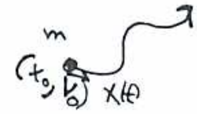
Chem. 1410
27 Aug. 07



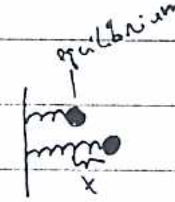
Features of Classical Mechanics : Central purpose : find trajectory $x(t)$

Basic Equation of motion (Newton) $\boxed{F(x) = m\ddot{x}(t)} = m\dot{v}(t) = \dot{p}(t)$

Example (1) Free particle $F = 0 \Rightarrow x(t) = \frac{p_0}{m} t + x_0$

(2) $F = \text{const}$; e.g. $m \downarrow g$, x ; $F = mg$; now $x(t) = x_0 + \frac{p_0}{m} t + \frac{1}{2}\frac{F}{m} t^2$

(3) Linear restoring force (Harmonic Oscillator) $F(x) = -kx$; Now $m\ddot{x} = -kx$



Or: $\ddot{x}(t) = -\omega^2 x(t)$ w/ $\omega \equiv \sqrt{k/m}$

Thus: $x(t) = \alpha \cos\omega t + \beta \sin\omega t = x_0 \cos\omega t + \frac{p_0}{m\omega} \sin\omega t$ $\leftarrow (x_0, p_0) \Leftrightarrow A, \delta$

$= A \sin(\omega t + \delta) = A[\sin\omega t \cos\delta + \cos\omega t \sin\delta]$

Features of H.O. motion: A = amplitude (magnitude of maximum displacement)

T = period of oscillation ; $\omega T = 2\pi$ or $T = \frac{2\pi}{\omega} = \frac{1}{\nu}$ ← frequency

Principle of Energy Conservation: define potential energy $V(x) = -\int_0^x F(x')dx'$

↑ lower limit is arbitrary

Thus, for
$$\begin{cases} F = 0, & V(x) = 0 \\ F = \text{const}, & V(x) = -Fx \\ F = -kx, & V(x) = \frac{1}{2}kx^2 \end{cases}$$

Now consider: $E =$ "total energy" $= \underbrace{\frac{1}{2} m v^2(t)}_{\text{Kinetic } E} + \underbrace{V(x(t))}_{\text{Potential } E}$

For free particle, $E = \frac{1}{2}\frac{p_0^2}{m} = \frac{1}{2} m v_0^2 = \text{const.}$

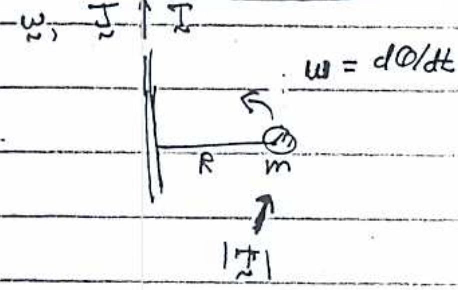
For constant force, $E = \frac{1}{2} m \left[\frac{p_0}{m} + \frac{F}{m} t\right]^2 - F\left[x_0 + \frac{p_0}{m} t + \frac{1}{2}\frac{F}{m} t^2\right] = \frac{p_0^2}{2m} - F x_0 = \text{constant}$

For H.O., $E = \frac{1}{2} m \left[-A\omega \cos(\omega t + \delta)\right]^2 + \frac{1}{2} m \omega^2 \left[A \sin(\omega t + \delta)\right]^2 = \frac{1}{2} m \omega^2 A^2 = \frac{1}{2} k A^2$

These are examples of <u>Principle of Conservation of Energy</u> (E)

Some basic characteristics of classical mechanics: ① Arbitrary E's allowed.

② Trajectories precisely specified



Classical Mechanical description of Rotational Motion.

linear	rotational
m	I $(= mR^2)$, moment of inertia
$\underset{\sim}{v}$	$\underset{\sim}{\omega}$, angular velocity
$\underset{\sim}{p}$	$\underset{\sim}{J}$, " momentum
$\underset{\sim}{F}$	$\underset{\sim}{\tau}$, torque

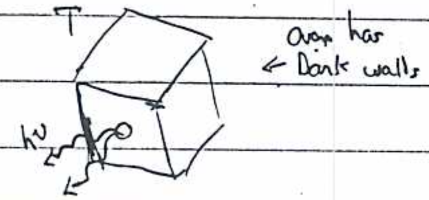
"Newton's Eq" $\boxed{\dot{J} = \tau}$

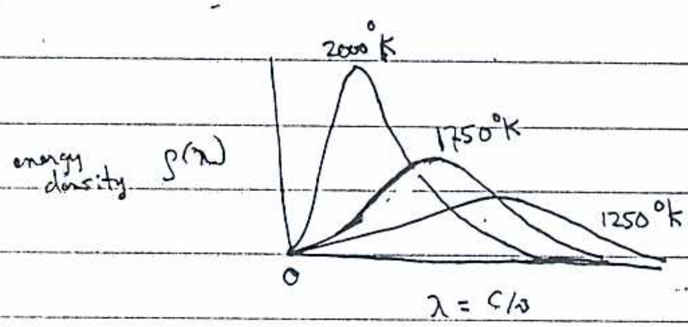
For constant torque: $\theta(t) = \theta_0 + \omega_0 t + \frac{1}{2}\frac{\tau}{I} t^2$

(rotational) $KE = \frac{1}{2} I \dot{\theta}^2(t) = \frac{\tau^2 t^2}{2I}$ if $\omega_0 = 0$

Failures of Classical Physics [~1900]

(I) Blackbody Radiation





Some Features: (1) $\lambda_{max} T = \text{const}$, where λ_{max} = wavelength at which intensity is max. [Wien's Law]

(2) $\int_0^\infty d\lambda\, \rho(\lambda) = a T^4$ [Stefan's Law]

$\uparrow$

$5.67 \times 10^{-8} \frac{W}{m^2} \frac{1}{°K^4}$

Theories [Raleigh-Jeans, Planck...]

Aside: Classical Equipartition Thm.: At thermal equilibrium [T = temp, °K], energy is partitioned into each molecule according to: $\frac{1}{2}k_BT$ in KE for each degree of freedom; and...

$\frac{1}{2}k_BT$ in PE for each vibrational degree of freedom

$\hookrightarrow k_B = 1.38E{-16}$ erg/°K

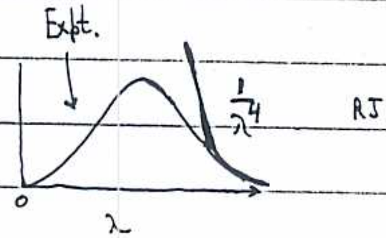
[Thus, ~~thm~~ → for a 1D H.O. $\bar{E} = k_BT$]

Now, Rayleigh-Jeans ... Assumed: (i) electromagnetic field = collection of h.o.'s, one for each possible frequency of light

(ii) classical equipartition thm. [each mode gets kT energy, indep. of frequency]

Then: (RJ) $\rho(\lambda) = \underbrace{\frac{8\pi}{\lambda^4}}_{\substack{\text{density of E.M.}\\ \text{modes w/ wavelength } \lambda\\ \text{in the cavity [per unit volume]}}} \cdot \overbrace{k_B T}^{\text{energy/mode}}$ ← $\frac{\text{energy}}{(\text{wavelength})(\text{volume})}$ } "energy density"

Disaster at high frequencies ["U.V. catastrophe"]:



Planck: for each field oscillator (frequency ν), restrict allowed energies to: $0, h\nu, 2h\nu, \ldots$ (1 photon) ["Quantization"]

Analysis then shows: $\bar{E}(\nu) = \frac{h\nu}{e^{h\nu/k_B T} - 1}$ $[\nu = \frac{c}{\lambda}]$ ← high frequency modes are not excited! [no photons in those modes]

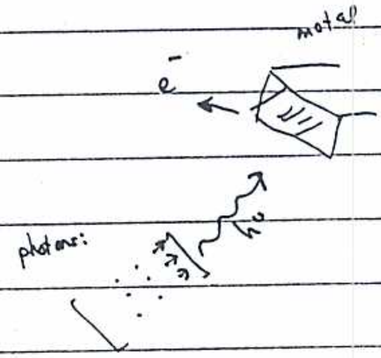
Thus:

$$\text{(Planck)} \quad \boxed{\rho(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{\left[e^{hc/\lambda k_B T} - 1\right]}}$$

; c = speed of light = 3 E10 cm/sec

h = Planck's const. = 6.625 E-27 erg-sec

Photo-electron effect [Einstein]

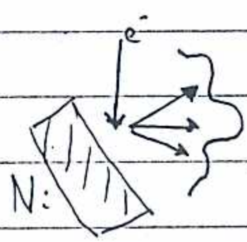


Expt: (1) no e^- for $\nu < \nu_0$

(2) for $\nu > \nu_0$, e^- off w K.E. $\propto (\nu - \nu_0)$ $\Rightarrow$ $\frac{1}{2}mv^2 = h\nu - \underbrace{h\nu_0}_{\Phi}$ ← "work fctn." of metal

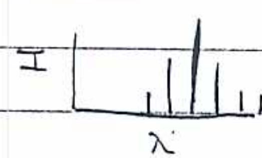
(3) e^- off instantaneously for $\nu > \nu_0$, even at low intensities

Davisson-Germer Expt. [1925] : Interference [Diffraction] in electron-surface scattering $\Rightarrow$ Matter is wavelike



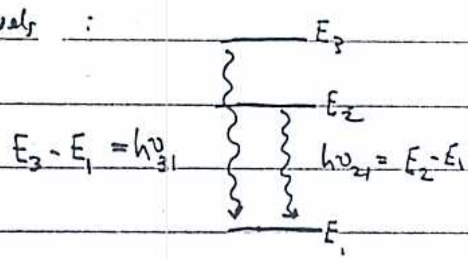
De Broglie : $\lambda = h/p$ for any particle

Atomic + Molecular Spectra - always composed of discrete lines



See Fig. 11.5-11.6 in Atkins

Suggests quantization of atomic/molecular E levels :

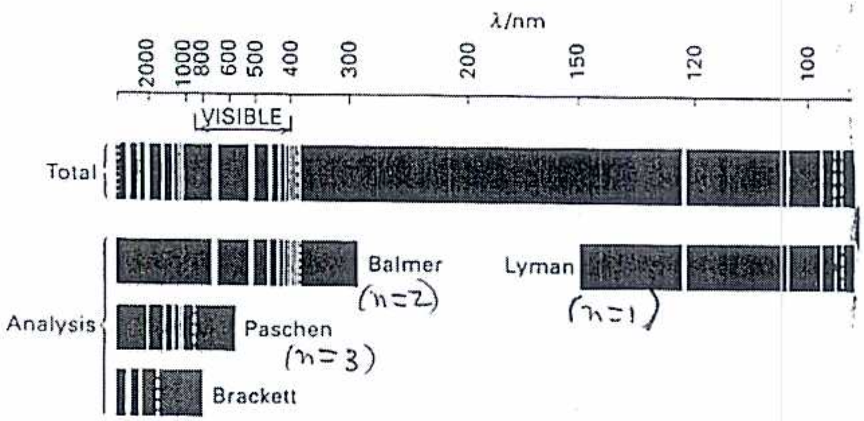


$[\nu_{31} > \nu_{21}]$

pass electric discharge thru $H_2(g) \rightarrow H\cdot + H\cdot$

highly energized!

consider emission spectra of the hydrogen atom [Balmer, Lyman ...]



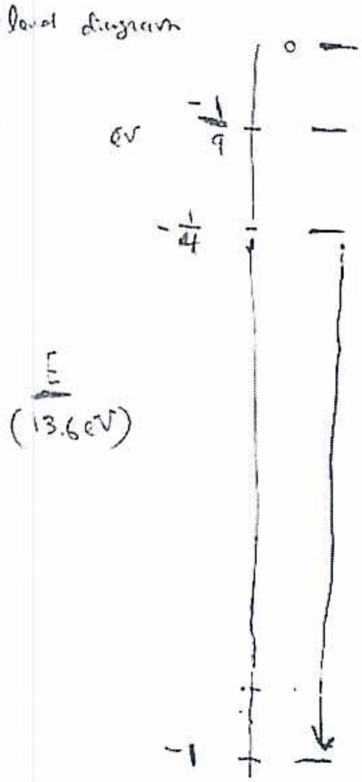
5th [Atkins]
Edition [→ 13.1 in 6th Ed.]
[8th Edition = 10.1]

13.2 The spectrum of atomic hydrogen. The observed spectrum and its resolution into overlapping series are shown. Note that the Balmer series lies in the visible region.

All lines in this emission spectrum are consistent w/ the following E-level diagram

E-levels of H:

$$\boxed{E_n = \frac{-13.6\,eV}{n^2} \quad ; n = 1, 2, 3, \dots, \infty}$$



Quantitatively, for any line in the emission spectrum

$$\boxed{h\nu = 13.6\,eV\left(\frac{1}{n^2} - \frac{1}{m^2}\right)}$$

$m, n = 1, 2, 3$
and $m > n$

J. Rydberg [1890]

$[1\,eV = 1.6 \times 10^{-12}\ ergs]$

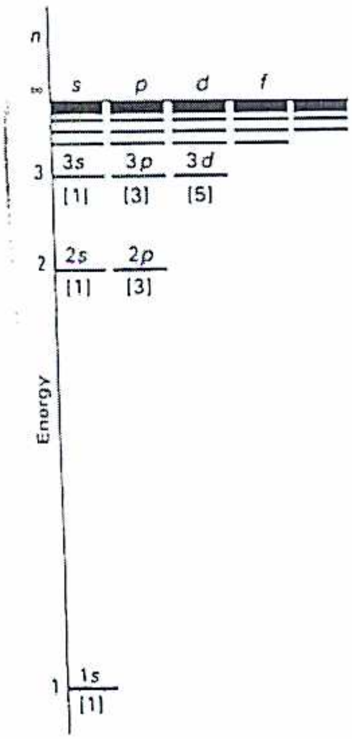
ν = frequency of emitted (or absorbed) light

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

λ: (free space) wavelength of the light

Energy levels, states + degeneracies

For some systems, ∃ two or more distinguishable states w/ the same energy, e.g. in the H-atom:



13.8 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. All orbitals of a given shell have the same energy in hydrogenic atoms.

Note also: spin degeneracy = 2 (↑↓) for each spatial orbital

so total degeneracies of energy levels:

	spatial degeneracy	× spin degeneracy	= total
(i) $n=1$	1	2	2
$=2$	4	2	
$=3$	9	2	18
generally: for n (principle quantum #)	n^2	2	$\boxed{2n^2}$

↑ # of electrs that can have energy E_n