Chemistry BC3253x:
Structure, Bonding, and Spectroscopy
aka Quantum Chemistry

Topic I: The Old Quantum Theory
(1900-1920)

I. The Old Quantum Theory
- A. Black body radiation
    - electromagnetic radiation: review
    - Empirical fit: Wien displacement law (1894)
    - Rayleigh-Jeans theory (1900) and the ultraviolet catastrophe
    - Solution: **the Quantum hypothesis** (Planck, 1900)
- B. The photoelectric effect
    - Experiment observing the effect (Hertz, 1887)
    - Theory (Einstein, 1905)
    - Refined experiments (Millikan, 1916)
    - Modern experiments using the photoelectric effect.
- C. The heat capacities of solids (Einstein, 1907)
- D. The structure of the atom
    - 1. Early studies on subatomic particles
        - a. Measurement of e/m (J.J. Thomson, 1897)
            - Application to modern mass spectrometry
        - b. Oil drop experiment (Millikan, 1909)
        - c. particle scattering experiment (Geiger and Marsden, 1909)
        - d. Planetary model (Rutherford, 1911)
    - 2. The spectrum of the **hydrogen atom** (Balmer 1885, Rydberg 1896)
    - 3. **Bohr model** of the one-electron atom (Bohr, 1913)
        - assumptions: Quantized angular momentum ℓ
            - The Correspondence Principle
        - results: explanation of line spectra
            - quantitative prediction of the Rydberg constant.

Electromagnetic radiation: review

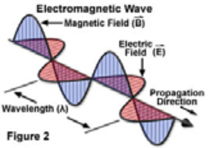
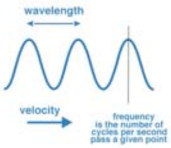


Figure 2

Light = oscillating electric and magnetic fields

Color defined by wavelength $\boldsymbol{\lambda}$ (lambda) or frequency $\boldsymbol{\nu}$ (nu)

Light travels at speed c: $\boldsymbol{\lambda \nu = c} = 2.9979245 \times 10^8$ m/s



Visible light ~ 400 to 700 nm

UV has $\lambda < 400$ nm, **IR** has $\lambda > 720$ nm [corrected 9/5/07]

Suppose $\boldsymbol{\lambda}$ = 500 nm = 500 x 10^{-9} m = 5 x 10^{-7} m.

Then $\boldsymbol{\nu}$ = (3 x 10^8 m/s)/(5 x 10^{-7} m) = 0.6 x 10^{15} = **6 x 10^{14} s^{-1}**

What does ν count per second? **cycles**. A cycle is 2π radians.

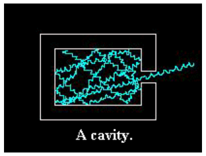
cycles/sec = **Hertz** unit often used for frequency

Radio stations: AM 535-1600 kHz FM: 88-108 MHz.

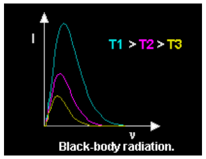
Microwave oven: 2.45 GHz.

Frequency in **radians**/sec, denoted (omega), $\boldsymbol{\omega = 2\pi\nu}$ [corrected 9/21/07]

Black body radiation



A cavity.



Black-body radiation.

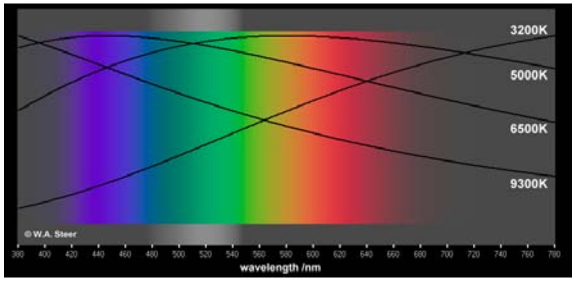
Black body emits light at any frequency, depending on T.

idealized black body: a cavity

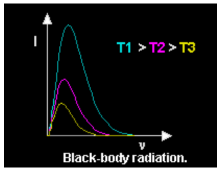
Real objects behave approximately so:

color changes with T ("red hot")

Temperatures of stars measured by color!



Black body radiation



How does intensity of light depend on ν?

Answer known experimentally: curves as shown

Wien: $\mathbf{I(\nu, T) = (8\pi k\beta/c^3)\,\nu^5\, e^{-\beta\nu/T}}$, β empirical constant.

Rayleigh-Jeans Theory:

black body = collection of oscillators, all possible frequencies

$I(\nu, T) = C\,\nu^2\, N(\nu)\, \langle\varepsilon(\nu, T)\rangle$ where

C = a constant (we are only concerned with shape)

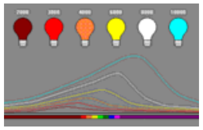
N(ν) = number of oscillators (per unit volume) with frequency ν

<ε(ν, T)> = average energy per oscillator with frequency ν at temperature T

Classical statistical mechanics and theory of waves says

$\mathbf{N(\nu) = 8\pi\nu^2/c^3}$ as ν increases, more waves can fit in volume.

Black body radiation



Rayleigh-Jeans Theory: $I(\nu, T) = C\,\nu^2\, N(\nu)\, \langle\varepsilon(\nu, T)\rangle$

How do we calculate <ε> the average energy per oscillator?

Boltzmann had shown that at temperature T, the probability of a system having energy E, P(E), is proportional to $\mathbf{e^{-E/kT}}$ where k, the Boltzmann constant, is equal to R/N_A

Digression: How do we calculate an **average**: <x> ?

1. n discrete values x_k, equal weight

$$\langle x\rangle = \frac{\sum_{k=1}^{n} x_k}{n}$$

2. n discrete values, with weights w_k

$$\langle x\rangle = \frac{\sum_{k=1}^{n} w_k x_k}{\sum_{k=1}^{n} w_k}$$

Black body radiation

Rayleigh-Jeans Theory: $I(\nu, T) = C\,\nu^2\, N(\nu)\, \langle\varepsilon(\nu, T)\rangle$

How do we calculate an **average**: <x> ?

<u>3. Continuous values</u>:

the limits for both integrals are all possible values of x, often **–∞ to +∞**, sometimes **0 to +∞**, sometimes a finite range **a to b**.

$$\langle x\rangle = \frac{\int x\,P(x)dx}{\int P(x)dx}$$

So

$$\langle\varepsilon\rangle = \frac{\int \varepsilon\,P(\varepsilon)d\varepsilon}{\int P(\varepsilon)d\varepsilon} = \frac{\int_0^\infty \varepsilon\, e^{-\varepsilon/kT} d\varepsilon}{\int_0^\infty e^{-\varepsilon/kT} d\varepsilon}$$

Both these integrals will be important in quantum calculations.

Black body radiation

Average energy from the Boltzmann distribution

use integral tables:

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$\text{so } (n=0)\quad \int_0^\infty e^{-ax} dx = \frac{1}{a} \quad \text{and } (n=1)\quad \int_0^\infty x e^{-ax} dx = \frac{1}{a^2}$$

$$\text{thus } \langle\varepsilon\rangle = \frac{\int_0^\infty \varepsilon\, e^{-\varepsilon/kT} d\varepsilon}{\int_0^\infty e^{-\varepsilon/kT} d\varepsilon} = \frac{(kT)^2}{kT} = kT$$

assuming that an equal number of oscillators exists at each ε.

This is **classical distribution of energy**.

Works well, for example, for translational energy of molecules.

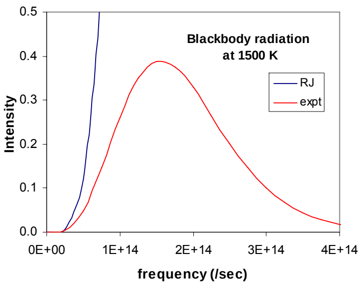
Black body radiation

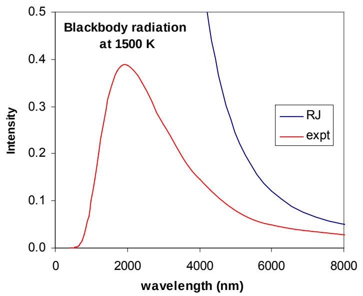
Rayleigh-Jeans Theory:

$I(\nu, T) = C\,\nu^2 N(\nu) \langle\varepsilon(\nu, T)\rangle = C\,(8\pi\nu^4/c^3)\,kT$

Works well for very small ν, ok for higher, but fails at large ν:

the ultraviolet catastrophe.





Black body radiation

Max Planck (1900) new theory. Key assumption:

oscillator cannot have any energy, but must be in fixed units

$\boldsymbol{\varepsilon_n = nh\nu}$ where **n is an integer** (0, 1, 2, ..)

oscillator energies are **quantized**. h = Planck's constant

radiation emitted when oscillator energy changes level (n)

Recalculate <ε>:

$$\langle\varepsilon\rangle = \frac{\sum_{n=0}^{\infty} w_n \varepsilon_n}{\sum_{n=0}^{\infty} w_n} = \frac{\sum_{n=0}^{\infty} \varepsilon_n e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

problem 1.2:
show that this is true.

This gives I(ν, T) that fits experiment perfectly

h is VERY small: 6.6256×10^{-34} J-s.

Black body radiation

$\mathbf{I(\nu, T)} = C\,\nu^2\,\mathbf{N(\nu)\,\langle\varepsilon(\nu, T)\rangle} = \mathbf{C\,(8\pi\nu^4/c^3)\,[h\nu/(e^{h\nu/kT}-1)]}$

h is VERY small: 6.6256×10^{-34} J-s.

If x is very small, $e^x = 1 + x$,

For **very small hν/kT** (small ν or large T),

$h\nu/(e^{h\nu/kT} - 1) = h\nu/(1 + h\nu/kT - 1) = kT$

which becomes the Rayleigh-Jeans equation.

At high T, the system follows the classical equation.

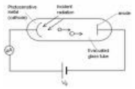
For **very large hν/kT** (large ν or small T),

$h\nu/(e^{h\nu/kT} - 1) = h\nu/(e^{h\nu/kT}) = h\nu\, e^{-h\nu/kT}$

which agrees with the empirical Wien equation

Planck actually *first* found this equation $\langle\varepsilon\rangle = h\nu/(e^{h\nu/kT} - 1)$, and then developed the theory that gives rise to it.

The Photoelectric Effect



Hertz (1887) Shine light on some polished metal surfaces:
electrons emitted. Emitted electrons = "photoelectrons"

Classical picture of light: waves, energy depend in intensity.

Yet photoelectric effect depends on λ (or ν):

for certain metals, very intense red light gives no signal,
while very pale blue light does.

Einstein (1905) [Nobel Prize 1921] explained this.

light is quantized in units $E = h\nu$ (beyond Planck!)

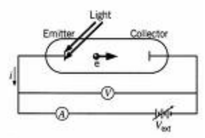
electrons in metal absorb these light quanta

There is a minimum energy Φ required to remove the electron,

Φ is a property of the metal, called work function.

if $h\nu < \Phi$, no light absorbed.

The Photoelectric Effect



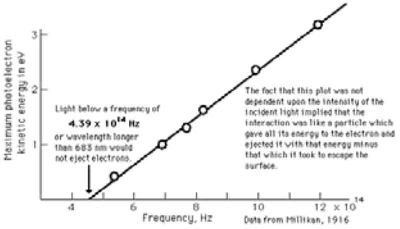
If $h\nu > \Phi$, electron has kinetic energy $E = h\nu - \Phi$.

Millikan (1916) [Nobel Prize 1923]

measured E vs ν:

found V needed to stop e^-.

Slope of plot gives same h
as in Blackbody radiation!



Many modern applications:

XPS, ESCA, MPS

observing threshold λ for generating photoelectron
to determining presence of a particular element.

Properties of materials related to Φ.

Heat Capacity of Solid Elements

Law of Dulong and Petit: $C_V \sim 3nR$ for solids at room T.

Why? [discussed in Chemistry BC3252y]

$C_v = (dU/\partial T)_V$

Each atom in a lattice can move in three directions (**x, y, z**)

n moles of atoms have $3nN_A$ degrees of freedom (d.o.f)

Classical equipartition of energy: $\langle\varepsilon\rangle = k_BT$ for each d.o.f.

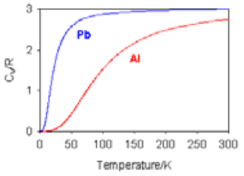
k_B = Boltzmann constant = R/N_A

$U = (3nN_A)(k_BT) = 3nRT$ $\quad C_V = (dU/\partial T)_V = 3nR$

But **as T falls, C_V decreases**. Why?

Einstein (1907): $\langle\varepsilon\rangle = h\nu/(e^{h\nu/kT} - 1)$

ν adjustable parameter
good fit to data.



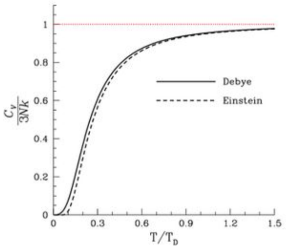
Heat Capacity of Solid Elements

Theory extended by **Debye** in **1912** to allow for
a distribution of frequencies.

Improved fit to data,

especially as T → 0 K

where C_V is proportional to T^3.



What is quantized?

1900 Planck	oscillators in black body
1905 Einstein	radiation for photoelectric effect
1907 Einstein	oscillations of real atoms in crystal

The Structure of Atoms and Atomic Spectroscopy

By late 1800's atom generally recognized as fundamental particle.

Faraday showed that a fixed quantity of charge (1 $\mathscr{F}$ = 96484 C)
reduces one **equivalent** of metal (one mole Ag^+, ½ mole Cu^{2+})

$Ag^+ + e^- \rightarrow Ag(s)$; $\quad Cu^{2+} + 2\,e^- \rightarrow Cu(s)$;

Storey (1894) used name "electron", estimated charge.

J.J. Thomson (1897) credited with "discovery of electron". How?

Experiments involving Cathode Ray Tube (CRT):
electrons (cathode rays) emitted from cathode,
accelerated by + voltage down tube,
collide with phosphorescent screen: emit light.
Add electric field, deflect beam.

Electron in CRT with Electric Field

Force (a vector) is $\mathbf{F} = q\,\mathbf{E}$ where $\mathbf{E}$ = Electric field (vector)

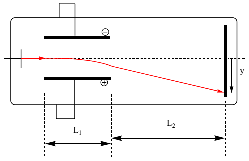
Let $\mathbf{E} = E_y = E$ and $q = e$. Then $F_y = eE$.

But $F_y = ma = m\,(dv_y/dt)$, so $dv_y = (eE/m)\,dt$ $v_y = (eE/m)t + c$

since $v_y = 0$ at $t = 0$, the constant c is zero.

$v_y = dy/dt$, so $dy = v_y\,dt \rightarrow y = (eE/m)\,t^2 + C$

define $y = 0$ at $t = 0$: so C is also 0.



The electric field extends for a length L_1.

v_x is constant, so $L_1 = v_x t_1$, $t_1 = L_1/v_x$

exiting the field, $v_y = (eE/m)(L_1/v_x)$ and $y = (eE/m)L_1^2/v_x^2$

From there the electron follows a straight line for $t_2 = L_2/v_x$

Deflection is $y = (eE/m)L_1^2/v_x^2 + (eE/m)(L_1/v_x)(L_2/v_x)$

$y = \{(eE/m)L_1/v_x^2\}(L_1+L_2)$

Electron in CRT deflected in a field

E field: deflection is $\{(eE/m)L_1/v_x^2\}(L_1+L_2)$

If you know L_1, L_2, v_x and E, can measure y and find (e/m)

But hard to determine v_x precisely.

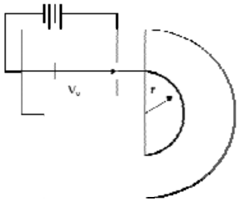
Different apparatus (Thomson): defect in **magnetic** field **B**

perpendicular to picture $\mathbf{F} = q\,(\mathbf{v} \times \mathbf{B})$

Coordinates: $\mathbf{B} = B_z$ and $v_0 = v_x$

v is always ⊥ **B**, so speed is constant

→ **motion is circular** in field:



F(centripetal) = $mv^2/r = qvB$

$r = (m/q)(v/B)$

If you know v and B, can measure r and find (q/m)

Charged (q) particle deflected in a Magnetic field

$r = (m/q)(v/B)$ How do you find v?

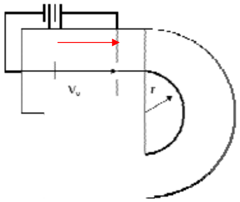
electron is accelerated with voltage E for distance d

As above, at time t, $v_x = qEt/m$ and $x = qEt^2/2m$

So when $x = d$, $t = (2md/qE)^{½}$

so $v_x = (qE/m)(2md/qE)^{½} = (2qEd/m)^{½}$

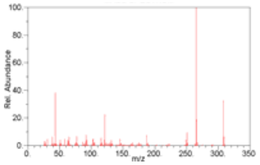
thus $r = (2Edm/qB^2)^{½}$



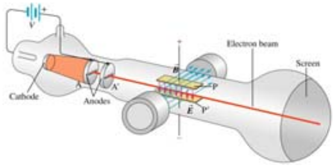
Modern mass spectrometers:

B and r fixed

Scan E, measure signal vs. (q/m)



back to J.J. Thomson...



Both these methods inaccurate:

hard to determine v_0 precisely.

Thomson combined these: perpendicular **E** and **B** fields.

Find the **B** and **E** for which the deflection is **zero**!

Result: $(q/m)_{\mathrm{electron}} \sim 10^{11}$ Coulombs/kg

whereas $(q/m)_{\mathrm{proton}} \sim 10^{8}$ C/kg

Conclusion: if they have the same charge, then $m_p \sim 1000\ m_e$

Thompson learned that the electron is very tiny!

Millikan's oil-drop experiment (1909): $q_e = e = 1.6 \times 10^{-19}$ C

from which $m_e = 9.1 \times 10^{-31\ \mathrm{kg}}$.

Thomson's "plum pudding" model of atom:

electrons, like raisins, buried in the large + charge.

Rutherford

more on atoms...

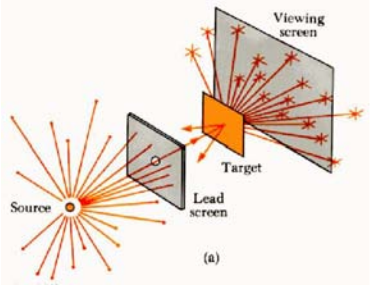
Geiger and Marsden (1909) in lab of **Ernst Rutherford** in Cambridge, England.

Radioactivity a recent discovery:

many experiments with α particles.

They aimed beam of α particles (He^{2+}) at a thin gold foil target.

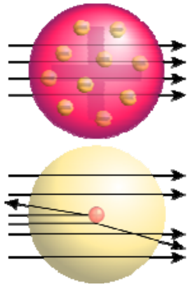
Expected to see weak deflections, but some bounced almost backwards!



Rutherford later said:

"It was almost as incredible as if you fired a fifteen-inch shell at a piece of tissue paper and it came back and hit you".

Rutherford model of Atom



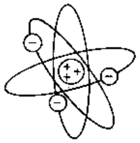
Rutherford (1911):

To explain behavior, need small dense + charge.

Proposal:

+ charge is in a very small nucleus

electrons orbit, like planets.



Planets have $F = GM_1M_2/R^2$

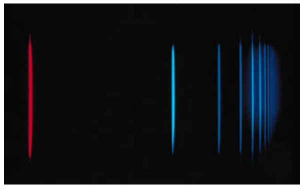
Charged particles have $F = q_1q_2/R^2$

Same equations for orbits (Kepler): ellipses or circles.

But...there is a problem.

Maxwell's equations say accelerating charges radiate; so electrons should lose energy, atoms collapse. But they don't.

Atomic Spectroscopy in the 19th C



Balmer (1885) saw sharp lines in the **visible emission spectrum of H atom**

"The Balmer Series"

positions (λ) fit to equation

$\tilde{\nu} = \mathbf{1/\lambda = a - b/n^2}$

where n = 3 for α (red), 4 for β (turquoise), ...

notice pattern of converging lines

Note: 1/λ is a quick convenient quantity for spectroscopy

e.g. IR lines are reported as at 3010 cm^{-1}, 1200 cm^{-1}

1/λ is **proportional to energy**.

If $\Delta E = h\nu = hc/\lambda$, then $\mathbf{1/\lambda = \Delta E/hc}$

Atomic Spectroscopy in the 19th C

Similar series seen in the UV and the IR (photographic plates).

Rydberg (1986) equation that fits all with single parameter:

$\tilde{\nu} = \mathbf{1/\lambda = R\{1/n_1^2 - 1/n_2^2\}}$ $\quad n_2 > n_1$

R = Rydberg constant = 109677.58 cm^{-1}

Note the exquisite precision!

Same pattern, different R for He^+, Li^{2+} (1 electron ions)

$\mathbf{n_1}$	**1**	**2**	**3**	**4**	**5**
Series	Lyman	Balmer	Paschen	Brackett	Pfund
region	UV	VIS	IR	IR	IR

The Bohr Atom (1913)

Background:

1) Rutherford planetary atom

2) Rydberg equation $1/\lambda = R\{1/n_1^2 - 1/n_2^2\}$

3) Classical mechanics of object with mass m in a circular orbit:

coordinates (r, θ): angular momentum $\ell = mr\,(d\theta/dt) = mr\omega$

U or E = $\frac{1}{2}m\,(dr/dt)^2 + \ell^2/mr^2 + V(r)$

1D equation in r with centrifugal potential (ℓ^2/mr^2)

If $V(r) = -Az/r$ (Coulomb's law), then

$E = -mA^2z^2/2\ell^2$, $r = \ell^2/mAz$, and $\nu = mAz^2/2\pi\ell^3$

i.e., for a given ℓ, we can find E, r, and ν. [$\nu = (d\theta/dt)/2\pi$]

But (1) why doesn't atom radiate? (2) where does R come from?

The Bohr Atom (1913)

Bohr made two postulates:

1) angular momentum is **quantized** $\boldsymbol{\ell = b_0 n}$, n = 1, 2, 3

b_0 an arbitrary parameter. This explains the Rydberg formula

$E(n) = -mA^2z^2/2\ell^2 = \mathbf{-mA^2z^2/(2b_0^2n^2) = E_n}$

$\Delta E_{atom} = E(n_2) - E(n_1) = -(mA^2z^2/2b_0^2)[1/n_2^2 - 1/n_1^2]$

But $1/\lambda = \Delta E/hc$ so $R = mA^2z^2/2hcb_0^2$

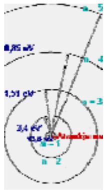
Circular orbits with

$r = \ell^2/mAz = (b_0 n)^2/mAz = \mathbf{a_0 n^2/z = r_n}$

where $a_0 = b_0^2/mA$ **...but what is b_0?**

Observe: as **n** increases, the spacing between adjacent energy levels *decreases*, while the spacing between orbits *increases*.

The Bohr Atom (1913)



...but what is b_0? **Bohr's second postulate**:

Bohr Correspondence Principle:

Quantum results approach classical in the limit as n →∞

What is ΔE for transition from (n+1) to n for large n?

$\Delta E = h\nu = E_{n+1} - E_n$ so $\nu = (mA^2z^2/2hb_0^2)[1/n^2 - 1/(n+1)^2]$

$\nu = (mA^2z^2/2hb_0^2)[(n^2+2n+1 - n^2)/\{n^2(n+1)^2\}]$

For large n, $2n+1 = 2n$ and $(n+1)^2 = n^2$ so $\nu = mA^2z^2/hb_0^2n^3$

But classically $\nu = mAz^2/2\pi\ell^3 = mAz^2/2\pi b_0^3n^3$

so $2\pi b_0 = h$ or $b_0 = h/2\pi = \hbar$

Conclusion: **the angular momentum is quantized in units $\boldsymbol{\hbar}$.**

Now there are no arbitrary parameters!

The Bohr Atom (1913)

Rydberg constant: $R = (mA^2z^2/2\hbar^2)/hc$

For $z = 1$, $m = m_e$, and $A = 1/(4\pi\varepsilon_0)$, this gives

$R_\infty = 109737\ \text{cm}^{-1}$. Stunning agreement with experiment.

Theory immediately accepted.

Denoted R_∞ since it assumes nucleus fixed: infinitely heavy

Improved value uses reduced mass $\mu = \{m_e m_p/(m_e + m_p)\}$

agrees to 8 digits!

$\mathbf{a_0 = \hbar^2/mA} = 0.529167 \times 10^{-10}$ m = 0.529167 Å = **1 bohr**

$\mathbf{r_n = a_0 n^2/z}$ 1 bohr = radius of orbit for H for n=1.

The Bohr Atom (1913)

$E_n = -hcR/n^2$

$E = 0$ when $n = \infty$ (and $r = \infty$): electron free, **atom ionized.**

All bound states have $E < 0$. Ground state, n=1, has **$E_1 = -hcR$**

hcR = energy needed to ionize ground state H.

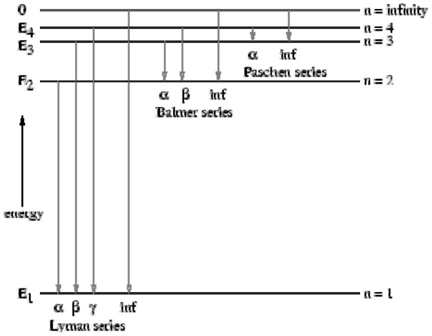
$hcR = 2.179908 \times 10^{-18}$ Joules (per atom)

= 1312.75 kJ/mole

= 13.0658 eV

When n=2, $E_2 = -hcR/4$

When n=3, $E_3 = -hcR/9$



The Bohr Atom (1913)

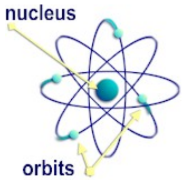
What this theory doesn't do...

describe many-electron atoms

this very common picture

(which is totally incorrect!) →

explain *why* the levels are quantized



Wave mechanics (1926) needed to do these.

Quantum history....

Recommended (short) book on the history of this era:

Uncertainty: Einstein, Heisenberg, Bohr, and the Struggle for the Soul of Science

by David Lindley

published February 2007