \langle l', m' | \hat{x}\boldsymbol{e}_x + \hat{y}\boldsymbol{e}_y | l, m \rangle = \boldsymbol{e}_+ \langle l', m' | \hat{r}_- | l, m \rangle,$$

is parallel to the right circularly polarization vector $\boldsymbol{e}_+$. The emitted photon with left circularly polarization ($\boldsymbol{e}_-$) can propagate along the z axis, since $M = \boldsymbol{\varepsilon} \cdot \boldsymbol{D}_{fi}$ and $\boldsymbol{e}_- \cdot \boldsymbol{e}_+ = 1$. A photon with the left-hand polarization carries a spin (-$\hbar$), that is, a spin direction opposite to the z direction.

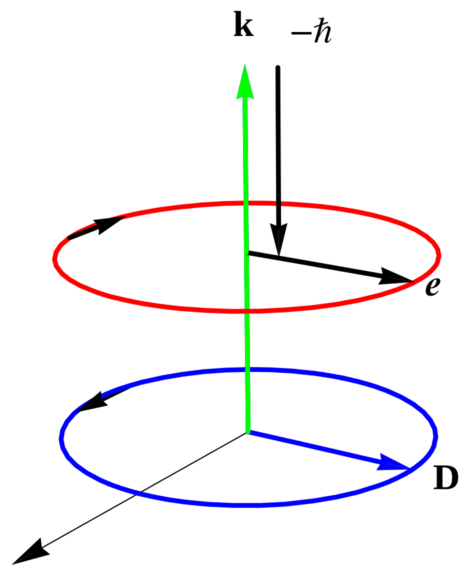

Fig. The case of $m' = m-1$ (left circularly polarization, σ^-). A left circularly polarized photon ($\boldsymbol{e}_-$) propagates with a wavevector $\boldsymbol{k}$ in the z direction. Note that the electric field is given by $\cos(kz-\omega t)\boldsymbol{e}_x - \sin(kz-\omega t)\boldsymbol{e}_y$. This electric field rotates in counter clock-wise sense with time t, and rotates in clock-wise sense with z (as the wave propagates forward). The corresponding spin of the photon is directed in the negative z direction, as -ħ. $\boldsymbol{D}_{f_i}(\approx \boldsymbol{e}_+)$. $\boldsymbol{\varepsilon}(\approx \boldsymbol{e}_-)$. ($\boldsymbol{e}_+ \cdot \boldsymbol{e}_- = 1$, $\boldsymbol{e}_+ \cdot \boldsymbol{e}_+ = 0$).

The rules on Δm can be understood by realizing that σ^+ and σ^- circularly polarized photons carry angular momenta of $+\hbar$ ans $-\hbar$, respectively, along the z axis, and hence m must change by one unit to conserve angular momentum. For linearly polarized light along the z axis, the photons carry no z-component of momentum, implying $\Delta m = 0$, while x or y-polarized light can be considered as a equal combination of σ^+ and σ^- photons, giving $\Delta m = \pm 1$.

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