## Flectro-magnetic radiation (light)

- The nature of light
- light is a wave
- The nature of waves
- What is a wave?
- What is waving?


## Waves



- Wave: some sort of periodic function
- something that periodicaly changes vs. time.
- wavelength ( $\lambda$ ): distance between equivalent points
- Amplitude: "height" of wave, maximum displacement of periodic function.


## Waves

- The number of waves passing a given point per unit of time is the frequency $(v)$.
- For waves traveling at the same velocity, the longer the wavelength, the smaller the frequency.
longer wavelength


## Waves


(a) Two complete cycles of wavelength $\lambda$

(b) Wavelength half of that in (a); frequency twice as great as in (a)

(c) Same frequency as (b), smaller amplitude

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## $v=$ wavelength $x$ frequency

meters $x(1 / \mathrm{sec})=\mathrm{m} / \mathrm{sec}$

$$
v=\lambda v
$$

## Waves

## Major question:

- What is waving?
- water wave:
- water height(pressure)
- Sound wave:
- air pressure
- Light?


## sight waves.



- What is waving? Electric field, and perpendicular magnetic field.
- Faraday thought this, Maxwell proved it.

- All electromagnetic radiation travels the speed of light (c), $3.00 \times 10^{8} \mathrm{~m} / \mathrm{s}$ (in a vacuum).
- Therefore: $\quad c=\lambda v$


## Speed of light in other materials

Index of refraction is:
$\mathrm{n}=\mathrm{c} / \mathrm{v}$
The index of refraction of some common materials are given below.
material $n$ material $n$

| Vacuum | 1 | Crown Glass | 1.52 |
| :--- | :--- | :--- | :--- |


| Air | 1.0003 Salt 1.54 |
| :--- | :--- | :--- | :--- |


| Water | $1.33 \quad$ Asphalt | 1.635 |
| :--- | :--- | :--- |

Ethyl Alcohol 1.36 Heavy Flint Glass 1.65
Fused Quartz 1.4585 Diamond 2.42
Whale Oil $\quad 1.460 \quad$ Lead 2.6
Values of $n$ come from the CRC Handbook of Chemistry and Physics

The major issue of late $19^{\text {th }}$ century physics

- What is light?
- Light and energy?
- How does light interact with matter?


## History of the atom

Atomic spectra
Bunsen, Kirchhoff, 1860
1st spectroscope
1st line spectrum
Lockyer, 1868
He in solar system
Balmer, 1885
H line spectrum
Rydberg 1890
generalized line
spectra, but no
explanatio!

## Quantum theory

- Plank,1900
> Black body radiation
- Einstein, 1905
> Photoelectric effect


## Atomic structure

- Dalton, 1803
$>$ atomic nature
- Faraday, 1834
$>$ Electricity \& Mag.
- Thompson, 1807
$>$ electrons e/m
- Millikan, 1911
$>$ oil drop
- Rutherford, 1911
> gold foil/nucleus
> Application of atomic theory to the electronic spectra of hydrogen


## History of the atom continued

- Bohr, 1913
> Application of atomic theory to the electronic spectra of hydrogen
- Pauli 1923
- De Broglie, 1924
- Wave properties of particles


## Discrete atoms

- Born, Heisenberg, Dirac, 1925
- Quantum mechanics
- Schrodinger, 1926
- Wave mechanics
- Heisenberg, 1927
- Uncertainty principle
- Heitler, London, 1927
- Valence Bond theory

Chemical bonding

- Pauling, 1928,1930
- hybridization, resonance
- Mulliken, 1928
- Molecular orbital theory


## Black Body Radiation

Spectral output of a black body.


Black shows that predicted from classical electricity \& magnetism
Colored curves are what you actually get.
Light is emitted when atoms vibrate (or oscillate), but they can only oscillate with an energy given by:

$$
\mathrm{E}=\mathrm{nh} v
$$

## Mystery 1: Black body radiation



- Higher T leads to shorter wavelength of light
- More K.E., more E
- Must be relationship between E and wavelength Plank concluded that energy is quantized. It comes in packets (like fruit snacks) and is proportional to frequency:
$E=h v$
where $h$ is Planck' s constant, $6.63 \times 10^{-34} \mathrm{~J}$-s. The minimum packet of $E$.


## What did Einstein get the Nobel Prize for?

## Mystery \#2: The Photo-electric effect



Note, this is what a photo cell does Turn light into work (current)
What might you expect what do you see? (from normal waves)

K. E. $\mathrm{e}^{-}$
K.E.



V

$V$

Einstein: Light is both a particle and a wave.
$\mathrm{E}_{\text {photon }}=1 / 2 \overbrace{\mathrm{mv}^{2}+\mathrm{h} v_{\mathrm{o}}=\mathrm{E}_{\text {electron }}}^{\mathrm{e}-\mathrm{K.E} \text {. "escape energy" }}$
light comes in packets of energy. Each packet runs into one electron. Each packet must have enough $E$ to break electron loose from metal. The rest of the energy goes into kinetic energy.

Frequency tells us the E of each packet. I tells us how many packets/second we get. More packets, more current (more electrons knocked off).


## Mystery number 3: element line spectrum



Gas discharge tube
(full of some elemental gas)
Gives off specific frequencies of light only.
Different elements give off different colors.
i.e. different energies.

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Hydrogen

Neon

## The Nature of Energy

- Energy, $\lambda, v$, related:

$$
\begin{aligned}
& c=\lambda v \\
& E=h v
\end{aligned}
$$

c= speed of light in vacuum, constant


## The Nature of Light



- A line spectrum of discrete wavelengths is observed from an element


## Hydrogen Line spectra <br> 



Johann Balmer, School teacher figured out that the lines fit a simple equation:

$$
\frac{1}{\lambda}=\left(R_{H}\right)\left(\frac{1}{n_{1}^{2}}-\frac{1}{n_{2}^{2}}\right)
$$

$\mathrm{R}_{\mathrm{H}}=$ constant
$\mathrm{n}_{1}$ and $\mathrm{n}_{2}$ are integers
But why?

## The Nature of Energy



- Niels Bohr adopted Planck' s assumption and explained these phenomena in this way:

1. Electrons in an atom can only occupy certain orbits (corresponding to certain energies).

## The Nature of Energy



- Niels Bohr adopted Planck's assumption and explained these phenomena in this way:

2. Electrons in permitted orbits have specific, "allowed" energies;

## The Nature of Energy



- Niels Bohr adopted

Planck's assumption and explained these phenomena in this way:
3. Energy is only absorbed or emitted in such a way as to move an electron from one "allowed" energy state to another; the energy is defined by

$$
E=h v
$$

## The Nature of Energy



The energy absorbed or emitted from electron promotion or demotion can be calculated by the equation:

$$
\Delta E=-R_{H} \quad\left(\frac{1}{n_{f}^{2}}-\frac{1}{n t}\right.
$$

where $R_{H}$ is the Rydberg constant, $2.18 \times 10^{-18} \mathrm{~J}$, and $n_{i}$ and $n_{f}$ are integers, the initial and final energy levels of the electron.

## Bohr.



- Using a model that had electrons orbiting the nuceus like planets, Bohr could explain H, but no other elements.
- Too simple.

$$
\begin{gathered}
\Delta E=-R_{H} \quad\left(\frac{1}{n_{f}^{2}}-\frac{1}{n t}\right. \\
R_{E}=1 / 2 m_{e} c^{2} \alpha^{2}
\end{gathered}
$$

## The Wave Nature of Matter

- Louis de Broglie: if light can be a particle, maybe matter can be wavelike.

$$
\begin{aligned}
& \text { Velocity }=\lambda v \\
& v=\frac{\text { velocity }}{\lambda} \\
& E=m(\text { velocity })^{2}=h v=h \frac{\text { velocity }}{\lambda} \\
& \lambda=\frac{h}{m(\text { velocity })}
\end{aligned}
$$

## Wave-like nature of matter

$$
\lambda=\frac{h}{m v}
$$

However, the higher the mass, the smaller the wavelength \& $\mathrm{h}=6.63 \times 10^{-34} \mathrm{~J}-\mathrm{s}$, a really small number.

Example; What is $\lambda$ for a 1 g ball?

$$
\lambda=\frac{6.63 \times 10^{-34} \mathrm{kgm}^{2} / \mathrm{s}}{.001 \mathrm{~kg}(1 \mathrm{~m} / \mathrm{s})}=6.63 \times 10^{-31} \mathrm{~m}
$$

wavelengths of everyday objects too small to measure.

## Wave-like nature of matter

- What about an electron? $\mathrm{v}=6 \times 10^{6} \mathrm{~m} / \mathrm{s}$ :
- $\mathrm{m}=9.1 \times 10^{-28} \mathrm{~g}$.
$\lambda=\frac{6.63 \times 10^{-34} \mathrm{kgm} 2 / \mathrm{s}}{9.1 \times 10^{-28}\left(6 \times 10^{6} \mathrm{~m} / \mathrm{s}\right)}=1.22 \times 10^{-10} \mathrm{~m}=.122 \mathrm{~nm}$
Wavelength of X-rays


## Electron microscopy



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## The Uncertainty Principle

- Heisenberg showed that the more precisely the momentum of a particle is known, the less precisely is its position known:

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

- our uncertainty of the whereabouts of an electron can be greater than the size of the atom!

This is a result of the wave/particle duality of matter

## "The clues"

- 1. Plank: $E$ of light is quantized $\&$ depends on frequency
- 2. Einstein/photo-electric effect: Light behaves like a particle when it interacts with matter
- 3. Emission spectra/Bohr: Potential E. of electrons are quantized in an atom
- 4. Debroglie: wave/particle duality of electrons (matter).
- 5. Standing waves: are quantized inherently

Born/Schroedinger/Jordan: use standing wave analogy to explain electron P.E. in atoms. Quantum Mechanics

$1=(1 / 2) \lambda$

## Standing waves

 $v_{\mathrm{O}}=$ frequency nodes $=2$ (gotta have 2$)$

$$
\begin{aligned}
& 1=(2 / 2) \lambda=\lambda \\
& 2 v_{\mathrm{O}}=\text { frequency } \\
& \text { nodes }=3
\end{aligned}
$$

$$
1=(3 / 2) \lambda
$$

$$
3 v_{0}=\text { frequency }
$$

$$
\text { nodes }=4
$$

$$
1=(4 / 2) \lambda=2 \lambda
$$

$$
4 v_{0}=\text { frequency }
$$

$$
\text { nodes }=5
$$

## Quantum mechanics

- Each electron can be explained using a standing wave equation (wavefunction)
- Quantized frequency corresponds to quantized Energy (Debroglie, Plank, etc.)
- Integer values are critical to this description: quantum numbers.


## Quantum mechanics



Examples of wave equations

Propagating wave


## Quantum mechanics

- Using math we do NOT want to deal with, you can do the same thing for an electron in hydrogen:

$$
\Psi=\frac{1}{\sqrt{\pi}} e^{-r}
$$



But what, physically is $\Psi$ ? What is waving?
Born (1926): $\Psi^{2}=$ probability/volume of finding the electron.

## Quantum Mechanics

Plot of $\Psi^{2}$ for hydrogen atom.
The closest thing we now have to a physical picture of an electron.

90\% contour, will find electron in blue stuff $90 \%$ of the time.


## Quantum Mechanics

- The wave equation is designated with a lower case Greek psi $(\psi)$.
- The square of the wave equation, $\psi^{2}$, gives a probability density map of where an electron has a certain statistical likelihood of being at any given instant in time.


## Quantum Numbers

- Solving the wave equation gives a set of wave functions, or orbitals, and their corresponding energies.
- Each orbital describes a spatial distribution of electron density.
- An orbital is described by a set of three quantum numbers (integers)
- Why three?


## Quantum numbers

- 3 dimensions.
- Need three quantum numbers to define a given wavefunction.
- Another name for wavefunction: Orbital (because of Bohr).


## Principal Quantum Number, $n$

- The principal quantum number, $n$, describes the energy level on which the orbital resides.
- Largest E difference is between E levels
- The values of $n$ are integers $\geq 0$.
- 1, 2, 3,..n.


## Azimuthal Quantum Number, l

- defines shape of the orbital.
- Allowed values of I are integers ranging from 0 to $n-1$.
- We use letter designations to communicate the different values of / and, therefore, the shapes and types of orbitals.


## Azimuthal Quantum Number, l $l=0,1 \ldots, n-1$

| Value of $I$ | 0 | 1 | 2 | 3 |
| :--- | :--- | :--- | :--- | :--- |
| Type of orbital | $s$ | $p$ | $d$ | $f$ |

So each of these letters corresponds to a shape of orbital.

## Magnetic Quantum Number, $m_{l}$

- Describes the three-dimensional orientation of the orbital.
- Values are integers ranging from - $/$ to $l$ :

$$
-l \leq m_{l} \leq l .
$$

- Therefore, on any given energy level, there can be up to:
- $1 \mathrm{~s}(\mathrm{l}=0)$ orbital $\left(\mathrm{m}_{1}=0\right)$,
- $3 p(l=1)$ orbitals, $\left(m_{1}=-1,0,1\right)$
- $5 d$ ( $l=2$ ) orbitals, ( $m_{1}=-2,-1,0,1,2$ )
- $7 f(l=3)$ orbitals, ( $m_{1}=-3,-2,-1,0,1,2,3$ )


## Magnetic Quantum Number, $m_{l}$

- Orbitals with the same value of $n$ form a shell.
- Different orbital types within a shell are subshells (s, p, d, f).

| $\boldsymbol{n}$ | Possible <br> Values of $\boldsymbol{l}$ | Subshell <br> Designation | Possible <br> Values of $m_{l}$ | Number of <br> Orbitals in <br> Subshell | Total Number <br> of Orbitals in <br> Shell |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 1 | 0 | $1 s$ | 0 | 1 | 1 |
| 2 | 0 | $2 s$ | 0 | 1 |  |
|  | 1 | $2 p$ | $1,0,-1$ | 3 | 4 |
| 3 | 0 | $3 s$ | 0 | 1 |  |
|  | 1 | $3 p$ | $1,0,-1$ | 3 | 9 |
| 4 | 2 | $3 d$ | $2,1,0,-1,-2$ | 5 |  |
|  | 0 | $4 s$ | 0 | 1 |  |
|  | $4 p$ | $1,0,-1$ | 3 | 16 |  |

## $s$ Orbitals

- Value of $I=0$.
- Spherical in shape.
- Radius of sphere increases with increasing value of $n$.


## $s$ Orbitals


s orbitals possess $n-1$ nodes, or regions where there is 0 probability of finding an electron.

## p Orbitals

- Value of $I=1$.
- Have two lobes with a nodal plane between them.


Note: always $3 p$ orbitals for a given $n$

## d Orbitals



- Value of $/$ is 2 .
- 2 nodal planes
- Four of the five orbitals have 4 lobes; the other resembles a $p$ orbital with a doughnut around the center.

Note: always 5 d orbitals for a given n .

## Orbitals and nodes



* $\mathrm{n}=$ the shell, with $\mathrm{n}=1$ the ground state or lowest possible energy shell. Thus n may have integral values from 1 - infinity.


## Energies of Orbitals

- For a one-electron hydrogen atom, orbitals on the same energy level have the same energy.
- That is, they are degenerate.



## Energies of Orbitals



- As the number of electrons increases, though, so does the repulsion between them.
- Therefore, in manyelectron atoms, orbitals on the same energy level are no longer degenerate.


## Energies of Orbitals



- For a given energy level (n):
- Energy:
- $s<p<d<f$
- s lowest energy, where electrons go first
- Next p
- Then d

Why?


The closer to the nucleus, the lower the energy

## The problem with quantum mechanics

- It's not hard to solve equations for the various wavefunctions if they are all alone (like H)
- The problem is what happens in the presence of other electrons
- The electron interaction problem
- Electron interaction so complex, exact solutions are only possible for H!
- Electron probabilities overlap a lot, must interact a lot, repulsion keeps them from ever "touching"


## Spin Quantum Number, $m_{s}$

- A fourth dimension required. Why?



## Spin Quantum Number, $m_{s}$

- A fourth dimension required. Why?
- Time. Adding time changes E
- Another integer (quantum number) needed.
- Time dependent Schroedinger equation.



## Spin Quantum Number, $m_{s}$

- This leads to a fourth quantum number, the spin quantum number $m_{s}$.
- The spin quantum number has only 2 values +1/2 and -1/2
- Describes magnetic
 field vector of electron


## Why do we call it "spin"



## Why do we call it "spin"

- And charges that spin produce magnetic fields



## Pauli Exclusion Principle

- No two electrons in the same atom can have exactly the same energy.
- For example, no two electrons in the same atom can have identical sets of quantum numbers.



## Electron Configurations Every electron has a name

- Name of each electron unique
- Name consists of four numbers:
- $\mathrm{n}, \mathrm{l}, \mathrm{m}_{\mathrm{l}}, \mathrm{m}_{\mathrm{s}}$
- Example:
- Mr. George Herbert Walker Bush
- We must learn to name our electrons
- Unlike people, there is a lot in the "name" of an electron.


## Electron Configurations

- Distribution of all electrons in an atom
- Consist of
- Number denoting the energy level


## Electron Configurations

- Distribution of all electrons in an atom
- Consist of
- Number denoting the energy level
- Letter denoting the type of orbital


## Electron Configurations

- Distribution of all electrons in an atom.
- Consist of

- Number denoting the energy level.
- Letter denoting the type of orbital.
- Superscript denoting the number of electrons in those orbitals.


## Orbital Diagrams

- Each box represents one orbital.
- Half-arrows represent the electrons.

Li

$1 s \quad 2 s$

- The direction of the arrow represents the $1 s^{2} 2 s^{1}$ spin of the electron.


# Hund's Rule <br> (of maximum multiplicity) 



## Electron configurations

| Element | Total <br> Electrons | Orbital Diagram |  |  |  |  |  | Electron Configuration |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $1 s$ | $2 s$ |  | $2 p$ |  | 3 s |  |
| Li | 3 | 11 | 1 |  |  |  |  | $1 s^{2} 2 s^{1}$ |
| Be | 4 | 11 | 11 |  |  |  |  | $1 s^{2} 2 s^{2}$ |
| B | 5 | 11 | 11 | 1 |  |  |  | $1 s^{2} 2 s^{2} 2 p^{1}$ |
| C | 6 | 11 | 11 | 1 | 1 |  |  | $1 s^{2} 2 s^{2} 2 p^{2}$ |
| N | 7 | 11 | 11 | 1 | 1 | 1 |  | $1 s^{2} 2 s^{2} 2 p^{3}$ |
| Ne | 10 | 11 | 11 | 11 | 11 | 11 |  | $1 s^{2} 2 s^{2} 2 p^{6}$ |
| Na | 11 | 11 | 11 | 11 | 11 | 11 | 1 | $1 s^{2} 2 s^{2} 2 p^{6} 3 s^{1}$ |

## Why do we accept this wacko stuff?

- It must explain all the data
- It should predict things
- Q.M. is consistent with all our data (photoelectric effect, emission spectra of elements, dual wave/ particle weirdness, etc.
- One prediction: elements with similar electron configuration should have similar chemical properties


## Why do we accept this wacko stuff?

 It predicts the periodicity of the periodic table!! $1 s$ $1 s$
$\square$ Representative s-block elements
$\square$ Transition metals
$\square$ Representative $p$-block elements
$\square f$-Block metals

- We fill orbitals in increasing order of energy.
- Different blocks on the periodic table, then correspond to different types of orbitals.


## Why do we accept this wacko stuff? It predicts the periodicity of the periodic table!!

- Remember: The periodic table was arranged the way it was based on chemical properties.
- Totally empirical, until now. Based only on observation.



## Periodic Table

$1 s$ $1 s$


$\square$ Representative s-block elements
$\square$ Representative $p$-block elements
$\square$ Transition metals
$\square f$-Block metals

- Periodic table tells you about the last electron that went in!!!
- Periodic table also makes it easy to do electron configurations.


## Short cut for writing electron configurations

## TABLE 6.4 Electron Configurations of the Group 2A and 3A Elements

Group 2A

| Be | $[\mathrm{He}] 2 s^{2}$ |
| :--- | :--- |
| Mg | $[\mathrm{Ne}] 3 s^{2}$ |
| Ca | $[\mathrm{Ar}] 4 s^{2}$ |
| Sr | $[\mathrm{Kr}] 5 s^{2}$ |
| Ba | $[\mathrm{Xe}] 6 s^{2}$ |
| Ra | $[\mathrm{Rn}] 7 s^{2}$ |
| Group 3A |  |
| B | $[\mathrm{He}] 2 s^{2} 2 p^{1}$ |
| Al | $[\mathrm{Ne}] 3 s^{2} 3 p^{1}$ |
| Ga | $[\mathrm{Ar}] 3 d^{10} 4 s^{2} 4 p^{1}$ |
| In | $[\mathrm{Kr}] 4 d^{10} 5 s^{2} 5 p^{1}$ |
| Tl | $[\mathrm{Xe}] 4 f^{14} 5 d^{10} 6 s^{2} 6 p^{1}$ |

## Electron configurations of the elements



## Some Anomalies



## Some irregularities occur when there are enough electrons to halffill $s$ and $d$ orbitals on a given row.

## Some Anomalies



For instance, the electron configuration for Chromium, is
[Ar] $4 s^{1} 3 d^{5}$
rather than the expected
[Ar] $4 s^{2} 3 d^{4}$.

## Some Anomalies

- This occurs because the $4 s$ and $3 d$ orbitals are very close in energy.
- These anomalies occur in $f$-block atoms, as well.

