12.10: Selection Rules (Hydrogen Atoms)

Let us now consider spontaneous transitions between the different energy levels of a hydrogen atom. Because the perturbing Hamiltonian ([e13.77]) does not contain any spin operators, we can neglect electron spin in our analysis. Thus, according to Section [s10.4], the various energy eigenstates of the hydrogen atom are labeled by the familiar quantum numbers n, l, and m.

According to Equations ([e3.106]) and ([e3.115]), a hydrogen atom can only make a spontaneous transition from an energy state corresponding to the quantum numbers n, l, m to one corresponding to the quantum numbers n', l', m' if the modulus squared of the associated electric dipole moment

$$d^{\,2}=|\langle n,l,m|e\,x|n',l',m'\rangle|^{\,2}+|\langle n,l,m|e\,y|n',l',m'\rangle|^{\,2}+|\langle n,l,m|e\,z|n',l',m'\rangle|^{\,2} \tag{12.10.1}$$

is non-zero. Now, we have already seen, in Section [s12.5], that the matrix element $\langle n,l,m|z|n',l',m'\rangle$ is only non-zero provided that $m'=m$ and $l'=l\pm 1$. It turns out that the proof that this matrix element is zero unless $l'=l\pm 1$ can, via a trivial modification, also be used to demonstrate that $\langle n,l,m|x|n',l',m'\rangle$ and $\langle n,l,m|y|n',l',m'\rangle$ are also zero unless $l'=l\pm 1$. Consider

$$x_{\pm}=x\pm{\rm i}\,y. \tag{12.10.2}$$

It is easily demonstrated that

$$[L_z,x_{\pm}]=\pm\hbar\,x_{\pm}. \tag{12.10.3}$$

Hence,

$$\langle n,l,m|[L_z,x_+]-\hbar\,x_+|n',l',m'\rangle=\hbar\,(m-m'-1)\,\langle n,l,m|x_+|n',l',m'\rangle=0, \tag{12.10.4}$$

and

$$\langle n,l,m|[L_z,x_-]+\hbar\,x_-|n',l',m'\rangle=\hbar\,(m-m'+1)\,\langle n,l,m|x_-|n',l',m'\rangle=0. \tag{12.10.5}$$

Clearly, $\langle n,l,m|x_+|n',l',m'\rangle$ is zero unless $m'=m-1$, and $\langle n,l,m|x_-|n',l',m'\rangle$ is zero unless $m'=m+1$. Now, $\langle n,l,m|x|n',l',m'\rangle$ and $\langle n,l,m|y|n',l',m'\rangle$ are obviously both zero if $\langle n,l,m|x_+|n',l',m'\rangle$ and $\langle n,l,m|x_-|n',l',m'\rangle$ are both zero. Hence, we conclude that $\langle n,l,m|x|n',l',m'\rangle$ and $\langle n,l,m|y|n',l',m'\rangle$ are only non-zero if $m'=m\pm 1$.

The previous arguments demonstrate that spontaneous transitions between different energy levels of a hydrogen atom are only possible provided

$$\begin{aligned} l' &= l\pm 1,\\ m' &= m,\; m\pm 1. \end{aligned}$$

These are termed the *selection rules* for electric dipole transitions (i.e., transitions calculated using the electric dipole approximation). Note, finally, that because the perturbing Hamiltonian does not contain any spin operators, the spin quantum number m_s cannot change during a transition. Hence, we have the additional selection rule that $m_s'=m_s$.

Contributors and Attributions

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