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Elementary Mathematics for Basic Atomic and Molecular Physics

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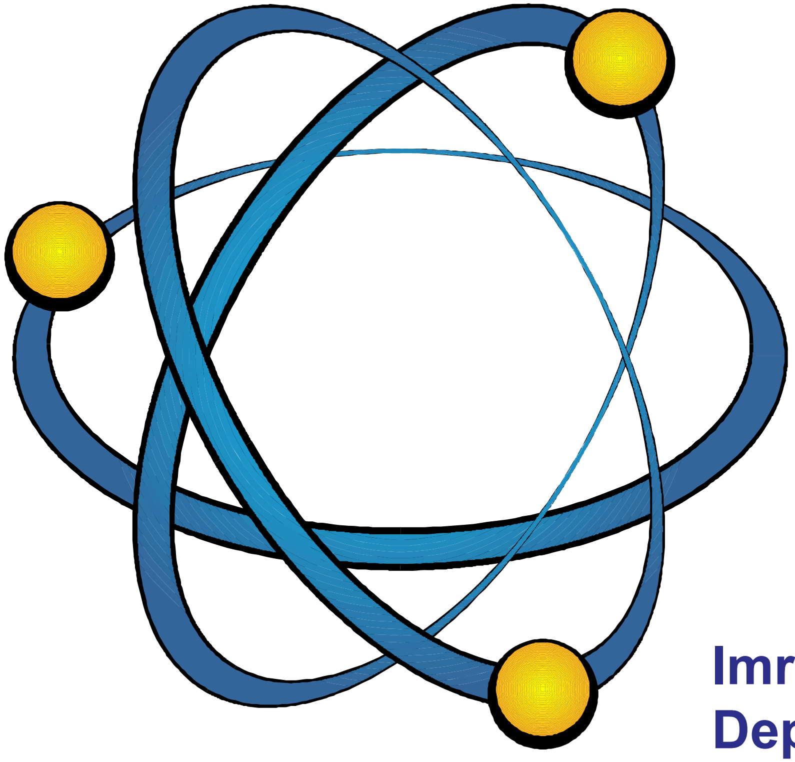

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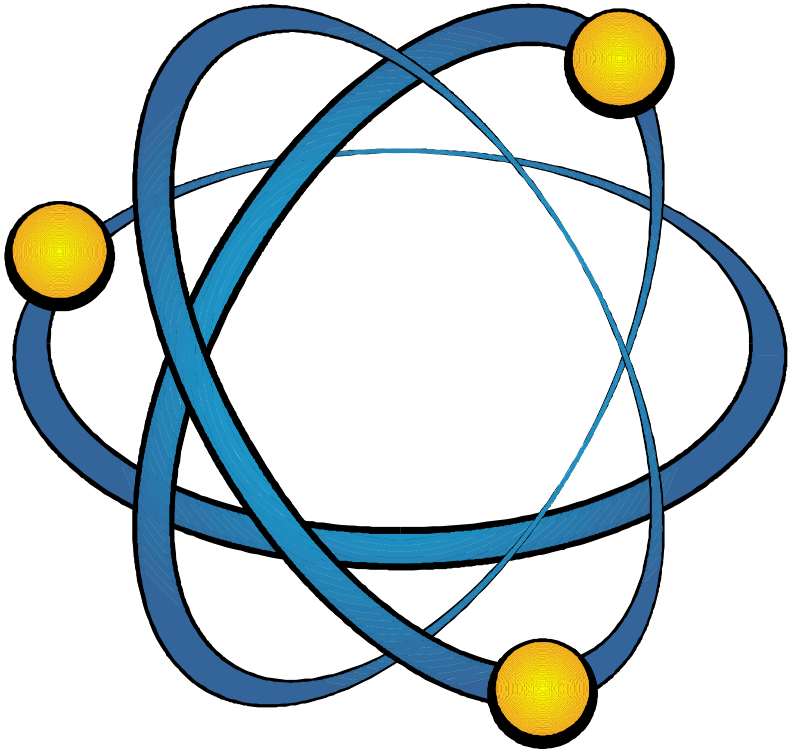
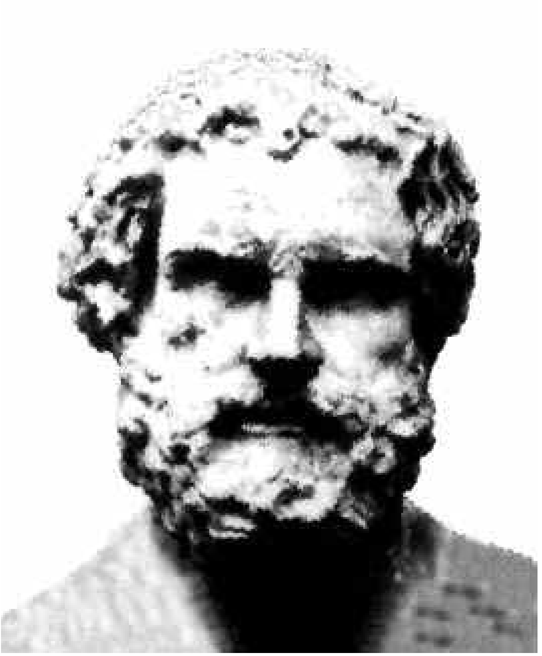
Models of the Atom



Historical Perspective

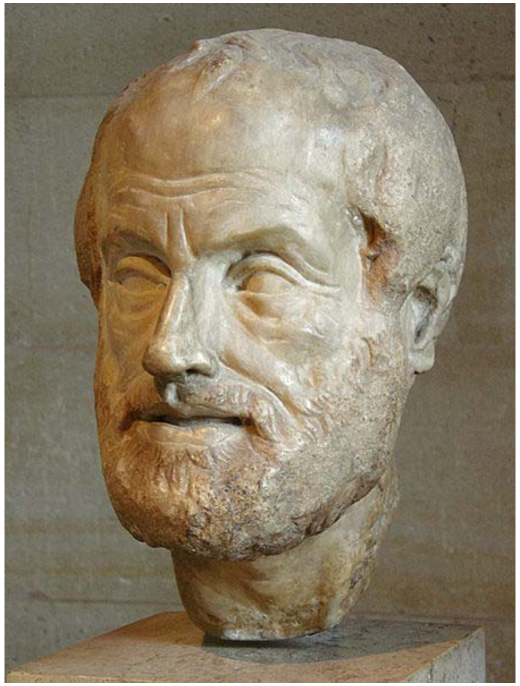
Early Greek Theories



Democritus (400 B.C.)

- That all matter is made up of various imperishable, indivisible elements which he called *atoma* (sg. *atomon*) or “indivisible units", from which we get the English word atom.
- This led to the idea of atoms in a void

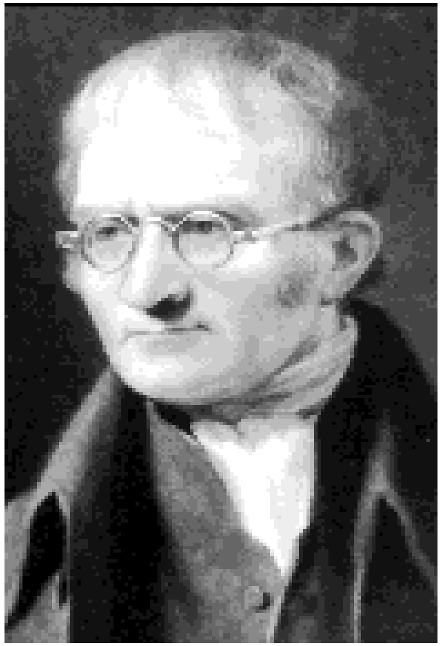
Early Greek Theories



Aristotle (350 B.C.)

- Aristotle modified an earlier theory that matter was made of four “elements”: earth, fire, water, air.
- Aristotle was wrong. However, his theory persisted for 2000 years.

John Dalton



1800- Dalton proposed a modern atomic model based on experimentation not on pure reason

- **Elements are made of tiny particles called atoms.**
- **All atoms of a given element are identical.**

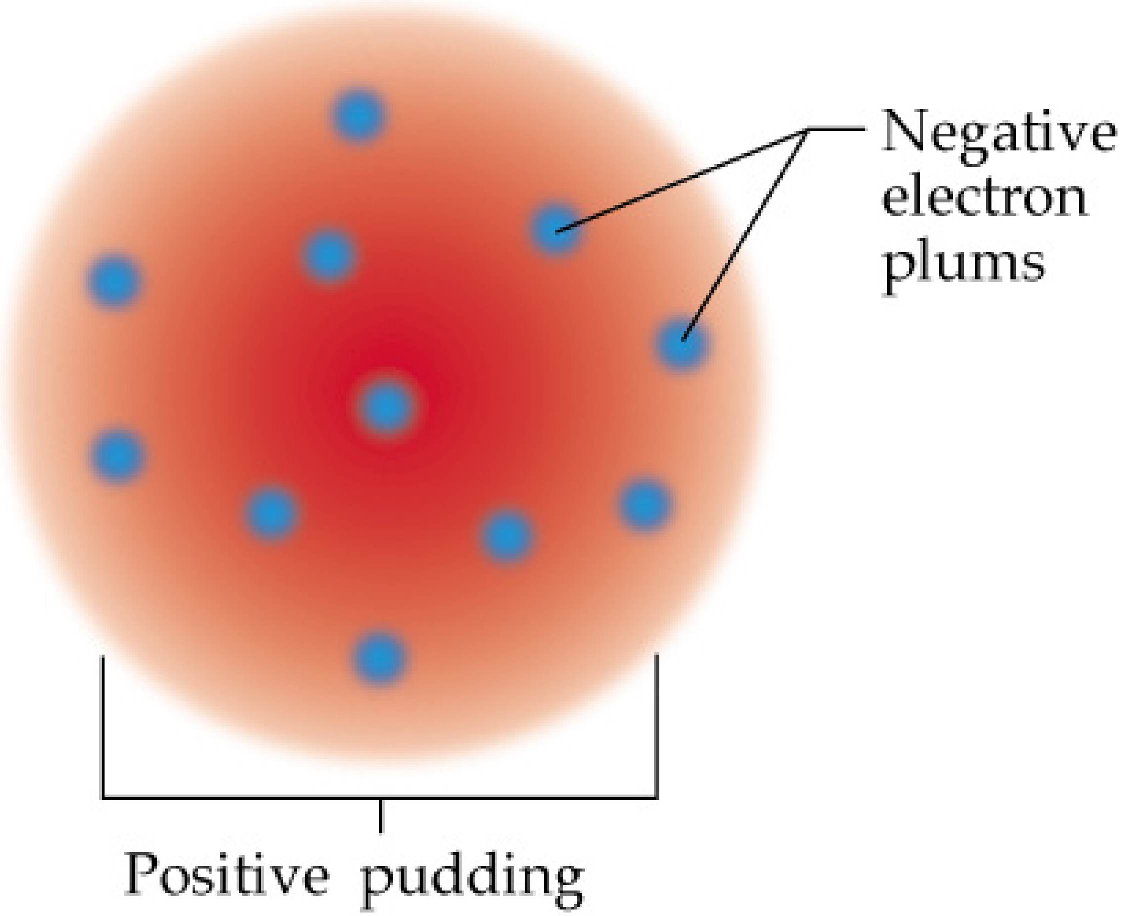
John Dalton

- The atoms of a given element are different from those of any other element; the atoms of different elements can be distinguished from one another by their respective relative weights.
- Atoms of one element can combine with atoms of other elements to form chemical compounds; a given compound always has the same relative numbers of types of atoms.
- Atoms cannot be created, divided into smaller particles, nor destroyed in the chemical process; a chemical reaction simply changes the way atoms are grouped together.

Sir Joseph John Thomson

- In 1897 J.J. Thomson determined that they were charged particles by using electric and magnetic fields
- Determined the mass to charge ratio (e/m) 1.76 x 10^{11} C/kg .
- No matter the metal used, you still get the same e/m. **Concluded that all atoms contained electrons**
- **Came up with the concept of “Plum pudding model”**

Thompson plum pudding model of the atom



400 BC

Democritus

Atomic concept

1800s

Dalton

Atomic model

(no subatomic particles)

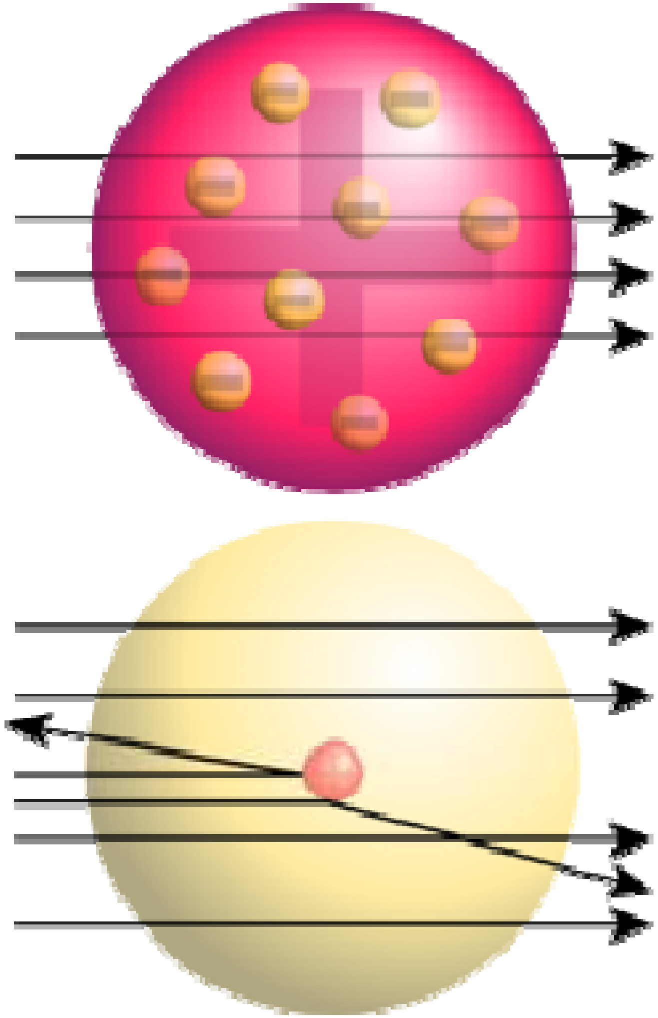
1897

Thomson discovers the electron

“Plum pudding model”

No nucleus or protons

1909 – Gold Foil Experiment

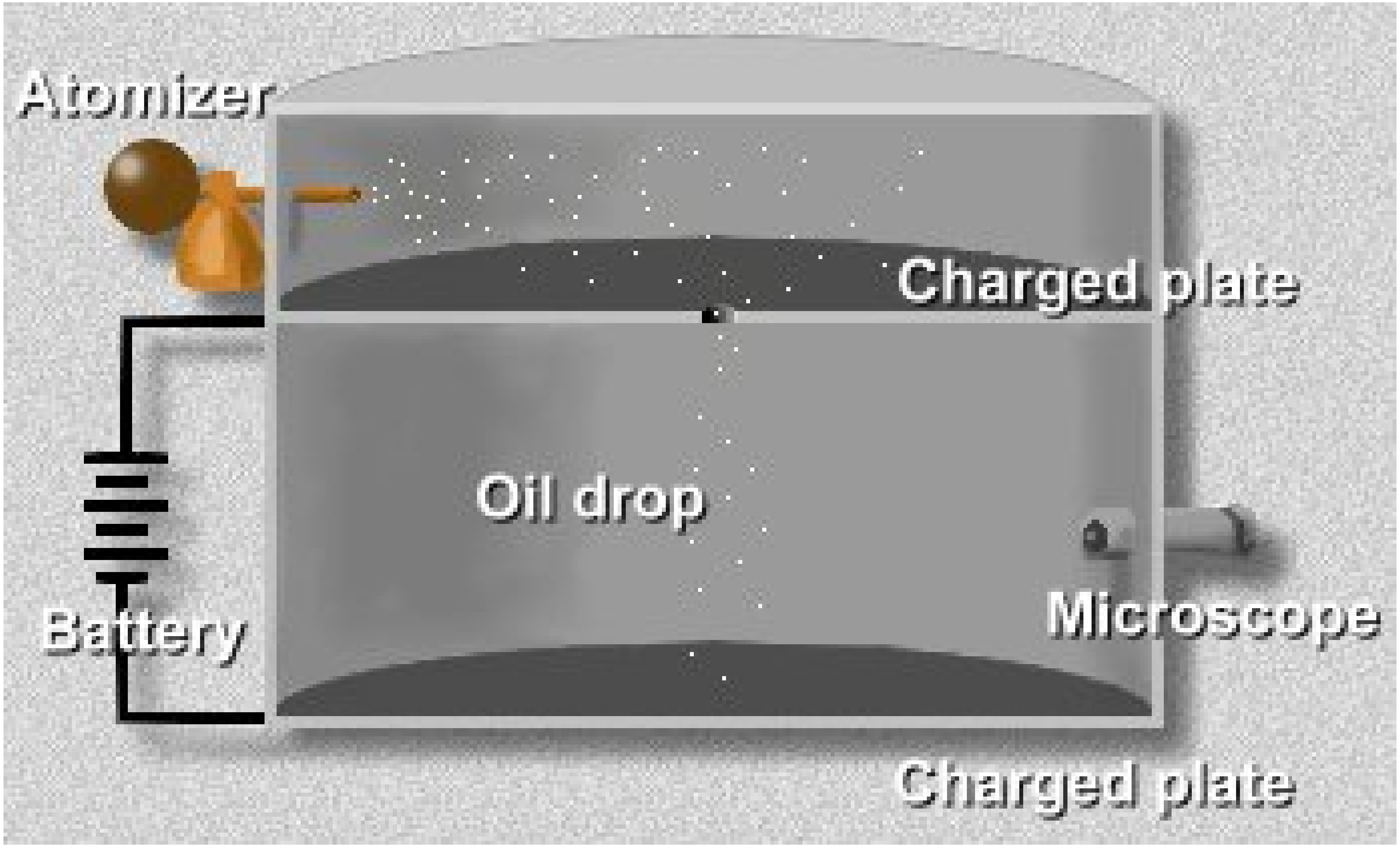


- Earnest Rutherford urged two of his graduate assistants – Geiger and Marsden – to create a way to probe the internal structure of the atom.
- Rutherford analyzed the data for two years before putting forth a new atomic model.

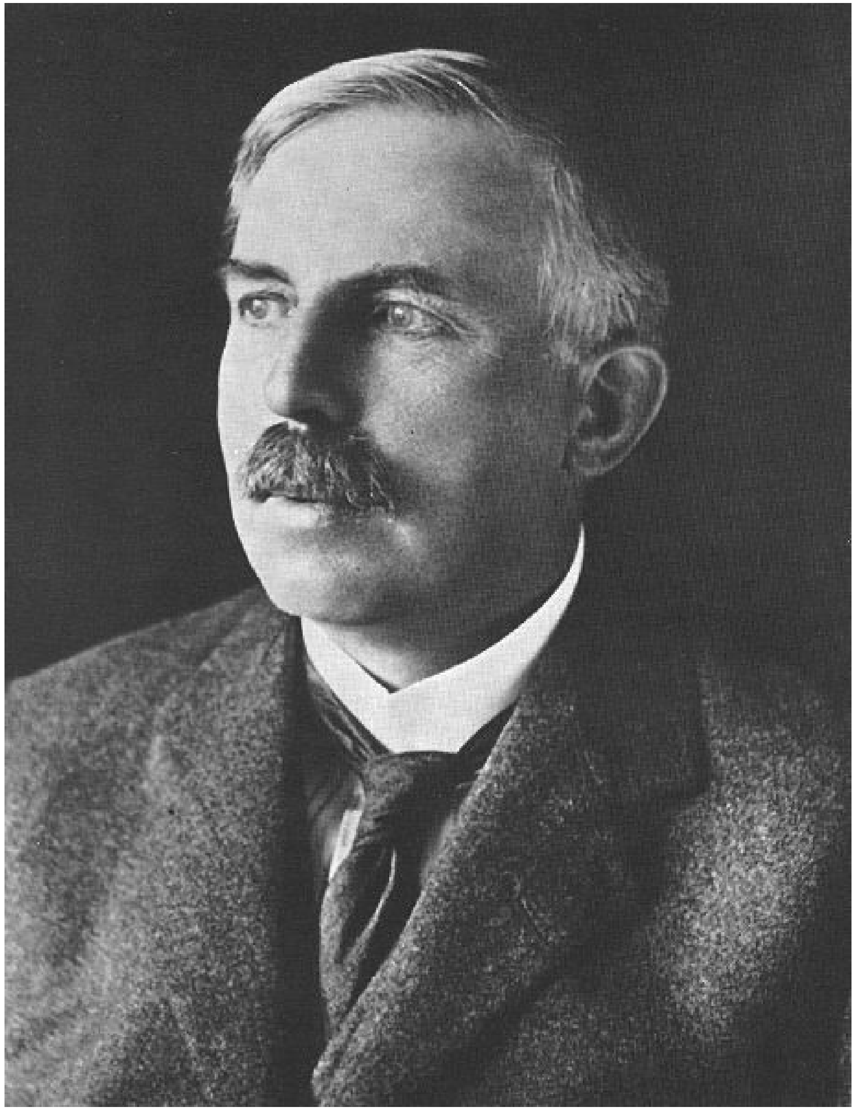
1910 – Robert Millikan

- In 1909 Millikan started the oil drop experiment that would determine the charge of an electron.
- Determined the charge of the electron to be 1.9 x10^{-10}C.
- Calculate the mass of the electron.
- Tried to prove Einstein's idea of a photon incorrect. Instead he proved Einstein right and won the Nobel Prize.

Oil-Drop Experiment



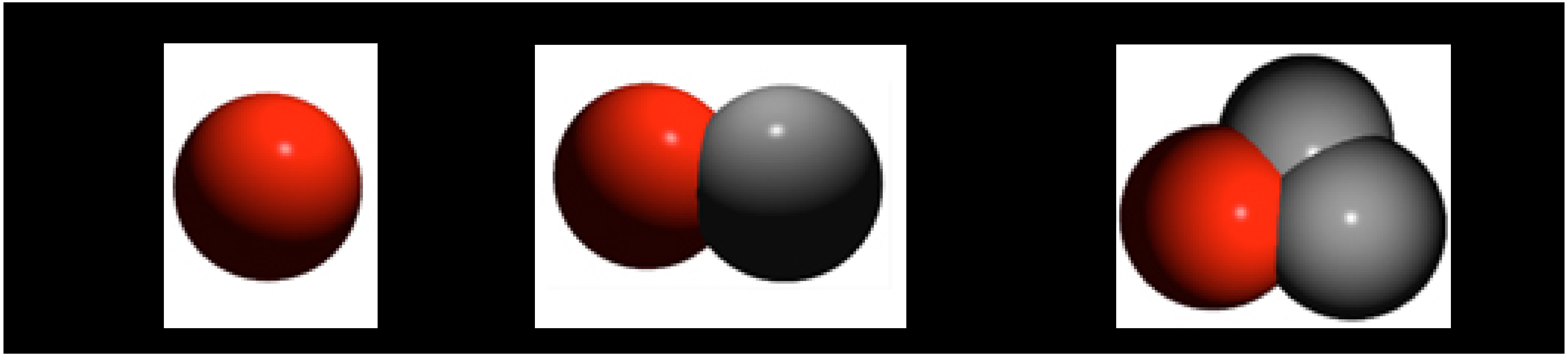
Earnest Rutherford



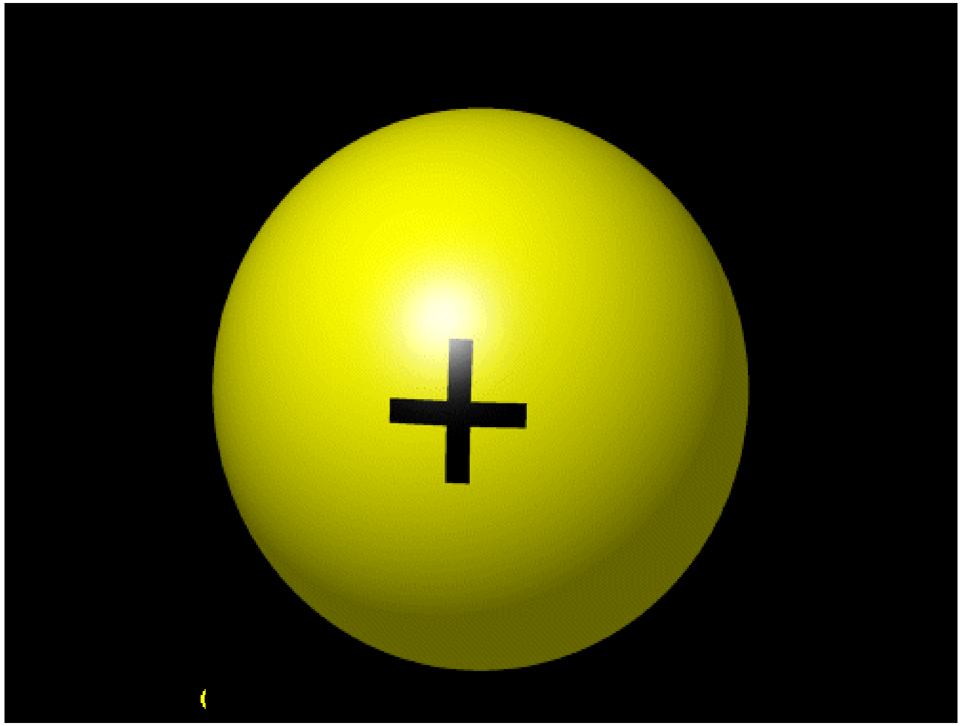
- Worked for Thomson in 1895 (two years before the discovery of the electron)
- 1909 – Urged Gieger and Marsden to create the Gold Foil Experiment
- 1911 – Created the nuclear model of the atom
- 1920 – Hypothesized the existence of the neutron

1913 – Isotopes

- J.J. Thomson discovered 3 isotopes of Neon in canal rays.
- All this proved was that the same element could have different atomic masses. The was no explanation why.
- Below are the three isotopes of hydrogen: hydrogen, deuterium, and tritium.



1919 – Protons



In 1919, Rutherford produced H^{1+} ions when alpha particles are shot into nitrogen gas. He concluded the ions had to come from the nitrogen gas and that since hydrogen had an atomic number of one, it must be a subatomic particle.

1932 – Neutrons

- 1920 Rutherford hypothesized the existence of neutrons.
- 1930 Bothe found a new type of ‘radiation’
- 1932 James Chadwick (on right) did a series of experiments that proved that this radiation is actually a neutral particle with approximately the same mass of a proton.

1905 – Einstein
proves atoms
exist

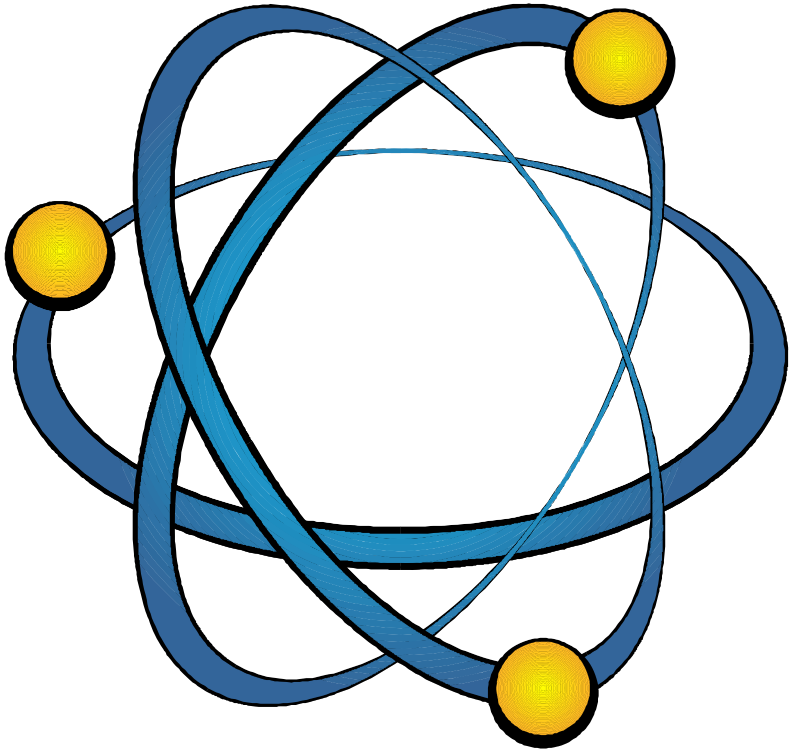
1909 – Rutherford Gold Foil
Experiment

1910 – Millikan
determined mass and
charge of electron

1911 – Rutherford
creates nuclear model
of atom

1913 – Thomson
discovers isotopes

Models of the Atom



Bohr’s Model

Bohr’s Model

In its final form, Bohr's theory used the following concepts, known as Bohr's hypotheses, to explain the spectrum of hydrogen.

A) The hydrogen atom included a positively charged nucleus (proton) and a negatively charged electron orbiting in a circular motion around the nucleus.

B) The electron could temporarily remain in a particular state (an orbit having a specific radius), provided that the angular momentum of the electron associated with that radius had a value that was an integral multiple of $\hbar$ ($\hbar = h/2\pi$, where h is Planck's constant).

C) Radiation is emitted from the atom when the electron "jumps" from a higher energy E2 (larger orbit) to a lower energy E1 (smaller orbit).

D) When such radiation is emitted, its frequency is determined by the Einstein frequency condition

$$h\nu_{21} = E_2 - E_1.$$

Bohr’s Model *Contd…*

- **Angular Momentum**

Bohr obtained values of the energies of various states or levels of the hydrogen atom by assuming that an electron with velocity v rotates in a circular orbit of radius r around the nucleus with an angular momentum of

$$m_e v r = nh/2\pi = n\hbar, \quad n = 1, 2, 3, \ldots . \tag{1}$$

This relationship expresses Bohr's second postulate in mathematical form. The electron mass is me, and the integer n is called the principal quantum number.

Bohr's Model *Contd…*

Using equations (1) and (2) to eliminate v leads to the formula for quantized orbits of the electron (Bohr orbits) described by the following radii:

$$r = \frac{\varepsilon_0 h^2}{\pi m_e e^2} n^2 = a_H n^2, \tag{3}$$

where a_H is the radius of the first Bohr orbit (n = 1) given by

$$a_H = \frac{\varepsilon_0 h^2}{\pi m_e e^2} = 0.53\ \text{Å}. \tag{4}$$

This value effectively describes the radius of the hydrogen atom in its ground state, or lowest-lying energy state (n =1).

Bohr’s Model *Contd…*

•Orbit

Newton's second law of motion, equating the sum of all forces acting on a body to the product of its mass and its acceleration, was then used to equate the electrical force of attraction between the negatively charged orbiting electron and the positively charged nucleus to the radial acceleration associated with the angular rotation of the electron around the much heavier nucleus (a proton):

$$\frac{e \cdot e}{4\pi\varepsilon_0 r^2} = \frac{m_e v^2}{r}, \tag{2}$$

where e is the electron charge and ε_0 is the permittivity of a vacuum.

Bohr's Model *Contd…*

- Energy

The total energy for a specific orbit can be obtained by summing the kinetic energy and the potential energy of the electron with respect to the nucleus:

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r}, \qquad (5)$$

where the first term is the kinetic energy of angular motion and the second term is the potential electrical energy of attraction.

Bohr’s Model *Contd…*

Using the value of r given in (3) as the separation distance of the positive and negative charges. Eliminating v by means of (2) gives the following value for the energy:

$$E = -\frac{e^2}{8\pi\varepsilon_0 r}. \qquad \textbf{(6)}$$

Bohr's Model *Contd…*

Substituting the expression (3) for r into (6), we find that the electron can have only certain discrete negative values of energy

associated with the various values of n, where n is a positive integer such that :

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \cdot \frac{1}{n^2} = -\frac{E_0}{n^2} \qquad \textbf{(7)}$$

and where E_0 **is given as**

$$E_0 = \frac{m_e e^4}{8\varepsilon_0^2 h^2} = 13.595 \text{ eV}. \qquad \textbf{(8)}$$

Bohr's Model *Contd…*

Inserting Reduced Mass

For a slightly more accurate value of the energy we must use the reduced mass μ of the combined electron and proton system

$$\mu = \frac{m_e}{1 + m_e/M_P} = \frac{m_e M_P}{M_p + m_e}, \qquad (9)$$

instead of the mass of the electron as in (8). We will use the reduced mass when we solve this problem using quantum mechanics. The reduced mass takes into account the finite size of the nucleus and the fact that both the electron and the proton rotate about the center of mass of the electron-proton system, rather than rotating about the center of mass of the proton as assumed in the Bohr theory.

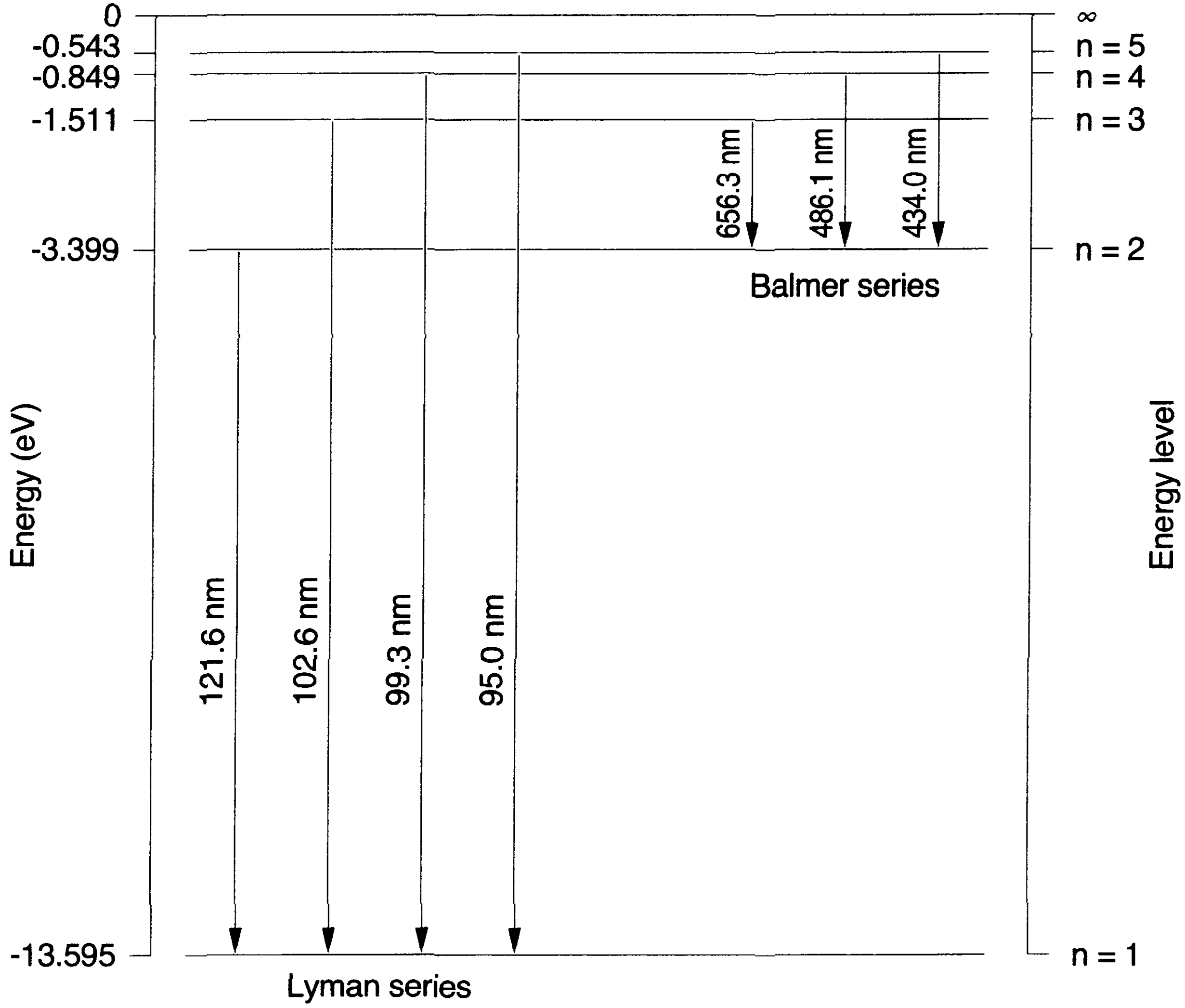
Bohr’s Model *Contd…*

Energy Levels

Thus, from (7) we find that the electron can have any one of a series of negative energies, which are referred to as energy states or levels (these terms are used interchangeably). The lowest value of energy (the most negative) corresponds to setting $n = 1$ in (7). Since this is the lowest energy, it is called the ground state; every atom has such a lowest energy state or ground state. The ground state is the energy state that normally occurs in nature unless additional energy in the form of heat or light is applied to the atom to raise it to a higher state.

Bohr's Model *Contd…*

The values of the negative energies for the hydrogen atom are shown in Figure below



Bohr's Model *Contd…*

Frequency and Wave Length of Emission Lines

Using Bohr's fourth hypothesis, one can estimate the frequency ν_{ji} of radiation occurring when an electron makes a transition from a higher energy level E_j to a lower level E_i as

$$\nu_{ji} = \frac{E_j - E_i}{h} = \frac{\Delta E_{ji}}{h} = \frac{E_0}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

$$= (3.28 \times 10^{15})\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)\ \mathrm{s}^{-1}. \qquad \textbf{(10)}$$

This formula relates the frequency of radiation to the energy differences between the various "quantized" negative energy states i and j.

Bohr’s Model *Contd…*

Using (10) and the relationship $\nu = c/\lambda$, we can obtain

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) = (1.0967758 \times 10^7)\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)\ \mathrm{m}^{-1}, \quad \textbf{(10)}$$

where $R_H = 1.0967758 \times 10^7\ \mathrm{m}^{-1}$ is referred to as the Rydberg constant for hydrogen.

Binding Energy

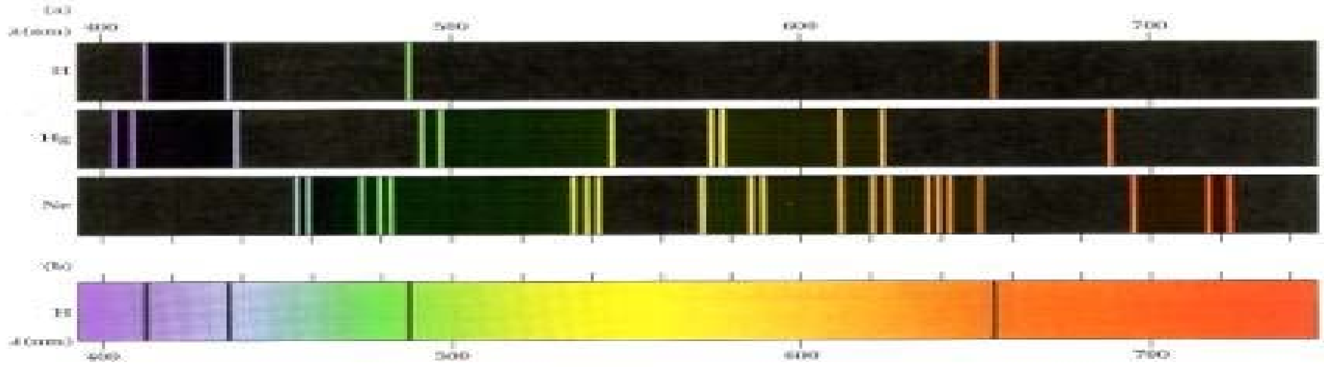
- **Energy needed to remove an electron (also known as ionization energy)**

- **For hydrogen measured ionization energy = 13.6eV**

- **This corresponds to the energy between the ground state and E=0**

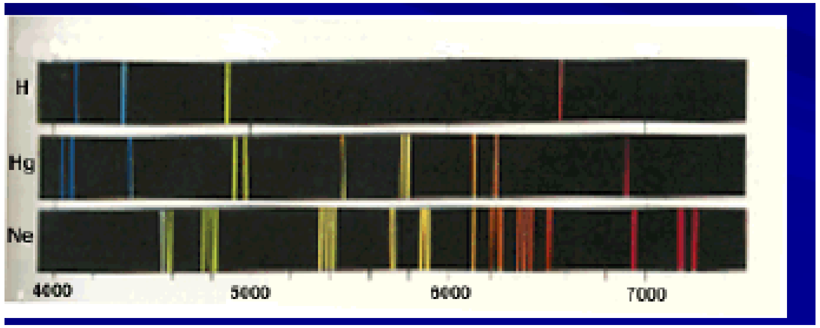
- **The transition between the energy levels give rise to the spectral lines**

Atomic Spectra



Line Spectra

The spectrum produced by a gas or vapour (following an electric discharge) contains only a few wavelengths (colours) and some of the wavelengths are missing. This is called a **Line Spectrum.** Each atom has its own spectrum



Line spectra of some elements

- The existence of these lines cannot be explained by classical Physics

Hydrogen spectrum

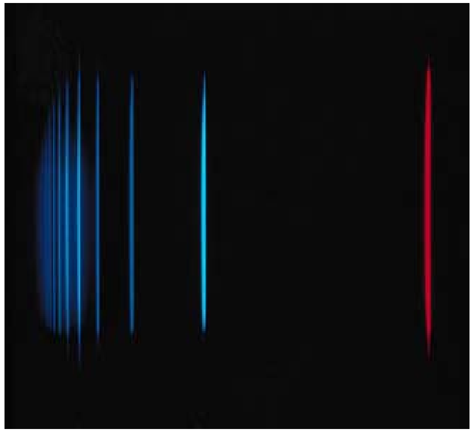


Figure shows hydrogen spectral lines in the visible region. These were the first lines to be discovered. There are 4 lines at 210 nm, 434 nm, 486nm and 656 nm (red). These lines form the **Balmer series** named after the scientist who came up with an empirical formula for the wavelengths of these lines.

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) where..n = 3,4,5......$$

R (Rydberg constant) = 1.097 x10^7 m^{-1}

Hydrogen spectrum

Later other series were discovered in the UV and IR region

Lyman Series: UV region

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right) where..n = 2,3,4......$$

Paschen Series : IR region

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right) where..n = 4,5,6......$$

Hydrogen spectrum

Brackett Series: IR region

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n^2}\right) where..n = 5,6,7......$$

Pfund Series ; IR region

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n^2}\right) where..n = 6,7,8......$$

Any proposed atomic theory must be able to explain these spectra.

Line spectra

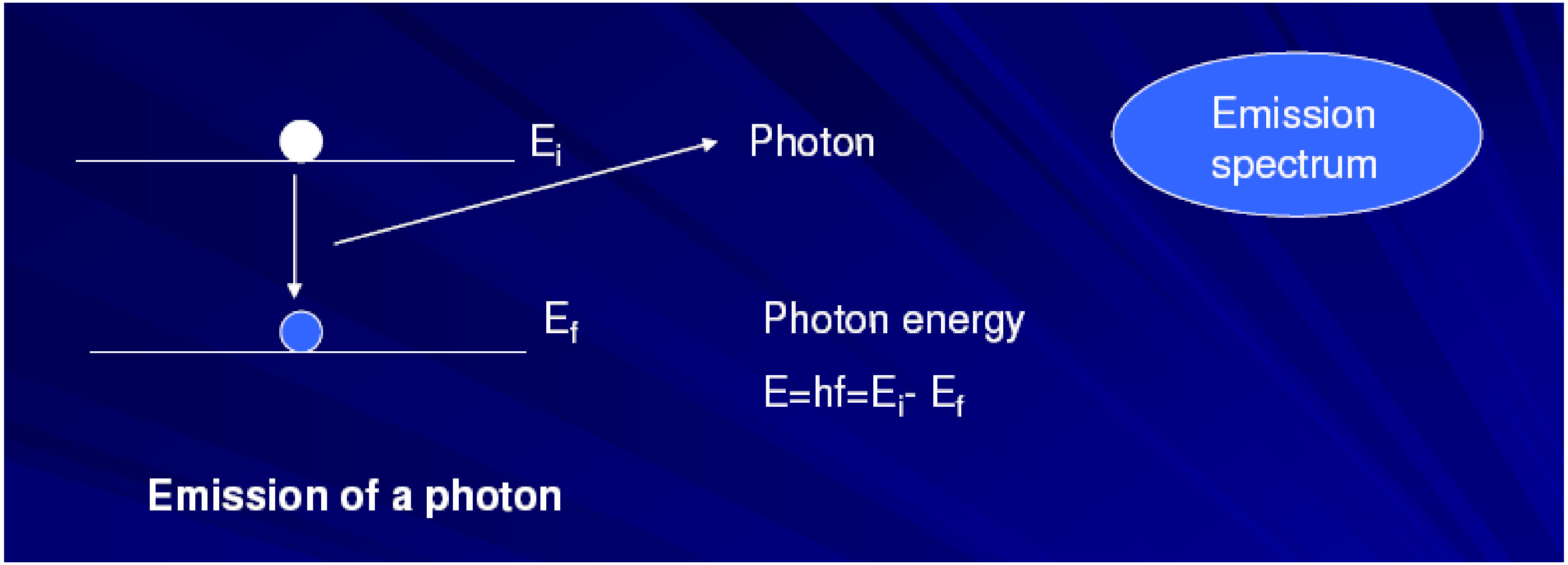
Line spectra cannot be explained by the classical physics.

We explain this phenomenon by utilizing two new concepts:

1. The particle nature of light (photons)
2. Energy levels: An atom can only have certain discrete energy values- we say that their energy is *quantized.* These energy values are called energy levels.

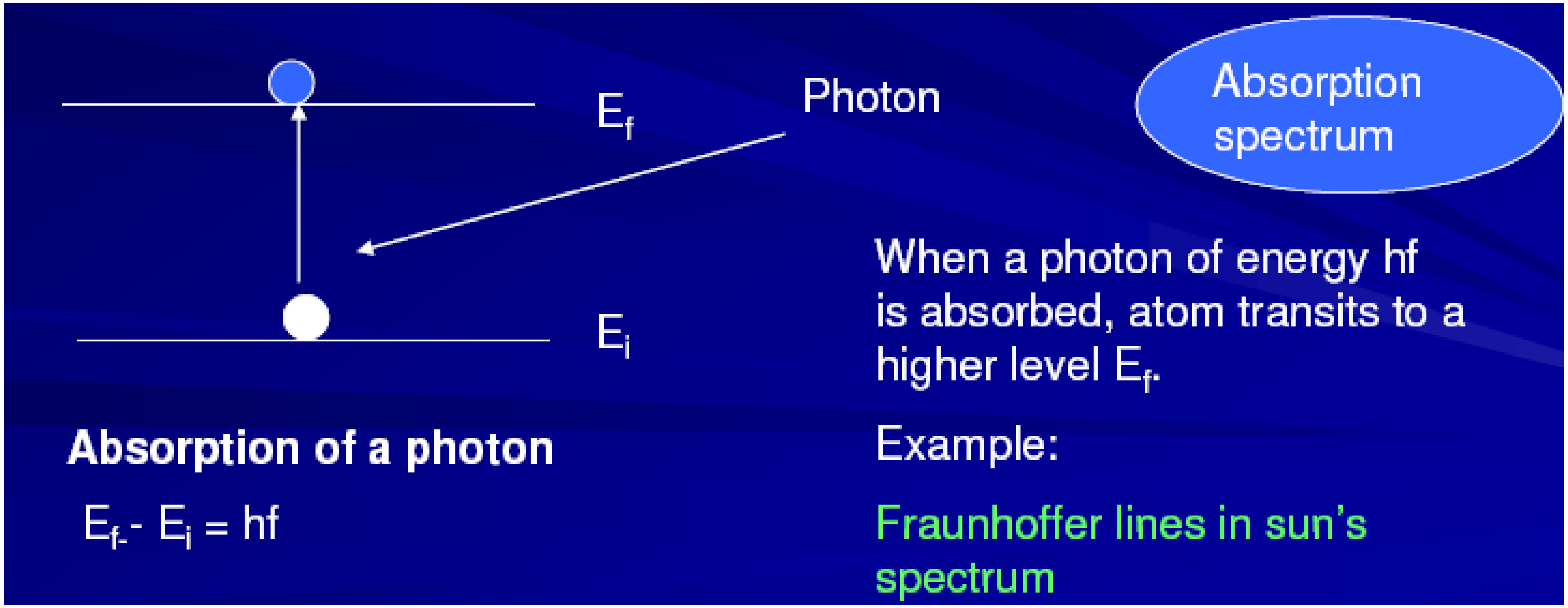
Emission spectrum

When an electron makes a transition from a higher energy level to a lower energy level ,the difference in the energy is emitted out as a photon . Each transition produces a photon of a certain energy and this appears as a line of certain wavelength on the spectrum. These lines constitute the Emission spectrum



Absorption spectrum

When white light passes through a gas, the gas absorbs light of certain wavelengths theta are present in its emission spectrum. The resulting spectrum has some colours (wavelengths) missing replaced by dark lines. This is called the Absorption spectrum.



Absorption spectrum

When a photon of energy hf is absorbed, atom transits to a higher level E_f.

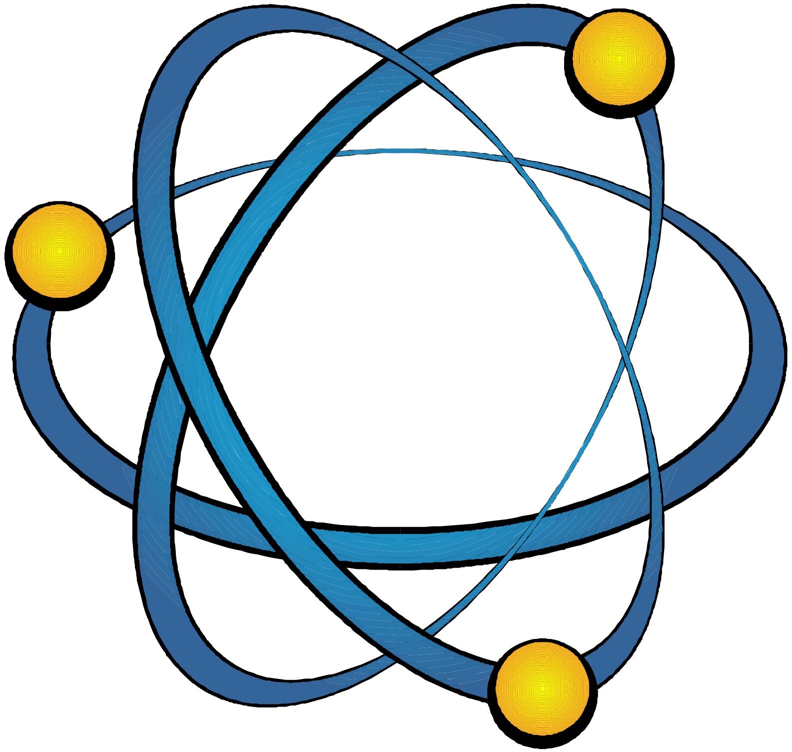
Example:

Fraunhoffer lines in sun's spectrum

Absorption of a photon

$E_{f} - E_i = hf$

Quantum Theory of Atomic Energy Levels



Quantum Mechanics

- Bohr’s theory established the concept of atomic energy levels but did not thoroughly explain the “wave-like” behavior of the electron.
- It can only be applied to one-electron systems like Hydrogen atom and not for heavier atoms.
- It cannot predict the intensity of spectral lines.
- Current ideas about atomic structure depend on the principles of quantum mechanics, a theory that applies to subatomic particles such as electrons. Electrons show properties of both waves and particles.

Quantum Mechanics

de Broglie

- The first clue in the development of quantum theory came with the discovery of the de Broglie relation.
- In 1923, Louis de Broglie reasoned that if light exhibits particle aspects, perhaps particles of matter show characteristics of waves.
- He postulated that a particle with mass *m* and a velocity *v* has an associated wavelength.
- The equation $\lambda_e = \frac{h}{p_e}$, is called the de Broglie relation.

Quantum Mechanics

- If matter has wave properties, why are they not commonly observed?

  The de Broglie relation shows that a baseball (0.145 kg) moving at about 60 mph (27 m/s) has a wavelength of about 1.7 x 10^{-34} m.

$$\lambda = \frac{6.63 \times 10^{-34}\ \frac{\text{kg}\cdot\text{m}^2}{\text{s}}}{(0.145\,\text{kg})(27\,\text{m}/\text{s})} = 1.7 \times 10^{-34}\,\text{m}$$

  This value is so incredibly small that such waves cannot be detected.

  Electrons have wavelengths on the order of a few picometers (1 pm = 10^{-12} m).

Quantum Mechanics

Heisenberg

- **Quantum mechanics** is the branch of physics that mathematically describes the wave properties of submicroscopic particles.
- We can no longer think of an electron as having a precise orbit in an atom.
- To describe such an orbit would require knowing its exact position and velocity.
- In 1927, **Werner Heisenberg** showed (from quantum mechanics) that it is <u>impossible</u> to know

  both simultaneously.

Quantum Mechanics

- **Heisenberg's uncertainty principle is a relation that states that the product of the uncertainty in position (Δx) and the uncertainty in momentum ($m\Delta v_x$) of a particle can be no smaller than $h/4\pi$.**

$$(\Delta x)(m\Delta v_x) \geq \frac{h}{4\pi}$$

When *m* is large (for example, a baseball) the uncertainties are small, but for electrons, high uncertainties disallow defining an exact orbit.

Wave Function

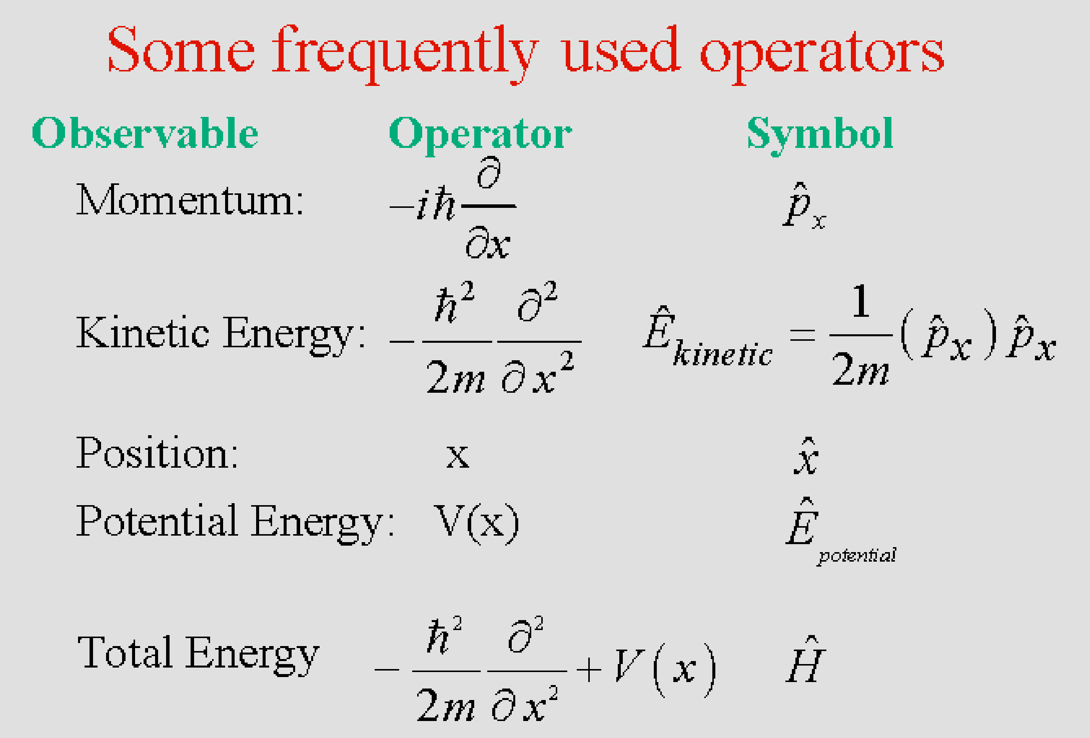
- **For every dynamical system there exists a *wave function* Ψ that is a single valued function of the parameters of the system and of time, and from which all possible predictions of the physical properties of the system can be obtained.**

Wave Function

- $\Psi = \Psi(\underline{r},t)$ in general, a complex number function
- (Real) Probabilty *density* $P(\underline{r},t) = \Psi^*\Psi = |\Psi(\underline{r},t)|^2$
- Probability (in volume $d^3\underline{r}$) $P(\underline{r},t)\, d^3\underline{r} = |\Psi(\underline{r},t)|^2\, d^3\underline{r}$
- Normalisation: $\int |\Psi(\underline{r},t)|^2\, d^3\underline{r} = 1$ over all space

Operators

- To every observable in classical mechanics (such as position, momentum, and energy), there corresponds a linear operator in quantum mechanics. An experiment that measures a value of such an observable is simulated in the theory by “operating” on the wave function of the system with the corresponding operator.



Some frequently used operators

Observable	Operator	Symbol
Momentum:	$-i\hbar\frac{\partial}{\partial x}$	$\hat{p}_x$
Kinetic Energy:	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$	$\hat{E}_{kinetic} = \frac{1}{2m}(\hat{p}_x)\hat{p}_x$
Position:	x	$\hat{x}$
Potential Energy:	V(x)	$\hat{E}_{potential}$
Total Energy	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)$	$\hat{H}$

Operators

- In any measurement of the observable *a* that corresponds to the operator *Â*, the only values that will ever be observed are the *eigenvalues* of that operator, which satisfy the *eigenvalue equation*

$$\hat{A}\Psi\left(x,t\right)=A\,\Psi\left(x,t\right)$$

Average

- If a system is in a state described by a wave function Ψ (*x*,*t*), then the average value of the observable *a* (measured once on many identical systems) is given by

$$\langle a\rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\hat{A}\,\Psi(x,t)\,dx}{\int_{-\infty}^{\infty} \Psi^*(x,t)\,\Psi(x,t)\,dx}$$

Time Evolution

Schrodinger

- **The wave function of a system evolves in time according to the time dependent Schrödinger equation**

$$i\hbar \frac{\partial \Psi\left(x,t\right)}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} + U\left(x\right) \right] \Psi\left(x,t\right)$$

Plausible Arguments for Schrödinger Equation

Electromagnetic waves:

$$\frac{\partial^2 \phi(x,t)}{\partial t^2} - c^2 \frac{\partial^2 \phi(x,t)}{\partial x^2} = 0$$

$$\phi(x,t) = A\exp\left[i(kx - \omega t)\right]$$

$$E = \hbar\omega \qquad p = \hbar k \qquad E = cp$$

thus, for a photon

$$\phi(x,t) = A\exp\left[\frac{i}{\hbar}(px - Et)\right]$$

de Broglie waves, non-relativistic case:

$$E = K + U = \frac{p^2}{2m} + U(x,t)$$

- we neglect the rest energy, it is now our reference (zero) for measuring the potential energy

$$\Psi(x,t) = A\exp\left[\frac{i}{\hbar}(px - Et)\right]$$

assume, by analogy, that this is a solution of the equation we are looking for

$$\frac{\partial \Psi(x,t)}{\partial t} = -\frac{iE}{\hbar} A\exp\left[\frac{i}{\hbar}(px - Et)\right] = -\frac{iE}{\hbar}\Psi(x,t)$$

$$\frac{\partial \Psi(x,t)}{\partial x} = \frac{ip}{\hbar} A\exp\left[\frac{i}{\hbar}(px - Et)\right] = \frac{ip}{\hbar}\Psi(x,t)$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\left(\frac{p}{\hbar}\right)^2 \Psi(x,t)$$

$$\underbrace{E = i\hbar \frac{\partial \Psi(x,t)}{\partial t} / \Psi(x,t) \qquad p^2 = -\hbar^2 \frac{\partial^2 \Psi(x,t)}{\partial x^2} / \Psi(x,t)}$$

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} / \Psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} / \Psi(x,t) + U$$

$$\boxed{i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x,t)\Psi(x,t)}$$

- the time-dependent Schrödinger Equation

Comments

This was a plausibility argument, not a derivation. We believe the Schrödinger equation not because of this argument, but because its predictions agree with experiment.

$$\boxed{i\hbar\frac{\partial\Psi(x,t)}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2}+U(x,t)\Psi(x,t)=\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U(x,t)\right]\Psi(x,t)}$$

- A differential equation by itself does not fully determine the solution, we need to impose ***boundary conditions***.

- This is a ***linear homogeneous partial differential equation***, it is first-order in the time derivative and the second-order in the space derivative (remember, non-relativistic $K \sim p^2$).

- In contrast to the classical mechanics, where both the initial coordinate and momentum must be specified to determine the subsequent motion (the Newton's 2nd Law contains the second-order derivative in time), in quantum mechanics it is sufficient to specify the wave function $\Psi(x,t_0)$ for all x at some time $t=t_0$ to determine it for all subsequent times.

- This equation is ***inherently complex***, and its solutions are complex (unlike classical waves, where the use of complex numbers is just a mathematical convenience).

Time-Independent Potential

Suppose that the potential is independent of time

$$V(x,t) = V(x)$$

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t)$$

This equation can be solved by the "separation of variables" method: $\Psi(x,t) = \psi(x)T(t)$

$$i\hbar \psi(x)\frac{dT(t)}{dt} = -\frac{\hbar^2}{2m}T(t)\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x)T(t)$$

- divide both sides by $\psi(x)T(t)$

$$i\hbar \frac{1}{T(t)}\frac{dT(t)}{dt} = \frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x)\right]$$

- two sides depend on different independent variables; thus, both sides must be equal to the same ***x***- and ***t***-independent constant!

$$i\hbar \frac{dT(t)}{dt} = ET(t)$$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)}$$

the time-independent S. Eq.

- the constant *E* is an eigenvalue of Hamiltonian operator

- The time-independent Schrödinger equation is an eigenvalue equation for the Hamiltonian operator:
  (operator × function=number × function)

$$\boxed{\hat{H}\psi = E\psi}$$

Time-Independent Potential (cont'd)

$$i\hbar\frac{dT(t)}{dt}=ET(t) \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x)$$

$$T(t)=\exp\left(\frac{-iEt}{\hbar}\right) \qquad \Psi(x,t)=\psi_E(x)\exp\left(\frac{-iEt}{\hbar}\right)$$

$\psi_E(x)-$ solution of the *t*-independent S.Eq. that corresponds to *E*

$\downarrow$

resembles $\exp(-i\omega t)$, thus, indeed, we can associate ***E*** with the total energy ***K+U***

- The *t*-dependent equation only tells us that *T*(*t*) depends on the energy *E*.
It doesn't tell us what the energy actually is. For that we have to solve the *x*-dependent eq.

- *T*(*t*) does not depend explicitly on the potential *V(x)*. But there is an implicit dependence because the potential determine possible values for the energy E.

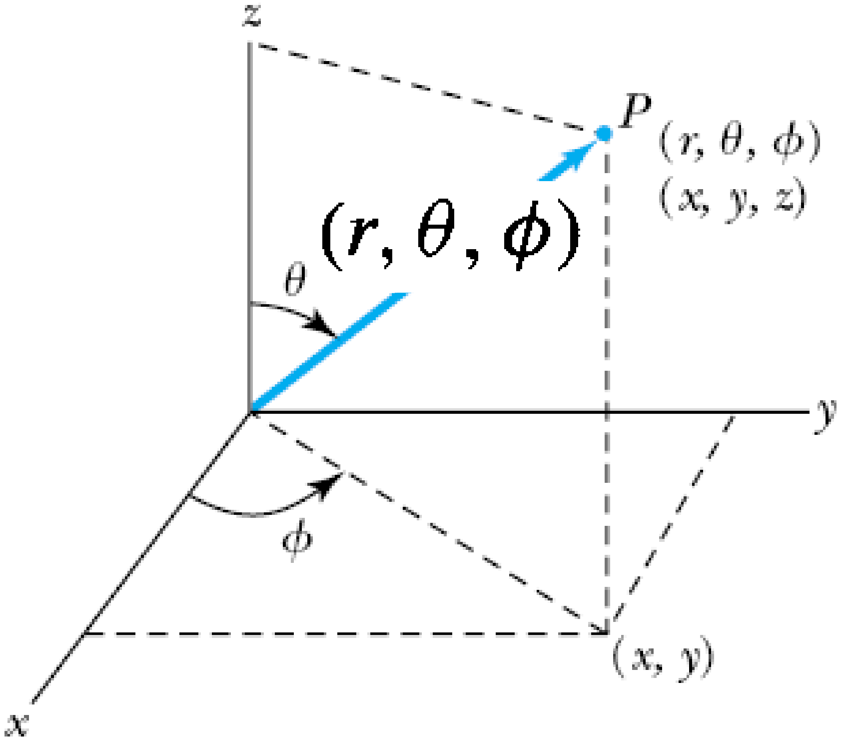
- Even though the potential is independent of time, the wavefunction still oscillates in time.
However, the probability ~ $\Psi^*(\mathbf{r},t)\,\Psi(\mathbf{r},t)$ is ***time-independent*** (***stationary solution***):

$$\left|\psi(x,t)\right|^2=\psi^*(x)e^{+iEt/\hbar}\psi(x)e^{-iEt/\hbar}=\psi^*(x)\psi(x)=\left|\psi(x)\right|^2$$

The rest of Chs. 5 and 6 – solving the TISE for several important potentials.

SCHRODINGER EQUATION IN SPHERICAL COORDINATES

- **Spherical Coordinates** (r, θ, ϕ)



SCHRODINGER EQUATION IN SPHERICAL COORDINATES

- Schrodinger's equation says

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi; \qquad \textbf{(1)}$$

the Hamiltonian operator H is obtained from the classical energy

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

SCHRODINGER EQUATION IN SPHERICAL COORDINATES

Using

$$p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}, \qquad p_y \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial y}, \qquad p_z \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial z}, \qquad (2)$$

or

$$\mathbf{p} \rightarrow \frac{\hbar}{i}\nabla, \qquad (3)$$

Thus

$$i\hbar\frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi, \qquad (4)$$

where

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \longrightarrow \textbf{Laplacian} \qquad (5)$$

SCHRODINGER EQUATION IN SPHERICAL COORDINATES

In spherical coordinates the Laplacian takes the form

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \quad (6)$$

the time-independent Schrodinger equation reads

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi. \quad (7)$$

Separation of Variables

- looking for solutions that are separable into products:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi). \qquad (8)$$

Equation (7) becomes,

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$+VRY = ERY. \qquad (9)$$

Separation of Variables

Dividing by YR and multiplying by $-2mr^2/\hbar^2$:

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]\right\}$$

$$+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0.$$

The term in the first curly bracket depends only on r, whereas the remainder depends only on θ and ϕ; accordingly, each must be a constant. $l(l+1)$

Separation of Variables

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1); \tag{10}$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} = -l(l+1). \tag{11}$$

The Angular Equation

- Equation (11) determines the dependence of ψ on θ and ϕ multiplying by $Y \sin^2\theta$, it becomes

$$\sin\theta \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)\sin^2\theta\, Y. \qquad (12)$$

This equation occurs in the solution to Laplace's equation in classical electrodynamics.

The Angular Equation

We try separation of variables

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi). \qquad (13)$$

Plugging this in, and dividing by $\Theta\Phi$, we find

$$\left\{ \frac{1}{\Theta} \left[\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) \right] + l(l+1)\sin^2\theta \right\} + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = 0. \quad (14)$$

The Angular Equation

The first term is a function only of θ , and the second is a function only of ϕ , so each must be a constant.

This time we'll call the separation constant m^2

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)\sin^2\theta=m^2; \quad (15)$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2. \quad (16)$$

The Angular Equation

The solution to equation (16) is simple

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \Rightarrow \Phi(\phi) = e^{im\phi}. \qquad (17)$$

Now, when ϕ advances by 2π we return to the same point in space (in spherical coordinates),

$$\Phi(\phi + 2\pi) = \Phi(\phi). \qquad (18)$$

Which means, $\exp[im(\phi + 2\pi)] = \exp(im\phi)$

or $\exp(2\pi im) = 1$

m must be an integer:

$$m = 0, \pm 1, \pm 2, \ldots. \qquad (19)$$

The Angular Equation

The θ equation,

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0, \quad (20)$$

may not be so familiar. The solution is

$$\Theta(\theta) = A P_l^m(\cos\theta), \quad (21)$$

where P_l^m is the associated Legendre function, defined by

$$P_l^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x), \quad (22)$$

The Angular Equation

and $P_l(x)$ is the $l\text{th}$ Legendre polynomial define by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l. \qquad (23)$$

For example,

$$P_0(x) = 1,\ \ P_1(x) = \frac{1}{2}\frac{d}{dx}(x^2-1) = x,$$

$$P_2(x) = \frac{1}{4\cdot 2}\left(\frac{d}{dx}\right)^2 (x^2-1)^2 = \frac{1}{2}(3x^2-1),$$

The Angular Equation

The first few Legendre polynomials, $P_l(x)$

$$P_0 = 1$$

$$P_1 = x$$

$$P_2 = \tfrac{1}{2}(3x^2 - 1)$$

$$P_3 = \tfrac{1}{2}(5x^3 - 3x)$$

$$P_4 = \tfrac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \tfrac{1}{8}(63x^5 - 70x^3 + 15x)$$

The Angular Equation

Note that,

- $P_l(x)$ is a polynomial (of degree *l*) in x, and is even or odd according to the parity of *l*
- But $P_l^m(x)$ is not, in general, a polynomial if m is odd it carries a factor of $\sqrt{1-x^2}$

$$P_2^1(x) = (1-x^2)^{1/2}\frac{d}{dx}\left[\frac{1}{2}(3x^2-1)\right] = 3x\sqrt{1-x^2},$$

- Since $\sqrt{1-\cos^2\theta} = \sin\theta$, therefore, $P_l^m(\cos\theta)$ is always a polynomial in $\cos\theta$,

The Angular Equation

Some associated Legendre functions, $P_l^m(\cos\theta)$.

$$P_1^1 = \sin\theta$$

$$P_1^0 = \cos\theta$$

$$P_2^2 = 3\sin^2\theta$$

$$P_2^1 = 3\sin\theta\cos\theta$$

$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$$

$$P_3^2 = 15\sin^2\theta\cos\theta$$

$$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$$

$$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

The Angular Equation

- Notice that *l* must be a nonnegative integer for the Rodrigues formula (23) to make any sense
- If $|m| > l$, then Equation (22) says $P_l^m = 0$. For any given *l*,
- Then for any given *l*, there are (2*l* + 1) possible values of m:

$$l = 0, 1, 2, \ldots; \; m = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l. \quad (24)$$

Spherical Harmonics

- Remembering the normalization equation

$$\int |\Psi|^2\, d^3\mathbf{r} = 1,$$

the volume element in spherical coordinates is

$$d^3\mathbf{r} = r^2 \sin\theta\, dr\, d\theta\, d\phi$$

so the normalization condition becomes,

$$\int |\psi|^2 r^2 \sin\theta\, dr\, d\theta\, d\phi = \int |R|^2 r^2\, dr \int |Y|^2 \sin\theta\, d\theta\, d\phi = 1$$

Spherical Harmonics

It is convenient to normalize R and Y individually:

$$\int_0^\infty |R|^2 r^2 \, dr = 1$$

and

$$\int_0^{2\pi} \int_0^{\pi} |Y|^2 \sin\theta \, d\theta \, d\phi = 1.$$

The normalized angular wave functions are called the **Spherical Harmonics**

Spherical Harmonics

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi}\, P_l^m(\cos\theta), \quad (25)$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

$$Y_l^{-m} = (-1)^m Y_l^m .$$

- These functions are orthogonal

$$\int_0^{2\pi} \int_0^{\pi} [Y_l^m(\theta, \phi)]^* [Y_{l'}^{m'}(\theta, \phi)] \sin\theta\, d\theta\, d\phi = \delta_{ll'} \delta_{mm'} . \quad (26)$$

Spherical Harmonics

$$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

$$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$$

Radial Equation

Notice that the angular part of the wave function, $Y(\theta, \phi)$ is the same for all spherically symmetric potentials; the actual shape of the potential, V(r), affects only the radial part of the wave function, R(r), which is determined by Equation (10):

Changing variabels in (10)

$$u(r) \equiv rR(r),$$

$$R = u/r$$

$$dR/dr = [r(du/dr) - u]/r^2$$

$$(d/dr)[r^2(dR/dr)] = rd^2u/dr^2,$$

Radial Equation

Hence,

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left[V+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u=Eu. \quad (27)$$

This is called the Radial Equation

With normalization condition

$$\int_0^\infty |u|^2\,dr=1.$$

Radial Equation

- Potential for hydrogen atom

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, \tag{28}$$

and the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu. \tag{29}$$

- Our problem is to solve this equation for u(r) and determine the allowed electron energies E.

The Radial Wave Function

Let

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \tag{30}$$

For bound states, $E < 0$, so κ is real.

manipulating equation (29)

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u$$

The Radial Wave Function

Again let

$$\rho \equiv \kappa r, \quad \text{and} \quad \rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}, \qquad (31)$$

So that

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u. \qquad (32)$$

Next we examine the asymptotic form of the solutions.
As $\rho \to \infty$ **the constant term in the brackets dominates, so (approximately)**

$$\frac{d^2u}{d\rho^2} = u \qquad (33)$$

The Radial Wave Function

The general solution of equation (33) is

$$u(\rho) = Ae^{-\rho} + Be^{\rho}, \qquad (34)$$

but e^{ρ} blows up (as $\rho \to \infty$), so $B = 0$. Evidently,

$$u(\rho) \sim Ae^{-\rho} \qquad (35)$$

for large ρ

The Radial Wave Function

As $\rho \to 0$, the centrifugal term in (32) dominates approximately then

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$$

The general solution of above equation is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l},$$

but ρ^{-l} blows up (as $\rho \to 0$), so $D = 0$. Thus

$$u(\rho) \sim C\rho^{l+1} \qquad (36)$$

The Radial Wave Function

- To peel off the asymptotic behavior introducing a new function $v(\rho)$

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho), \qquad (37)$$

Finding $\frac{du}{d\rho}$ and $\frac{d^2u}{d\rho^2}$ interms of $v(\rho)$

$$\frac{du}{d\rho} = \rho^l e^{-\rho}\left[(l+1-\rho)v + \rho\frac{dv}{d\rho}\right], \qquad (38)$$

$$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho}\left\{\left[-2l-2+\rho+\frac{l(l+1)}{\rho}\right]v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right\}. \qquad (39)$$

The Radial Wave Function

Using (38) and (39) in (32),

$$\rho \frac{d^2 v}{d\rho^2} + 2(l + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0. \quad (40)$$

Finally seek the solution interms of power series of $v(\rho)$

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j.$$

Our problem is to determine the coefficients $(a_0, a_1, a_2, \ldots)$.

The Radial Wave Function

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j a_j \rho^{j-1}$$

Replacing dummy index *j* by *j*+1

$$= \sum_{j=0}^{\infty} (j+1) a_{j+1} \rho^{j}. \qquad (41)$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1} \qquad (42)$$

The Radial Wave Function

Inserting (41) and (42) in (40),

$$\sum_{j=0}^{\infty} j(j+1)a_{j+1}\rho^j + 2(l+1)\sum_{j=0}^{\infty}(j+1)a_{j+1}\rho^j$$

$$-2\sum_{j=0}^{\infty} ja_j\rho^j + [\rho_0 - 2(l+1)]\sum_{j=0}^{\infty}a_j\rho^j = 0.$$

Equating the coefficients of like powers yield

$$j(j+1)a_{j+1} + 2(l+1)(j+1)a_{j+1} - 2ja_j + [\rho_0 - 2(l+1)]a_j = 0,$$

or

$$a_{j+1} = \left\{\frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}\right\}a_j. \quad (43)$$

The Radial Wave Function

$$a_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} a_j .$$

This recursion formula determines the coefficients, and hence the function $v(\rho)$.

For large *j* above recursion formula becomes

$$a_{j+1} \cong \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j ,$$

so

$$a_j \cong \frac{2^j}{j!} A .$$

Where,

$a_0 = A$ (a constant to be fixed by normalization)

The Radial Wave Function

Therefore

$$v(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho},$$

and hence

$$u(\rho) = A \rho^{l+1} e^{\rho}, \qquad (44)$$

which blows up at large ρ.

The Radial Wave Function

- There is only one way out of this dilemma: The series must terminate. There must occur some maximal integer, $j_{\max}$, such that

$$a_{j_{\max}+1} = 0$$

Evidently from equation (43)

$$2(j_{\max} + l + 1) - \rho_0 = 0. \qquad (45)$$

The Radial Wave Function

Defining

$$n \equiv j_{\max} + l + 1$$

the so-called principal quantum number, we have from (45)

$$\rho_0 = 2n. \qquad (46)$$

But

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2},$$

so the allowed energies are

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots \quad (47)$$

This is famous Bohr's Formula

The Radial Wave Function

Using (31) and (46), we find that

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an},$$

where

$$a \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\ \mathrm{m}$$

is called the Bohr’s radius.

The Radial Wave Function

- Evidently the spatial wave functions for hydrogen are labeled by three quantum numbers (*n*, *l*, and *m*):

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_l^m(\theta,\phi), \qquad (48)$$

where

$$R_{nl}(r) = \frac{1}{r}\rho^{l+1}e^{-\rho}v(\rho), \qquad (49)$$

The ground state (that is, the state of lowest energy) is the case n = 1;

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\ \mathrm{eV}. \qquad (50)$$

Evidently the binding energy of hydrogen

Quantum Numbers

The three quantum numbers:

- n: **Principal quantum number**
- ℓ: **Orbital angular momentum quantum number**
- m_ℓ: **Magnetic (azimuthal) quantum number**

The restrictions for the quantum numbers:

$n = 1, 2, 3, 4, \ldots$

$\ell = 0, 1, 2, 3, \ldots, n - 1$

$m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$

Equivalently:

$n > 0$

$\ell < n$

$|m_\ell| \leq \ell$

The energy levels are: $E_n = -\frac{E_0}{n^2}$

Degeneracy

For arbitrary *n,* the possible value of *l* are

$$l = 0, 1, 2, \ldots, n - 1.$$

For each *l*, there are (2/+ 1) possible values of m so the total degeneracy of the energy level *En* is

$$d(n) = \sum_{l=0}^{n-1} (2l + 1) = n^2.$$

The first few radial wave functions for hydrogen, $R_{nl}(r)$

$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$

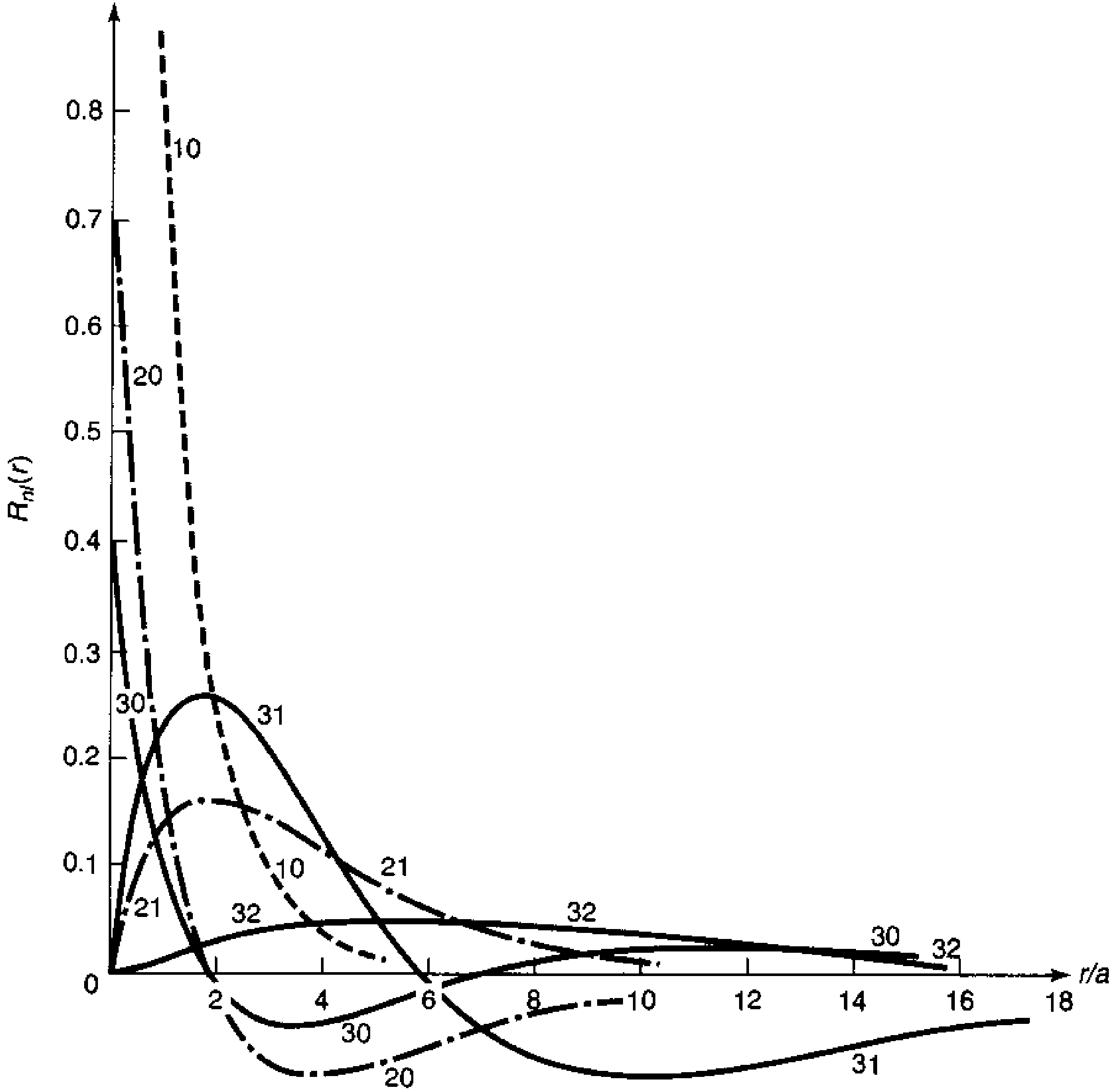
$$R_{40} = \frac{1}{4}a^{-3/2}\left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right)\exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}}a^{-3/2}\left(1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right)\frac{r}{a}\exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}}a^{-3/2}\left(1 - \frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2\exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}}a^{-3/2}\left(\frac{r}{a}\right)^3\exp(-r/4a)$$

Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$



Normalized Hydrogen Wave Function

The polynomial $v(\rho)$ can be written as

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho),$$

where

$$L_{q-p}^{p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \qquad (51)$$

is an associated **Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right) \qquad (52)$$

is the qth **Lagnerre** polynomial

The first few Laguerre polynomials, $L_q(x)$

$$L_0 = 1$$

$$L_1 = -x + 1$$

$$L_2 = x^2 - 4x + 2$$

$$L_3 = -x^3 + 9x^2 - 18x + 6$$

$$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$$

$$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$$

$$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$$

Some associated Laguerre polynomials, $L_{q-p}^{p}(x)$

$L_0^0 = 1$

$L_1^0 = -x + 1$

$L_2^0 = x^2 - 4x + 2$

$L_0^1 = 1$

$L_1^1 = -2x + 4$

$L_2^1 = 3x^2 - 18x + 18$

$L_0^2 = 2$

$L_1^2 = -6x + 18$

$L_2^2 = 12x^2 - 96x + 144$

$L_0^3 = 6$

$L_1^3 = -24x + 96$

$L_2^3 = 60x^2 - 600x + 1200$

Normalized Hydrogen Wave Function

The normalized Hydrogen wave functions are

$$\psi_{nlm}=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}}\,e^{-r/na}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_l^m(\theta,\phi)$$

These are exactly solvable and mutually orthogonal

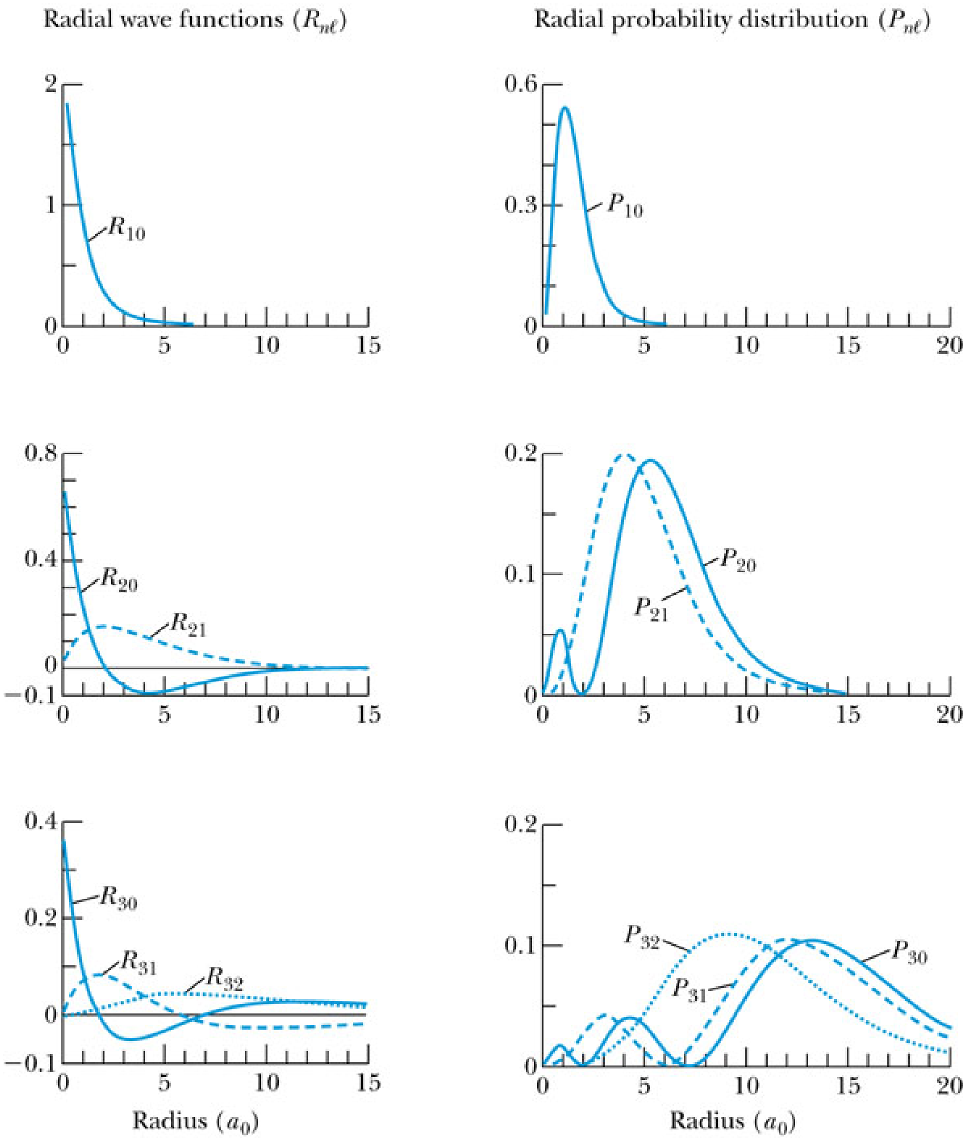
$$\int \psi_{nlm}^{*}\,\psi_{n'l'm'}\,r^2\sin\theta\,dr\,d\theta\,d\phi=\delta_{nn'}\delta_{ll'}\delta_{mm'}$$

Probability Distribution Functions

- We use the wave functions to calculate the probability distributions of the electrons.
- The “position” of the electron is spread over space and is not well defined.
- We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element $d\tau$ is:

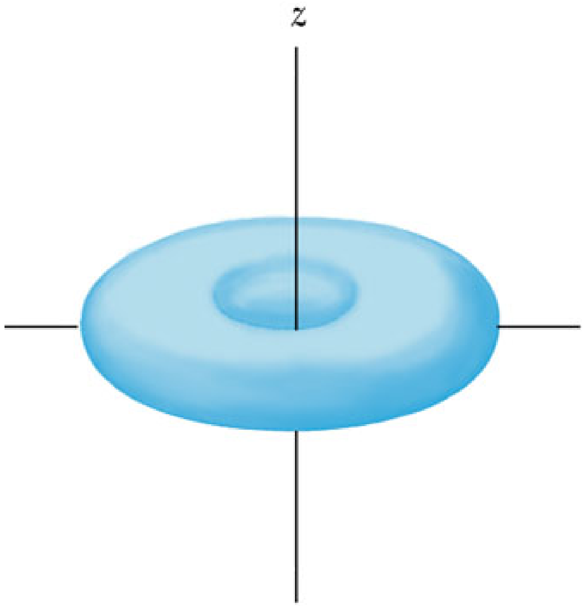
$$dP = \psi^*(r,\theta,\phi)\ \psi(r,\theta,\phi)\, d\tau$$

Probability Distribution Functions

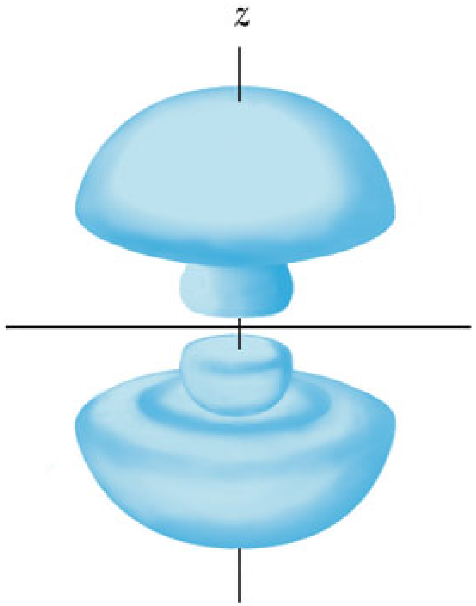


***R*(*r*) and *P*(*r*) for the lowest-lying states of the hydrogen atom.**

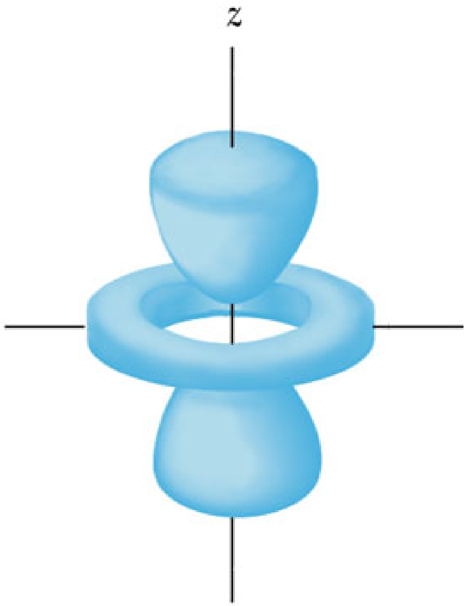
Probability Distribution Functions



$n = 2$
$\ell = 1$
$m_\ell = \pm 1$



$n = 3$
$\ell = 1$
$m_\ell = 0$



$n = 3$
$\ell = 2$
$m_\ell = 0$

ANGULAR MOMENTUM OF ATOMS

Orbital Angular Momentum

- The orbital angular momentum **L** is a vector quantity that is found to have a magnitude given by

$$|\mathbf{L}| = [l(l+1)]^{1/2}\frac{h}{2\pi} = [l(l+1)]^{1/2}\hbar,$$

where / is the azimuthal quantum number.

Orbital Angular Momentum

- For / = 0 (s states), there is no orbital angular momentum, which implies that there is no net rotation of the electron charge cloud.
- This does not imply that there is no electron motion but only no net motion for this particular s state.
- The solution for the angular momentum (using the Schrödinger equation) also suggests that the z component of the angular momentum L_z is quantized and of the form

$$L_z = m\frac{h}{2\pi} = m\hbar.$$

Orbital Angular Momentum

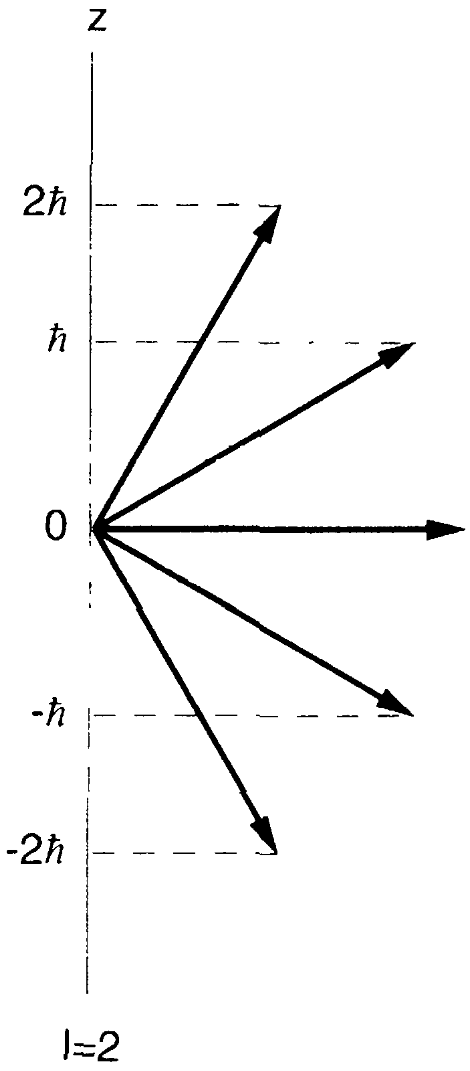
- **The magnetic quantum number *m* is associated with rotation of the electron about the *z* axis through the angular rotation ϕ, with integral values up to** $m = \pm l.$

- **The various possible values of angular momentum $m\hbar$ represent the *z* components of the angular momentum, for which there will be 2/ +1 different values.**

- **Thus, various states will have their angular momentum vectors precisely oriented in certain discrete orientations, as shown in Figure in next slide.**

Orbital Angular Momentum

Possible values of the orbital angular momentum vector for the case / = 2, along with the components projected onto the z axis



$$|\mathbf{L}| = \hbar[l(l+1)]^{1/2}$$

$$L_z = -l\hbar,\ -(l-1)\hbar, \ldots, (l-1)\hbar,\ l\hbar$$

Orbital Angular Momentum

Zeeman Effect

- **If a magnetic field is applied to an ensemble of atoms, the levels will split into the associated angular momentum states (except for *s* states, in which *m* is always zero).**

- **This will provide 2*l* + 1 states of slightly different energy for each *l* value associated with the nth quantum number.**

- **This is due to the alignment of electrons with the magnetic field and the splitting of energy into components associated with the field.**

- **The multiple values for the energies of these states lead to many more possible transitions between states.**

- **Thus, when electrons jump from one state to another, more wavelengths are emitted when a magnetic field is present than when it is not present; this is known as the Zeeman effect.**

ANGULAR MOMENTUM OF ATOMS

Spin Angular Momentum

- When the spectral lines of hydrogen (produced when radiative transitions occur between energy levels) were first observed with an extra-high-resolution spectrograph
- It was seen that there was a splitting of the emission lines similar to that observed with the Zeeman effect, except that there was no magnetic field present.
- This implied that the energy levels were split into several components, and that the theoretical interpretation of this splitting would require another component in the energy Hamiltonian in Schrodinger's equation.

Spin Angular Momentum

- Pauli suggested that the electron had an intrinsic spin angular momentum around its own axis with a value of either +h/2 or -h/2.
- **The value of the electron spin angular momentum vector *S* was obtained from the appropriate Schrodinger equation to be**

$$|\mathbf{S}| = [s(s+1)]^{1/2}\hbar,$$

where s is the spin quantum number with a value of 1/2 .

- **The *z* components have values of**

$$S_z = \pm\hbar/2 = \pm s\hbar.$$

ANGULAR MOMENTUM OF ATOMS

Total Angular Momentum

- In classical terms, the total angular momentum vector J consists of the vector sum of the orbital angular momentum vector L and the spin angular momentum vector S:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}.$$

The total angular momentum could have any possible value between L + S and L - S.

Total Angular Momentum

- The magnitude of **J** is given by

$$|\mathbf{J}| = [j(j+1)]^{1/2}\hbar,$$

where j has values for a one-electron system of either

$$j = l + s = l + \tfrac{1}{2}$$

or

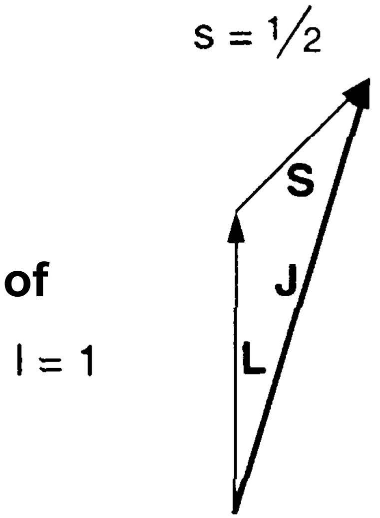
$$j = l - s = l - \tfrac{1}{2} \quad (l \neq 0).$$

If $l = 0$, the total quantum number j is just equal to s

Total Angular Momentum

The two possible values of the total angular momentum J for a one-electron atom

Spin and orbit angular momenta - same direction



$j = l + s = 3/2$

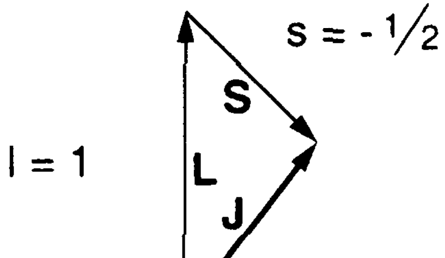
Magnitudes:

$|\mathbf{S}| = \sqrt{s(s+1)}\ \hbar$

$|\mathbf{L}| = \sqrt{l(l+1)}\ \hbar$

$|\mathbf{J}| = \sqrt{j(j+1)}\ \hbar$

Spin and orbit angular momenta - opposite direction



$j = l - s = 1/2$

Total Angular Momentum

Few Examples

$$\text{for } l = 1$$

$$j = \tfrac{1}{2} \text{ or } \tfrac{3}{2}$$

$$\text{for } l = 2$$

$$j = \tfrac{3}{2} \text{ or } \tfrac{5}{2}$$

For $l = 0$, a special case exists in which there is only one value of j $\left(j = \frac{1}{2}\right)$.

ENERGY LEVELS ASSOCIATED WITH ONE-ELECTRON ATOMS

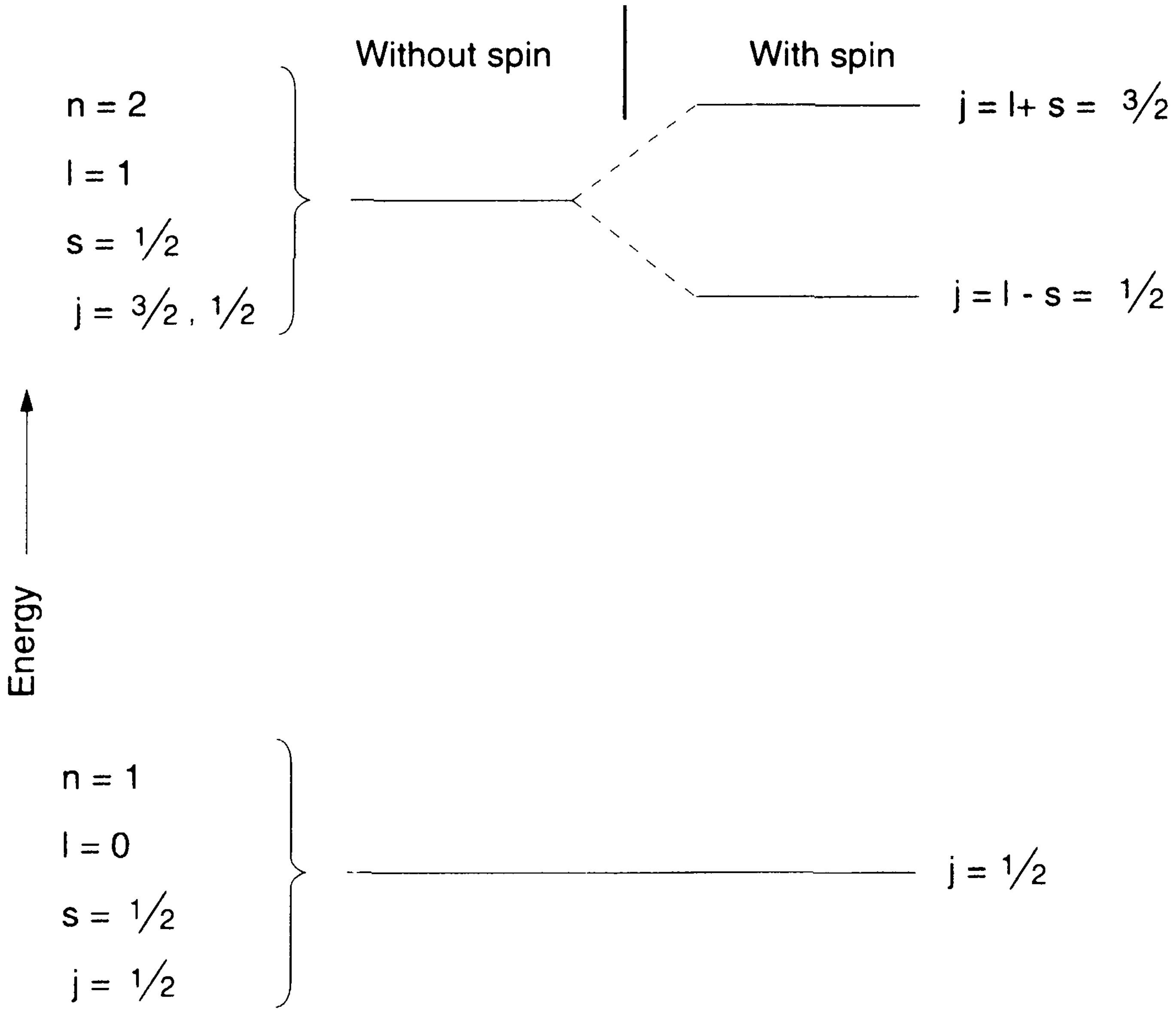
- **With the Bohr theory, energy levels of the hydrogen atom are arranged according to the value of the n quantum number**

- **Using quantum mechanics, we realize that the electron also has quantum numbers associated with the orbital angular momentum *l* and the magnetic quantum number *m***

- **We later added as a relevant quantum number of either +1/2 or -1/2 (called spin quantum number *s*)**

- **most useful four quantum numbers for designating energy levels are n, *l*, s, and j rather than n, *l*, m, and s, since j indicates the relative orientation of the electron orbital and spin angular momenta.**

Energy-level splitting due to the electron spin for n = 2 and / = 1 and also for n = 1 and / = 0



Pauli Exclusion Principle

- Pauli suggested that no two electrons could occupy the same state.

- This means that no two electrons could have all of the same quantum numbers, including the n and / and m quantum numbers as well as the spin quantum number of either +1/2 or -1/2

- This is referred to as the Pauli exclusion principle

Periodic Table of Elements

- The periodic table is built up of elements (atoms) that have various numbers of protons, neutrons, and electrons.
- The periodic table of the elements can be viewed as sequentially adding protons, neutrons, and electrons such that charge neutrality is satisfied.
- In developing the periodic table of the elements, as more protons and electrons are added to produce new elements
- the electrons are added sequentially into shells according to their n, /, m, and s quantum numbers, beginning with the lowest allowed values and working toward higher values, with the maximum number of electrons determined by the number of protons in the nucleus.

Periodic Table of Elements

Keeping in mind the restrictions on quantum numbers n, *l*, and m. And also have the restrictions on s of ±1/2, and the Pauli exclusion principle (i.e., all four quantum numbers cannot be the same). The Table shows how the various elements evolve according to the way electrons fill the possible quantum states.

Quantum Numbers for Various Shells and Subshells

Shell	**K**	**L**		**M**			**N**				**O**					**P**		
n	**1**	**2**		**3**			**4**				**5**					**6**		
Subshell	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d
l	0	0	1	0	1	2	0	1	2	3	0	1	2	3	4	0	1	2
Number of electrons	2	2	6	2	6	10	2	6	10	14	2	6	10	14	18	2	6	10

Periodic table of the elements showing the s, p, d, and f subshells

1s	1 H																			2 He
2s	3 Li	4 Be												2p	5 B	6 C	7 N	8 O	9 F	10 Ne
3s	11 Na	12 Mg												3p	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4s	19 K	20 Ca	3d	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	4p	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5s	37 Rb	38 Sr	4d	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	5p	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6s	55 Cs	56 Ba	5d	57-71 *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	6p	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7s	87 Fr	88 Ra	6d	89 Ac	90 †															

4f *	Rare Earths	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
5f †	Heavy Elements	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Energy Levels of Multi Electron Atoms

- For the hydrogen atom, we used both the kinetic and potential energy of the electron in the Hamiltonian when determining the values of bound energy states or levels of the atom.

- There are a number of possible interactions that must be included in the Hamiltonian in order to obtain a more exact solution for the possible energy levels of atoms, especially for multi-electron atoms.

Energy Levels of Multi Electron Atoms

- Kinetic energy of the electrons - the energy associated with the electron ve-velocities.
- Electrostatic interaction energy of the electrons with the nucleus. For hydrogen, this was the coulomb potential between the proton and the electron.
- Mutual electrostatic energy of the electrons, or the electrons being repulsed by each other.
- Spin-orbit interaction - the alignment of the electron spin angular momentum with respect to the orbital angular momentum.
- Spin-spin interactions of the electrons - the perturbations caused by the spin of one electron interacting with the spin of another electron.
- Interaction between the orbital magnetic moments of different electrons.
- Interactions between the electron spins and the nuclear spin.
- Nuclear spin interaction with the orbital angular momentum of the electrons. Relativistic effects.
- An "exchange correlation" that tends to align electronic spins parallel to each other.

Energy Levels of Multi Electron Atoms

The technique that has been the most successful in determining energy levels when such interactions are considered is referred to as Russell-Saunders or LS coupling. For some atoms, mainly heavier atoms (4th point), the spin-orbit energy dominates; that condition is referred to as j-j coupling.

LS Coupling

RULES FOR OBTAINING *S*, *L*, AND *J* FOR *LS* COUPLING

(1) Consider only those electrons not in closed subshells; for example,

$$1s^2 2s \rightarrow 2s,$$
$$1s^2 2s^2 2p^2 \rightarrow 2p2p,$$
$$1s^2 2s^2 2p3d \rightarrow 2p3d,$$
$$1s^2 2s^2 2p^2 3d \rightarrow 2p2p3d.$$

(2) If a subshell is nearly full, treat it as though the missing electron(s) is (are) the active electron(s). In other words, take the difference between the filled subshell and the unfilled subshell. Examples:

F $\quad 1s^2 2s^2 2p^5$ or $2p^5 \rightarrow 2p^6 - 2p^5 = 2p,$

Cd^{3+} $\quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^9 5s$ or $4d^9 5s \rightarrow 4d5s.$

LS Coupling

(3) First consider both possibilities of the electron spin orientation (up or down, $\pm\frac{1}{2}$) for each electron in an unfilled subshell. For two electrons in unfilled subshells, take the sum of the two spin angular momenta by adding the individual spins to obtain 1 and then take the difference by subtracting them to obtain 0. For three electrons, add all three for the sum $\left(\frac{3}{2}\right)$ and then add two and subtract one for the difference $\left(\frac{1}{2}\right)$ because the total S cannot be negative.

(4) Second, consider all possible values of L for each value of S. For two electrons in unfilled shells, take the sum of the two orbital angular momenta by adding the individual l values, and then take the difference by subtracting them, making sure you subtract the smaller from the larger. For three electrons you would add all three l values for the sum and then add two and subtract one for the difference, because the total L cannot be negative. Then take all possible values of L in between the sum and difference by changing the value of L in integral units. Example: 2p3d, where $l_1 = 2$ and $l_2 = 1$. Therefore $L = 2 + 1 = 3$, $2 - 1 = 1$, and (stepping down in unit intervals) $3 - 1 = 2$.

(5) Finally, compute all values of J in the range from $J = L + S$ to $J = L - S$, decreasing J by 1 each time.

(6) Label the energy levels according to:

$$^{2S+1}L_J$$

j-j Coupling

Using the j–j coupling scheme for two electrons involves, first, coupling the spin and orbit values so that $\mathbf{J}_1 = \mathbf{L}_1 + \mathbf{S}_1$ and $\mathbf{J}_2 = \mathbf{L}_2 + \mathbf{S}_2$ for each of the two electrons. Then the total angular momentum is obtained by combining $\mathbf{J}_1$ and $\mathbf{J}_2$ such that $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. The quantum numbers would therefore take on values ranging from $|j_1 + j_2|$ to $|j_1 - j_2|$. The reader may consult those references at the end of this chapter and other books on spectroscopy for further details about j–j coupling. We will use LS notation for energy levels throughout the rest of this text because LS coupling is more common for laser transitions.

Molecular Orbital's

- What is an orbital?
  - a wave function for a single particle

Molecular orbital's are composed of wave functions of the electrons in the molecule

Basis Sets

To study molecules quantum mechanically, we need to construct molecular orbital's

- We use a set of atomic orbital's

$$\Phi = \sum_{i=1}^{N} a_i \varphi_i$$

Φ is the molecular orbital, φ is an atomic orbital and *a* is a coefficient

Basis Sets

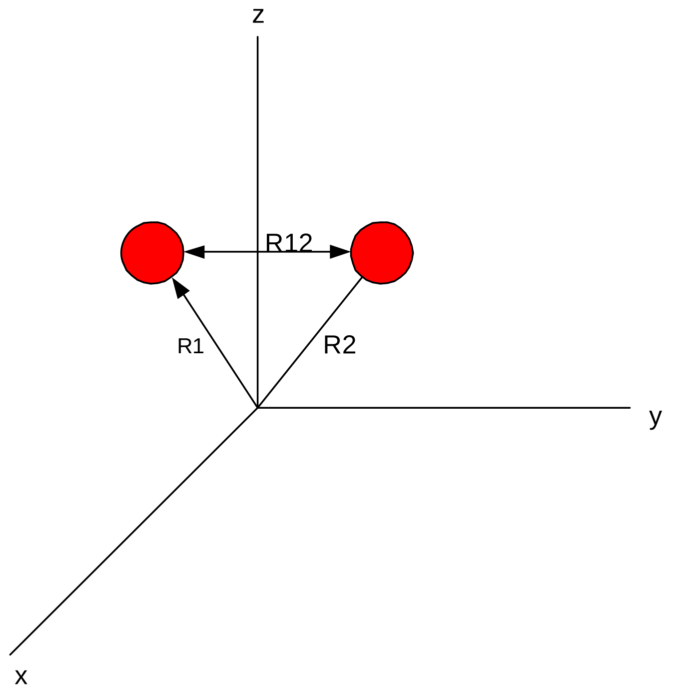
- The set of *N* atomic orbital's and their coefficients compose a molecular orbital
- This approach is referred to as the

Linear Combination of Atomic Orbitals (LCAO)

The greater the value of *N* the more complete our molecule will be described quantum chemically.

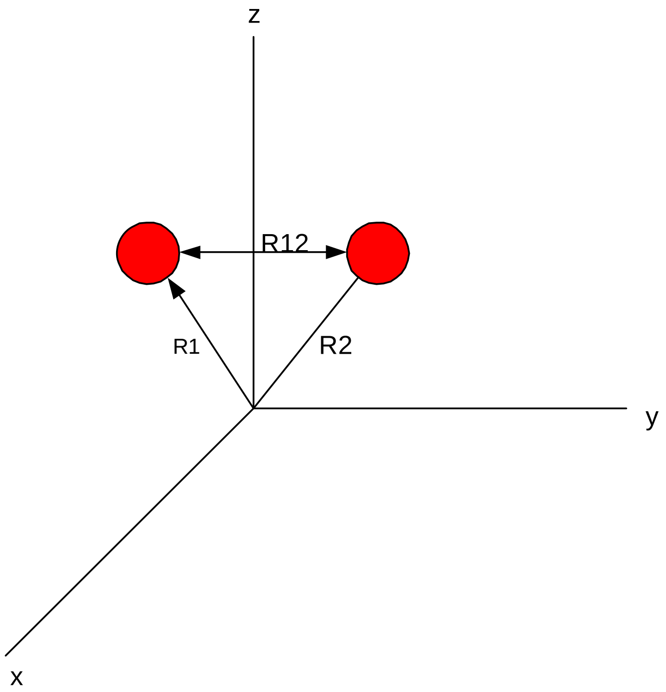
The H_2 Model

- Each hydrogen atom has a 1*s* orbital
- Molecular orbitals (MOs) are formed as the atomic orbitals approach each other (remember LCAO)



The H_2 Model

- The 1s orbitals are centred on the atoms
- If we use these two orbitals, they comprise a minimal basis set



The Born-Oppenheimer Approximation

- Central to quantum chemisty
- The approximation is based on nuclei being much heavier than electrons
- One considers electrons in a molecule to be moving in a field of fixed nuclei
- Necessary since Schrödinger equation cannot be solved exactly for molecular systems

The H_2 Model

- Total Hamiltonian:

$$H = -\frac{\hbar}{2m_e}\nabla_e^2 - \frac{\hbar}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

- After applying the Born-Oppenheimer approximation:

$$H = -\frac{\hbar}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} + \frac{e^2}{4\pi\varepsilon_0 R}$$

THANK YOU