8.4: Rydberg Formula

An electron in a given stationary state of a hydrogen atom, characterized by the quantum numbers \(n\), \(l\), and \(m\), should, in principle, remain in that state indefinitely. In practice, if the state is slightly perturbed—for instance, via interaction with a photon—then the electron can make a transition to another stationary state with different quantum numbers. (See Chapter \([s13]\).)

Suppose that an electron in a hydrogen atom makes a transition from an initial state whose radial quantum number is \(n_i\) to a final state whose radial quantum number is \(n_f\). According to Equation (\([e9.55]\)), the energy of the electron will change by \(\Delta E = E_0 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)\). If \(\Delta E\) is negative then we would expect the electron to emit a photon of frequency \(\nu = \frac{\Delta E}{h}\). [See Equation (\([ee3.15]\)).] Likewise, if \(\Delta E\) is positive then the electron must absorb a photon of energy \(\nu = \frac{\Delta E}{h}\). Given that \(\frac{1}{\lambda} = \frac{1}{\nu} = \frac{1}{\nu c}\), the possible wavelengths of the photons emitted by a hydrogen atom as its electron makes transitions between different energy levels are

\[
\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right),
\]

where \(R = \frac{E_0}{h c}\) and \(R = 1.097 \times 10^7 \text{ m}^{-1}\). Here, it is assumed that \(n_f < n_i\). Note that the emission spectrum of hydrogen is quantized: that is, a hydrogen atom can only emit photons with certain fixed set of wavelengths. Likewise, a hydrogen atom can only absorb photons that have the same fixed set of wavelengths. This set of wavelengths constitutes the characteristic emission/absorption spectrum of the hydrogen atom, and can be observed as “spectral lines” using a spectroscope.

Equation (\([e9.77]\)) is known as the Rydberg formula. Likewise, \(R\) is called the Rydberg constant. The Rydberg formula was actually discovered empirically in the nineteenth century by spectroscopists, and was first explained theoretically by Bohr in 1913 using a primitive version of quantum mechanics. Transitions to the ground-state (\(n_f = 1\)) give rise to spectral lines in
the ultraviolet band—this set of lines is called the Lyman series. Transitions to the first excited state ($n_f=2$) give rise to spectral lines in the visible band—this set of lines is called the Balmer series. Transitions to the second excited state ($n_f=3$) give rise to spectral lines in the infrared band—this set of lines is called the Paschen series, and so on.

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