Line Spectra and Energy Levels
A Chem 101A Tutorial
A normal incandescent light bulb contains a hot piece of metal wire, which produces white light.

A hydrogen discharge tube contains hot hydrogen gas, which produces lilac-colored light.

Let’s explore how these differ!
When we pass the white light from the normal light bulb through a prism, we see the entire visible spectrum (the “colors of the rainbow”).

The colors we see are our brain’s way of representing wavelengths.

Note that our eyes can only detect wavelengths from roughly 400 nm to 700 nm. Light bulbs also produce infrared and ultraviolet light, but we cannot see these types of radiation.
When we pass the lilac-colored light from the hydrogen discharge tube through a prism, we only observe four specific colors, which appear as colored vertical lines.

This pattern is called the line spectrum of hydrogen.
Here is the line spectrum of hydrogen superimposed on the entire visible spectrum.
Other elements also produce line spectra when we pass an electrical discharge through them.

For example, helium produces bright blue-white light.

When we pass this light through a prism, we separate it into the line spectrum of helium.
The line spectrum of every element is unique.

For example, both mercury and krypton produce light blue light in a discharge tube, but their line spectra are obviously different.

As a result, we can use line spectra to identify the elements in an unknown substance.
Some line spectra are very complex, while others are simple.

Neon produces many visible lines, while sodium produces only one.
Before we explore line spectra in more detail, we need to change the way we observe them.

Instead of looking at wavelengths, we will now focus our attention on the photon energy of the light.

Photon energy is inversely proportional to wavelength:

\[
E_{\text{photon}} = \frac{hc}{\lambda}
\]

The photon energy of visible light ranges from 170 kJ/mol to 300 kJ/mol. Here is the visible spectrum plotted using energy as the scale. Wavelength is shown below the spectrum for comparison. Note that higher energies correspond to shorter wavelengths.
Here is the hydrogen line spectrum plotted on our energy scale.

Problem: our eyes can only detect radiation whose wavelength is in the range 400 – 700 nm.

Does the hydrogen discharge tube produce other wavelengths that we cannot observe with our eyes?
Yes, it does!!

If we use film that is sensitive to wavelengths outside the visible range, we observe a vast number of additional lines that we cannot see with our eyes.

Some of these lines are widely spaced, while others are bunched tightly together.
If we look farther into the ultraviolet region, we find still more spectral lines.

This diagram shows the complete line spectrum of hydrogen.
When we look at the line spectrum of hydrogen, we notice several groups of lines.

In each group, the lines start out widely spaced, then get closer and closer until they blur together.

Each of these groups of lines is called a series.
The first group of lines, lying at the shortest wavelengths and highest energies, is called the **Lyman series**.
The second group, which includes the lines we can see with our eyes, is called the **Balmer series**.
The third group, which lies in the infrared region and overlaps the fourth group, is called the **Paschen series**.
Why does the line spectrum of hydrogen look like this?

To understand, we must start with the fact that the electron in a hydrogen atom can only have certain energies.

These allowed energies can be calculated from the following formula:

\[ E = \frac{-1313 \text{ kJ/mol}}{n^2} \]

The symbol \( n \) here stands for a counting number (1, 2, 3…).

Note that all of the possible energies for the hydrogen electron are negative numbers.
There are infinite possible energies for the hydrogen atom, because there are infinite counting numbers.

However, the electron cannot have any energy we choose. For instance, the electron cannot have $E = -1000 \text{ kJ/mol}$.

\[
-1000 \text{ kJ/mol} = \frac{-1313 \text{ kJ/mol}}{n^2}
\]

\[
\begin{align*}
 n^2 &= \frac{-1313 \text{ kJ/mol}}{-1000 \text{ kJ/mol}} = 1.313 \\
 n &= 1.146 \text{ (not a counting number)}
\end{align*}
\]
Here are the first few energies that the electron can have in a hydrogen atom:

\[
E_1 = \frac{-1313 \text{ kJ/mol}}{1^2} = -1313 \text{ kJ/mol}
\]

\[
E_2 = \frac{-1313 \text{ kJ/mol}}{2^2} = -328.2 \text{ kJ/mol}
\]

\[
E_3 = \frac{-1313 \text{ kJ/mol}}{3^2} = -145.9 \text{ kJ/mol}
\]

\[
E_4 = \frac{-1313 \text{ kJ/mol}}{4^2} = -82.1 \text{ kJ/mol}
\]

\[
E_5 = \frac{-1313 \text{ kJ/mol}}{5^2} = -52.5 \text{ kJ/mol}
\]

\[
E_6 = \frac{-1313 \text{ kJ/mol}}{6^2} = -36.5 \text{ kJ/mol}
\]

If we let \( n \) become infinitely large, \( E \) becomes infinitesimally small (it gets closer and closer to zero):

\[
\lim_{{n \to \infty}} E_n = 0 \text{ kJ/mol}
\]
$E_2 = -328.2 \text{ kJ/mol} \quad (n = 2)$

$E_3 = -145.9 \text{ kJ/mol} \quad (n = 3)$

$E_4 = -82.1 \text{ kJ/mol} \quad (n = 4)$

$E_5 = -52.5 \text{ kJ/mol} \quad (n = 5)$

$E_6 = -36.5 \text{ kJ/mol} \quad (n = 6)$

We can represent these allowed energies by plotting them on a vertical graph.

This graph is called the energy level diagram for the hydrogen atom.

Remember that every allowed energy for a hydrogen atom fits the formula

$$E = \frac{-1313 \text{ kJ/mol}}{n^2}$$
If we have a collection of cold hydrogen atoms, each atom’s electron will have the lowest possible energy (-1313 kJ/mol), because that is the most stable state for the electron.

This lowest energy level is called the **ground state**.
If we add a lot of energy, though, many of the hydrogen atoms will absorb this energy and their electrons will rise to higher energy levels, called excited states. We will end up with electrons in a variety of levels.
Any electron that is above the ground state will eventually drop back to the ground state. It can do so in one step or in several.

For instance, an electron that is in level 5 might drop to level 4, then to level 2, and finally to level 1.
As the electron drops from one level to another, it loses energy. This energy comes out in the form of a photon of electromagnetic radiation (light).

The energy of the photon exactly equals the size of the energy change for the electron.
We can calculate the energy of each photon by calculating the difference between the starting and final energy levels for each jump.

\[ \Delta E = -82.1 - (-52.5) = -29.6 \text{ kJ/mol} \]

\[ \Delta E = -328.2 - (-82.1) = -246.1 \text{ kJ/mol} \]

\[ \Delta E = -1313 - (-328.2) = -985 \text{ kJ/mol} \]
Electron Energy (kJ/mol)

$\Delta E = -29.6 \text{ kJ/mol}$

$\Delta E = -246.1 \text{ kJ/mol}$

$\Delta E = -985 \text{ kJ/mol}$

The photon energy equals the energy change for the electron, but it is a positive number.

$E_{\text{photon}} = 29.6 \text{ kJ/mol}$

$E_{\text{photon}} = 246.1 \text{ kJ/mol}$

$E_{\text{photon}} = 985 \text{ kJ/mol}$
Here is what we will observe. We will see three specific wavelengths of light being emitted from the atom, corresponding to the three photon energies we calculated.
If we compare these wavelengths with the actual line spectrum of hydrogen, we find an exact match!
In fact, every line in the hydrogen line spectrum corresponds to an electron jump.

The energy of the photon equals the amount of energy the electron loses (the change in the electron energy).

\[ E_{\text{photon}} = |\Delta E_{\text{electron}}| \]
Let’s see how the lines in the spectrum match up with electron transitions (jumps between energy levels).
We’ll begin with the Lyman series.
Here is an expanded view of the Lyman series, with the wavelengths and energies of some lines.

We can match each of these lines with an electron transition.
The first line in the Lyman series... is produced by electrons moving from level 2 to level 1.
The second line in the Lyman series... is produced by electrons moving from level 3 to level 1.

\[ E_{\text{photon}} = 1167 \text{ kJ/mol} \]

\[ \Delta E_{\text{electron}} = -1167 \text{ kJ/mol} \]
The third line in the Lyman series...

...is produced by electrons moving from level 4 to level 1.

\[ E_{\text{photon}} = 1231 \text{ kJ/mol} \]

\[ \Delta E_{\text{electron}} = -1231 \text{ kJ/mol} \]

97.18 nm
$E_{\text{photon}} = 1260 \text{ kJ/mol}$

Line 4

94.90 nm

$\Delta E_{\text{electron}} = -1260 \text{ kJ/mol}$

The fourth line in the Lyman series...

...is produced by electrons moving from level 5 to level 1.
The series limit for the Lyman series... is produced by electrons moving from the “infinitieth” energy level to level 1.
Any line in the line spectrum corresponds to an electron transition (a jump from one level to another).

For the Lyman series, the electron always ends up in level 1.

This diagram shows the electron transitions that correspond to the first six lines of the Lyman series, plus the series limit.
Now that we’ve explored the Lyman series, let’s apply the same ideas to the other series we observe in the line spectrum of hydrogen.

If will help us see the individual series if we expand that section of the line spectrum….
Here is the region of the spectrum from 0 to 350 kJ/mol.

The four lines we can observe with our eyes are shown in their actual colors.
Let’s start with the Balmer series. This series contains the second most energetic photons (after the Lyman series).
Here is the Balmer series with the wavelengths and energies of a few of its lines.

Let’s match these photon energies with the $\Delta E$ values for the electron.
The first line in the Balmer series...

...is produced by electrons moving from level 3 to level 2.
The second line in the Balmer series... is produced by electrons moving from level 4 to level 2.
$E_{\text{photon}} = 275.7 \text{ kJ/mol}$

The third line in the Balmer series...

...is produced by electrons moving from level 5 to level 2.

$\Delta E_{\text{electron}} = -275.7 \text{ kJ/mol}$
The Balmer series corresponds to a new set of electron transitions.

For the Balmer series, the electron always ends up in level 2.

This diagram shows the electron transitions that correspond to the first five lines of the Balmer series, plus the series limit.
We now know how the Lyman and Balmer series lines are formed.

The Lyman series is produced by electrons dropping from higher levels into level 1.

The Balmer series is produced by electrons dropping from higher levels into level 2.
The Lyman series falls in a much higher energy range than the Balmer series, because electrons lose a very large amount of energy when they drop into level 1. All of the possible drops into level 2 release far less energy.
We can analyze the remaining series in the same fashion. However, all of the remaining series overlap with one another to some extent, so it becomes difficult to tell which lines belong to which series.

Let’s expand the remaining series to make them a little easier to see.
This diagram highlights the Paschen series (series #3) and the Brackett series (series #4).

Notice that these two series overlap one another, and the Brackett series overlaps with some of the lower-energy series.
Here is the Paschen series with all of the other series removed.
The Paschen series contains all of the photons produced when the electron drops into **level 3**.

For example, the first line in this series (at 63.8 kJ/mol = 1874 nm) is produced when the electron drops from level 4 to level 3.

\[
\Delta E = -63.8 \text{ kJ/mol}
\]
Here is the Brackett series with all other series removed.
The Brackett series contains all of the photons produced when the electron drops into level 4.

For example, the second line in this series (at 45.6 kJ/mol = 2624 nm) is produced when the electron drops from level 6 to level 4.

\[
\begin{align*}
\text{level 5} & \quad \downarrow \\
\text{level 6} & \quad \downarrow \\
7 & \quad \downarrow \\
\text{level 4} & \quad \downarrow \\
\text{level 4} & \quad \downarrow \\
8 & \quad \downarrow \\
9 & \quad \downarrow \\
\text{level 4} & \quad \downarrow \\
4 & \quad \downarrow \\
4 & \quad \downarrow \\
4 & \quad \downarrow \\
\end{align*}
\]

\[\Delta E = -45.6 \text{ kJ/mol}\]
Each series in the line spectrum of hydrogen correlates with the final energy level for an electron transition.

- **Lyman** series: transitions that end up in **level 1**
- **Balmer** series: transitions that end up in **level 2**
- **Paschen** series: transitions that end up in **level 3**
- **Brackett** series: transitions that end up in **level 4**
- **Pfund** series: transitions that end up in **level 5**
Let’s practice!
Can we answer these questions…
Where is the fifth line of the Paschen series?
What is the corresponding electron transition?
What is the energy of this line?
First, we need to find the Paschen series. It is the third series, counting from the right (i.e. it has the lines with the third-highest energies).

You should learn the sequence: Lyman, Balmer, Paschen (from highest energy to lowest).
Next, we need to find the fifth line in the series. The lines in each series are numbered from left to right (from lowest energy to highest energy).

Now we need to identify the electron transition that produces this line.
The light we observe is the result of the electron moving between two levels. The Paschen series is the third series, which means that for all lines in the Paschen series, the electron ends up in level 3. But where does it start?

??

3 -145.9 kJ/mol
We can work this out systematically.

For the first line, the electron makes the smallest possible jump: level 4 to level 3

For the second line, the electron jumps from level 5 to level 3

Third line: level 6 to level 3

Fourth line: level 7 to level 3

Fifth line: level 8 to level 3
To get the energy of this light, we subtract the energies of the two levels. 
\[
\Delta E_{\text{electron}} = (-145.9 \text{ kJ/mol}) - (-20.5 \text{ kJ/mol}) = -125.4 \text{ kJ/mol}
\]

The photon energy is positive: 
\[
E_{\text{photon}} = 125.4 \text{ kJ/mol}
\]
All other elements have line spectra, as do all ions that contain at least one electron.

What can we tell from their line spectra?
Ions that have **only one electron** show line spectra that are similar to that of hydrogen. Examples are He⁺, Li²⁺, and Be³⁺.

However, the energies are much larger.

The energies of all lines are increased by a factor of $Z^2$, where $Z$ is the atomic number of the element.
Here is a comparison of the line spectra of H and He$^+$.  

For He, the atomic number (Z) is 2. Therefore, the energies of all helium lines are 4 times as large as they are for hydrogen ($2^2 = 4$).
For example, the energies of the Lyman series for H range from 984.8 kJ/mol to 1313 kJ/mol. The energies of the corresponding series in the He\(^{+}\) spectrum range from 3939 kJ/mol to 5252 kJ/mol.

\[984.8 \text{ kJ/mol} \times 2^2 = 3939 \text{ kJ/mol}\]
\[1313 \text{ kJ/mol} \times 2^2 = 5252 \text{ kJ/mol}\]
However, line spectra for uncharged elements other than hydrogen do not resemble the line spectrum for hydrogen, and they do not fit any simple pattern.

Here is the line spectrum of uncharged helium as it appears to our eyes. Remember that we can only see wavelengths from 400 nm to 700 nm.
The line spectrum of sodium (shown here) is unusually simple.

There are many other lines, but they are so faint and the prominent yellow line at 590 nm is so bright that the other lines are usually not visible.

What can we tell from this spectrum?
The photon energy of 590 nm light is 203 kJ/mol.

This tells us that sodium atoms can lose 203 kJ/mol of energy.

Somewhere among the allowed energy levels of Na, there must be two levels that are 203 kJ/mol apart.

But we cannot determine the energies of these two levels, or whether there are other levels between them.
However, other measurements have shown that the lower energy level for this electron transition is -495 kJ/mol.

Therefore, we can calculate that the upper energy level must be -292 kJ/mol.

Line spectra tell us how far apart energy levels are, but they do not give us the actual energies of the levels.