SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

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## SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

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ROAD MAP
THE DISCOVERY OF ATOMIC STRUCTURE

A simple example of the energy changes involved in particular transitions and the resulting spectrum is the hydrogen emission spectrum. This spectrum is especially interesting for historical, theoretical and practical reasons. Over a period of 40 years, from 1885 to 1925, all of the lines in the emission spectrum in the ultraviolet, visible and infrared regions were found experimentally and were identified with various electron transitions. Spectroscopic experiments like the above gave the major experimental evidence for the Bohr theory of the atom and eventually for the modern quantum theory.

By 1885 the concept of the atom was generally accepted by chemists although not by all physicists. However, little was known about the structure of the atom. What was known was a reasonably good idea of the size and mass of atoms and the belief that electric charge was somehow involved.

Around 1897 two major advances occurred. One was the discovery of radioactivity by H. Becquerel through the accidental exposure of a photographic plate left in a closed drawer with a piece of uranium. The other discovery was no accident at all, but was the discovery that negative electric charge was carried by a discrete particle, which came to be called the electron, by J. J. Thomson in his laboratory in Cambridge, England. Earnest Rutherford, a New Zealand scientist working in Thomson’s laboratory, discovered one type of radiation called alpha particles and studied their properties, such as their scattering by various substances. In 1909 he asked two of his younger colleagues, Hans Geiger and Ernest Marsden, to experiment with scattering alpha particle by a thin gold foil. They discovered, to their surprise, that a very few of the alpha particles were scattered almost straight back. Rutherford drew the conclusion that the atom must consist of a very small, hard and heavy positively charged center and a larger and looser negatively charged part, and thus was born the idea of the nuclear atom.

To return to spectroscopy. Now that the general structure of an atom was known, the questions of how hydrogen atoms, which were known to have a positive nucleus and only one electron, could emit several series of discrete spectra, needed answering. In 1913 the Danish scientist, Niels Bohr, published a new idea that the electron could only ‘orbit’ the nucleus in a finite number of energy states and never in between. He was able to mathematically calculate the spectral series so his idea was taken seriously and eventually became one of the fundamental steps towards modern quantum mechanics.
The discovery of the electron by J. J. Thomson (1897) and the research on radioactivity by H. Becquerel and M. Curie showed that the atom contained negative and positive particles. But where were they? Thomson suggested a 'raisin toast' model in which negative electrons were spread through a positive cloud. E. Rutherford and his co-workers in a brilliant sequence of experiments in which α-particles were used as atomic probes developed the NUCLEAR ATOM.

This is a picture of a Crooke’s tube, the apparatus with which J. J. Thomson discovered the electron.

Other scientists attempted this experiment before Thomson but the beam did not deflect. Thomson got the beam to deflect by making sure that the tube contained a high vacuum. Can you explain why this made a difference?

This is a picture of an experiment separating α, β, and γ radiation. Explain how you can determine the sign of the charges on the different forms of radiation.
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GEIGER-MARSDEN EXPERIMENT

This is the experimental arrangement by which Geiger and Marsden produced the data from which Rutherford developed the idea of the nuclear atom. The next page will show the essential chemistry of the experiment and then we show a picture of an atom where the nucleus is drawn to correct scale relative to the electron cloud.

Using the fact that the alpha particle is positive and the experimental results on the next page, decide which of the three atomic models shown on the right is correct.
From a stream of alpha particles, one of them hits a hydrogen nucleus and knocks it away, while being itself only slightly deflected.

When an alpha particle hits a helium nucleus, both of them are deflected equally, showing that they are equal in mass. Why does this deflection show that the alpha particle and the helium nucleus have the same mass?

When an alpha particle hits a nitrogen nucleus, the alpha can be returned to sender while moving the nitrogen much less.

Most alpha particles will pass straight through many layers of atoms, showing that the atom is mostly empty space. An occasional alpha particle, however, will be deflected at a large angle.

For a given nuclear mass and charge, how much an alpha particle is deflected by a nucleus depends upon how close it approaches the nucleus.
A picture of the hydrogen atom, showing the actual size comparison between the electron cloud (in red) and the nucleus (in black).
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ATOMIC SIZE

Let us imagine making an atom of hydrogen. Start with a proton and an electron far apart and not moving with respect to each other. Call the energy of this situation zero. Then allow the electron and proton to attract each other as opposite charges do. As they approach each other the electrostatic potential energy will become negative but they will also speed up (mostly the electron) and the kinetic energy will become positive. At a certain distance (about 32 picometers) the sum of the potential and kinetic energy will be at a minimum and that will set the size of the atom.

The kinetic energy of an electron in an atom is mostly determined by the Heisenberg uncertainty principle, which has the equation

$$(\Delta x)(\Delta p) > \frac{h}{4}$$

where $\Delta x$ is the uncertainty in the location and $\Delta p$ is the uncertainty in the momentum. If we tried to constrain the electron too close to the proton, then the uncertainty in the momentum would increase and with that the kinetic energy would increase, according to the equation.

$$K = \frac{p^2}{2m} = \frac{mv^2}{2}$$

where $K$ is the kinetic energy of a particle, $p$ is the momentum and $m$ is the mass of the particle.

Total Energy = Kinetic Energy + Potential Energy

Why can we disregard the kinetic energy of the proton?
WHAT AND WHERE ARE ELECTRONS?

We know that each electron has a definite electrical charge, which we can write as $e$ and that $e = 1.602 \times 10^{-19}$ C and we know that each electron has a definite (small) mass $m$ and that $m = 9.11 \times 10^{-31}$ kg.

What is harder to know is where an electron is located. We know from quantum mechanics that an electron can only be probably located in any given volume of space, although for a given electron, the probability of it being somewhere, in all space, is one.

There is a finite probability of an electron being anywhere in space. We often represent this by drawing electron cloud pictures, where the deeper color represents a greater probability of the presence of an electron.

In an isolated atom the electron probability forms a spherical cloud around the nucleus. It is thickest at the nucleus and falls off away from the nucleus. The electron cloud and the nucleus together form the atom.

Suppose the blue dot in picture 2 represents an atomic nucleus with four protons, what kind of force would the black arrows represent? How would you interpret the red arrows in picture 3? Why are the black arrows drawn thicker than the red arrows? What kind of atom will be neutral when it has four electrons? Where is it located on the periodic table? In picture number 4, is the size of the nucleus (blue dot) drawn correctly to scale with the size of the electron cloud? If not, would it be larger or smaller and by about how much?
The red arrow above shows the energy transition from the \( n = 3 \) state of the hydrogen atom to the \( n = 2 \) state. This transition will produce the red emission line in the Balmer spectrum.

Find the transitions (arrows) which will produce the other visible lines in the hydrogen spectrum.
The wavelengths of one electron atomic emission spectra can be calculated from the Rydberg equation:

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where $\lambda$ = wavelength (in m.) and Z is the atomic number. Z = 1 for hydrogen.

R is called the Rydberg constant and $R = 1.096776 \times 10^7$ m$^{-1}$

$n_1 = 1, n_2 = 2, 3, 4 ...$

$n_1 = 2, n_2 = 3, 4, 5 ...$

$n_1 = 3, n_2 = 4, 5, 6 ...$
SPECTROSCOPY AND THE STRUCTURE OF THE ATOM

FROM THE SPECTRUM TO ATOMIC STRUCTURE

STEP ONE: Measure the energy difference between \( n = 3 \) and \( n = 2 \) on the Energy Diagram for H.

STEP TWO: Using the Spectral Chart for H, measure the wavelength and calculate the energy of the longest wavelength Balmer line, using \( E = \frac{hc}{\lambda} \).

STEP THREE: Compare your results for Step 1 and Step 2. They should be about the same, up to the limits of accuracy.

STEP FOUR: Repeat the procedures for Steps 1 through 3, finding the energy difference between \( n = 2 \) and \( n = 1 \), and comparing it with the energy of the longest wavelength Lyman line.

STEP FIVE: Measure the wavelengths of the left edge of each of the five series. Calculate the energy for each of those wavelengths.

STEP SIX: Find and mark the five energies you calculated in Step Five on the Energy Diagram for H.

STEP SEVEN: Interpret and discuss your results.

For further practice:
1. Use the Energy Diagram for H to find the difference in energy between \( n = 5 \) and \( n = 3 \). Calculate the wavelength of the electromagnetic radiation that would have this energy and locate it on the Spectral Chart for H.
2. Using the third longest wavelength line in the Balmer series, calculate its energy and find two energy levels on the Energy Chart for H whose difference would produce light of that wavelength.

NOTE: Although these energies are usually considered negative, it is only the differences in energy that concern us here, so do not worry about the sign for now.
The scale for orbital radii is given in picometers (pm).
1.00pm = 1.00x10^{-12}m
The radius of the nucleus is less than 6.00x10^{-3}pm.

A hydrogen atom consists of a negatively charged electron with a probability of being in a region of space around a tiny, positively charged nucleus, which in the case of hydrogen is just a single proton. The probability of finding the electron always peaks at the nucleus and always descends as we look farther and farther away from the nucleus. But how rapidly that probability descends away from the nucleus and in what directions it descends less or more depends upon the quantum state of the atom. In any case, the shape and extent of that region within which we can expect to find the electron (usually with a 95% probability) is called an orbital. In the simplest cases (those with no angular momentum) the orbital is spherical and depends for its size upon the energy of the atom. That energy is described by the quantum number n.
The energy is lowest for n = 1, which also has the smallest orbital. Both the energy and the radius of the orbital rise as the square of n.
What happens to the atomic radius as the energy approaches zero?
What can you say about the atomic radius when the energy is positive?
The Rydberg equation shows the wavelength, $\lambda$, of the photon emitted when a single electron atom of nuclear charge $Z$ falls from energy level $n_1$ to energy level $n_2$. R is the Rydberg constant.

\[ \frac{1}{\lambda} = R Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

R = 1.096776 x 10$^{-7}$ m$^{-1}$

Qualitatively describe the difference between the energy levels of H, He$^+$, and Li$^{2+}$. What is the cause of these differences?
When the excited hydrogen atom is in a magnetic field, something new happens. The spectral lines are split!

In order to explain these observations we introduce another quantum number, \( l \), which is called the azimuthal quantum number or the angular momentum quantum number.

For all atoms with more than one electron the spectral lines are split by \( l \) even without a magnetic field, due to the interaction of the excited electron with the other electrons in the atom.

For hydrogen we have pictured the orbitals as circular. Circular orbitals correspond to the case where \( l = 0 \).

From quantum mechanics it is known that \( l \) can take on any integral value between 0 and \( n-1 \), for the principle quantum number \( n \).

Now we can make a table of quantum states for \( n \) and \( l \).

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>etc</td>
<td></td>
</tr>
</tbody>
</table>

We have shown hydrogen orbitals as circles in this module. These correspond to the \( l = 0 \) states. For the other states it is best to represent the orbitals in three dimensions, as we do in our module Chemical Bonding.

Chemists and other spectroscopists also have a special system of naming the orbitals corresponding to the different \( l \) values:

- \( l = 0 \) is called an s state.
- \( l = 1 \) is called a p state.
- \( l = 2 \) is called a d state.
- \( l = 3 \) is called an f state.

Thus, for example, an state with \( n = 3 \) and \( l = 2 \) would be called a 3d state.

A basic principle is that, except for one electron atoms, for a given principle quantum number \( n \) the energy of a state increases with increasing \( l \).

Chemists use spectroscopic studies to determine the energy differences between the various states, from which they can determine the actual energy levels of the states. In general, the energy states are ordered as follows, with 1s being the lowest (most strongly bound) and 7f the highest (least strongly bound) energy states.

Finish the table for \( n = 4 \) and extend it through \( n = 5 \).
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LITHIUM

Picture 1 shows the some of the lower energy levels for lithium. The 2s and 2p levels are labeled, you label the rest of the levels. Draw in all of the transitions between levels which involve a change in $l$ of plus or minus 1.

Lithium Energy Levels

Measure the wavelength of each of the lines shown in the lithium spectrum (picture 2). In picture 1, find the energy of the 2p–2s transition. Would this transition produce one of the lines in the lithium spectrum shown in picture 2? Which one?
In picture 1 the magnetic fields of the electron and the nucleus of a hydrogen atom are shown parallel. In picture 2 the magnetic fields are shown antiparallel. Recalling the experiment with bar magnets, you know that the parallel state has a higher energy than the antiparallel state.

The wavelength of electromagnetic radiation given off when the hydrogen atoms drops from the parallel state to the antiparallel state is 21 cm. What is the frequency of the 21 cm photon? What is the difference in energy between the hydrogen atom in the parallel state and in the antiparallel state? What happens if a 21 cm photon is absorbed by a hydrogen atom in the antiparallel state?

It is known from experiment and from quantum mechanics that the magnetic field of an electron can have only two directions, up and down, and nothing in between. For historical reasons this property of electrons has been named ‘spin’ and assigned the letter $m_s$.

For spin up $m_s = + \frac{1}{2}$
For spin down $m_s = -\frac{1}{2}$

The proton has the same spin property as the electron.

What is the total spin of the hydrogen atom in the parallel state? What is the total spin of the hydrogen atom in the antiparallel state?

In the 1930’s astronomers trying to map our galaxy were frustrated by the vast lanes of dust blocking our vision of the inner galaxy. In the early 1940’s the Dutch astronomers Oort and van Hulst proposed using the 21 cm hydrogen line to explore the galaxy and beyond. Eventually the technology to do this was developed and now this is a major probe of the universe, since most of the universe is made of hydrogen.
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SPECTROSCOPIC LINE SPLITTING

Since the electron is a moving charged particle when \( l \neq 0 \), it has a magnetic field, as indicated by the vertical arrow in picture 1.

Many energy levels are actually split by the interaction between the magnetic field of the electron (spin) and the magnetic field of the charged electron moving in its orbital. This is called the fine structure.

Obtain two bar magnets with their north and south poles labeled. Align the magnets parallel to each other with their north poles pointing in the same direction. Hold onto one magnet while you let the other one go. Then align the magnets parallel so that the south pole of one magnet is aligned with the north pole of the other magnet, then let go. Compare the two situations. Which one, N-N or N-S has the higher energy? Which one is more stable. Explain the relationship between energy and stability.

The electrons themselves also have their own magnetic fields, as shown in pictures 2 and 3.

We call the magnetic effect of an electron by the name 'spin' because it is what would be produced by a spinning charge. According to quantum mechanics the direction of the electron spin can only have two values, one aligned with the magnetic field it is in and one opposite. Having done the experiment with bar magnets above, explain which arrangement, either picture 4 or picture 5, would have the higher energy.

Picture 6 shows the fine structure of an alkali atom (solid horizontal lines). The principle quantum number, \( n \), is shown next to the \( s \) state for which \( l = 0 \).

The electron shown in picture 2 has spin \( s = +\frac{1}{2} \)
The electron shown in picture 3 has spin \( s = -\frac{1}{2} \)
In all of the orbital diagrams on this page, the same external magnetic field is shown by the vertical black arrow. The magnetic field of the electron in its orbital is shown by the blue arrow. Assuming, for simplicity, that all of the orbital magnetic fields are of equal strength (not necessarily true), list the orbitals from lowest energy state to highest energy state.
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THE PAULI EXCLUSION PRINCIPLE

Each orbital is determined by three quantum numbers. They are:
- \( n \), the principal quantum number, which can take any positive integer,
- \( l \), the azimuthal quantum number, which can take any value \( 0 \leq l \leq n-1 \),
- \( m \), the magnetic quantum number, which can take any value \( -l \leq m \leq l \).

In addition, each electron has its spin quantum number \( s \), where either \( s = +\frac{1}{2} \) or \( s = -\frac{1}{2} \).

The PAULI EXCLUSION PRINCIPLE says that no two electrons (in the same atom) can have the same set of quantum numbers.

\[
\begin{array}{ccc}
n = 1 & l = 0 & m = 0 \\
n = 2 & l = 0 & m = 0 \\
& l = 1 & m = -1 \\
& l = 1 & m = 0 \\
& l = 1 & m = +1 \\
n = 3 & l = 0 & m = 0 \\
& l = 1 & m = -1 \\
& l = 1 & m = 0 \\
& l = 2 & m = -1 \\
& l = 2 & m = 0 \\
& l = 2 & m = +1 \\
& l = 2 & m = +2 \\
n = 4 & & \\
\end{array}
\]

As done in the above chart, write out all of the sets of quantum numbers with principal quantum number \( n = 4 \).

AUFBAU

With each increase of one in the atomic number, one more electron has to be added to the atom to balance the nuclear charge. In the ground state, this electron will be added to the lowest energy unoccupied orbital, with a maximum of two electrons per orbital. The following diagram is a useful aid to help remember in which order the electrons are added, going along the path of each arrow from top down.

The orbitals are named according to the following system. First comes the principal quantum number, \( n \). This is followed by a letter representing the \( l \) value, according to the following rules:
- For \( l = 0 \) we have \( s \) orbitals.
- For \( l = 1 \) we have \( p \) orbitals.
- For \( l = 2 \) we have \( d \) orbitals.
- For \( l = 3 \) we have \( f \) orbitals.

Using the Pauli exclusion principle and the fact that electrons can have either of two spin states, calculate how many electrons can be in each orbital.
Using the spin assignments given on the previous page, what is the total spin of the parahelium atom? What is the total spin of the orthohelium atom? (You can ignore the nucleus for these questions.)
1. When the spectroscope is pointed at a Bunsen burner flame with NaCl(s) held in the flame a single yellow line appears. Explain.

2. The same flame viewed against a 100 Watt incandescent bulb shows a dark line at the same wavelength as the bright yellow line. Explain.

3. What is the wavelength of the dark line?
When a light bulb is connected to a variable resistor we observe the following sequence of events as the power is gradually increased.

<table>
<thead>
<tr>
<th>POWER</th>
<th>APPEARANCE</th>
<th>SPECTRUM</th>
<th>POWER CURVE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Power</td>
<td><img src="image1.jpg" alt="Light Bulb" /></td>
<td><img src="image2.jpg" alt="Spectrum" /></td>
<td><img src="image3.jpg" alt="Power Curve" /></td>
</tr>
<tr>
<td>Medium Power</td>
<td><img src="image4.jpg" alt="Light Bulb" /></td>
<td><img src="image5.jpg" alt="Spectrum" /></td>
<td><img src="image6.jpg" alt="Power Curve" /></td>
</tr>
<tr>
<td>High Power</td>
<td><img src="image7.jpg" alt="Light Bulb" /></td>
<td><img src="image8.jpg" alt="Spectrum" /></td>
<td><img src="image9.jpg" alt="Power Curve" /></td>
</tr>
</tbody>
</table>

The curves shown on the right are mathematically generated to show the amount of relative emission power at different wavelengths from a source at temperatures from 100K to 1000K. Something which emits electromagnetic radiation according to this law is called a black body.
LAMBERT-BOUGER-BEER LAW

PICTURES FOR CONCENTRATION AND PATH LENGTH EFFECTS

Original Solution

Path Length Effect

Concentration Effect

\[ A = a \times b \times c \]

- **A**: absorption
- **a**: absorptivity
- **b**: path length
- **c**: concentration
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ABSORPTION SPECTRA FROM LIQUIDS AND SOLIDS WITH DIFFERENT CONCENTRATIONS OF DYE

Principles behind Lambert-Beuger-Beer Law

a. Particular kinds of molecules absorb light in particular wavelength regions.

b. More molecules absorb more light.

c. More molecules absorb more light.

Explain what is happening to produce each of the three spectral sequences above. Be particular. Explain the differences between the spectral sequences and explain how and why the spectra are changing in each spectral sequence.
Describe the spectra shown on this page; e.g., tell everything you can about it including the wavelengths and energies associated with its emission and/or absorption regions and lines, the type and state of matter which produced it, whether it is an emission or absorption spectrum or both, and everything else you can observe or think of.