Structures and Properties of Matter

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CONTENTS

ATOMIC THEORIES

Dalton's Atomic Theory

Matter is composed of indestructible, indivisible atoms, which are identical for one element, but different from other elements. This model is commonly referred to as the **billiard ball model.**

Table 0.1: Creating the Dalton Atomic Theory (1805)

Key Experimental Work	Theoretical Explanation
Law of definition composition: elements combine in a characteristic mass ratio	Each atom has a particular combining capacity
Law of multicple proprtions: there may be more than one mass ratio	Some atoms have more than one combining capacity
Law of conservation of mass: total mass remains	Atoms are neither created nor destroyed constant in a chemical reaction

Thomson Atomic Model

Thomson's quantitiative work with the cathode ray resulted in the discovery of the electron. Thomson was able to deflect the cathode ray towards a positively charged plate to deduce that the particles in the beam were negatively charged. Thomson's model is commonly referred as the **plum pudding model**. See Figure 1.
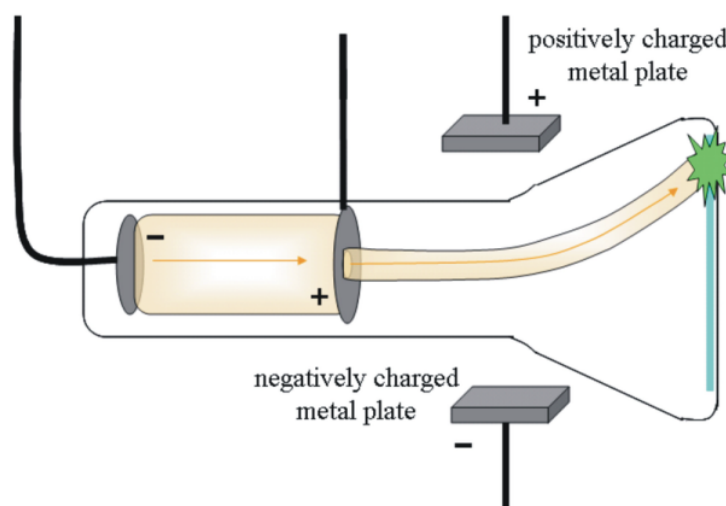
Figure 1: The charged particles were directed in the direction of the positively charged plate, thus he concluded that these particles, which were smaller than the smalles atom, where negatively charged. A **cathode ray** is a stream of electrons.

Rutherford Atomic Theory

Rutherford used radium as a source of alpha radiation and directed it at a thin film of gold. **Note:** it is kind of fortunate that Rutherford used gold because the nucleus is so large which produced desireable results.

Table 0.2: Creating the Thomson Atomic Theory (1897)

Key experimental work	Theoretical explanation
Arrhenius: the electrical nature of chemical solutions	Atoms may gain or lose electrons to form ions in solution
Faraday: quantitative work with electricity and solutions	Particular atoms and ions gain or lose a specific number of electrons
Crookes: qualitative studies of cathode rays	Electricity is composed of negatively charged particles
Thomson: quantiative studies of cathode rays	Electrons are a component of all matter
Milikan: charged oil drop experiment	Electrons have a specific fixed electric charge

- Most particles passed right through the gold foil, meaning that most of the atom is empty space

- Based on Thomson's model, some electrons should only be deflected at *small angles*, but instead deflected at even larger angles.

- All of the positive charge in the atom had a relatively small volume compared to the size of the atom. See Figure **??**

- There had to be a nuclear attractive force to explain how the what came to be nucleus occupied such little volume

- The nuclear force of attraction also had to be **much stronger** than the electrostatic force repelling the positive charges in the nucleus.

- It was also in this experiment that he discovered the α, β, and γ radiation.
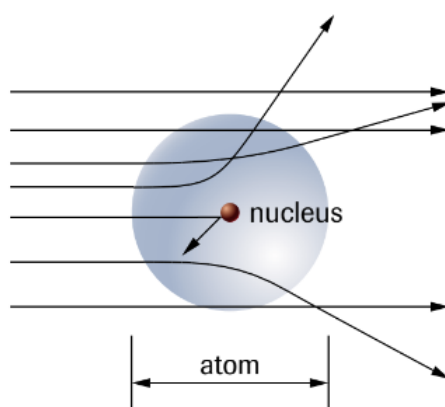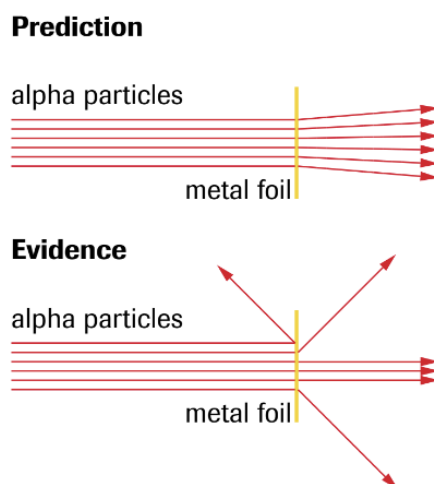
Figure 2: Prediction vs. Evidence: the particles were deflected at large angles instead of small angles

Table 0.3: Creating the Rutherford Atomic Theory (1911)

Key experimental work	Theoretical experiment
Rutherford: a few positive particles are deflected at large angles when fired at a gold foil	The positive charge in the atom must be very concentrated at a small volume
Most materials are very stable and do not fly apart (break down)	A very strong nuclear force holds the positive charges with the nucleus
Rutherford: most alpha particles pass straight through the gold foil	Most of the atom is empty space

Protons, Isotopes, and Neutrons

Definitions:

- **Proton:** a positively charged subatomic particle found in the nucleus of atoms

- **Isotope:** a variety of atoms of an element; atoms of this variety have the same number of protons as all of the elements, but a different number of neutrons

- **Neutron:** a neutral/uncharged subatomic particle present in the nucleus of atoms

- Previous studies by scientists found that the smallest positive charge possible was from ionized gas (leaving just the proton). This in turn became the **proton**

- By bending the hydrogen-gas positive rays in a magnetic field, they were able to determine the charge and mass of the hypothetical proton

- The proton was shown to have a charge equal to but opposite to that of the electron and a mass 1836 times that of an electron

- Evidence from radioactivity and mass spectrometer falsified Dalton's theory that all atoms of a particular element were identical. There were actually **isotopes**

- James Chadwick used alpha particle bombardment to propose the existence of the **neutron**

Table 0.4: Creating the concepts of protons, isotopes, and neutrons

| Key experimental work	Theoretical explanation
Rutherford (1914): the lowest charge on an ionized gas particle is from the hydrogen ion (the proton)	The smallest particle of positive charge is the proton
Soddy (1913): radioactive decay suggest different atoms of the same element	Isotopes of an element have a fixed number of protons but varying stability and mass
Aston (1919): mass spectrometer work indicates different masses for some atoms of the same element. See Figure 3. Chadwick: (1932): Radiation is produced by bombarding elements with alpha particles	The nucleus contains neutral particles called neutrons
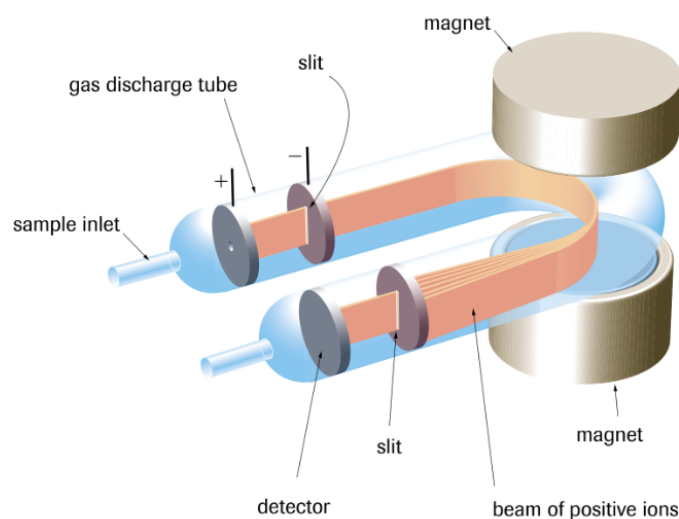
Figure 3: A mass spectrometer is used to determine the masses of ionized particles by measuring the deflection of these particles as they pass through a strong magnet

Problems

1. Present the experimental evidence that led to the Rutherfor model

2. How did Rutherford infer that the nucleus was

(a) very small (compared to the size of the atom)?

(b) positively charged?

3. (a) State the experimental evidence that was used in the discovery of the proton

    (b) Write a description of a proton

4. (a) State the experimental evidence that was used in the discovery of the neutron

    (b) Describe the nature of the neutron

5. (a) State the experimental evidence that was used in the discovery of the neutron

    (b) Describe the nature of the neutron

6. What is meant by a "black box" andw why is this an appopriate analogy for the study of atomic structure?

7. Theories are often created by scientists to explain scientific laws and experimental results. To some people it seems strange to say that theories come after laws. Compare the scientific and common uses of the term "theory"
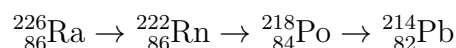
Solutions

1. The gold foil experiment. As predicted, most of the α-particles passed right through. However, some were deflected backwards, meaning that there was a densely positive center, called the nucleus

2. (a) According to Dalton, some particles should be deflected at rather small angles. However, the particles were actually deflected at much larger angles than predicted. This means that the nucleus was very dense and small in volume

    (b) The particles didn't pass through and were deflected

3. (a) In Figure 2, you can see the prediction vs. evidence. The evidence was that some particles were deflected at large angles, and some even backwards

    (b) The proton is a subatomic particle with a charge equal to but opposite to that of an electron and a mass of 1836 times greater

4. (a) Chadwick used alpha particle bombardment to prove the existence of the neutron

    (b) The proton is a neutral/uncharged subatomic particle present in the nucleus of atoms

5. The term "black box" refers to a system or object that can be understood and analyzed based on its inputs and outputs, regardless of its internal workings or structure. In the study of atomic structure, scientists could not directly observe the internal workings of an atom, but could analyze the results they presented. For instance, in Rutherford's gold foil experiment, they didn't know the internal workings of an atom, yet still proved the existence of a nucleus. Another example is Bohr's model; the model was based on the observed spectral lines of hydrogen–he could predict the behaviour of electrons in an atom without directly observing them

6. Theories are scientific assumptions made based solely on previously proven knowledge, namely laws. Thus, it would be contradictory to assume that laws come after theories because there would be no laws to prove the pre-existing theories in the first place

Case Study: A Canadian Nuclear Scientist

An exceptional female student, who was Rutherford's first graduate student at McGill University, is Canadian **Harriet Brooks**. Before the gold foil experiment, Rutherford was researching radioactivity and invited Brooks. Brooks studied the reactivity of radium and found an "emanation", which is radon from the radioactive decay of radium

$$^{226}_{86}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\alpha$$
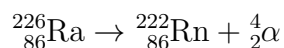
- At the time, everyone believed that an element remained the same when it emitted radiation. Brookes disagreed and gathered evidence to falsify that claim

- Brooks used diffusion of the emanated gas to determine the molar mass of what we now know as radon

- In the process, she gathered evidence that led to Rutherford's theoretical interpretation that radiation resulted in the recoil (action-rejection) of the radiating nucleus. Often the recoiling nucleus was ejected from the radioactive sample

- Brook's third significant contribution was important evidence that Rutherford interpreted as a series of radioactive transformations. For example:

$$^{226}_{86}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb}$$

(emitting an alpha particle in each step)

ORIGINS OF QUANTUM THEORY

- **Max Planck** is credited with starting the quantum revolution with a surprising interpretation of the experimental results obtained from the study of the light emitted by hot objects

- **Gustav Kirchhoff** was interested in the light emitted by blackbodies

- The term **blackbody** is used to describe an ideal, perfectly black object that does not reflect any light and emits various different forms of light (electromagnetic radiation) as a result of its temperature

Planck's Quantum Hypothesis

- As a solid is heated, it changes colours. Initially it is red, then white. Recall that white is a combination of all colours, so the light emitted by the hotter object must now be accompanied by, for example, blue light

- The changes in the colours and the corresponding spectra do not depend on the composition of the solid

- The intensity (brightness) of the different colours observed in the spectrum of emitted light resembles a bell curve. See Figure 4

Table 1 Brooks's Place in the History of Radioactivity

1896	Becquerel discovers radioactivity (of uranium)
1898	Radium, polonium, and thorium are identified as radioactive (by the Curies)
1898	Brooks earns B.S. (first in her class) from McGill University and starts graduate work with Rutherford
1900	Rutherford's team identifies radioactive emissions as alpha, beta, and gamma
1901	Brooks identifies radon as a product of the radioactivity of radium
1901	Brooks earns M.A. from McGill University
1901–02	Brooks starts Ph.D. in Pennsylvania
1902–03	Brooks earns fellowship to work with J. J. Thomson in Cambridge, England
1903–04	Brooks returns to work with Rutherford at McGill and publishes further evidence for radon as a radioactive decay product
1904–06	Brooks works at Barnard College, New York
1906–07	Brooks works with Marie Curie in Paris, France
1907	Brooks marries and discontinues her research life
1908	Rutherford wins Chemistry Nobel Prize for Canadian research
1911	Rutherford scattering experiment and the nuclear atom
1913	Soddy invents isotopes to explain his experimental results
1913	Bohr publishes his atomic interpretation of the periodic table and line spectra
1914	Rutherford coins the word "proton"
1916	Lewis theorizes that valence electrons are shared to form covalent bonds
1932	Chadwick creates the neutron to explain the mass of the alpha particle
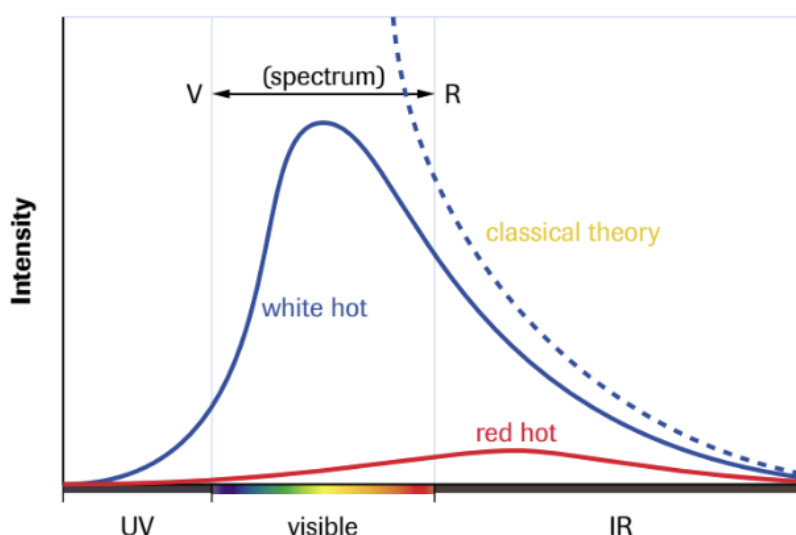
Figure 4: The solid lines show the intensity of the colours of light emitted by a red-hot wire and a white-hot wire. Notice how the curve becomes higher and shifts toward the higher UV as the temperature increases. The dotted line represents the predicted curve for a white-hot object, according to the classical theory before Planck

- For many years, scientists struggled to explain the curves shown in Figure 4. Some were able to describe it at the endpoints, but not the overall curve obtained from experiments.

See Figure 5

- Planck hypothesized that the energies of the oscillating atoms in the heated solid were multiples of a small quantity of energy; in other words, energy is **not continuous**

- Einstein later pointed out that the inevitable conclusion of Planck's hypothesis is that light emitted by a hot solid is also quantized–it comes in "bursts", not as a continuous stream of energy

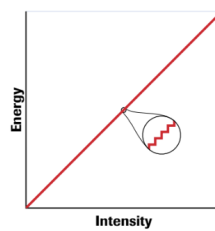- One little burst or packet of energy is called **quantum** of energy

Figure 5: For many years, scientists could not explain the intensity curve, because they believed that as the intensity of light changes, the total energy increases continuously. However, as a consequence of Planck's work, Einstein suggested the slope is actually a staircase with tiny steps, where each step is a quantum of energy

- An interpretation of the evidence from heating a solid is that a sequence of quanta emissions from IR to red to blue to UV occurs. A logical interpretation is that as the temperature increased, the proportions of each larger quantum becomes greater

- The temperature of a heated object is due to a complex combination of the number and kind of quanta

Sample: How would observations of a star allow astronomers to obtain the temperature of the star?

Answer: The colour of the star corresponds to its temperature. It is important to account for luminosity instead of apparent colour because the intensities are different at different distances

Sample: Draw staircase diagrams to show the difference between low-energy red light quanta versus higher-energy violet light quanta.

Answer:
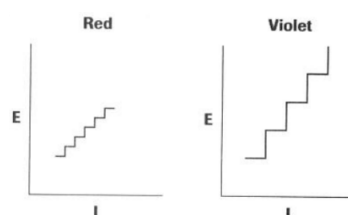
Sample: Liquids and solids, when heated, produce continuous spectra. What kind of spectrum is produced by a heated gas?

Answer: Heated gas produces a **bright-line spectrum**. This is because the quantized energy causes the transition of electrons between energy levels, releasing energy, which produces a birght-line spectrum.

The Photoelectric Effect

- Early on, scientists believed that light acted like a stream of particles, or a wave so to speak. Many scientists, including Newton, bitterly opposed this. But, evidence from experiments with, for example, reflection, refraction, and diffraction facourde the wave hypothesis over the particle view

- In the mid-19th century, **James Maxwell** proposed a theory explaining the known properties of light, electricity, and magnetism. He proposed that light is an electromagnetic wave composed of electric and magnetic fields that can exert forces on charged particles. This electromagnetic-wave theory, known as the **classical theory of light** became widely accepted

- The spectrum derived from this theory is seen in Figure 6

Important. The reason why light is sometimes a wave and other times a particle is because scientists used the **black-box model**. Scientists cannot say for sure because we are only observing the inputs and outputs, thus we treat light as both a wave and particle
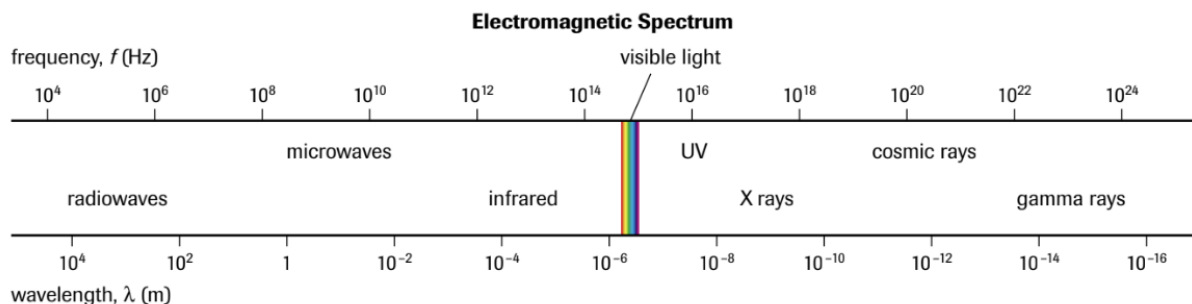
Figure 6: The electromagnetic spectrum originally prediced by Maxwell. It includes all forms of electromagnetic radiation from very short wavelength gamma (γ) rays to oridnary visible light to very long wavelength radio waves

- **Heinrich Hertz** discovered the **photoelectric effect** by accident in 1887. It involves the effect of electromagnetic radiation or light on substances, particularly certain metals. See Figure 7

- According to the classical theory, the intensity/brightness of the light shone on the metal would determine the kinetic energy of the liberated electrons; the brighter the light, the greater the current. But this was shown to be **false**

- Further experimental work showed that the frequency (colour/energy) of the light was the most important characteristic of the light in generating current. In other words, the classical theory was unacceptable for explaining the photoelectric effect

- Einstein built on Planck's idea of a quantum of energy to propose that light consisted of a stream of energy packets or quanta–later called **photons**. A photon of red light contains less energy than a photon of UV light, for example.

- Einstein suggested that the ejection of an electron from the metal surface could be explained in terms of **photon-electron** collision. The energy of the photon is transferred to the electron, some of the energy used for the electron to break free from the atom and the rest is left over as kinetic energy of the ejected atom

- The key thing is that the electron cannot break free from the atom unless a cretain minimum quantity of energy is absorbed from a single photon

Important. Increasing intensity increases the number of photons, but not the energy of each photon. This is why the classical theory treating the relationship between energy and intensity as linear is wrong. In other words, if there is great intensity but the energy of each individual photon is not sufficient, then no electrons are ejected
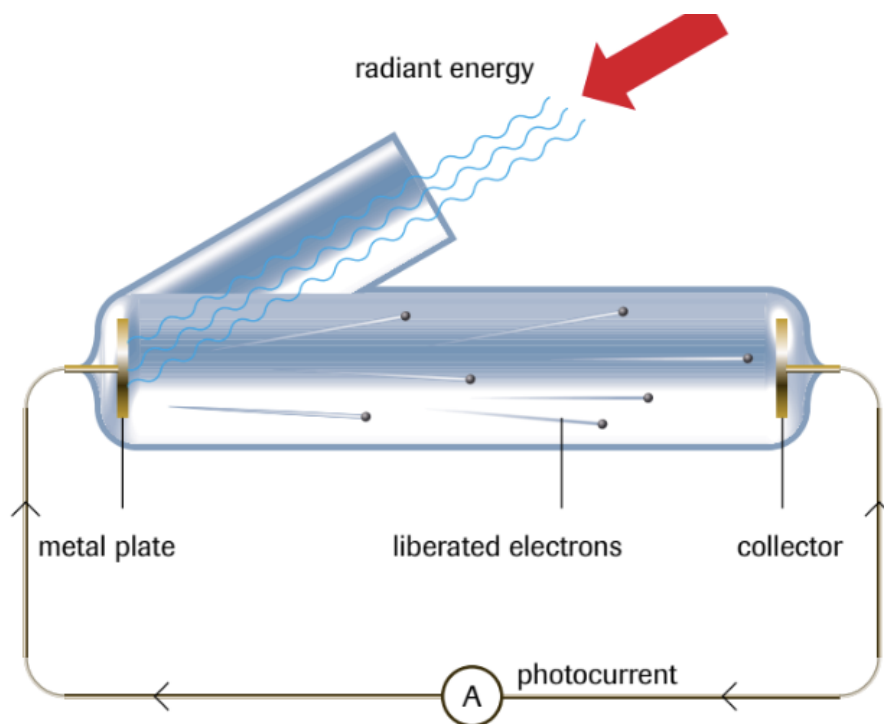
Figure 7: In the photoelectric effect, light shining on a metal plate liberates electrons from the metal surface. The ammeter (A) records the electric current in the circuit. In other words, light shining on a metal plate magically produced current

A possible analogy is the bowl analogy, where a marble is trapped statically in a bowl:

- A certain, minimum quantity of potential energy is required by the marble to escape from the bowl

- This is the same idea with the photoelectric effect–a minimum quanta of energy is required by the electron to escape from the atom

- No electrons are detected at low photon energies because the energy of the single photon captured was insufficient for the electron to escape

Figure 8
(a) Using a bowl analogy, different atoms would be represented with bowls of different depths.
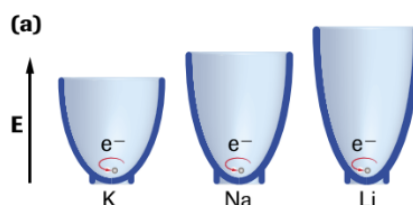
(b) For most atoms, the energy of a red photon is not great enough to boost the electron (marble) out of the atom (bowl). The electron can absorb the energy but is still stuck in the atom. This process simply results in the heating of the sample.
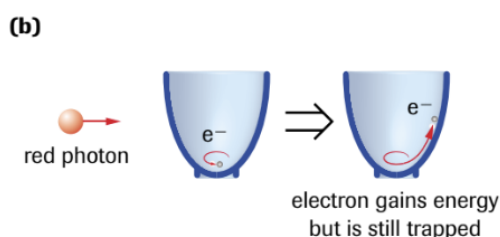
(c) A higher-energy photon, such as a UV photon, has more than enough energy to boost the electron out of many atoms.

(a)

K   Na   Li

(b)

red photon

electron gains energy but is still trapped

(c)

UV photon

electron escapes from atom
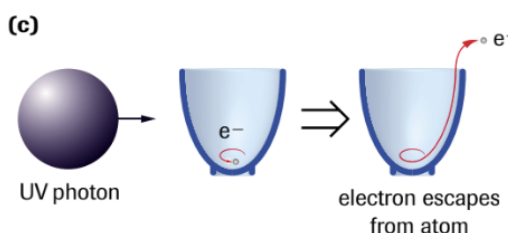
Quantum Theory

Electromagnetic energy is not infinitely subdivisible; energy exists as packets or quanta, called photons. A photon is a small packet of energy corresponding to a specific frequency of light $(E = h\nu)$

Table 0.5: Creating Quantum Theory

Key experimental work	Theoretical explanation
Kirchhoff (1859): blackbody radiation	Plan (1900): the energy from a blackbody is quantized; i.e., restricted to whole number multiples of certain energy
Hertz (1887): the photoelectric effect	Einstein (1905): the size of a quantum of electromagnetic energy depends directly on its frequency; one photon of energy ejects one electron

Problems

1. State the two important experimental obsevations that established the quantum theory of light

2. Although Einstein received the Nobel Prize for this explanation of the photoelectric effect, should Max Planck be considered the father of quantum theory?

3. Write a brief descrption of the photoelectric effect experiment

4. Distinguish between the terms "quantum" and "photon"

5. What effect does the type or colour of light have on the release of electrons from a sodium metal surface?

   (a) Write a brief experimental design to answer this question, based on Figure 7

   (b) Would you expect all colours of light to release electrons from the sodium metal? Justify your answer, in general terms, using the idea of photons

6. Einstein won the Nobel Prize in 1921 for explaining the photoelectric effect in 1905. Einstein calculated the energy of an incoming photon from the Planck equation

$$E = h\nu$$

   (a) If the minimum frequency of light required to have an electron escape from sodium is 5.5×10^{14} Hz, calculating the late energy of photons of this frequency.

   (b) Whati s the minimum energy of t4he quantum leap that an electron makes to escape the sodium atom as a photoelectron?

7. UV light that causes tanning and burning of the skin has a higher energy per photon that infrared light from a heat lamp.

   (a) Use the Planck equation to calculate the energy of a 1.5×10^{15} Hz UV photon and a 3.3×10^{14} Hz IR photon

   (b) Compare the energy of the UV and IR photons, as a ratio.

   (c) From your knowledge of the electromagnetic spectrum, how does the energy of visible-light photons and X-ray photons compare with the energy of UV and IR photons?

Solutions

1. From the photoelectric effect experiment, the two important observations that established the quantum theory of light is that light displaces/ejects electrons from atoms and the intensity of the light doesn't have any effect on the amount of electrons ejected

2. Yes, because by definition, quantum theory is "a theory of matter and energy based on the concept of **quanta**, especially quantum mechanics". Although Einstein built on the ideas of Planck and quanta and popularized it, Planck is considered the father of quantum theory, by definition

3. The experiment involved shooting light rays at a metal plate, which ejected electrons and produced current that was picked up by an ammeter. The experiment also concluded that the intensity of the light was not directly proportional to the current generated

4. "Quantum" refers to a burst/packet of energy while a "photon" is a manifestation of the energy–the photon is a particle that carries quantum which can then be transferred to electrons

5. (a) Using a photoelectric effect apparatus, light of a constant intensity is varied in colour (frequency/wavelength) and electric current is measured. The light colour is the independent variable, and the current is the dependnt variable; and the light intensity and type of metal surface are the controlled variables.

   (b) Not all colours of light will release electrons from the sodium metal because the photons in some colours of light do not carry enough quanta to be able to eject the electrons from the atom

6. (a) Substituting in the values

$$E = (6.63 \times 10^{-34}\,\text{J s})(5.5 \times 10^{14}\,\text{Hz})$$
$$= 3.65 \times 10^{-19}\,\text{J}$$

   (b) The energy absorbed by a photoelectron is the same as the energy supplied by the photon that "hits" it, so the minimum photoelectron energy increase is also 3.65×10^{-19} J.

7. (a) Substituting in the values

$$\text{UV:}\ (6.63 \times 10^{-34}\,\text{J s})(1.50 \times 10^{15}\,\text{Hz}) = 9.95 \times 10^{-19}\,\text{J}$$
$$\text{IR:}\ (6.63 \times 10^{-34}\,\text{J s})(3.30 \times 10^{14}\,\text{Hz}) = 2.19 \times 10^{-19}\,\text{J}$$

   (b) Dividing

$$\frac{E_{\text{UV}}}{E_{\text{IR}}} = \frac{9.95 \times 10^{-19}}{2.19 \times 10^{-19}}$$
$$= 4.54$$

   (c) The UV has more energy than the visible-light and the IR less energy than the visible-light.

QUANTUM THEORY

The energy of a photon of electromagnetic radiation is **proportional** to its frequency, not to its intensity/brightness as had been believed up to that time. This is used to derive the Planck equation

$$E = h\nu$$

Where E is the energy, $h = 6.63 \times 10^{-34}$ J s, the Planck constant, and $\nu =$ the frequency of the wave.

Flaw with Rutherford's Model

- Rutherford believed that the electrons orbited around the nucleus like planets

- Only problem was that they should be emitting energy, meaning that they would eventually collapse into the nucleus. See Figure 8

- This would leave the atom unstable, so chemists knew this was not the case
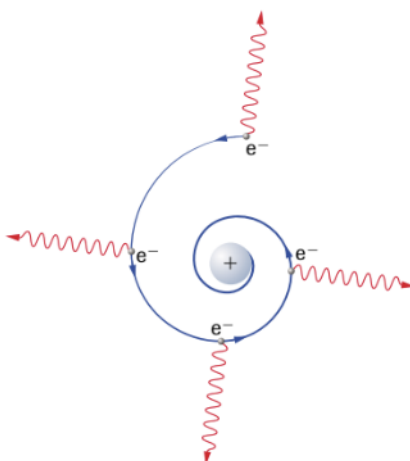

Figure 8: According to Rutherford's model, an obiting electron should continuously emit electromagnetic radiation, losing energy, and collapse the atom. The evidence is to the contrary

Atomic Spectra

- Robert Bunsen and Gustav Kirchhoff worked together to invent the **spectroscope**. See Figure 9

- The spectroscope forms the basis of an analytic method called **spectroscopy** [1]

- Bunsen and Kirchhoff studied the spectra of chemicals, especially elements, heated in a Bunsen burner flame, and the spectrum of the Sun. They discovered that an element not only produced a characteristic flame colour but, on closer examination through a spectroscope, also produced a **bright-line spectrum** [2] that was characteristic of the element

- This techique was used to catalogue known elements and when a new spectrum was found, the spectrum was used as evidence of a new element

- The elements **cesium** and **rubidium** were discovered within a year of the invention of spectroscopy

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[1]**Spectroscopy:** a tehcnique for analyzing spectra; the spectra may be visible light, infrared, ultraviolet, X-ray, and other types

[2]**Bright-line spectrum:** a series of bright lines of light produced or emitted by a gas excited by, for example, heat or electricity

- **Note:** spectroscopes may separate the light by using a prism, or a **diffraction grating**. The most modern, compact, and inexpensive school spectrometers use a diffraction grating

Important. Different elements have different spectrums because they have different number of protons, and different arrangement of electrons. The differences in spectra reflects the differences in the amount of energy that the atoms absorb or give off when their electrons move between energy levels. Hence, this is an effective technique in identifying new elements.
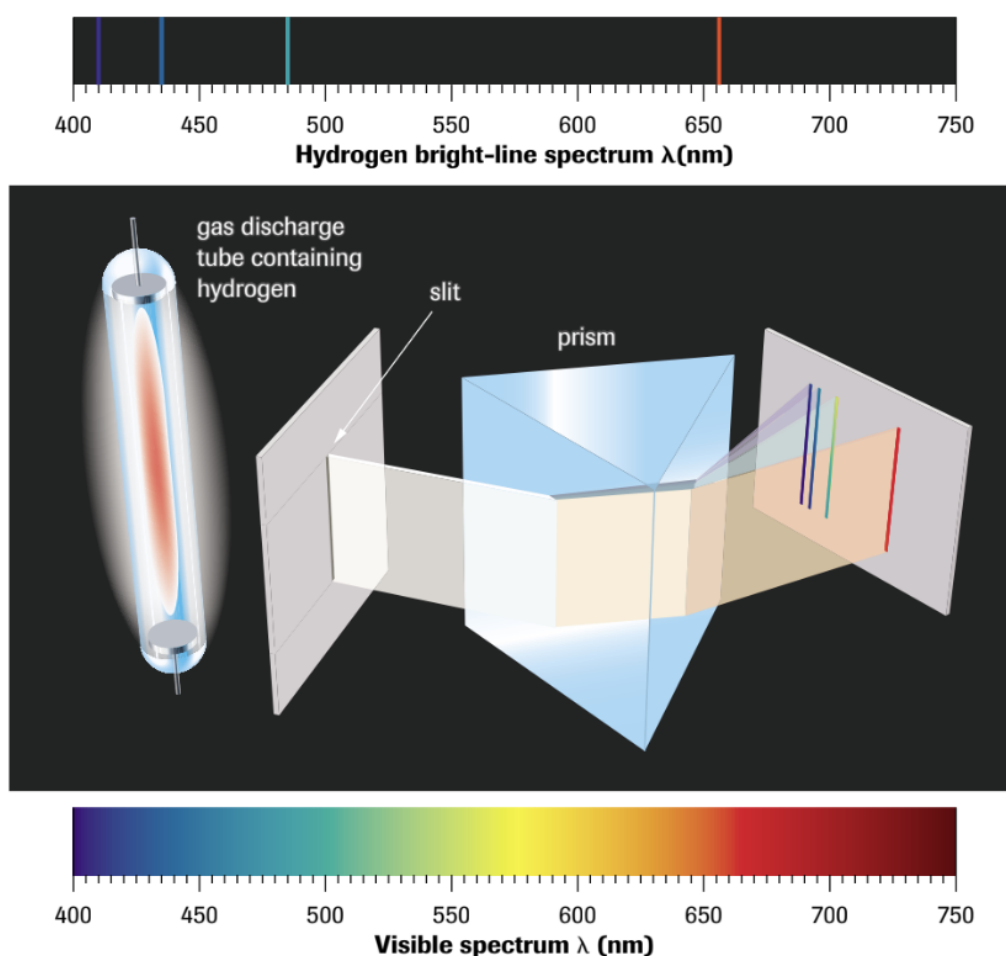
Figure 9: Light from a source of light is passed through slits to form a narrow beam. This beam is split into its components by the prism to produce a series of coloured lines. The visible region of the hydrogen spectrum includes four coloured lines at the wavelengths shown by the scale

- Around 1814, **absorption** or **dark-line spectra** were investigated by Joseph von Fraunhofer

- Kirchhoff, among others, was able to show in the 1860s that dark lines in an element's spectrum were in the same position as the bright lines in the spectrum of the same element. See Figure 10

- This provided a powerful tool to determine the composition of gases far away in the universe. When light passes through a gas, for example, the atmosphere around the Sun, some light is absorbed by the atoms present in the gas

Figure 10: If you start with a complete colour spectrum of all possible colours, then pass this light through a gas and analyze what is left, you get a dark-line spectrum; in other words, the complete spectrum with some lines missing.

Bohr's Model

Bohr's First Postulate
Electrons do not radiate energy as they orbit the nucleus. Each orbit corresponds to a state of constant energy called a **stationary state**.
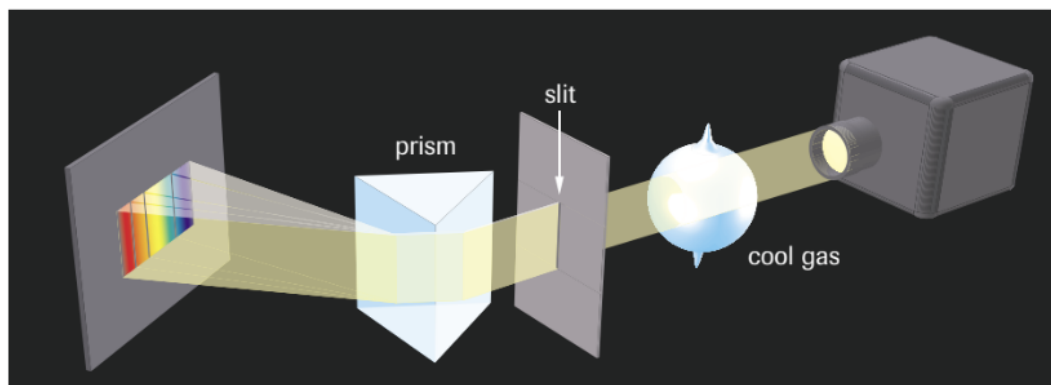
- Bohr reasoned that if the light released or absorbed from an atom was quantized, then the energy of the electron inside the atom must also be quantized. In other words, an electron can only have certain energies. The simplest arrangement would be a planetary model with each electron orbit at a fixed distance with a fixed energy

- Electrons do move in a circular orbit around the nucleus, with the motion described by classical physics

- Electrons have only a **fixed set of allowed orbits**, called **stationary states**. [3] Stationary in the sense that the energy is constant. As long as an electron remains in its orbit, its energy is constant and gives off no energy

- An electron can only pass from one allowed orbit to another. That is, electrons cannot lie between orbits

Bohr's Second Postulate
Electrons can change their energy only by undergoing a **transition** from one stationary state to another.

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[3]**Stationary state:** a stable energy state of an atomic system that does not involve any emission of radiation.

- Bohr observed the spectrum lines when observing hydrogen. The non-continuous colours suggested only certain energies were released. See Figure 12

- There are two states for electrons:

  1. **Ground state:** the "expected" arrangement of electrons. This is because this is the lowest amount of energy the electrons can possess

  2. **Excited state:** When an electron temporarily occupies an energy state higher than its ground state–it transitioning between energy levels. The more energy the electron absorbed, the higher the energy levels the electrons can move to. Eventually, the electron returns back to the ground state, releasing energy in the form of **photons**. This is called an electron **transition**. [4]

- A transition from a higher energy state to a lower energy state means that the electron loses energy and this energy is released as a photon of light, explaining a bright line in a bright-line spectrum. When some energy is absorbed, for example from a photon of light, the electron undergoes a transition from a lower energy state to a higher one, explaining a dark line in an absorption spectrum. These dark lines indicate the amount of energy that was absorbed when the electrons transitioned. See Figure 11

(a) An electron gains a quantum of energy.   **(b)** An electron loses a quantum of energy.
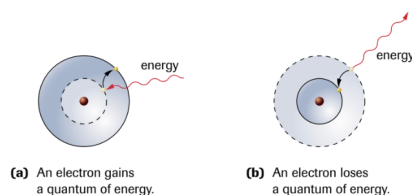
Figure 11

The Successes and Failures of the Bohr Model

Successes

- The Bohr model of the atom is able to offer a reasonable explanation of Mendeleev's periodic law and its representation in the periodic table

- According to the Bohr model, periods in the periodic table result from the filling of electron energy levels in the atom. E.g., atoms in Period 3 have electrons in 3 energy levels

- Although Bohr did his calculations as if electrons were in circular orbits, the most important property of the electrons was their energy, not their motion

- Bohr's model was also able to successfully predict the infrared and ultra-violet spectra for hydrogen

Failures

---

[4]**Transition:** the jump of an electron from one stationary state to another.

Figure 12: Because there are so many atoms, and thus a lot of electrons, in a sample of hydrogen gas, there would be a continuous spectrum and not individual lines. These lines indicate that energy is released in quanta and not continuous

- It only works very well for the spectrum of hydrogen atoms, or ions with only one electron

- The calculations of spectral lines using Bohr's theory for any atom or ion containing more than one electron did not agree with the empirical results
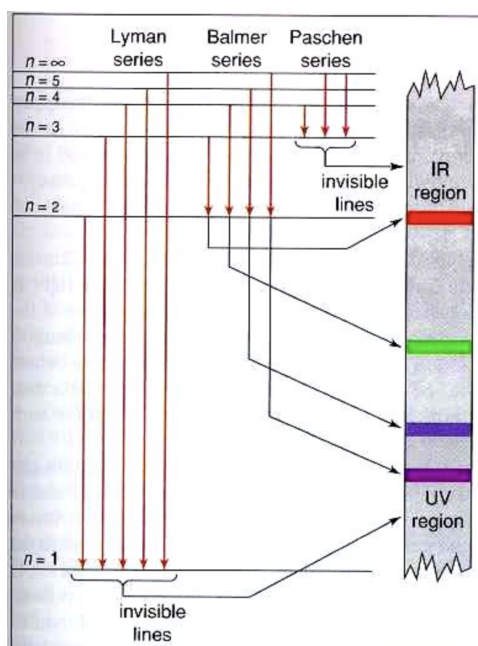
- The disrepancy became worse as the number of electrons increased [5]

Sample: Use the Bohr theory and the periodic table to draw energy-level diagrams for the phosphrous atom.

Answer: Phosphorus is in period 3–there are 2, 8, and 5 electrons per energy level. To draw the energy-level diagram, work from the bottom up:

Sixth, the 3rd energy level,	5 e$^-$	(from group **15**)
Fifth, the 2nd energy level,	8 e$^-$	(from eight elements in **period 2**)
Fourth, the 1st energy level	2 e$^-$	(from two elements in **period 1**)
Third, the protons:	15 p$^+$	(from the **atomic number**)
Second, the symbol:	P	(uppercase symbol from the table)
First, the name of the atom	phosphorus	(lowercase name)

Sample: Use the Bohr theory and the periodic table to draw energy-level diagrams for hydrogen, carbon, and sulfur atoms.

Answer: Using the same method as above

---

[5]Despite the failures, Bohr's theory was a great success because it was the start of a new approach–including the new quantum ideas in a model of the atom

	4 e$^-$	6 e$^-$
		8 e$^-$
1 e$^-$	2	2 e$^-$
1 p$^+$	6 p$^+$	16 p$^+$
H	C	S
hydrogen	carbon	sulfur

Table 0.6: Creating the Bohr Atomic Theory (1913)

Key experimental evidence	Theoretical explanation
Mendeleev (1869-1872): there is a periodicity of the physical and chemical properties of the elements	A new period begins in the periodic table when a new energy level of electrons is started in the atom
Mendeleev (1872): there are two elements in the first period and eight elements in the second period of the periodic table	There are two electrons in the first energy level and eight in the next level
Kirchhoff, Bunsen (1859), Johann Balmer (1885): emission and absorption of line spectra, and not continuous spectra, exist for gaseous elements	Since the energy of light absorbed and emitted is quantized, the energy of electrons in atoms is quantized

Timeline
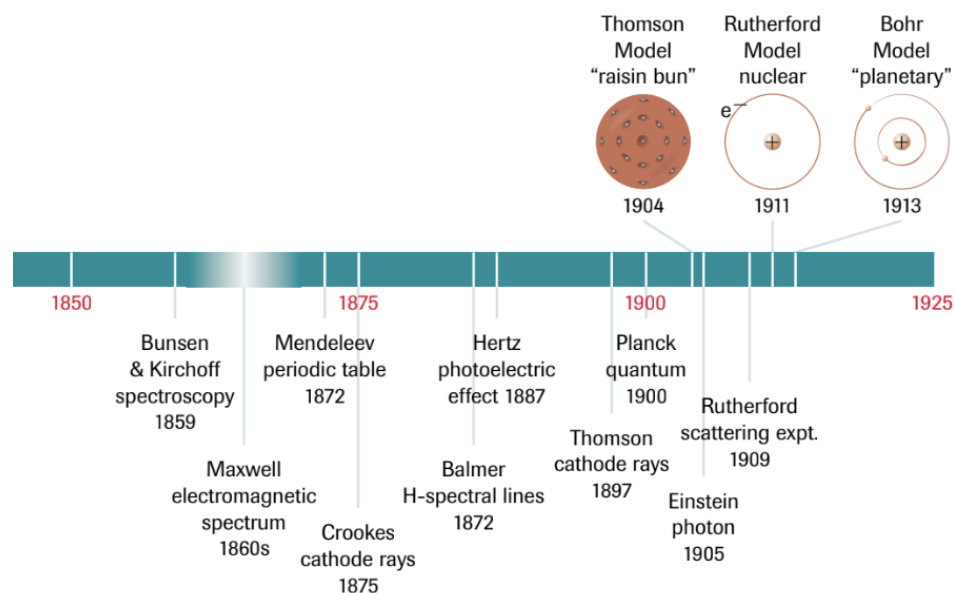
Figure 13 is the timeline up to the Bohr model.

Figure 13: In a little over a hundred years, the idea of an atom has changed from the original indivisible sphere of Dalton to a particle with several components and an internal organization

Problems

1. What was the main achievement of the Rutherford model? What was the main problem with this model?

2. State Bohr's solution to the problem with the Rutherford atomic model.

3. When creating his new atomic theory, Bohr used one important new idea (theory) and primarily one important experimental area of study. Identify each of these.

4. (a) What is the empirical distinction between emission and absorption spectra?

   (b) In general terms, how did Niels Bohr explain each one of these spectra?

5. Draw an energy-level diagram for each of the following:

   (a) Fluorine atom

   (b) Neon atom

   (c) Sodium atom

6. What do the atomic, periodic, and group numbers contribute in energy-level diagrams?

7. State two or more reasons why Bohr's theory was considered a success.

8. Identify one significant problem with the Bohr theory.

9. In 1885, Balmer created an equation that described the visible light spectrum for hydrogen. This evolved to become the Rydberg equation presented below. Bohr used Balmer's work as an insight into the structure of the hydrogen atom.

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Where $R_H = 1.10 \times 10^7 \text{ m}^{-1}$. [6]

   (a) The visible portion of the hydrogen spectrum is called the Balmer series. The visible light photons emitted from the hydrogen atom all involve electron transitions from higher (excited) energy levels down to the $n_f = 2$ level. Calculate the wavelength of the light emitted from the quantum leap of an electron from $n_i = 4$ to $n_f = 2$.

   (b) Use the wave equation, $\lambda = \frac{c}{\nu}$, to calculate the frequency of the light emitted.

   (c) Use the Planck equation, $E = h\nu$, to calculate the energy of the electron transition and, therefore, the difference in energy between the $n_i = 4$ and the $n_f = 2$ levels

   (d) Repeat (a) through (c) for the $n_i = 3$ to the $n_f = 2$ electron transition.

   (e) Draw an energy-level diagram for hydrogen showing the $n_i = 3$ and 4 to the $n_f = 2$ transitions. Add the energy difference values to the diagram. From these values, what is the energy difference between $n = 4$ and $n = 3$?

10. Using your knowledge of the history of atomic theories from Dalton to Bohr, state what you think will happen next in the historical story.

---

[6]The alternative Ryderberg equation, $\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$, where $R_H = 2.18 \times 10^{-18}$ J, is derived by using the equation $\Delta E = \frac{hc}{\lambda}$

Solutions

1. The main achievement of the Rutherford model was the discovery of the nucleus. This model proposed that electrons orbited the nucleus in a solar system like fashion. The problem with this model is that the electrons emit electromagnetic radiation when orbiting, meaning that they would eventually collapse into the nucleus

2. Bohr's solution was that these electrons orbited in stationary states around the nucleus. Each electron orbited the nucleus in a fixed energy level and maintained a constant energy when orbiting. This way, the electrons do not lose energy and collapse into the nucleus.

3. (a) Emission spectra consist of light emitted by a sample of substance. Absorptions spectra consist of missing frequencies (colours) of light after the source light passes through a sample of substance.

   (b) Bohr explained each one of these spectra as energy being emitted by electrons transitioning from a higher energy state to a lower energy state, emitting energy in the form of protons

4. (a) Fluorine has 9 protons and electrons

   $$7\,e^-$$
   $$2\,e^-$$
   $$9\,p^+$$

   F   fluorine

   (b) Neon has 10 protons and electrons

   $$8\,e^-$$
   $$2\,e^-$$
   $$10\,p^+$$

   Ne   neon

   (c) Sodium has 11 protons and electrons

   $$1\,e^-$$
   $$8\,e^-$$
   $$2\,e^-$$
   $$11\,p^+$$

   Na   sodium

5. The atomic number is the number of protons and electrons the atom has, the period is the number of energy levels the atom has, and the group number is the number of valence electrons the atom has.

6. Bohr's theory explained the known emission spectral lines for hydrogen, the periodic trend in Mendeleev's periodic table, helped predict UV and infrared spectra for hydrogen, and solved the problem with the Rutherford model.

7. The Bohr theory only worked well for the spectrum of hydrogen atoms, or ions with only one electron. Calculations for spectrum lines with this theory didn't match with empircal evidence. The disrepancy became worse as the number of electrons increased.

8. (a) Using the equation

$$\frac{1}{\lambda} = (1.10 \times 10^7 \, \text{m}^{-1}) \left(\frac{1}{2^4} - \frac{1}{4^2} \right)$$
$$\frac{1}{\lambda} = (1.10 \times 10^7 \, \text{m}^{-1}) \left(\frac{3}{16} \right)$$
$$\lambda = \frac{16}{3.30 \times 10^7 \, \text{m}^{-1}}$$
$$= 4.85 \times 10^{-7} \, \text{m}$$

(b) Substituting into the equation

$$\nu = \frac{c}{\lambda}$$
$$= \frac{3.0 \times 10^8 \, \text{m s}^{-1}}{4.85 \times 10^{-7} \, \text{m}}$$
$$= 6.19 \times 10^{14} \, \text{Hz}$$

(c) Substituting into the equation

$$E = (6.63 \times 10^{-34} \, \text{J s})(6.19 \times 10^{14} \, \text{Hz})$$
$$= 4.10 \times 10^{-19} \, \text{J}$$

However, because the electron is moving from the $n_i = 4$ to $n_f = 2$ level, energy is released, meaning that the sign of our final answer should be negative. Thus

$$E = -4.10 \times 10^{-19} \, \text{J}$$

(d) We will skip the steps and use the alternative Rydberg equation

$$\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$
$$= -(2.18 \times 10^{-18} \, \text{J}) \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$
$$= -3.03 \times 10^{-19} \, \text{J}$$

(e) This is the same diagram seen in Figure 12. The difference in energy is $4.10 \times 10^{-19} \, \text{J} - 3.03 \times 10^{-19} \, \text{J} = 1.07 \times 10^{-19} \, \text{J}$.

9. The most likely assumption is that theories would advance to try and describe arrangements and energies for atoms more complex than hydrogen.

QUANTUM NUMBERS

There are 4 distinct numbers, coupled together as coordinates, to represent the location of an electron in an atom. This is called **quantum numbers**

1. Principle quantum number

2. Secondary quantum number

3. Magnetic quantum number

4. Spin quantum number

Principle Quantum Number

This represents the energy level in the atom. Denoted by n, it has the range

$$\text{theoretical: } [1, \infty)$$
$$\text{practical: } [1, 7] \quad \text{7 periods on the periodic table}$$

The theoretical number of total electrons given a quantum number is $2n^2$. This is the only quantum number that matters, because the other numbers are considered "labels". This quantum number was **invented by Bohr**, and is still used to designate the main energy levels of electrons. Bohr's theory used only one quantum number, which is why it worked so well for hydrogen but not for other atoms. See Figure 14.
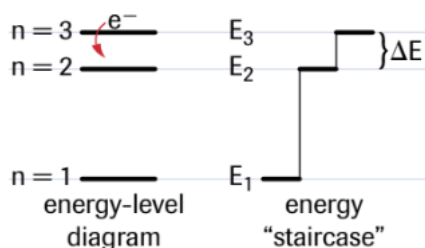

Figure 14: Bohr's principle energy levels, designated by n, are like unequal steps on an energy staircase. If an electron "falls" from a higher energy level, such as $n = 3$, to a lower energy level, such as $n = 2$, the difference between the steps is released as a photon of light.

Secondary Quantum Number

This represents the shape of the orbital. Denoted by ℓ, it has the range

$$\text{theoretical: } [0, n-1]$$
$$\text{practical: } [0, 4]$$
$$\text{notation } (s, p, d, f)$$

- **Arnold Sommerfeld** expanded on Bohr's theory when he realized many of the lines Bohr observed were actually **multiple lines** very tightly together.
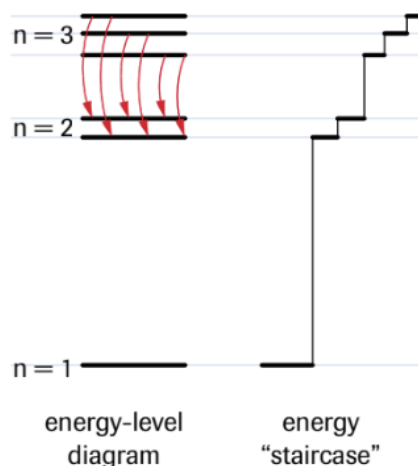
Figure 15: Sommerfield's model adds more sublevels to all of the Bohr main levels. Compare with Figure 14 to see the difference.

- Sommerfield decided to split energy levels into **sub-energy** levels, having only slightly different energies. This is how they derived the secondary quantum number. See Figure 15.

Sample: What is the similarity in the type of observations used by Bohr and Sommerfield?
Answer: The similarity is that there are main energy levels for the electrons. Both models use the principle quantum number to describe the main energy sublevel.

Sample: What is the difference in the electron orbits proposed by Bohr and those of Sommerfield?
Answer: Bohr proposed that there was only one energy level, while Sommerfield proposed that there were actually many sublevels within each energy level. Sommerfield used the observation that the bright-lines in the emission spectrum of hydrogen were actually composed of many more lines to create his hypothesis.

Magnetic Quantum Number

This represents the orientation of the orbital. Denoted by m_ℓ, it has the range

$$m_\ell \in [-\ell, \, \ell]$$

- If a gas discharge tube is placed near a strong magnet, some single lines split into new lines. This is called the **Zeeman effect**, see Figure 16.

- Sommerfield and Debye's explanation was that orbits could exist at various angles. The idea is that if the orbits are oriented in space in different planes, the energies of the orbits are different when an atom is near a strong magnet, hence the lines splitting.
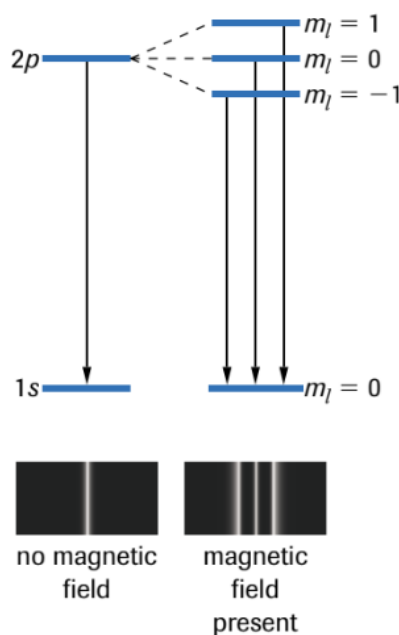
Figure 16: The triplets in spectra produced in a magnetic field are explained by creating a third quantum number, corresponding to the angled orbits in an orbit type

Spin Quantum Number

This represents the spin of the electron in the orbital. Denoted by m_s, it has the range

$$m_s \in [-\frac{1}{2}, +\frac{1}{2}]$$

Where $+\frac{1}{2}$ corresponds to "spin up" and $-\frac{1}{2}$ corresponds to "spin down".

- This was introduced because when they experimented with hydrogen, some electrons repelled, and some attracted. Therefore, they concluded that the way the electron must be spinning around the nucleus is different.

- Some elements and compounds are **paramagnetic**, like $O_{2(\ell)}$.

- The spins are equal in magnitude but opposite in value, hence $\pm\frac{1}{2}$

Problems

1. What is the main kind of evidence used to develop the description of electrons in terms of quantum numbers?

2. Briefly, what is the theoretical description of electrons in atoms provided by each of the four quantum numbers?

3. Theoretical knowledge in science develops from an need to explain what is observed. What is the fourth quantum number and why is it necessary?

4. If every electron must have a unique set of four quantum numbers, how many different electrons can there be for each principle number from $n = 1$ to $n = 3$?

Solutions

1. Line and continuous spectra is the main kind of evidence used to develop the description of electrons in terms of quantum numbers. These spectra are created through the practice of spectroscopy.

2. n represents the energy level, ℓ represents the shape of the orbital in the energy level, m_ℓ represents the orientation of the orbitals, and m_s represents the spin of the electron in the orbital.

3. The fourth quantum number helps explain the paramagnetism traits of some elements and compounds. Because the spins are equal in magnitude but opposite in charge, $m_s = \pm\frac{1}{2}$.

4. There are a maximum of $2n^2$ electrons in a given energy level

$$
\begin{aligned}
n = 1 &: \quad 2 \\
n = 2 &: \quad 8 \\
n = 3 &: \quad 18
\end{aligned}
$$

ATOMIC STRUCTURE AND THE PERIODIC TABLE

The main thing to understand from the previous section is that there are four quantized values that describe an electron in an atom. Quantized means that the values are restricted to certain discrete values.

Table 0.7: Values and letters for the secondary quantum number

Value of ℓ	0	1	2	3
Letter designation	s	p	d	f
Name designation	**s**harp	**p**rincipal	**d**iffuse	**f**undamental

Electron Orbitals

- Bohr's theory was based on the idea of an electron travelling in a orbit path. A more modern view is that of an electron **orbital** [7]

- As we move from focusing on the energy of electrons to focusing on their position, the terminology will change from using principal energy level to **shell** [8], and from energy sublevel to **subshell**. [9]

- Chemists usually use the number for the main energy level and a letter designation for the energy sublevel. For example, a $1s$ orbital, a $2p$ orbital, a $3d$ orbital, or a $4f$ orbital in that energy sublevel can be specified.

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[7]**Orbital:** a region of space around the nucleus where an electron is likely to be found.
[8]**Shell:** main energy level; the shell number is given by the principal quantum number n
[9]**Subshell:** orbiatls of different shapes and energies, given by the secondary quantum number ℓ

Table 0.8: Orbits and orbitals

Orbits	Orbitals
2-D path	3-D region in space
Fixed distance from nucleus	Variable distance from nucleus
Circular or elliptical path	No path; varied shape of region
$2n^2$ electrons per orbit	2 electrons per orbital

Creating Energy-Level Diagrams

- The previous energy level diagrams only included the principal quantum number. Now, it also use the secondary quantum number

- In Figure 17, as the atoms become larger and the main energy levels become closer together, some sublevels start to overlap in energy

- The energy of an electron increases with an increasing value of the principal quantum number. For a given value of n, the sublevels increase in energy, in order s < p < d < f
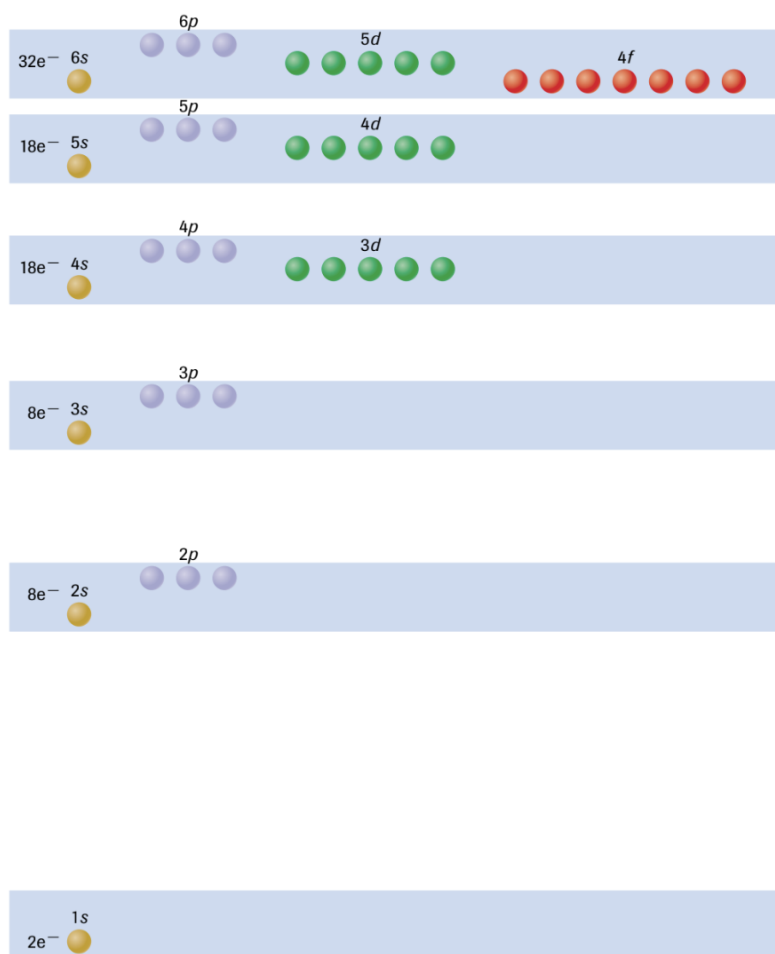

Figure 17: Diagram of relative energies of electrons in various orbitals. Each orbital (circle) can potentially contain up to two electrons.

- Show an electron in an orbital by placing an up arrow or a down arrow, or both to represent an electron pair. According to the **Pauli exclusion principle** [10] , the two electrons cannot point in the same direction

- An energy sublevel must be filled before moving onto the next higher energy sublevel, according to the **Aufbau principle** [11]. See Figure 19.

- Spread out the electrons as much as possible horizontally before doubling up any pair of electrons, according to **Hund's rule** [12]

- In Figure 18, for (a), according to the Aufbau principle, the 1s orbital must be filled up first before moving onto the 2s orbital. For (b) and (c), according to Hund's rule, all of the orbitals must have one electron

- As you move across the periodic table, each atom has one more electron than the previous. Because the electrons are added sequentially to the lowest energy orbital available (Aufbau principle), the elements can be classified by the sublevel currently being filled. See Figure 20
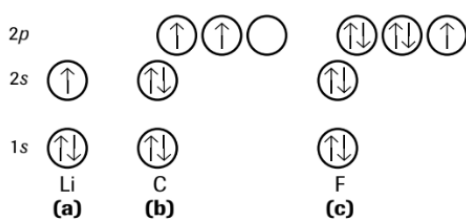

Figure 18: Energy-level diagrams for lithium, carbon, and fluorine atoms

Figure 19: Start and the top and move in the direction of the arrows for the orbiatls

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[10]**Pauli exclusion principle:** no two electrons in an atom can have the same four quantum numbers.
[11]**Aufbau principle:** "aufbau" is German for building up; each electron is added to the lowest energy orbital available in an atom or ion.
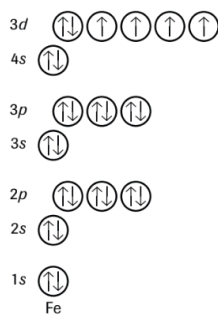[12]**Hund's rule:** one electron occupies each of several orbitals at the same energy before a second electron can occupy the same orbital.

Figure 20: Classification of elements by the sublevels that are being filled

Sample: Draw the energy-level diagram for an iron atom.
Answer:

Creating Energy-Level Diagrams for Anions and Cations

- For anions, simply add the corresponding number of electrons to the configuration

- For cations, remove the number of electrons from the orbitals with the **highest** principal quantum number, because they represent the valence shell

Sample: Draw the energy-level diagram for the sulfide ion.
Answer: Sulfur is an anion, so we add the corresponding 2 electrons to the energy-level diagram.

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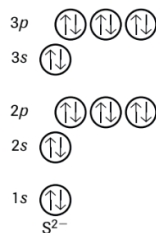
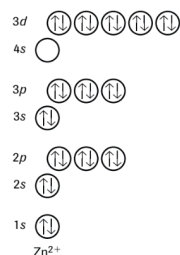**Sample:** Draw the energy-level diagram for the zinc ion.

Answer: Zinc is a cation, so we remove the corresponding 2 electrons from the orbitals with the highest principal quantum number, in this case being 4s.

Sample: State the names of the three main rules/principles used to construct an energy-level diagram. Briefly describe each of these in your own words.

Answer: The three rules/princples are

(a) Pauli exclusion principle: no two electrons can have the same four quantum numbers

(b) Aufbau principle: each electron is added from the lowest energy orbital available

(c) Hund's rule: all of the orbitals must have a single electron before doubling up

Sample: How can the periodic table be used to help complete energy-level diagarams?

Answer: As you move across the periodic table, each atom has one more electron than the previous. Because the electrons are added sequentially to the lowest energy level (Aufbau principle), the atom can be classified by the current sublevel being filled.

Sample: Complete the electron energy-level diagrams for

(a) phosphorus atom

(b) potassium atom

(c) manganese atom

(d) nitride ion

(e) bromide ion

(f) cadmium ion

Answer: Watch out for the word ion.

Sample:

(a) Complete the electron energy-level diagrams for a potassium ion and a chloride ion

(b) Which noble gas atom has the same electron energy-level diagram as these ions?

Answer:

(a) The potassium ion is a cation and the chloride ion is an anion

(b) This is asking the same question as "which element is isoelectronic to the potassium cation and which element is isoelectronic to the chloride anion?". Argon is isoelectronic to both the potassium cation and the chloride anion

Electron Configurations

An electron configuration is a listing of the number and kinds of electrons in order of increasing energy. You can also shorthand it by writing the noble gas from the period above it first in square followed by the rest of the configuration in the period.

Sample: Write the electron configuration for the chlorine atom.
Answer: Cl: $1\,s^2\,2\,s^2\,3\,s^2\,3\,p^5$, or $[\mathrm{Ne}]\,3\,s^2\,3\,p^5$

Sample: Identify the atoms that have the following electron configurations:

(a) $1\,s^2\,2\,s^2\,2\,p^6\,3\,s^2\,3\,p^6\,4\,s^2\,3\,d^{10}\,4\,p^5$

(b) $1\,s^2\,2\,s^2\,2\,p^6\,3\,s^2\,3\,p^6\,4\,s^2\,3\,d^{10}\,4\,p^5\,5\,s^2\,4\,d^5$

(c) $1\,s^2\,2\,s^2$

(d) $1\,s^2\,2\,s^2\,2\,p^5$

(e) $1\,s^2\,2\,s^2\,2\,p^6\,3\,s^1$

(f) $1\,s^2\,2\,s^2\,2\,p^6\,3\,s^2\,3\,p^4$

Answer:

(a) Br, bromine

(b) Tc, technetium

(c) Be, beryllium

(d) F, fluorine

(e) Na, sodium
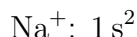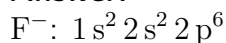
(f) S, sulfur

Sample: Write the shorthand electron electron configuration for the lead atom and the lead(II) ion.
Answer:
Pb: $[\mathrm{Xe}]\,6\,s^2\,4\,f^{14}\,5\,d^{10}\,6\,p^2$
Pb^{2+}: $[\mathrm{Xe}]\,6\,s^2\,5\,d^{10}$

Sample: Write the full electron configurations for a fluoride ion and a sodium ion.
Answer:
F^-: $1\,s^2\,2\,s^2\,2\,p^6$
Na^+: $1\,s^2$

Sample: A fluoride ion and neon atom are theoretically described as isoelectronic. State the meaning of this term.
Answer: Isoelectronic means two atoms that have the same number of electrons and theoretically the same electron configuration.

Explaining the Periodic Table

- The four quantum numbers were developed using experimental studies of atomic spectra and the experimentally determined arrangement of elements in the periodic table. It is no coincidence that the maximum number of electrons in the s, p, d, and f orbitals correspond exactly to the number of columns of elements in the s, p, d, and f blocks in the periodic

- **Representative elements** [13] have their properties much more precisely defined because they can be explained with having s and p orbitals

- **Transition elements** [14] can now be explained as having d orbitals, hence why they can store so many electrons in some sublevels

- The lathanides and actinides can also be explained as a series of elements filling an f energy level. The f block of elements is 14 elements wide, as expected by filling 7 orbitals with 14 electrons

Table 0.9: Electron subshells and the periodic table

Period	# of elements	groups: 1-2 orbitals: s	13-18 p	3-12 d	- f
Period 1	2	2			
Period 2	8	2	6		
Period 3	18	2	6	10	
Period 4-5	18	2	6	10	
Period 6-7	18	2	6	10	14

Explaining Ion Charges

Many of the transition metals are multivalent, and this theory helps explain it. For instance, the electron configuration for a zinc atom:

$$Zn:\ [Ar]\,4\,s^2\,3\,d^{10}$$

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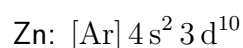
[13]**Representative elements:** the metals and nonmetals in groups 1-2 and 13-18. In other words, the s and p blocks.

[14]**Transition elements:** the metals in groups 3-12; elements filling d orbitals with electrons.
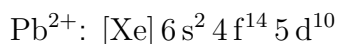
If another atom removes 2 of the 4s electrons, this would leave zinc with filled 3d orbitals, which is much more stable:

$$\text{Zn}^{2+}: \ [\text{Ar}] \, 3 \, \text{d}^{10}$$

Another example is the formation of either a 2+ or 4+ ion in lead. The electron configuration for lead is

$$\text{Pb}: \ [\text{Xe}] \, 6 \, \text{s}^2 \, 4 \, \text{f}^{14} \, 5 \, \text{d}^{10} \, 6 \, \text{p}^2$$
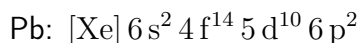
Which shows filled 4f, 5d, and 6s orbitals with a partially filled 6p orbital. Lead could either lose 2 electrons from the 6p orbitals or 4 electrons from both the 6s and 6p orbitals:

$$\text{Pb}^{2+}: \ [\text{Xe}] \, 6 \, \text{s}^2 \, 4 \, \text{f}^{14} \, 5 \, \text{d}^{10}$$

$$\text{Pb}^{4+}: \ [\text{Xe}] \, 4 \, \text{f}^{14} \, 5 \, \text{d}^{10}$$

Explaining Magnetism

- Paramagnetism is explained for elements that have unpaired electrons

- Ferromagnetism occurs in elements that can form magnet domains

- Ferromagnetism is based on the properties of a collection of atoms, rather than just one atom

Problems

1. Determine the maximum number of electrons with principal quantum numbers 1, 2, 3, 4

2. State the Aufbau principle and describe two methods that can be used to employ this method

3. If 4 electrons are to be placed into a p subshell, describe the procedure, including the appropriate rules

4. The last electron represented in an electron configuration is related to the position of the element in the periodic table. For each of the following sections of the periodic table, indicate the sublevel (s, p, d, f) of the last electron:

   (a) Groups 1 and 2
   (b) Groups 3-12 (transition metals)
   (c) Groups 13-18
   (d) Lanthanides and actinides

5. (a) When the halogens form ionic compounds, what is the ion charge of the halide ions?

   (b) Explain this similarity, using electron configurations

6. The sodium ion and the neon atom are isoelectronic

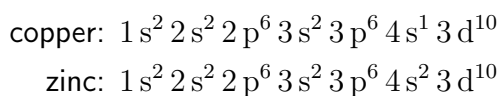   (a) Write the electron configurations for the sodium ion and the neon atom

(b) Describe and explain the similarities and differences in properties of these two chemical entities

7. Use electron configurations to explain the common ion charges for antimony, i.e. Sb^{3+} and Sb^{5+}

8. Evidence indicates that copper is paramagnetic, but zinc is not. Explain the evidence

Solutions

1. Using $2n^2$, the maximum number of electrons for principal numbers 1-4 is $2, 8, 18, 32$

2. The Aufbau principle states that sublevels with the lowest energy must be filled first before the sublevels with higher energy levels

3. According to Hund's rule, there must be one electron in each orbital before doubling them up. Therefore, there will be one orbital with 2 electrons and two with 1 electron

4. (a) Sublevel s

    (b) Sublevel d

    (c) Sublevel p

    (d) Sublevel f

5. (a) The ion charge is -1

    (b) This is because they have p-orbitals with 7 electrons, meaning that they are 1 short of a full sublevel. This is why they gain an electron, hence the -1 charge

6. (a)
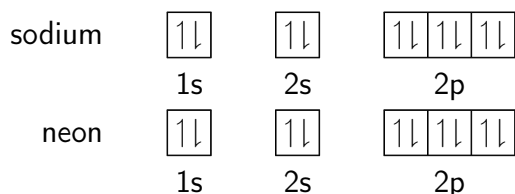
    (b) They have the same noble electron configuration, but sodium has more protons than neon

7. The electron configuration for the neutral Sb is $[\text{Kr}]\, 5\,\text{s}^2\, 4\,\text{d}^{10}\, 5\,\text{p}^3$. The 3+ charge comes from removing 3 electrons from the $5\,\text{p}^3$ sublevel and the 5+ charge comes from removing the 5 electrons from both the $5\,\text{s}^2$ and $5\,\text{p}^3$ sublevels

8. The electron configuration for neutral copper and zinc are

$$\text{copper: } 1\,\text{s}^2\, 2\,\text{s}^2\, 2\,\text{p}^6\, 3\,\text{s}^2\, 3\,\text{p}^6\, 4\,\text{s}^1\, 3\,\text{d}^{10}$$
$$\text{zinc: } 1\,\text{s}^2\, 2\,\text{s}^2\, 2\,\text{p}^6\, 3\,\text{s}^2\, 3\,\text{p}^6\, 4\,\text{s}^2\, 3\,\text{d}^{10}$$

The reason that zinc isn't paramagnetic is because copper promoted one of its electrons into the 3d orbitals, leaving an unpaired electron in the 4s orbital, while zinc doesn't have any unpaired electrons.

WAVE MECHANICS AND ORBITALS

- Broglie hypothesized that if a wave can behave like a particle, then a particle should also be able to behave like a wave. His hypothesis was that electrons behaved like a wave

- According to Schrodinger, the electron can only have certain quantized energies because of the requirement for only whole numbers of wavelengths for the electron wave

Electron Orbitals

- Heisenberg realized that to measure any particle, we essentially had to "touch" it. The only way to do this is to shoot a photon at the electron and measure the photon. However, the process of hitting a subatomic particle with a photon means that the particle is no longer where it was and it has also changed it speed. This is **Heisenberg's uncertainty principle** [15]

- Since the position of an electron is described as a region of probability, scientists use the term **orbital** to describe the region in space where electrons may be found. See Figure 21
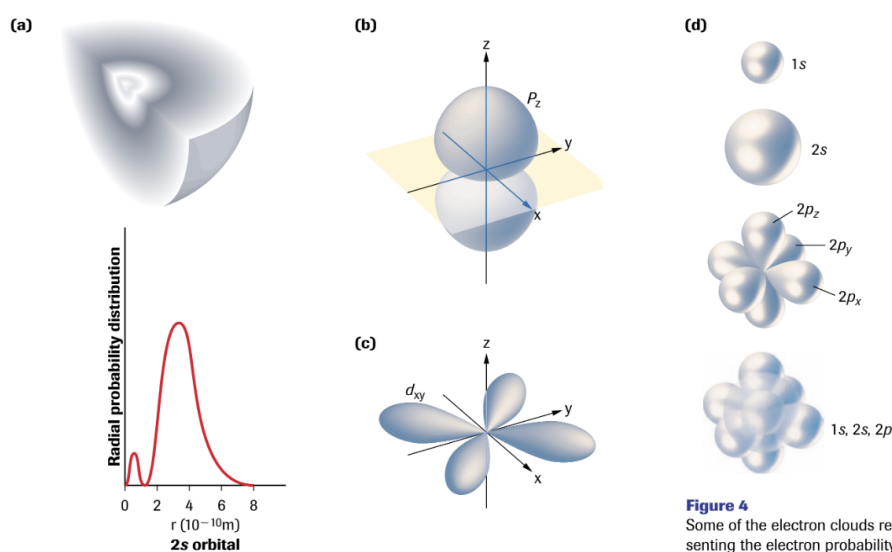

Figure 21: (a): In the cross-section, the darker theshading, the higher the **electron probability density**. (b): A $2p_z$ orbital. (c): A d_{xy} orbital. (d): A superposition of a 1s, 2s, and 2p orbitals.

Problems

1. Briefly state the main contribution of each of the following scientists to the development of quantum mechanics:

---

[15]**Heisenberg's uncertainty principle:** it is impossible to know simultaneously the position and velocity of an electron.

    (a) de Broglie

    (b) Schrodinger

    (c) Heisenberg

2. What is an electron orbital and how is it different from an orbit?

3. State two general characteristics of any orbital provided by the quantum mechanics atomic model

4. What information about an electron is not provided by the quantum mechanics atomic model?

5. Using diagrams and words, describe the shapes of the 1s, 2s, and three 2p orbitals

6. Theoretically, what is the maximum number of electrons in an atom that could have the following sets of quantum numbers

    (a) $n = 4$

    (b) $n = 5$, $m_\ell = +1$

    (c) $n = 5$, $m_s = +\frac{1}{2}$

    (d) $n = 3$, $\ell = 2$

    (e) $n = 2$, $\ell = 1$

    (f) $n = 0$, $\ell = 0$, $m_\ell = 0$

    (g) $n = 2$, $\ell = 1$, $m_\ell = -1$, $m_s = -\frac{1}{2}$

    (h) $n = 3$

    (i) $n = 2$, $\ell = 2$

    (j) $n = 1$, $\ell = 0$, $m_\ell = 0$

7. Using the Peridic Table, list elements (you may ignore the lathanides and actinides) that have ground state electron configurations that differ from those we would predict

8. The electron configurations are determined experimentally for atoms in the gas phase. Would you expect the electron configurations to be the same in the solid and liquid states as in the gas phase?

Solutions

1. (a) de Broglie theorized that if a wave can behave like a particle, then a particle should also behave like a wave. His hypothesis was that an electron behaved like a wave

    (b) Schrodinger theorized that electrons can only have certain quantized energies because of the requirement for only whole number wavelengths for the electron wave

    (c) Heisenberg created the uncertainty principle which states that we cannot simultaneously know both the position and velocity of an electron

2. Bohr's and Rutherford's model both included electrons orbiting around the nucleus. An orbital on the other hand, is a electron probability dense region where electrons have a probability of appearing.

3. The energy level that it is in and the shape.

4. Position and velocity, according to Heisenberg's uncertainty principle

5. The 1s orbital is a sphere that is not as dense in the center. The 2s orbital looks the same as the 1s orbital but larger. The three 2p orbitals look like dumbbells stacked perpendicular on top of each other

6. (a) $e = 2(4^2) = 32$

   (b) $e = \frac{1}{2}(2)(5^2) = 25$

   (c) $e = 2(5) = 10$

   (d) $e = 2(3) = 6$

   (e) $e = 2$

   (f) $e = 1$

   (g) $e = 2(3^2) = 18$

   (h) $e = 2(3) = 6$

   (i) $e = 2$

7. The transition metals because they have d orbitals and can hybridize orbitals

8. The electron configurations can differ in solid and liquid states compared to the gas states. This is because in solid and liquid states, the atoms are more closely packed, leading to interactions between neighbouring atoms

LEWIS THEORY OF BONDING

- **Ionic bonding**: the electrostatic attraction between positive and negative ions in the crystal lattice of a salt

- **Covalent bonding**: the sharing of valence electrons between atomic nuclei within a molecule or complex ion

- **Valence**: the number of unpaired electrons in the outermost energy level

- The Dalton atom theory starts before the Mendeleev periodic table with Franklind stating that each element has a fixed valence that determines its bonding capacity

- Friedrich Keule extended the idea of illustrating a bond as a dash between bonding atoms; i.e. what we now call structural diagram

- Jacbobus van't Hoff and Joseph Le Bel extended these structures to three dimensions

- Gilbert Lewis combined the knowledge of many chemical formulas, the concept of valence, the octet rule, and the electron-shell model of the atom to explain chemical bonding

- The electrons that do not participate in bonding but move between bonded molecules are said to be **delocalized electrons**

> **Important.** The key ideas of Lewis theory of bonding are:
>
> - Atoms and ions are stable if they have a noble gas-like electron structure; i.e. a stable octet of electrons
>
> - Electrons are most stable when they are paired
>
> - Atoms form chemical bonds to achieve a stable octet of electrons
>
> - A stable octet may be achieved by an exchange of electrons between metal and nonmetal atoms

Sample: Place the following chemistry concepts in the order that they were created by chemists:

(a) Lewis structures

(b) Empirical formnulas

(c) Dalton atom

(d) Kekule structures

(e) Schrodinger quantum mechanics

Answer: (b), (c), (d), (e), (f)

Sample: Place the following chemistry concepts in the order that they were created by chemists and briefly explain how one concept led to the next:

(a) Bohr atom

(b) Empirical formulas

(c) Dalton atom

(d) Lewis structures

Answer: The order is empirical formulas, Dalton atom, Bohr atom, and Lewis structures. Empirical formulas were developed to express the simplest whole-number ratio of elements in a compound. Dalton built on the concept of empirical formulas by suggesting that atoms of different elements combined in fixed ratios form compounds. Bohr's model built on Dalton's model. Lastly, Lewis structures built on Bohr's understanding of electron orbits–note that the whole idea of Lewis structures is built on the valence shell of the electron, which implies Bohr's atom

VALENCE BOND THEORY

- A half-filled orbital in one atom can overlap with another half-filled orbital of a second atom to form a new, bonding orbital

- When atoms bond, they arrange themselves in space to achieve the maximum overlap of their half-filled orbitals. Maximum overlap produces a bonding orbital of lowest energy

VSEPR THEORY

VSEPR Theory stands for Valence Shell Electron Pair Repulsion Theory; pairs of electrons in the valence shell of an atom stay as far apart as possible to minimize the repulsion of their negative charges. There are two forms of geometry:

1. Electron-pair geometry

2. Molecular geometry

The electron-pair geometry and molecular geometry are sometimes the same (CH_4 for example), but the majority of the time they are different (NH_3 for example)

> **Important.** In VSEPR bonding
>
> - Only the valence shell electrons of the central atoms are important for molecular shape
>
> - The molecular shape is determined by the positions of the electrons when they are a maximum distance apart to yield the lowest repulsion possible

VSEPR Notation

VSEPR notation is denoted as AXE, where

- A represents the number of central atoms (always just 1)

- X represents the number of atoms bonded to the central atom

- E represents the number of electron pairs on the central atom

INTERMOLECULAR FORCES

Intermolecular forces are forces of attraction that exist **BETWEEN** molecules.
Intramolecular forces are forces of attraction that exist **WITHIN** a molecule.

> **Important.** Bonds do NOT BREAK/BROKEN in changes of state. Instead, you should say: more energy is required to overcome the **intermolecular attraction** between the molecules. We are simply separating molecules.

Interionic Forces

Generally, the attractive force between a pair of oppositely charged ions is greater the larger the charge on the ions with a decrease in ionic size. For ionic compounds, the intramolecular forces are equivalent to the intermolecular forces, since they are both electrostatic forces.

CONTENTS: Structures and Properties of Matter

London Dispersion Forces

These forces involve the displacement of elcetrons in molecules. They result from the **random motion** of electrons and occur when the concentration of electrons is higher in one particular region than another. This results in what is called a **instantaneous dipole**. Once the electrons "realize" that there are too many in one particular area, they **disperse**.

- The instantaneous dipole from one atom can also affect the neighbouring molecules. For instance, if a molecule on the right had a partial negative charge on the left, then the molecule on the left will have a partial repulsion force on the right

- This effect creates an **induced dipole**, creating a force of attraction between the two atoms

- These induced dipoles of course have a chain-effect, where one induced-dipole creates another induced-dipole

- I.e. the random motion of electron creates induced dipoles. This is also why nonpolar substances have lower melting/boiling points, and can be liquid, soft solid, and gas.

> **Important.** A dipole is more easily induced as the number of electrons increases and in turn as molar mass increases. As atomic radius increases, so does induction. Because dispersion forces become stronger as molar mass increasees, melting/boiling point of covalent compounds also increases with molar mass. For instance, helium has a BP of 4 K and radon has a BP of 211 K.

Dipole-Dipole Interactions

In a polar substance, molecules tend to line up the "positive" end of one dipole with the "negative" end of neighbouring dipoles. This type of interaction requires a polar substance; therefore, it is often called a **permanent dipole**. This yields higher melting/boiling points.

> **Important.** When comparing substances of roughly the same molar mass, the dipole forces will produce significant differences in melting/boiling point. However, when comparing substances of widely different molar masses, the dispersion forces are usually more significant than dipole forces. That is, as molar mass increases, the london forces are stronger than the dipole forces.

Hydrogen Bonding

A form of dipole-dipole interaction, this is primarily only seen in atoms that have a highly electronegative atom, for instance N, O, or F. This way, the proton in the nucleus of the hydrogen is revealed and the bonding force becomes extremely evident. For water to have such a high boiling point, it is due to the hydrogen bonding, since oxygen is extremely electronegative.

STRUCTURES AND PROPERTIES OF MATTER

We can classify solids with the table below

Table 0.10: Classifying Solids

Clas of substance	Elements combined	Examples
ionic	metal + nonmetal	$NaCl_{(s)}$, $CaCO_{3(s)}$
metallic	metal(s)	$Cu_{(s)}$, $CuZn_{3(s)}$
molecular	nommetal(s)	$I_{2(s)}$, $H_2O_{(s)}$, $CO_{2(s)}$
covalent network	metalloids/carbon	$C_{(s)}$, $SiC_{(s)}$, $SiO_{2(s)}$

Ionic Crystals

The arrangement of ions within form a **crystal lattice structure**, see Figure 22

- Relatively hard but brittle

- Conducts electricity in liquid state

- Forms solutions in water because of dissociation

- High melting points

Ionic bonding is defined theoretically as the simultaneous attraction of an ion by surrounding ions of opposite charge.
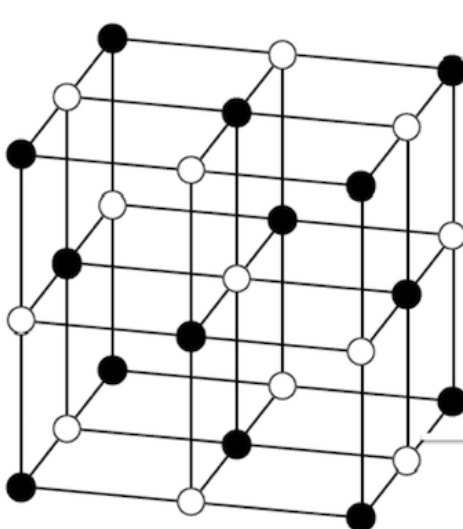

Figure 22: Crystal lattice structure

Metallic Crystals

All metals have a continuous and very compact crystalline structure. The properties of metals are the result of the bonding between fixed, positive nuclei and loosely held, mobile valence electrons. This attraction is not localized or directed between specific atoms, as occurs with ionic crystals. Instead, the electrons act like a negative "glue" around the positive nuclei.

- Low ionization energy of metal atoms to explain loosely held electrons

- Empty valence orbitals to explain electron mobility

- Electrostatic attraction of positive centers and the negatively charged electron "sea" to explain the strong, nondirectional bonding

Important. Metals are malleable, ductile, and flexible because the bonding between atoms in metals is nondirectional, since the bonding is due to the "electron sea".
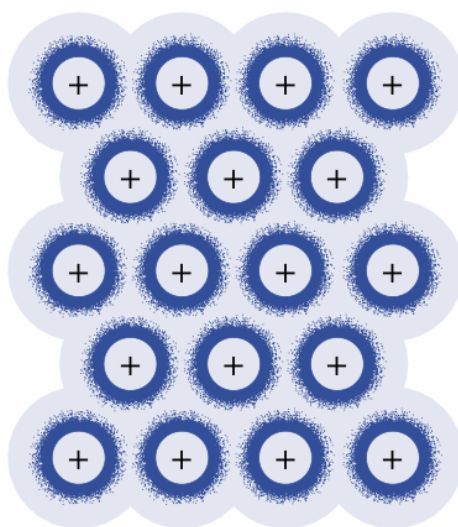

Figure 23: Each positive charge represents the nucleus and inner electrons of a metal atom, surrounded by a mobile "sea" of valence electrons.

Molecular Crystals

The intermolecular forces that keep molecular crystals together are the same: LDP, dipole-dipole, and hydrogen bonding.

- These forces are relatively weak compared to ionic and covalent bonds

- **Relatively low-degree hardness of the solids**

- **Low melting points** (compared to ionic compounds)

Covalent Network Solids

In most covalent solids, intermolecular forces are quite weak. This is why covalent substances of low molecular masses are generally gaseous at room temperature.

In a few substances, known as **covalent network solids**, covalent bonds are extended throughout the crystalline solid. In these cases, the **entire crystal is held together by covalent bonds**–the intermolecular and the intramolecular forces are the same. Common examples are **diamond** and **graphite**.

- Much **harder** and **higher melting/boiling point** that ionic and molecular crystals

Diamond

A pure carbon compound that has a bonding scheme in which each carbon atom is bonded to 4 other carbon atoms. This bonding results from sp^3 hybridization and gives a **tetrahedral shape**.

- Diamond is **very hard**

- Diamond is a **non-conductor of electricity**

- Diamond melts at $3500°$C

In this case, there are no other intermolecular forces, but instead the entire molecule is held together by covalent bonds–carbon only has a covalent bond to carbon. See Figure 24
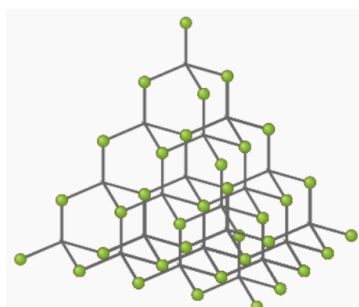

Figure 24: The structure of diamond

Graphite

A pure carbon compound that contains carbon atoms that are bonded together in a very different way compared to diamonds (see Figure 25. The type of bonding involves the orbital set $sp^2 + p$. Recall that the three sp^2 orbitals are directed in a plane at $120°$ angles. The p orbital is perpendicular to the plane, directed above and below.

Each carbon atom forms strong covalent bonds with three other carbon atoms in a hexagonal arrangement. The electrons in the p orbitals of the carbon atoms are **delocalized** [16]. In graphite, the p orbitals in each carbon are equally as close to each other. Therefore, the delocalized electrons are free to move around.

- Graphite **conducts electricity** because the electrons are moving between the plane perpendicular to the traditional p orbital bonding plane (see Figure 25)

- The bonding **within layers is very strong** (because they are a covalent network) but the bonding **between layers is very weak** (because they are held with delocalized electrons)

- The delocalized electrons moving between covalent planes is not considered to be intermolecular forces

- Acts as a lubricant because the covalent network planes slide over one another while maintaining the weak intermolecular attractions

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[16]**Delocalized:** electrons in a molecule, ion, or solid metal that are not associated with a single atom or a covalent bond; electrons that can move throughout atoms in a molecule.
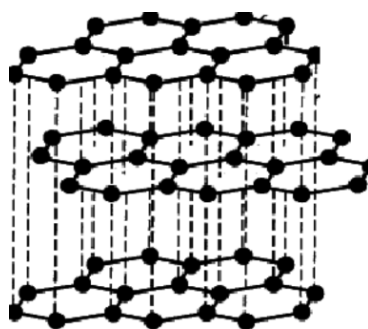
Figure 25: The structure of graphite