Ch. 29 Part 1
The Hydrogen Spectrum

In this chapter, we will draw on a number of ideas we have used all semester to see what we can learn about atoms and molecules. There is more in this chapter than we have time for; we will primarily focus on the Hydrogen atom (which we can study in detail) and on the general lessons we can apply to broad classes of atoms and molecules.

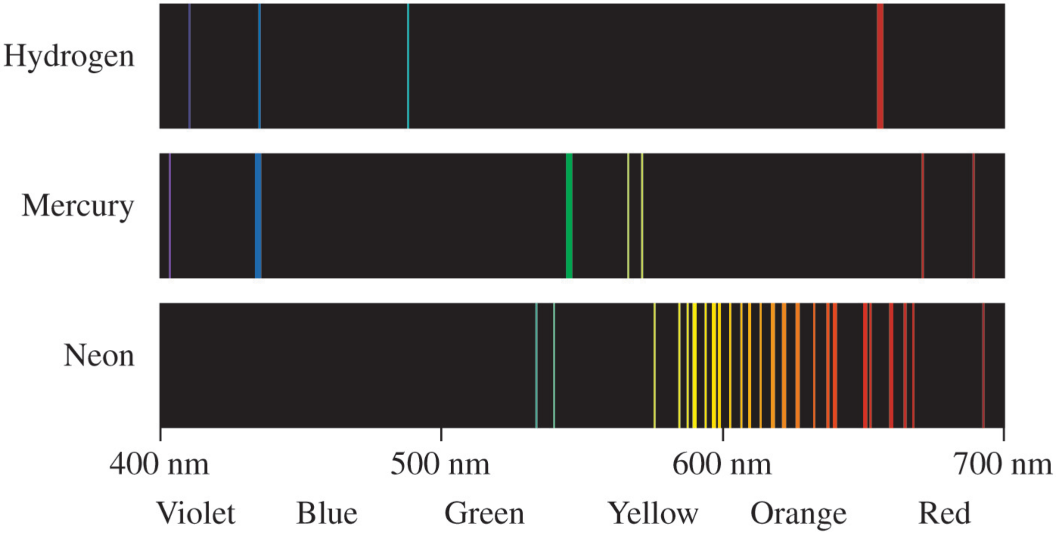
29.1: Spectroscopy

We have seen that a transition between energy levels is accompanied by the emission or absorption of a photon:

$$\Delta E = \frac{hc}{\lambda}$$

Looking at the wavelengths of light emitted and absorbed by various atoms, only certain discrete λ values are seen, which implies that only certain energy jumps occur. Broadly speaking, how can we use the pattern of observed wavelengths to learn about the structure of atoms?

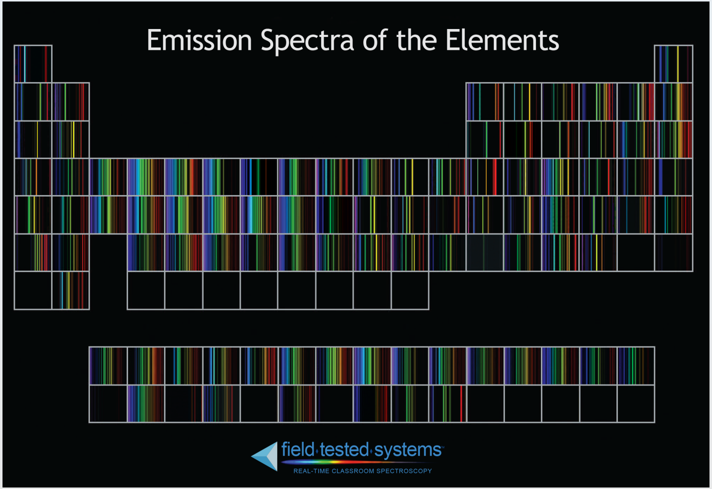
29.1: Spectroscopy



Where did this picture come from? See the first pre-lecture video. Send the broad light from a glowing gas through a diffraction grating with spacing d. We will see bright spots (vertical lines) at any angle θ where

$$d \sin\theta = m\lambda$$

The Periodic Table of Spectra



https://www.fieldtestedsystems.com/ptable/

The Hydrogen spectrum

Is there a pattern to these lines? Look at the simplest atom, hydrogen. It turns out that there is a simple pattern:

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)}$$

where m can be any positive integer $1, 2, \ldots$, and n is an integer greater than m. Can we develop a theory that reproduces this pattern?

29.2 Atoms

This section discusses the nuclear model of the atom. Most of this should already be familiar, and we will not work through the process of scattering that led to this picture. (For example, problem 29.13 is really just a review of a basic Chapter 21 problem.)

29.2 Atoms

Basic nuclear model:

- Typical atomic size is of the order of 1×10^{-10} m.
- Most of the mass of an atom is concentrated in a tiny nucleus, on the order of a few femtometers (fm), where $1\,\text{fm} = 1 \times 10^{-15}$ m.
- The nucleus contains Z protons and N neutrons. The atomic mass number $A = N + Z$.
- More detail about the nucleus is in Ch. 30.
- A neutral atom contains Z electrons.

29.3 Bohr's Model of Atomic Quantization

Basic assumptions:

- An atom can exist in discrete energy states.
- Transitions between states are accompanied by the absorption or emission of energy. That could be a photon, or it could be an interaction (*e.g.* a collision) with another particle.
- The lowest energy state is called the ground state.
- Normally, atoms tend to be in the lowest energy state.
- If excited to a higher energy state, the atom can relax to the ground state by emitting photons corresponding to various possible energy transitions. There may be additional quantum constraints on which transitions will be observed. (For example, conservation of angular momentum may rule out certain transitions.)

Basic assumptions (*continued*):

- **Emissions:** If you excite an atom to sufficiently high energy, you can see emissions from any allowed transition.
- **Absorption:** Since the atom is normally in the ground state, absorption spectra normally show only transitions that involve the ground state.

What do the photon energies tell us? They tell us about transitions between energy levels. Pick $m = 2$ (which gives us visible light).

- $n = 3 \rightarrow m = 2$.

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{2^2} - \frac{1}{3^2}\right)} = 656\,\text{nm}$$

This is the red line in the hydrogen spectrum.

29.3 Bohr's Model of Atomic Quantization **Skip**

What do the photon energies tell us? They tell us about transitions between energy levels. Pick $m = 2$ (which gives us visible light).

- $n = 3 \rightarrow m = 2$.

$$\lambda = \frac{91.1\,\mathrm{nm}}{\left(\frac{1}{2^2} - \frac{1}{3^2}\right)} = 656\,\mathrm{nm}$$

  This is the red line in the hydrogen spectrum.

- $n = 4 \rightarrow m = 2$.

$$\lambda = \frac{91.1\,\mathrm{nm}}{\left(\frac{1}{2^2} - \frac{1}{4^2}\right)} = 486\,\mathrm{nm}$$

  This is the aqua line in the hydrogen spectrum.

- $n = 5 \rightarrow m = 2.$

$$\lambda = \frac{91.1\,\mathrm{nm}}{\left(\frac{1}{2^2} - \frac{1}{5^2}\right)} = 434\,\mathrm{nm}$$

This is the violet line in the hydrogen spectrum.

- $n = 5 \to m = 2.$

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{2^2} - \frac{1}{5^2}\right)} = 434\,\text{nm}$$

This is the violet line in the hydrogen spectrum.

- $n = 6 \to m = 2.$

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{2^2} - \frac{1}{6^2}\right)} = 410\,\text{nm}$$

This is not easily visible—it is nearly in the ultraviolet.

29.3 Bohr's Model of Atomic Quantization Skip

If the lower state is $m = 1$, all the transitions are in the ultraviolet.

- $n = 2 \rightarrow m = 1$.

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)} = 122\,\text{nm}$$

29.3 Bohr's Model of Atomic Quantization **Skip**

If the lower state is $m = 1$, all the transitions are in the ultraviolet.

- $n = 2 \rightarrow m = 1$.

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)} = 122\,\text{nm}$$

- $n = 3 \rightarrow m = 1$.

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{1^2} - \frac{1}{3^2}\right)} = 103\,\text{nm}$$

- $n = 4 \rightarrow m = 1$.

$$\lambda = \frac{91.1\,\text{nm}}{\left(\frac{1}{1^2} - \frac{1}{4^2}\right)} = 97.2\,\text{nm}$$

These are all in the ultraviolet.

29.3 Bohr's Model of Atomic Quantization **Skip**

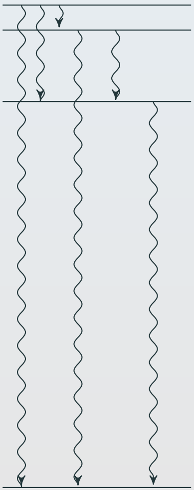
We can then tabulate the corresponding energy gaps using $\Delta E = \frac{hc}{\lambda}$. These give energy differences. To find the actual energy levels, we need to set a reference level. If the atom is ionized, the electron is removed to infinity, and the energy is 0 eV. (More on this later.)

m	n	λ	E_{photon}
3	5	1280 nm	0.968 eV
3	4	1870 nm	0.662 eV
2	5	434 nm	2.86 eV
2	4	486 nm	2.55 eV
2	3	656 nm	1.89 eV
1	5	94.9 nm	13.1 eV
1	4	97.2 nm	12.8 eV
1	3	103 nm	12.1 eV
1	2	122 nm	10.2 eV

We can then tabulate the corresponding energies, noting that the limiting value is indeed 0 eV.

n	E_n
100	$-0.001\,36$ eV
...	...
6	-0.378 eV
5	-0.544 eV
4	-0.851 eV
3	-1.51 eV
2	-3.40 eV
1	-13.6 eV

29.3 Bohr's Model of Atomic Quantization



$E_4 = -0.851\,\text{eV}$

$E_3 = -1.51\,\text{eV}$

$E_2 = -3.40\,\text{eV}$

$E_1 = -13.6\,\text{eV}$

Transitions between levels result in photons with corresponding energy and wavelength. Thus, for example, if the atom transitions from state 3 to 2, the corresponding photon wavelength is

$$\lambda = \frac{hc}{\Delta E} = \frac{hc}{E_3 - E_2}$$

$$\lambda = \frac{1240\,\text{eVnm}}{(-1.51\,\text{eV}) - (-3.40\,\text{eV})}$$

$$\lambda = \frac{1240\,\text{eVnm}}{1.89\,\text{eV}} = 656\,\text{nm}$$

Emission and Absorption

Normally, the atom is found in the lowest energy state, $n = 1$, known as the ground state. The atom can absorb energy and transition to a higher state, but only photons with enough energy to match a transition from $n = 1$ can be absorbed. So, for example, a photon with $E = 1.89\,\text{eV}$ (corresponding to the $2 \to 3$ transition) will not be absorbed by an atom in the ground state.

However, if you add a photon with enough energy to go from 1 to 3, (*i.e.* $E_3 - E_1 = (-1.51\,\text{eV}) - (-13.6\,\text{eV}) = 12.1\,\text{eV}$), the atom can transition to the $n = 3$ state. The atom can then relax to the ground state either directly $3 \to 1$, or in multiple steps $3 \to 2$ then $2 \to 1$. (Other quantum constraints may limit the possible relaxation routes; we will not worry about them for the moment.)

The net result is that *absorption* spectra usually only show energy levels reachable from the ground state, while *emission* spectra can show all reachable energy levels.

What's Next?

- Develop the Bohr model—a *simple* solar-system-like model to explore the hydrogen atom.
- Extend some of the lessons of the Bohr model to other atoms and molecules