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 \(|n\rangle, |l\rangle, |m\rangle\).

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 \(|n\rangle, |l\rangle, |m\rangle\) to one corresponding to the quantum numbers \(|n'\rangle, |l'\rangle, |m'\rangle\) if the modulus squared of the associated electric dipole moment

\[
|d|^2 = |\langle n,l,m|e\,x|n',l',m'\rangle|^2 + |\langle n,l,m|e\,y|n',l',m'\rangle|^2 + |\langle n,l,m|e\,z|n',l',m'\rangle|^2
\]

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 \(|m'=m\rangle\) and \(|l'=l\pm 1\rangle\). It turns out that the proof that this matrix element is zero unless \(|l'=l|\) 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 \(|l'=l|\pm 1\rangle\). Consider \(|x_\pm = x \pm iy\rangle\). It is easily demonstrated that \(|[L_z,x_\pm| = \pm \hbar x_\pm\rangle\) Hence, \(|\langle n,l,m|L_zx_+\rangle = \langle n,l,m|x_+\rangle = \langle n,l,m|x\rangle = 0\rangle\) and \(|\langle n,l,m|L_zx_-\rangle = \langle n,l,m|x_-\rangle = \langle n,l,m|x\rangle = 0\rangle\). Clearly, \(|\langle n,l,m|x_-\rangle = \langle n,l,m|x_-\rangle = \langle n,l,m|x\rangle = 0\rangle\). Now, \(|\langle n,l,m|y|n',l',m'\rangle\) 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 \(|m'=m|\pm 1\rangle\).

The previous arguments demonstrate that spontaneous transitions between different energy levels of a hydrogen atom are only
\[
\begin{aligned}
l' &= l \pm 1, \\
m' &= m, m \pm 1.
\end{aligned}
\]
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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