

The Hydrogen Atom

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Contents

| | | |
|----------|--|-----------|
| 1 | Introduction | 3 |
| 2 | The Bohr Quantum Model of the Hydrogen Atom | 4 |
| 2.1 | The Spectroscope and Collimated Light | 4 |
| 2.2 | Atomic Spectra | 5 |
| 2.3 | A Mass Point in Circular Motion | 5 |
| 2.4 | The Bohr Model of the Atom | 7 |
| 3 | Classical Mechanics | 12 |
| 3.1 | Harmonic Oscillators | 12 |
| 3.2 | The Equipartition of Energy Theorem | 13 |
| 3.3 | Degrees of Freedom of a Vibrating String | 14 |
| 4 | Problems With Classical Physics | 14 |
| 4.1 | Blackbody Radiation | 14 |
| 4.2 | The Photoelectric Effect | 15 |
| 4.3 | De Broglie Wave-Particle Duality | 16 |
| 4.4 | De Broglie and the Hydrogen Spectra | 17 |
| 5 | Normal Coordinates and Degrees of Freedom | 17 |
| 6 | Specific Heat of Molecules | 17 |
| 7 | The Vibrating String, and the One Dimensional Wave Equation | 18 |

| | | |
|----|--|----|
| 8 | The Ultraviolet Catastrophe: Plank's Solution. | 18 |
| 9 | The Photoelectric Effect | 18 |
| 10 | Solving Differential Equations by the Method of Frobenius | 18 |
| 11 | The Phase Velocity and Group Velocity of Waves | 18 |
| 12 | The Schrödinger Equation | 18 |
| 13 | Derivation of the Schrödinger Equation | 19 |
| 14 | Laplace's Equation in Spherical Coordinates | 21 |
| 15 | The Schrödinger Equation in Spherical Coordinates | 22 |
| 16 | Solving Partial Differential Equations by the Technique of Separation of Variables | 22 |
| 17 | The Angular Momentum Operator | 23 |
| 18 | Solving Schrödinger's equation for the Hydrogen Atom | 24 |
| 19 | Quantum Numbers | 24 |
| 20 | Spherical Harmonics | 24 |
| 21 | Legendre Functions and Polynomials | 25 |
| 22 | Laguerre Polynomials | 25 |
| 23 | Matrix Operators | 26 |
| 24 | Eigenvalues | 26 |
| 25 | Differential Operators and Integral Operators | 26 |
| 26 | Linear Operators in Hilbert Space | 26 |
| 27 | What is an Atomic Orbital? | 26 |

| | | |
|-----------|---|-----------|
| 28 | The Atomic Orbitals of Hydrogen | 26 |
| 29 | Pictures and Representations of Orbitals | 26 |
| 30 | Quantum Numbers | 26 |
| 31 | The Pauli Exclusion Principle | 27 |
| 32 | Spin Quantum Number | 27 |
| 33 | Bibliography | 27 |

1 Introduction

Magic and theology are not necessary for an explanation of atomic structure and atomic orbitals. The quantum mechanical structure and behavior of the hydrogen atom can be understood with a reasonable amount of ordinary work (Perhaps this depends upon the readers concept of reasonable and ordinary).

Introductory chemistry books often start with a chapter on atomic orbitals. The information is usually presented magically, pulled out of thin air so to speak, treated as some kind of scientific dogma and revelation. Most students will just memorize this information, as they are trained to do in school. They deal with it like material from a catechism. Elementary school teaches, by its instructional examples, that education is memorization. We do not think it is! So good students may be puzzled and bothered by this lack of explanation of these atomic orbitals, and by the lack of any evidence for them. Some with a mathematical inclination will be bothered by the lack of even an indication of proof. They should at least be told that proof does exist. And if they are adventurous types and well equipped for long distance travel, they should be pointed toward the road to orbital knowledge through the perhaps wolf infested forest of physics and quantum mechanics.

The goal of this document is to show how this magic is not magic at all, but arises from physical principles, mathematics, and logic. This is a difficult goal to reach in a short time. We will not reach it, but perhaps we may see at least a shadow of reality off in the distance, and see the path that must be followed to reach enlightenment. A difficulty in learning science is that learning courses X,Y,Z depends upon knowing courses A, B, C, ..., and vice versa. My optimistic remarks should be tempered by the famous remark:

"I think I can safely say that nobody understands quantum mechanics."
Richard Feynman, in **The Character of Physical Law** (1965).

2 The Bohr Quantum Model of the Hydrogen Atom

Bohr presented his theory of the atom in 1913. His goal was to explain the discrete nature of atomic spectra. A classic spectroscope consists of a heated source that gives off light, a collimating lens to make the light rays from the source approximately parallel, a slit through which the light is viewed, a prism that refracts the light and a telescope that makes visible a distant virtual image of several multiple images of the slit, which are due to the light being composed of various wavelengths. If the wavelengths were continuous with no gaps, one would see shifted images of the slit, all smeared together in the final image. But it turns out that these images are separated. From this we conclude that the light consists of discrete wavelengths rather than a continuous spread of wavelengths. If we look at the image of white light through a prism, or through a diffraction grating, we see the familiar visible spectrum, first written about by Isaac Newton. This spectrum consists of the colors red through violet, with no apparent gaps. But under enough magnification we find that this spectrum is discrete. If a gas such as Hydrogen is heated and viewed through a spectroscope we see certain discrete lines which are unique to Hydrogen. It was discovered that these lines are characteristic of a particular atom, and therefore that atoms could be identified by such images or "spectra."

2.1 The Spectroscope and Collimated Light

The word "collimate" comes from the Latin verb collimare, which originated in a misreading of collineare, "to direct in a straight line." So collimate is directly related to the word collinear. When we view an image of a slit in a spectroscope we want the rays from the slit image to pass through the prism as nearly parallel rays. Then the rays are diffracted by the prism into multiple images corresponding to each wavelength composing the light. These images then appear to come from a distant source, with the slit image rays at slightly different angles for different wavelengths. Viewing these distant

virtual images through a telescope, we get a magnified image of these separated lines. We may collimate the light by using a lens with the slit image near the focus of the lens. Light can also be collimated by passing it through a pair of parallel slits, although in this case the intensity is decreased.

2.2 Atomic Spectra

In 1885 Balmer discovered a formula for the visible part of the hydrogen spectrum. The lines of this Balmer spectrum start at a red line at wavelength $\lambda = 6562.8$ Angstroms and extend to a limit of $\lambda = 3645.6$ Angstroms in the near ultraviolet. An angstrom equals 10^{-10} meters. The velocity of light is approximately $c = 3 \times 10^8$ meters per second. The frequency ν of the first red line is

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^8}{6562.8} = 4.5712 \times 10^{14}$$

Hertz. This is 457.12 Thz, or 457120 Ghz. The visible spectrum ranges from a frequency of about 400 Thz to 800 Thz. The formula that Balmer found was

$$\lambda = 3646 \frac{n^2}{n^2 - 4}$$

where $n = 3, 4, 5, 6, \dots$ Rydberg extended this work to the other hydrogen spectral series, where he worked with the wave number k , which is the reciprocal of the wavelength,

$$k = \frac{1}{\lambda}.$$

For example Balmer's formula can be written as

$$k = R_H(1/2^2 - 1/n^2),$$

where the R_H is the Rydberg constant

$$109677.576 \text{ cm}^{-1}.$$

2.3 A Mass Point in Circular Motion

Let a mass point be specified in polar coordinates (θ, r) . Let the point be constrained to lie on a circle of radius r . Let the polar coordinate unit vectors be

$$\mathbf{u}_r = \cos(\theta)\mathbf{i} + \sin(\theta)\mathbf{j},$$

$$\mathbf{u}_\theta = -\sin(\theta)\mathbf{i} + \cos(\theta)\mathbf{j}.$$

The first vector is perpendicular to the circle and the second is tangent to it. Let the position vector of the point be

$$\mathbf{r} = r\mathbf{u}_r.$$

The velocity is

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} = \frac{dr}{dt}\mathbf{u}_r + r\frac{d\mathbf{u}_r}{dt} = r\frac{d\mathbf{u}_r}{dt},$$

because here r is constant. We have

$$\begin{aligned}\frac{d\mathbf{u}_r}{dt} &= \frac{d\mathbf{u}_r}{d\theta} \frac{d\theta}{dt} \\ &= \mathbf{u}_\theta \frac{d\theta}{dt}.\end{aligned}$$

So

$$\mathbf{v} = r\frac{d\theta}{dt}\mathbf{u}_\theta = r\omega\mathbf{u}_\theta,$$

where ω is the angular velocity. The acceleration is

$$\begin{aligned}\mathbf{a} &= \frac{d\mathbf{v}}{dt} = r\frac{d\omega}{dt}\mathbf{u}_\theta + r\omega\frac{d\mathbf{u}_\theta}{dt} \\ &= r\frac{d\omega}{dt}\mathbf{u}_\theta - r\omega^2\mathbf{u}_r \\ &= r\frac{d\omega}{dt}\mathbf{u}_\theta - \frac{v^2}{r}\mathbf{u}_r,\end{aligned}$$

where $d\omega/dt$ is the angular acceleration, and $v = r\omega$ is the tangential velocity. If the angular acceleration is zero

$$\frac{d\omega}{dt} = 0,$$

then the acceleration is

$$\mathbf{a} = -\frac{v^2}{r}\mathbf{u}_r,$$

which is the centripetal acceleration directed toward the center of the circle. The magnitude is v^2/r .

The momentum of the mass point is

$$\mathbf{p} = m\mathbf{v}.$$

The angular momentum is the moment of momentum about the center of motion

$$\begin{aligned}\mathbf{L} &= \mathbf{r} \times \mathbf{p} \\ &= \mathbf{r} \times m\mathbf{v} \\ &= mr\mathbf{u}_r \times r\omega\mathbf{u}_\theta,\end{aligned}$$

which in this case just has magnitude $mr^2\omega = mrv$ because \mathbf{u}_r and \mathbf{u}_θ are perpendicular unit vectors.

2.4 The Bohr Model of the Atom

Consider a classical electron of charge e orbiting around in a circle of radius r about the atomic nucleus, which has a charge Ze . The magnitude of the Coulomb electrical force exerted by the positive charge of the nucleus on the electron, is given in the rationalized MKS (Meter, Kilogram Second) system of units by

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2},$$

where ϵ_0 is the permittivity of free space and e is the charge of the electron. In the case of the hydrogen atom, the nucleus contains one proton, so $Z = 1$. This attractive force supplies the centripetal force for the circular motion of the electron around the nucleus. So the Coulomb force equals the mass times acceleration of the electrons circular motion

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m \frac{v^2}{r},$$

where m is the mass of the electron. There is a problem with this in classical physics. According to Maxwell's electromagnetic theory, an accelerated charge radiates electromagnetic waves, so the electron will constantly lose energy and spiral into the nucleus.

Bohr made several assumptions that contradicted classical physics. He assumed that there were static orbits where the electron did not radiate

energy. He assumed that electrons in jumping between these orbits lost or gained energy as radiation, where the energy is given by $h\nu$, where h is Planck's constant and ν is the frequency of radiation. He also assumed that the electron has orbital angular momentum given by

$$L = mvr = \frac{nh}{2\pi} = n\hbar,$$

for some integer n . \hbar , pronounced h bar, is by definition Planck's constant divided by 2π . A mystery of Bohr's model is where this assumption came from. It comes to some extent apparently in remarks and calculations in papers published by J. W. Nicholson (John William Nicholson, FRS (1 November 1881, 3 October 1955) was an English mathematician. Based on the results of astronomical spectroscopy of nebula he proposed in 1911 the existence of several yet undiscovered elements.) More on this later.

The energy of the electron in this circular orbit consists of the kinetic energy K and the potential energy V .

The potential energy increases as the electron moves to an orbit of larger radius, because work is done against the attractive force of the nucleus. It is convenient to define the potential of the electron to be zero at infinity. So the work done in taking the electron from an orbit of radius r to infinity is

$$\begin{aligned} W &= \int_r^\infty \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} dr \\ &= \frac{1}{4\pi\epsilon_0} Ze^2 \int_r^\infty \frac{1}{r^2} dr \\ &= \frac{1}{4\pi\epsilon_0} Ze^2 \left[-\frac{1}{r} \right]_r^\infty \\ &= \frac{1}{4\pi\epsilon_0} Ze^2 \left[0 + \frac{1}{r} \right] \\ &= \frac{1}{4\pi\epsilon_0} Ze^2 \frac{1}{r} \\ &= V(\infty) - V(r) = -V(r). \end{aligned}$$

So the potential energy is

$$V(r) = -\frac{1}{4\pi\epsilon_0} Ze^2 \frac{1}{r}.$$

Using the orbit equation above

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m \frac{v^2}{r},$$

the kinetic energy is

$$K = \frac{1}{2}mv^2 = \frac{1}{8\pi\epsilon_0} \frac{Ze^2}{r}.$$

So the total energy in an orbit of radius r is

$$E(r) = K(r) + V(r) = -\frac{1}{8\pi\epsilon_0} Ze^2 \frac{1}{r}.$$

Now we will find the allowed orbits using Bohr's angular momentum quantization condition

$$mvr_n = \frac{nh}{2\pi}.$$

Let us rewrite this as

$$v^2 = \left[\frac{nh}{2\pi mr_n} \right]^2 = \frac{n^2 h^2}{4\pi^2 m^2 r_n^2}.$$

The orbit equation is

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_n^2} = m \frac{v^2}{r_n}.$$

Solving this for v^2 we find

$$v^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{mr_n}.$$

Equating these two expressions for v^2 and solving for r_n we find

$$r_n = n^2 \frac{h^2 \epsilon_0}{\pi m Z e^2}.$$

For the hydrogen atom $Z = 1$ so the n th radius is

$$r_n = n^2 \frac{h^2 \epsilon_0}{\pi m e^2}.$$

For $n = 1$ we have

$$r_1 = a_0 = \frac{h^2 \epsilon_0}{\pi m e^2}.$$

a_0 is called the Bohr radius. Using for the mass of the electron

$$m = 9.1093897 \times 10^{-31} \text{Kg},$$

for the charge of the electron

$$e = 1.6021773 \times 10^{-19} \text{C},$$

and for Plank's constant

$$h = 6.626076 \times 10^{-34} \text{J} \cdot \text{s},$$

$$\pi = 3.14159265358979,$$

$$\epsilon_0 = 8.854187817 \times 10^{-12}$$

we find the Bohr radius to be

$$a_0 = .0529 \text{nm}$$

The radius is quantized. n is called the principal quantum number. Selecting n we compute the radius of the orbit from

$$r_n = n^2 a_0.$$

And then the corresponding energy from

$$E(r_n) = -\frac{1}{8\pi\epsilon_0} Z e^2 \frac{1}{r_n}.$$

The difference in energy corresponding to two quantum states with principle quantum numbers m and n is

$$\Delta E(m, n) = E(r_n) - E(r_m).$$

The frequency of radiation emitted when an electron falls from energy level n to m is

$$\nu = \frac{\Delta E(m, n)}{h}.$$

The wave length is

$$\lambda = \frac{c}{\nu}.$$

It is found that the Balmer spectral series corresponds to $m = 2$, and $n = 3, 4, 5, 6, \dots$. Here is a Python program calculating these wavelengths:

```

# bohr.py calculations with the bohr model of the hydrogen atom
#2/4/2011
#mass of the electron
m = 9.1093897E-31
#charge of the electron
e = 1.6021773E-19
#Plank's constant
h = 6.626076E-34
pi = 3.14159265358979
#Permittivity of free space
e0=8.854187817E-12
#Smallest electron orbit of the hydrogen atom
a0 = h*h*e0/(pi*m*e*e)
#Speed of light
c=2.99792458e8
#nanometer
nm=1.0e-9
print "Bohr radius=" , a0
#
#Energy of the nth Bohr orbit
def energy(n):
    #mass of the electron
    m = 9.1093897E-31
    #charge of the electron
    e = 1.6021773E-19
    #Plank's constant
    h = 6.626076E-34
    pi = 3.14159265358979
    e0=8.854187817E-12
    a0 = h*h*e0/(pi*m*e*e)
    r=n*n*a0
    f=-e*e/(8.*pi*e0*r)
    return f
#
#Difference of energy between the n1 Bohr orbit and the n2 Bohr orbit
def de(n1,n2):
    d=energy(n2)-energy(n1)
    return d
n=1 print "n=",n print "energy(n)=",energy(n), "Joules" print
"=",energy(n)/e," electron volts" n=2 print "n=",n print
"energy(n)=",energy(n)/e," electron volts" n=1 m=2 print " n=",n,"
m=",m print "Energy difference=",de(n,m)/e, "electron volts" print
"=",de(n,m), "joules" nu=de(n,m)/h print "Frequency=",nu, "Hertz"
print "Wavelength=", (c/nu)/nm, "nm" # n=2 m=3 print " n=",n,"
m=",m print "Energy difference=",de(n,m)/e, "electron volts" print
"=",de(n,m), "joules" nu=de(n,m)/h print "Frequency=",nu, "Hertz"
print "Wavelength=", (c/nu)/nm, "nm" # The Balmer Spectrum n=2
k=20 print "Balmer Spectrum, n=",n for m in range(3,k+1):
    delta=de(n,m)
    nu=delta/h
    wavelength=(c/nu)/nm
    print "m=",m, " Wavelength=",wavelength, " nm"
print "Balmer Limit"
delta=-energy(n)
nu=delta/h
wavelength=(c/nu)/nm

```

```
print "m= infinity"," Wavelength=",wavelength," nm"
```

We run the program like so:

```
python bohr.py
```

Here is the output:

```
Bohr radius= 5.2917735715e-11 n= 1 energy(n)= -2.1798735699e-18
Joules = -13.605695012 electron volts n= 2 energy(n)=
-3.40142375301 electron volts
n= 1 m= 2
Energy difference= 10.204271259 electron volts = 1.63490517742e-18
joules Frequency= 2.46738066002e+15 Hertz Wavelength=
121.502313306 nm
n= 2 m= 3
Energy difference= 1.88967986278 electron volts =
3.02760218042e-19 joules Frequency= 4.56922344449e+14 Hertz
Wavelength= 656.112491854 nm Balmer Spectrum, n= 2 m= 3
Wavelength= 656.112491854 nm m= 4 Wavelength= 486.009253225 nm
m= 5 Wavelength= 433.936833237 nm m= 6 Wavelength=
410.070307409 nm m= 7 Wavelength= 396.9075568 nm m= 8
Wavelength= 388.80740258 nm m= 9 Wavelength= 383.442365369 nm
m= 10 Wavelength= 379.694729082 nm m= 11 Wavelength=
376.968715643 nm m= 12 Wavelength= 374.921423916 nm m= 13
Wavelength= 373.343471796 nm m= 14 Wavelength= 372.1008345 nm
m= 15 Wavelength= 371.104350596 nm m= 16 Wavelength=
370.292764362 nm m= 17 Wavelength= 369.622826795 nm m= 18
Wavelength= 369.063276668 nm m= 19 Wavelength= 368.59105129 nm
m= 20 Wavelength= 368.188828201 nm Balmer Limit m= infinity
Wavelength= 364.506939919 nm
```

3 Classical Mechanics

3.1 Harmonic Oscillators

The harmonic oscillator is a linear system that vibrates in harmonic sinusoidal waves. Such a system displaced by distance x experiences a restoring force of the form $F = -kx$. An example of this is a simple mass spring system, where two masses are connected by a spring, and such that when displaced from equilibrium by distance x , experience a restoring force $F = -kx$,

where k is the spring constant. Considering the acceleration of the masses, we obtain a differential equation of the form

$$m \frac{d^2x}{dt^2} + kx = 0,$$

where for simplicity we consider a single mass m being displaced with respect to a fixed body. We find that the motion is harmonic, that is, it is a sin wave, with frequency determined by the mass m and the elastic constant k . Two masses connected by a spring will behave in the same way with respect to a coordinate system located at their center of mass. The state of such a system is characterized by two variables, x_1 and x_2 , namely the coordinates of the two masses, and the associated velocities. The total energy of such a system is the instantaneous sum of the kinetic energies, and the elastic potential energy stored in the spring. These energies are quadratic functions of the positions and the velocities. The system is said to have two degrees of freedom. If we had a system of n masses coupled by elastic forces, the system would have n degrees of freedom. It is often possible to introduce normal coordinates for such a system so that the system is uncoupled, so is characterized by a set of n uncoupled differential equations, where each normal coordinate appears in a single differential equation. This may be done by computing matrix eigenvalues and eigenvectors.

The sum of the kinetic and potential energies of a classical system is called the Hamiltonian H of the system.

3.2 The Equipartition of Energy Theorem

Using the kinetic theory of gases, treating the molecules of the gas as simple independent elastic masses, one can derive the ideal gas law

$$PV = nRT,$$

where P is the pressure, V is the gas volume, n is the number of moles, R is the gas constant, and T is the absolute temperature.

By definition we have

$$R = N_A k,$$

where $N_A = 6.03 \times 10^{23}$ is Avogadro's number, the number of molecules in a mole, and k is Boltzman's constant. Boltzman's constant k is defined by the ideal gas law for a monotonic gas.

One can compute that one mole of a monatomic ideal gas, consisting of N_A molecules, has energy

$$E = N_A \frac{3}{2} kT.$$

Now such a gas has $3N_A$ degrees of freedom, since each molecule is specified by the three coordinates of its center of mass. Hence one concludes that each individual molecule has average energy

$$\frac{1}{2} kT,$$

per degree of freedom.

The Equipartition of Energy Theorem says that this is universal: Any system in thermal equilibrium has average energy

$$\frac{1}{2} kT$$

per degree of freedom.

In statistical mechanics one can prove this, provided that the Hamiltonian is a quadratic function of the generalized coordinates and velocities, and that the system is able to exchange energies between modes. This is a classical result only approximately correct because of quantum effects.

3.3 Degrees of Freedom of a Vibrating String

Consider an approximation of the vibration of a string consisting of a system of n masses connected together by small elastic forces. Because we can increase the degree of approximation by increasing the number of masses, the string must have an infinite number of degrees of freedom. These modes are the string harmonics.

4 Problems With Classical Physics

4.1 Blackbody Radiation

Consider electromagnetic waves in thermal equilibrium in a box. Using the equipartition theorem and assigning energy

$$\frac{1}{2} kT$$

to each mode of vibration, we get good agreement with the measured intensity of the radiation in the box for low temperatures. This intensity can be measured by having a small hole in the box where radiation can escape. For low temperatures the measured values agree with the classical theory, but for high temperatures the measured intensities of radiation coming out of the little hole does not correspond to the classical theoretical value. The box is a black body because radiation entering the box has little chance of escaping back out of the hole, thus radiation is completely absorbed, so the body is black, no radiation is reflected.

Planck replaced an integral over a continuum of modes, by a summation over a discrete countable set of frequencies. He assumed that modes of radiation mode could only occur at energies certain multiples of a constant h , hereafter called Planck's constant. So he was able to construct a theory that agreed with experiment at high temperatures also. This suggested that there was a problem with classical physics.

4.2 The Photoelectric Effect

The photoelectric effect is the emission of electrons from a metal surface when the surface is exposed to light. The photoelectric effect was first noticed by Heinrich Hertz in 1887, in connection with his work on electromagnetic radiation (See Kenneth Krane p70). James Clerk Maxwell had presented his mathematical theory of electromagnetism in the 1880's (See James Clerk Maxwell **A Treatise on Electricity and Magnetism** two volume, Dover reprint) In this work Maxwell had shown that his famous Maxwell equations led to a wave equation for electromagnetic waves that are propagated at the speed of light c , where

$$c = \frac{1}{\sqrt{\epsilon_0 \mu_0}},$$

where the speed is determined by the permittivity of free space ϵ_0 , and the permeability μ_0 of free space. Hertz conducted an experiment where he created a spark between two spheres using an oscillator. This first spark generated a second spark between two spheres located some distance from the original spark. This demonstrated the existence of Maxwell's electromagnetic waves, which travelled from the first spark to generate the second. Hertz noticed that the second spark occurred less easily when the light from the first spark was shaded from the second set of spheres. He concluded that the light from the first spark was ionizing the air between the second set of

spheres making the spark generation easier. Subsequent researchers were able to determine that the light was ejecting electrons from the metal surfaces, thus ionizing the air gap.

In the photoelectric effect experiments it was later shown that the energy of the ejected electrons depended only on the frequency of light, not on the intensity. Classical physics predicted that the greater the intensity of the light, the more energy would be given to the electrons. This was quite puzzling to classical physicists.

Einstein constructed a nonclassical theory where electrons are ejected from a charged plate by ultraviolet light, but only in discrete packets of energy where

$$E = h\nu$$

using Plank's new constant h . Einstein showed that this was a non-classical quantum effect.

4.3 De Broglie Wave-Particle Duality

The photoelectric effect showed that light is both a particle and a wave. De Broglie extended this to all particles. This also gave some explanation for the angular momentum quantum numbers of Bohr and suggested Heisenberg's uncertainty principle. De Broglie's idea was that electrons are standing waves and an integral number of them fit in some sense around the Bohr orbits. See the recent translation of his PhD thesis in the bibliography.

So suppose λ is the wavelength of these electron waves and r is a Bohr radius. Then De Broglie said that

$$\frac{2\pi r}{\lambda} = n,$$

where n is some integer. Multiplying both sides by h

$$\frac{hr}{\lambda} = \frac{nh}{2\pi} = n\hbar.$$

Bohr's orbit condition says that the angular momentum of the rotating electron is equal to some integer multiple of \hbar ,

$$mvr = pr = \frac{nh}{2\pi} = n\hbar.$$

This follows from De Broglie's equation if we set

$$p = \frac{h}{\lambda}.$$

De Broglie suggested that this relationship holds for all particles and so all particles have a wave nature.

See also the Wilson-Sommerfeld quantization rules given in Eisberg.

4.4 De Broglie and the Hydrogen Spectra

Bohr constructed a planetary theory of hydrogen structure with electrons circling the nucleus in orbits of radii determined by energy changes give with Plank's constant. De Broglie speculated that the orbits are such that the electrons are waves that fit in integral multiples of the wave length and that not only are electrons waves but that all particles have wave properties. Schrödinger thought that if this were so then there must be a wave equation governing the motion of the particles. And he proceeded to construct such an equation based on various requirements of both optics and mechanics. This new kind of mechanics was called Quantum mechanics.

http://en.wikipedia.org/wiki/Hydrogen_spectral_series

5 Normal Coordinates and Degrees of Freedom

See my document on Mechanics.

<http://www.stem2.org/je/mechanics.pdf>

6 Specific Heat of Molecules

See my document on Statistical mechanics.

<http://www.stem2.org/je/statmech.pdf>

7 The Vibrating String, and the One Dimensional Wave Equation

The theory of the vibrating string and its harmonics might lead to an understanding of the modes of black body radiation. Plank's solution of the problem of Black Body radiation and the introduction of the quantum of energy and Plank's constant provided the first step towards Quantum Mechanics.

<http://www.stem2.org/je/vibratingstring.pdf>

8 The Ultraviolet Catastrophe: Plank's Solution.

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11 The Phase Velocity and Group Velocity of Waves

12 The Schrödinger Equation

For a single particle of mass m experiencing a potential energy $V(\mathbf{r})$, the time dependent Schrödinger Equation is

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H} \psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t) + V(\mathbf{r}) \psi(\mathbf{r}, t),$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

is the Hamiltonian operator consisting of the kinetic energy operator

$$-\frac{\hbar^2}{2m} \nabla^2,$$

and the potential energy

$$V(\mathbf{r}).$$

∇^2 is the Laplacian operator. The square of the complex magnitude of $\psi(\mathbf{r}, t)$ is the probability density function of the probability for finding the particle at position \mathbf{r} at time t .

The time invariant version of the Schrödinger Equation for a bound particle of energy E is

$$E\psi(r) = -\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r).$$

E is an eigenvalue of the Hamiltonian operator. This solution is like a standing wave for the particle in a state having energy E . This interpretation of the wave function ψ is due to Max Born.

13 Derivation of the Schrödinger Equation

Schrödinger became aware of De Broglie's hypothesis that particles are waves determined by the momentum of the particle, which was published in De Broglie's PhD thesis of 1924. De Broglie's idea was to extend the idea that photons are both waves and particles to all particles, specifically to electrons found in atoms. His idea was that the electrons are some kind of standing waves surrounding the nucleus. Schrödinger thought this over and decided that if particles are waves they must have an associated wave equation. He retired to the mountains with a lover to work on this problem between his love sessions. By this time Arnold Sommerfeld had extended Bohr's quantum theory by adding some relativistic modifications. So Schrödinger first tried to find a relativistic wave equation, but he ran into difficulties and gave up for a short time. But shortly decided to work on a more classical approach. He looked at the case of a complex plane wave of the form

$$\psi(x, t) = A \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t)),$$

propagated in the direction \mathbf{k} , where

$$\mathbf{k} = k_x \mathbf{u}_x + k_y \mathbf{u}_y + k_z \mathbf{u}_z,$$

and

$$\mathbf{r} = x\mathbf{u}_x + y\mathbf{u}_y + z\mathbf{u}_z.$$

A general wave can be obtained as an integral of such plane waves.

The total energy of the particle equals the classical expression

$$E = T + V = \frac{1}{2}mv^2 + V = \frac{(mv)^2}{2m} + V = \frac{(p)^2}{2m} + V,$$

where p is the momentum of the particle. He used Einstein's photon energy relation

$$E = h\nu = \hbar\omega$$

and De Broglie's relation defining the wavelength in terms of the momentum p

$$p = \frac{h}{\lambda} = \hbar k,$$

where k is the wave number. Extending this to three dimensions

$$\mathbf{p} = \hbar\mathbf{k}.$$

Let us differentiate the plane wave equation,

$$\psi(x, t) = A \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t))$$

with respect to time. We get

$$\frac{\partial\psi}{\partial t} = -i\omega\psi = -i\frac{E}{\hbar}\psi$$

Or

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi.$$

Differentiating with respect x we get

$$\frac{\partial}{\partial x}\psi = ik_x\psi,$$

and differentiating again

$$\frac{\partial^2}{\partial x^2}\psi = -k_x^2\psi = -\left(\frac{p_x}{\hbar}\right)^2\psi.$$

Then

$$-\hbar^2 \frac{\partial^2}{\partial x^2} \psi = -k_x^2 \psi = p_x^2 \psi.$$

Continuing with y and z we get

$$p^2 \psi = -\hbar^2 \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi.$$

Dividing by $2m$ we get the kinetic energy

$$T\psi = \frac{p^2}{2m} \psi = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi.$$

So we have by substituting in the energy equation

$$E = T + V,$$

$$\begin{aligned} i\hbar \frac{\partial \psi}{\partial t} &= E\psi = (T + V)\psi \\ &= \left(-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V \right) \psi. \\ &= \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi. \end{aligned}$$

Or

$$i\hbar \frac{\partial \psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi.$$

which is Schrödinger's equation. When the total energy E is constant we get Schrödinger's time independent equation

$$E\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi.$$

14 Laplace's Equation in Spherical Coordinates

The Laplacian in spherical coordinates is

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

See Emery **Vector Analysis**, where the labelling of the angles is switched and written in the common form used in mathematics.

15 The Schrödinger Equation in Spherical Coordinates

To solve the Schrödinger equation for the hydrogen atom we write the time invariant equation using spherical coordinates (r, θ, ϕ) . The ordering of these coordinates is important, because the coordinate system must be right handed. Here θ is the angle from the z axis to the point vector. Consider a point $\mathbf{r} = (x, y, z)$. The coordinate r is the length of the vector \mathbf{r}

$$r = \sqrt{x^2 + y^2 + z^2}$$

the coordinate θ is the polar angle from the z axis to \mathbf{r} and the coordinate ϕ is the azimuthal angle in the xy plane from the x axis to the projection of \mathbf{r} to the xy plane. Thus

$$x = r \sin(\theta) \cos(\phi)$$

$$y = r \sin(\theta) \sin(\phi)$$

$$z = r \cos(\theta)$$

The Laplacian in spherical coordinates is

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

So the Schrödinger equation becomes

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

16 Solving Partial Differential Equations by the Technique of Separation of Variables

One of the most simple partial differential equations is the one dimensional heat equation, whose solution gives the temperature distribution in a one dimensional rod. We looked at this equation in the document on Joseph

Fourier and on the creation of Fourier Series. This gives an introduction of separation of variables and the conversion of a partial differential equation into a set of ordinary differential equations that usually take the form of eigenvalue problems. Here is a link to the Fourier paper:

<http://www.stem2.org/je/fourier.pdf>

The Schrödinger equation is much more complicated than the one dimensional heat equation, but also yields to separation of variables, and the restrictions on the solutions of the resulting ordinary differential equations leads to the quantum numbers.

17 The Angular Momentum Operator

A reference for this section is chapter 9 of Norwood. Let E be the energy of a particle in a central force field.

$$E = \frac{p^2}{2m} + V(r) = \frac{p_p^2}{2m} + \frac{p_o^2}{2m} + V(r),$$

where p_p is the momentum magnitude in the direction parallel to \mathbf{r} , p_o is the momentum magnitude in the direction orthogonal to \mathbf{r} , and V is the potential energy. The angular momentum is

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

so the magnitude is

$$\|\mathbf{L}\| = rp_o$$

So in spherical coordinates (r, θ, ϕ) p_p corresponds to motion in the radial direction, and p_o to motion in the θ and ϕ directions. So considering that the magnitude of \mathbf{L} is rp_o , we write

$$E = \frac{p_p^2}{2m} + \frac{L^2}{2mr^2} + V(r).$$

Schrödinger's equation in spherical coordinates is

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

So we may identify the angular momentum operator with

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right]$$

Then we may write Schrödinger's equation as

$$-\frac{\hbar^2}{2m} \left[\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} \right] \psi + \frac{\hat{L}^2}{2mr^2} \psi + V(r, \theta, \phi) \psi = E \psi$$

18 Solving Schrödinger's equation for the Hydrogen Atom

We write the wave function as

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

We separate the variables and arrive at first a radial differential equation in r , which gives eigenvalues for the energy and involves the Laguerre polynomials, and second a partial differential equation in θ and ϕ and the angular momentum operator. This equation is further separated into two ordinary differential equations, one of which involves the Legendre functions, and the other has complex exponential solutions. These differential equations lead to the angular momentum quantum numbers and to the magnetic quantum numbers. Details later.

19 Quantum Numbers

The quantum numbers are (n, ℓ, m_ℓ) , where
 n is the principal quantum number $n = 1, 2, 3, \dots$ defining the energy,
 ℓ is the angular momentum quantum number $\ell = 0, 1, 2, \dots, (n - 1)$
 m_ℓ is the magnetic quantum number $m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$

20 Spherical Harmonics

The Spherical Harmonics appear as solutions of Laplace's equation in spherical coordinates. The Laplace operator appears in the Schrödinger equation.

21 Legendre Functions and Polynomials

The Legendre equation appears in the solution of the azimuthal part of the solution of the hydrogen atom.

22 Laguerre Polynomials

The Laguerre equation appears in the solution of the radial part of the solution of the hydrogen atom. The Laguerre polynomials, named after Edmond Laguerre (1834 to 1886), are solutions of Laguerre's equation:

$$x y'' + (1 - x) y' + n y = 0.$$

This equation has nonsingular solutions only if n is a non-negative integer. These polynomials, usually denoted by L_0, L_1, \dots are a polynomial sequence, which may be defined by the Rodrigues formula

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^n).$$

They are orthogonal polynomials with respect to the inner product given by

$$\langle f, g \rangle = \int_0^\infty f(x)g(x)e^{-x} dx.$$

The Laguerre polynomials arise in quantum mechanics, in the radial part of the solution of the Schrödinger equation for a one-electron atom. Physicists often use a definition for the Laguerre polynomials that is larger, by a factor of $n!$, than the definition used here.

Here are a few of the Laguerre polynomials:

$$L_0(x) = 1$$

$$L_1(x) = 1 - x$$

$$L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$$

$$L_3(x) = \frac{1}{6}(-x^3 + 9x^2 - 18x + 2)$$

$$L_4(x) = \frac{1}{24}(x^4 - 16x^3 + 72x^2 - 96x + 24)$$

23 Matrix Operators

Matrices can be identified with linear operators in some vector spaces. An alternate version to the wave mechanics version of quantum mechanics is matrix mechanics.

24 Eigenvalues

The eigenvalue λ of a linear operator L is a number such that

$$L\phi = \lambda\phi,$$

where ϕ is a vector in some vector space, which may be a function in some space of functions. ϕ is called an eigenfunction.

25 Differential Operators and Integral Operators

26 Linear Operators in Hilbert Space

27 What is an Atomic Orbital?

Reference: Wikipedia Atomic Orbitals.

28 The Atomic Orbitals of Hydrogen

29 Pictures and Representations of Orbitals

<http://www.orbitals.com/orb/ov.htm>

30 Quantum Numbers

<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/quantum.html>

31 The Pauli Exclusion Principle

It is found that no two electrons can be in the same quantum state and hence occupy same quantum numbers.

32 Spin Quantum Number

In order to explain the fine structure of the hydrogen atom one is led to the idea that the angular momentum consists of more than just the orbital momentum of the electron in the Bohr atom. It was first proposed that the nucleus was perhaps the source of this alteration in momentum, however this was found to not be possible. So the electron is assigned an intrinsic momentum that can take on one of two values. It is called spin because a simple minded idea is to assign the addition of angular momentum to the conception of the electron being some small mass spinning on its axis. This however is incorrect. The electron spin is a relativistic effect not part of the Schrödinger equation analysis.

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