2.11: Atomic Spectroscopy and the Correspondence Principle

Bohr's correspondence principle states that the predictions of classical and quantum mechanics agree in the limit of large quantum numbers (An Introduction to Quantum Physics, French and Taylor, p. 27). This principle can be illustrated using the Bohr model of the hydrogen atom, which is an ad hoc mixture of established classical and newly proposed quantum concepts.

On the basis of Rutherford's nuclear model of the atom, Bohr envisioned the hydrogen atom's electron executing circular orbits around the proton with quantized angular momentum. This gave rise to a manifold of allowed electron orbits with discrete (as opposed to continuous) radii and energies. By fiat Bohr called these stationary states, because the orbiting (accelerating) electron did not radiate energy as required by classical electromagnetic principles.

Initial speculation, however, suggested that the observed line spectrum of the hydrogen atom might be interpeted in terms of electromagnetic emissions related to orbital frequencies of the electron. Subsequently, Bohr achieved agreement with experiment by postulating that the observed frequencies were due to photon (hv) emissions as the electron made a quantum jump from one allowed orbit to another. As will be shown below these two explanations, the first classical and the second quantum mechanical, can be used to illustrate the correspondence principle.

The calculations below are carried out in the Mathcad programming environment using the following information.

$$\text{Planck's constant:} \quad h = 6.62608(10)^{-34}\text{joule sec} \quad \text{Electron mass:} \quad m_e = 9.1093897(10)^{-31}\text{kg}$$
$$\text{Speed of light:} \quad c = 2.9979(10)^8 \tfrac{m}{sec} \quad \text{Bohr radius:} \quad a_0 = 5.29177(10)^{-11}\text{m}$$
$$\text{Conversion factors:} \quad pm = 10^{-12}m \quad aJ = 10^{-18}\text{joule}$$
$$\text{Energy of a photon:} \quad E_{photon} = h\nu = \tfrac{hc}{\lambda}$$

Energy of the hydrogen atom's electron (n is a quantum number and can have integer values).

$$E_{atom} = \frac{-2.18aJ}{n^2}$$

Emission Spectroscopy

In emission spectroscopy a photon is created as the electron undergoes a transition from a higher to a lower energy state. Energy conservation requires

$$E_{atom}^{initial} = E_{atom}^{final} + E_{photon}$$

Using Bohr's quantum jump model we calculate the frequency of the photon emitted when an electron undergoes a transition from the n=2 to the n=1 state.

$$n_i = 2 \quad n_f = 1 \quad \frac{-2.178aJ}{n_i^2} = \frac{-2.178aJ}{n_f^2} + h\nu \quad \left| \begin{array}{l} solve, \nu \\ float, 3 \end{array} \right. \rightarrow \frac{2.47e15}{sec}$$

This result is in agreement with the experimental hydrogen atom emission spectrum.

Next we calculate the orbital frequencies of these two quantum states. This requires knowing the classical orbital velocity and orbit circumference. These are most easily obtained by using postulates and results of the Bohr model.

Quantized orbital angular momentum: $m_e vr = \frac{nh}{2\pi}$

Allowed orbit radius: $r = n^2 a_0$

Orbit circumference: $C = 2\pi r$

Orbit frequency: $\nu = \frac{v}{C} \quad \nu(n) = \frac{h}{4\pi^2 m_e n^3 a_0^2}$

The classical orbital frequencies for the n = 1 and n = 2 orbits bracket the photon frequency, but are not in good agreement with the quantum result.

$$\nu(1) = 6.58 \times 10^{15} \tfrac{1}{s} \quad \nu(2) = 8.22 \times 10^{14} \tfrac{1}{s}$$

Next we explore high energy electronic states. Recently an electronic hydrogen atom emission transition was observed at 408.367 MHz in interstellar space. Assuming the transition occurs between adjacent states, calculate the quantum number of the destination

state.

$$\frac{-2.18aJ}{(n+1)^2} = \frac{-2.18aJ}{n^2} + h\,\frac{408.367(10)^6}{\text{sec}} \quad \begin{array}{c} \text{solve, n} \\ \text{float, 3} \end{array} \rightarrow \begin{pmatrix} -0.5 \\ 252.0 \\ -127.0 - 219.0i \\ -127.0 + 219.0i \end{pmatrix}$$

Thus the transition is from n = 253 to n = 252. Below we see that the classical orbital frequencies for these states again bracket the quantum result, but now are in much closer agreement with it.

$$\nu(252) = 4.11 \times 10^8 \tfrac{1}{s} \quad \nu(253) = 4.06 \times 10^8 \tfrac{1}{s}$$

As the n quantum number increases the predictions of classical and quantum mechanics converge as required by Bohr′s correspondence principle.

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