HANDOUT SET

GENERAL CHEMISTRY I

Periodic Table of the Elements

	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 **H** 1.00794																	2 **He** 4.00262
2	3 **Li** 6.941	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.179
3	11 **Na** 22.9898	12 **Mg** 24.305											13 **Al** 26.98154	14 **Si** 28.0855	15 **P** 30.97376	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9380	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.69	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.59	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.9055	46 **Pd** 106.42	47 **Ag** 107.8682	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.710	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.9045	54 **Xe** 131.29
6	55 **Cs** 132.9054	56 **Ba** 137.34	57 **La*** 138.91	72 **Hf** 178.49	73 **Ta** 180.9479	74 **W** 183.85	75 **Re** 186.207	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.9665	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.9804	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** 226.0254	89 **Ac**** 227.0278	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (264)	108 **Hs** (265)	109 **Mt** (266)	110 (270)	111 (272)	112 ***** (277)						

*Lanthanides	58 **Ce** 140.12	59 **Pr** 140.9077	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.9342	70 **Yb** 173.04	71 **Lu** 174.967

**Actinides	90 **Th** 232.038	91 **Pa** 231.0659	92 **U** 238.0289	93 **Np** 237.0482	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)

Mass numbers in parenthesis are the mass numbers of the most stable isotopes. As of 1997 elements 110-112 have not been named.

***Peter Armbruster and Sigurd Hofman synthesized a single atom at the Heavy-Ion Research Center in Darmstadt, Germany in 1996. The atom survived for 280 μs after which it decayed to element 110 by loss of an α-particle

Chapter 8

Quantum Theory

ATOMIC STRUCTURE

CHAPTER 8

INTRODUCTION

Knowledge of the electronic structure of the atom explains many observed phenomena, ranging from the emission of light from a glowing gas to why metals form cations and nonmetals form anions. The development of quantum mechanics ushered in a new branch of physics and chemistry and the quantum mechanical model of the atom remains the model in use today. The current model has its roots in spectroscopy; the study of electromagnetic radiation and its interaction with matter. Using electromagnetic radiation, it is possible to probe the microscopic structure of atoms and molecules. Possibly the most unique property of electromagnetic radiation, however, is its property of behaving like a wave and a particle simultaneously - known as wave-particle duality. With this seemingly paradoxical observation of wave-particle duality, it is possible to explain both the line spectrum observed for excited gas-phase atoms and the photoelectric effect, as well as many other observed phenomena. An essential part of understanding many of the subtle aspects of chemistry require a basic understanding of light and quantum mechanics.

GOALS

1. It is important to be able to relate wavelength, frequency, velocity, and energy of light. Additionally, knowledge of the region from the complete electromagnetic radiation spectrum a particular wavelength is in is very important.
2. You must be able to describe the difference between a line spectrum and a continuous spectrum and be able to explain the source of the line spectrum of a gas-phase atom.
3. You should be able to trace the history of the model of the atom up to the quantum mechanical model in use today. You should be also be able to discuss the strengths and weaknesses of each model.
4. Evidence exists that particles, such as electrons, exhibit wave-like characteristics, a hypothesis proposed by de Broglie. You should be able to calculate the apparent wavelength of a moving particle using de Broglie relationship.

5 Bohr's model of the atom placed the electrons in planetary orbits around the nucleus. Bohr's model is very compelling since it is quite intuitive and calculations with the Rydberg equation yield nearly perfect correlation between experiment and theory for the hydrogen atom line spectrum. It is important to know when the model breaks down (any atom except hydrogen) and what this model led to.

6. The quantum mechanical model of the atom describes the electronic structure of the atom in terms of probability regions around the nucleus *(orbitals).* These probability regions are described by wave-functions which have quantized solutions called the quantum numbers (n, l, m_1). It is essential that you be able to assign the quantum numbers to each electron in an atom.

7 Just as in Bohr's model, the quantum mechanical model places electrons in progressively higher energy levels defined by the orbital's quantum numbers. You must be able to draw the atomic orbital energy level diagram through at least the 5*p* subshells. You must also be able to properly place the electrons in the orbital energy diagram (using Aufbau, Pauli exclusion, and Hund's rule) and write the correct electron configuration.

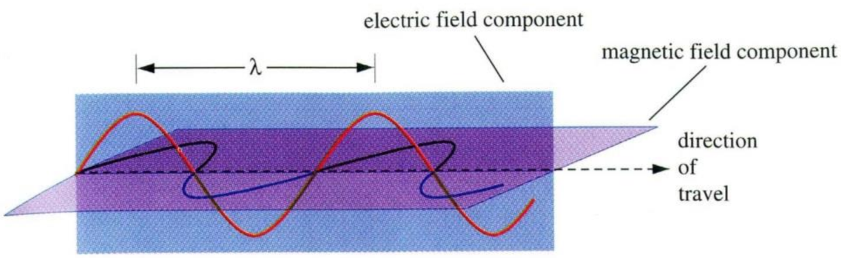
8. You should be able to correctly identify whether an atom is in an excited state based on the electron configuration or the atomic energy level diagram.

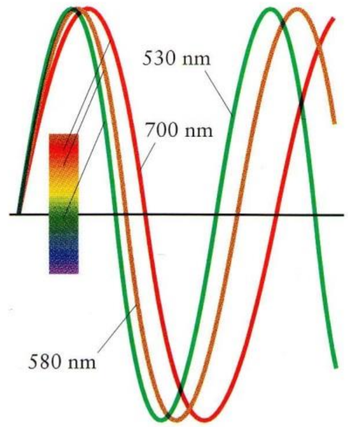
DEFINITIONS

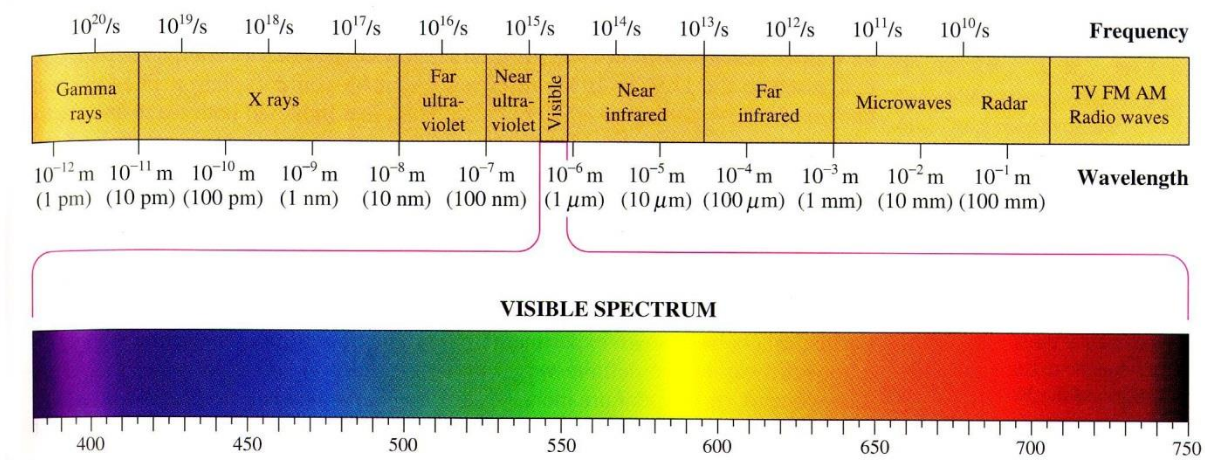
You should have a working knowledge of at least these terms and any others used in lecture

Light
Electromagnetic radiation
Angular-momentum quantum number
Spectrum
Line spectrum
Continuum
Continuous spectrum
Wavelength
Frequency
Speed of light
Hertz
Energy
Planck's constant
Photoelectric effect
Quantum
Photon
Wave
Rydberg's equation
Wave-particle duality
Ground state
Excited state
Orbit
Orbital
Principal quantum number
de Broglie relationship
Heisenberg uncertainty quantum number
Magnetic quantum number
Spin quantum number *n, 1*, m_l, m_s
s, p, d, f
Subshell
Aufbau
Pauli exclusion
Hund's rule
Degenerate energy
Atomic orbital energy-level diagram
Electron configuration

ELECTROMAGNETIC RADIATION







MEASURED QUANTIZED EVENT IN EACH REGION

γ-ray

x-ray

UV

Visible

IR

Microwave

Radiowave

Some Important Equations and Constants

Constants

$c = 3.00 \times 10^{8}$ m/s

$h = 6.63 \times 10^{-34}$ J·s

$\sigma = 5.67 \times 10^{-8}$ $\frac{W}{m^2 \cdot K^4}$

Equations

$c = \lambda \nu$

Planck's Law: $E = h\nu = \frac{hc}{\lambda}$

de Broglie's Law: $\lambda = \frac{h}{m\mathrm{v}}$ [v (velocity) not ν (frequency)]

Wien's Law: $\lambda_{max} = \frac{0.0029}{T}$

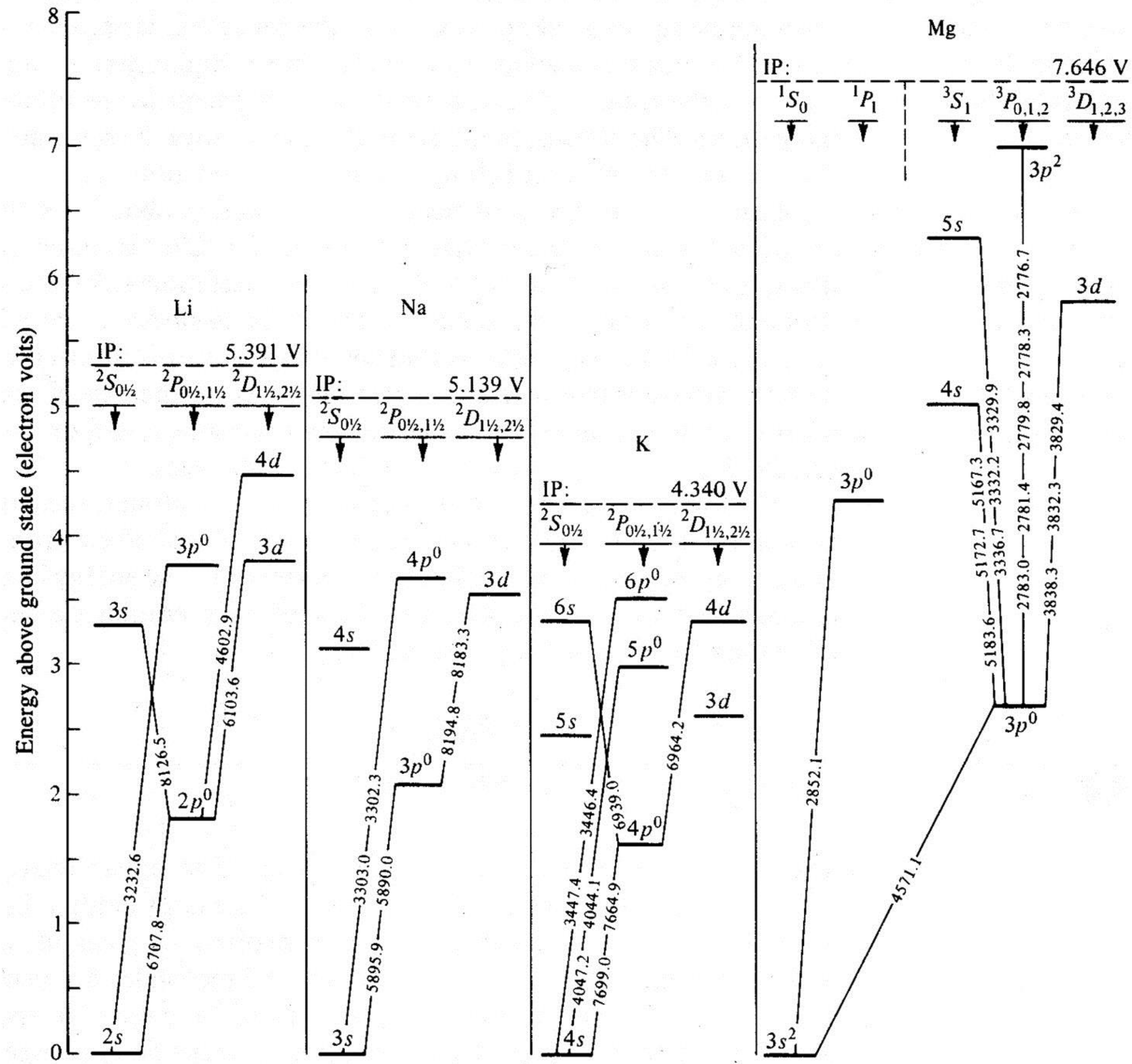
Stephan-Boltzmann Law: $F = \sigma T^4$

Inverse-Square Law of Light: $F = \frac{L}{4\pi d^2}$

Einstein's Energy/Mass Relationship: $E = mc^2$

Schwarzschild Radius: $R = \frac{2GM}{c^2}$

Atomic term diagram for Li, Na, K, and Mg. Wavelengths are given in angstroms. (IP = ionization potential in eV.)



Atomic Structure I: Electromagnetic Radiation

1. What are the colors of the visible light spectrum in order from short to long wavelength? What is the approximate wavelength of each color?

2. If the thermonuclear reactor in the center of our sun emits an x-ray photon, how fast will that photon be travelling?

3. What is the wavelength of a 650 nm photon in meters?

4. The "oldies" FM radio station, KRTH, transmits on 101.1 MHz. What is the wavelength of the radiation (in meters)?

5. The Sun emits the highest intensity of light at about 520 nm. What is the color and the energy (in J) of this radiation?

6. A particular star emits light with a λ_{max} of 485 nm. What is the surface temperature of the star? (Stellar emission can be considered to be blackbody.)

7. What is the kinetic energy of the electrons ejected from silver metal when it is struck by light with a wavelength of 200 nm?

Work Functions for Photoelectric Effect

Element	**Work Function (eV)**	**Work Function (J)**
Aluminum	4.08	6.54×10^{-19}
Beryllium	5.0	8.01×10^{-19}
Cadmium	4.07	6.52×10^{-19}
Calcium	2.9	4.65×10^{-19}
Carbon	4.81	7.71×10^{-19}
Cesium	2.1	3.36×10^{-19}
Cobalt	5.0	8.01×10^{-19}
Copper	4.7	7.53×10^{-19}
Gold	5.1	8.17×10^{-19}
Iron	4.5	7.21×10^{-19}
Lead	4.14	6.63×10^{-19}
Magnesium	3.68	5.90×10^{-19}
Mercury	4.5	7.21×10^{-19}
Nickel	5.01	8.03×10^{-19}
Niobium	4.3	6.89×10^{-19}
Potassium	2.3	3.68×10^{-19}
Platinum	6.35	1.02×10^{-18}
Selenium	5.11	8.19×10^{-19}
Silver	4.73	7.58×10^{-19}
Sodium	2.28	3.65×10^{-19}
Uranium	3.6	5.77×10^{-19}
Zinc	4.3	6.89×10^{-19}

Adapted from *CRC Handbook of Chemistry and Physics*.

8. The technique of photoelectron spectroscopy (an instrumental method that measures the kinetic energy of electrons produced photoelectrically from metallic targets) was used to identify the metals in an alloy. The electromagnetic radiation source was the Mg K_α x-ray emission at 0.9898 nm. The spectrum showed two photoelectron peaks; the first of which was at 2.0008×10^{-16} J and the other at 2.0014×10^{-16} J. The relative ratios of the two photoelectron emissions was 14:8. What is the composition of the alloy?

Atomic Structure II: Wave-Particle Duality

1. Using de Broglie's equation, calculate the apparent wavelength of an electron with a velocity of 40.2 m/s. ($m_{electron}$ = 9.11 x 10^{-28} g)

2. What is the "wavelength" of a baseball (0.181 kg) pitched at this speed? (FYI, 40.2 m/s = ~90 mi/hr)

3. What prevents us from actually measuring the wavelength calculated in problem 2?

4. Just for fun… What is the velocity of a rubidium atom when its de Broglie wavelength is equal to its atomic radius? The atomic radius of Rb is 248 pm. Approximately what temperature is this? Incidentally, this is called the Bose-Einstein condensate.

Atomic Structure III: Quantum Mechanics

1. Consider a hydrogen atom which has been electrically excited into emission. What is the energy of the light emitted when the electron falls from the $n = 4$ state to the $n = 2$ state?

2. What is the wavelength of the light produced in question 1? What is the color of the photon?

3. What region of the electromagnetic radiation spectrum is a photon produced by hydrogen atom in which the electron falls from $n = 7$ to $n = 6$?

4. The ionization energy of hydrogen atom is 2.179×10^{-18} J. When an electron recombines with an ionized hydrogen, it emits a continuum of radiation rather than a line spectrum. Explain this observation.

5. What is the wavelength of light emitted by a hydrogen atom when an electron at the ionization potential (*i.e.*, the electron is just beyond the $n = 7$ energy level) recombines with the hydrogen $n = 7$ energy level?

6. Explain the observation that, in the solar blackbody spectrum, dark lines are seen at exactly the same wavelengths as the emission lines for hydrogen.

7. What are the allowed quantum numbers for a ground-state electron in the outer-most orbital of magnesium metal?

9. Write the full electron configuration for ground-state

   nitrogen atom

   vanadium atom

   chromium atom

10. Write the abbreviated electron configuration for ground-state

    oxygen atom

    zirconium atom

    copper atom

11. What are one possible set of quantum numbers for an excited-state electron of magnesium metal in the which the electron has been promoted to a *d*-orbital in the fifth principle quantum shell?

12. When gaseous lithium metal is excited to emission in a flame, it produces a striking and beautiful red emission. One of the emission lines of lithium is 610.4 nm and is due to the excited state electron falling from a 3*d* orbital to a 2*p* orbital.

    What is the energy difference between the lithium 3*d* and 2*p* orbital?

    After the transition, is lithium at ground state?

A Review of That Weird Thing Called Light

Light has unique properties which are often nonintuitive. For example, the speed of light is a constant 3.00×10^8 m/s regardless of its wavelength, λ, or frequency, ν.

$$c = \lambda\nu$$

This is not true for other forms of energy, such as sound energy. Also, light behaves simultaneously as a wave or a particle (a photon), a characteristic shared by quantum-sized particles but not a much for macroscopic particles or objects.

1. Violet light has a wavelength of about 410 nm. What is the frequency of this light?

2. It is very difficult to transmit electromagnetic radiation appreciable distances underwater. The U.S. Nave has developed a system for communicating with submerged submarines using very long wavelengths. The system uses radiowaves with a frequency of 76 Hz. What is the wavelength of this radiation? (The Hz is the unit of frequency and is equivalent to /s or s^{-1}. It is an honorific given to Heinrich Hertz[1])

As postulated by Max Planck[2] and rigorously verified, the energy possessed by a photon is independent of its intensity and dependent upon its frequency.

$$E = h\nu$$

where E is the energy of the photon in J, ν is the frequency of oscillating energy in the photon, and h is Planck's constant, 6.626×10^{-34} J·s

3. The most prominent line in the line spectrum of aluminum is found at 396.15 nm. What is the energy of one photon of light with this wavelength?

[1] Heinrich Rudolf Hertz (1857-1894)
[2] Max Karl Ernst Ludwig Planck (1858-1947)

4. What is the energy of the light in problem 3 in kJ/mol?

5. The most prominent line in the spectrum of magnesium is 285.2 nm. Other prominent lines are found at 383.8 and 518.4 nm. In what region of the electromagnetic radiation spectrum is each line? Which line is the most energetic?

6. Referring to problem 5, would the most energetic line have sufficient energy to initiate a chemical reaction by breaking a chemical bond which has a bond strength of 405 kJ/mol?

7. The amount of power being produced by the Sun is 1370 W/m^2. Assume for this problem that the Sun produces only 525 nm light. What is the approximate number of photons striking 1 m^2 of illuminated Earth surface per second? (A watt, W, is a J/s)

Albert Einstein[3] earned the 1921 Nobel Prize in physics for the discovery of the law of the photoelectric effect – the concept which definitively validates the particle nature of light.

$$KE_{e^-} = h\nu - \Phi_b$$

8. A particular metal has a binding energy of 6.7×10^{-19} J/atom. What will be the kinetic energy of the photoelectrons produced if the metal is illuminated by x-ray radiation with a wavelength of 1.1 nm?

9. To cause a metallic cesium surface to eject an electron, a photon with a minimum energy of 200(±10) kJ/mol is required. What is the longest possible wavelength of light that will cause cesium metal to lose an electron?

The concept of the quantized nature of matter and, in particular, the quantized electronic energy levels in atoms was first postulated by Niels Bohr[4] in 1913. Through the Rydberg[5] equation (1890) it is possible to calculate all of the line emission energies for hydrogen atom.

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

[3] Albert Einstein (1879-1955)
[4] Niels Henrik David Bohr (1885-1962)
[5] Johannes Robert Rydberg (1854-1919)

R_H (the Rydberg constant) in this form of the Rydberg equation has the value of 1.0974×10^7 m^{-1}. It is possible to convert the Rydberg constant to units of joules and rewrite the equation

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

where, in this case, the Rydberg constant is 2.179×10^{-18} J. This new form of the Rydberg equation predicts with a high level of accuracy the differences in energy between energy levels in the hydrogen atom. The negative sign corrects the equation for direction of energy travel; *i.e.*, if an electron falls from high energy to low, the atom gives off light (an "exothermic" process). When $n_f = 2$, the equation is known as the Balmer equation since if predicts the wavelengths or energies of the Balmer emission lines (visible light lines) of hydrogen atom almost exactly.

10. What is energy of the photon produced when an electron in an excited-state hydrogen atom falls from $n = 4$ to $n = 2$?

11. What is the wavelength of the photon in problem 10? What color is this photon?

12. The Rydberg equation can be used to calculate the energy (or wavelength) of a photon absorbed by a hydrogen atom. Could the photon produced in problem 10 be absorbed by a ground-state hydrogen atom?

But why should the energy levels (or in Bohr's model, the electron orbits) be quantized at all? When quantum-sized particles in motion, they also possess wave-like characteristics. This was first postulated by Louis de Broglie[6] in 1925 to help explain quantization in the Bohr model of the hydrogen atom. De Broglie proposed that, if the electron is behaving as a wave (like a photon), then the electron "wave" must constructively interfere with itself as it completes an orbit (inspect the drawing of a standing wave on an orbit, below). If the wave does not constructively interfere (that is, create a standing wave), the electron will move in toward or away from the nucleus until the distance traveled in orbit establishes a standing wave. Despite Bohr's atomic theory having been invalidated, de Broglie's equation that relates the apparent wavelength of a moving particle to its mass and velocity has been verified in a wide variety of experimental situations.

$$\lambda = \frac{h}{mv}$$

The reader is referred to a discussion of de Broglie waves, Compton scattering, Young's double-slit experiment, and the photoelectric effect for a more in-depth treatment of wave-particle duality.

The presentation of quantum mechanics by Schrödinger[7] in 1926 revolutionized physics and, ultimately, chemistry. The details of quantum mechanics are complex but not inaccessible and are a work of exquisite beauty and "*...spring from true genius...*" (Einstein,1926).

13. What is the apparent wavelength of an electron (9.11×10^{-31} kg) moving at 90.0% the speed of light?

Almost everything we know about the microscopic nature of matter is encoded in the way light interacts with the matter. For example, quantum mechanics is inextricably tied to the energies of light absorption and emission from atoms and molecules. The energy of light absorbed is the difference in energy between the atomic or molecular orbitals in the substance.

14. An atom has an emission line at 630.7 nm. What is the difference in energy between the orbitals which produce this emission line?

[6] Louis Victor Pierre Raymond duc de Broglie (1892-1987)
[7] Erwin Rudolf Josef Alexander Schrödinger (1887-1961)

15. A dye molecule has a wavelength of maximum absorption of 495 nm. What is the difference in energy between the molecular orbitals which account for this absorption?