

(Appendix) Where do the selection rules originate from and what is the dipole approximation?

The following paragraph offers a simplified explanation of the derivation of selection rules. It should, however, be emphasised that not all simplifying assumptions are necessarily mentioned explicitly.

According to Fermi's golden rule, the intensity of a transition between two states $|i\rangle$ and $|f\rangle$ ('final state' and 'initial state') is generally proportional to the square of a matrix element

$$I \sim |M_{fi}|^2$$

where the matrix elements are those of the electromagnetic interaction operator

$$M_{fi} \sim \langle f | \mathcal{H}_{WW} | i \rangle$$

The electromagnetic interaction operator of a non-relativistic 1 electron-1 photon process can be derived from the integral

$$\mathcal{H}_{WW} = -\frac{1}{c} \int d^3 r \hat{j}(\vec{r}) \hat{A}(\vec{r})$$

Here, $\hat{j}(\vec{r})$ is the current density operator of the electron; \hat{j} leads to a term $\sim \frac{e}{2m_e} \hat{p} \sim \hat{p}$ and is therefore proportional to the momentum operator of the electron.

$\hat{A}(\vec{r})$ is the vector potential eventually leading to a term $\sim \vec{\epsilon} e^{i\vec{k}\vec{r}}$, where $\vec{\epsilon}$ is the polarisation and \vec{k} is the photon wave vector.

Inserting the respective values thus yields the expression

$$M_{fi} \sim \left\langle f \left| e^{i\vec{k}\vec{r}} \hat{\vec{\epsilon}} \hat{\vec{p}} \right| i \right\rangle$$

This matrix element now needs to be evaluated.

The term $e^{i\vec{k}\vec{r}}$ can be simplified using a Taylor series expansion:

$$e^{i\vec{k}\vec{r}} = \underbrace{1}_{\text{yields el. dipole term (E1)}} + \underbrace{i\vec{k}\vec{r} + o(i\vec{k}\vec{r})^2}_{\text{yields magnetic dipole moment M1, electric quadrupole moment E2 etc.}}$$

The electric dipole radiation usually dominates by far (if it is allowed!), as can be shown by a simple estimation of an optical transition ($\lambda \simeq 6000 \text{ \AA}$, $r \simeq 1 \text{ \AA}$)

$$kr \simeq \frac{2\pi}{6000 \text{ \AA}} 1 \text{ \AA} \simeq \underbrace{\frac{1}{1000}}_{\text{M1, E2 etc}} \ll \underbrace{1}_{\text{E1}}$$

In this example, the amplitudes (E1 and M1, E2 etc) differ by 3 orders of magnitude ($10^3 : 1$) and this difference is even squared in the case of their ratios ($\simeq 10^6 : 1$).

In dipole approximation, the matrix element to be evaluated is therefore

$$M_{fi} \sim \langle f | \vec{\epsilon} \vec{p} | i \rangle$$

The operator $\hat{\vec{p}}$ can be simplified:

$$\begin{aligned} \langle \Phi_m | \vec{\epsilon} \vec{p} | \Phi_n \rangle &= \vec{\epsilon} \left\langle \Phi_m \left| m_e \frac{d\vec{r}}{dt} \right| \Phi_n \right\rangle \\ \text{(Time derivative of an operator)} &\sim m_e \vec{\epsilon} \left\langle \Phi_m \left| \frac{i}{\hbar} [H_0, \vec{r}] \right| \Phi_n \right\rangle \\ ([H_0, r] \sim p, \text{ see Bethe/Salpeter, p.52}) &\sim \frac{im_e}{\hbar} \vec{\epsilon} \langle \Phi_m | H_0 r - r H_0 | \Phi_n \rangle \\ (\Phi_i \text{ are eigenstates of } H_0) &\sim im_e \vec{\epsilon} \left(\frac{E_m - E_n}{\hbar} \right) \langle \Phi_m | \vec{r} | \Phi_n \rangle \\ &\sim -im_e \omega \langle \Phi_m | \vec{\epsilon} \vec{r} | \Phi_n \rangle \end{aligned}$$

Therefore, in the present context

$$\vec{\epsilon} \vec{p} \sim \vec{\epsilon} \vec{r}$$

This corresponds to a dipole energy $\sim \vec{E} \vec{\mu} = q \vec{E} \vec{r} \sim r \cos \vartheta$.

Thus, the selection rules for dipole radiation (E1) can be regarded as conditions under which

$$\langle f | \vec{\epsilon} \vec{r} | i \rangle \neq 0$$

Application of the calculation to an H atom

If we perform the calculation for atoms similar to H with the known energy eigenstates $\Phi_m = R_{n,l}(r)Y_{l,m}(\vartheta, \varphi)$, we obtain

$$\langle \Phi_m | \vec{e}r | \Phi_n \rangle = \underbrace{\int_0^\infty dr r^2 R_{n_f, l_f}^*(r) r R_{n_i, l_i}(r)}_{\text{radial part, const.}} \underbrace{\int \int d\varphi d\vartheta \sin \vartheta Y_{l_f, m_f}^*(\vartheta, \varphi) Y_{l_i, m_i} \vec{e} \frac{r}{|r|}}_{\text{angular part, is evaluated in the following}}$$

Expressing $\vec{e}r$ via spherical surface functions $Y_{l,m}$

$$\begin{aligned} \vec{e}r &= \epsilon_x \sin \vartheta \cos \varphi + \epsilon_y \sin \vartheta \sin \varphi + \epsilon_z \cos \vartheta \\ &= \sqrt{\frac{4\pi}{3}} \left(\epsilon_z Y_{1,0} + \frac{-\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1,1} + \frac{\epsilon_x + i\epsilon_y}{\sqrt{2}} Y_{1,-1} \right) \end{aligned}$$

shows that the matrix element needs to be evaluated using an integral over three $Y_{l,m}$.

$$0 \stackrel{!}{\neq} \text{angular part} = \int \int d\vartheta d\varphi \sin \vartheta Y_{l_f, m_f}^* Y_{(l=1)(m=-1,0,1)} Y_{l_i, m_i}$$

This expression is only $\neq 0$ if:

$$m_f - m_i = \pm 1 \quad \text{and} \quad l_f - l_i = 0, \pm 1$$

(The selection rule $\Delta S = 0$ is due to the fact that \mathcal{H}_{WW} does not contain — and therefore cannot change — the spin.)

References

- Bethe/Salpeter
- Gasiorowicz