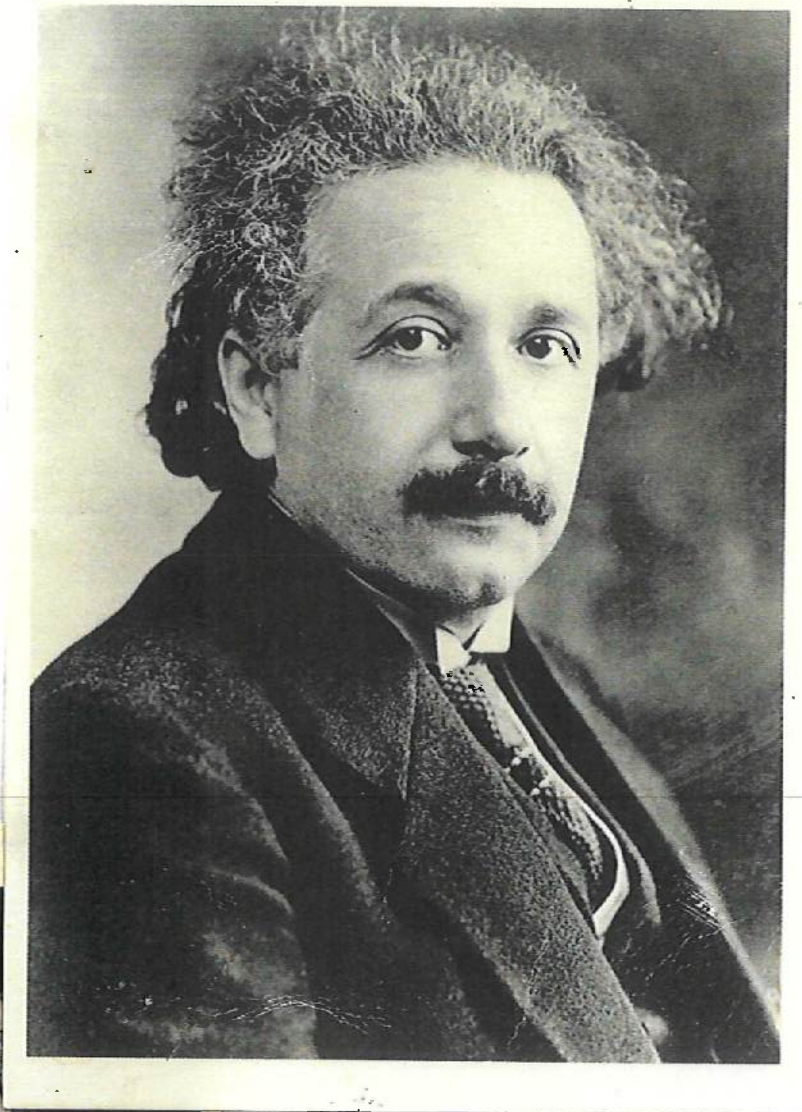
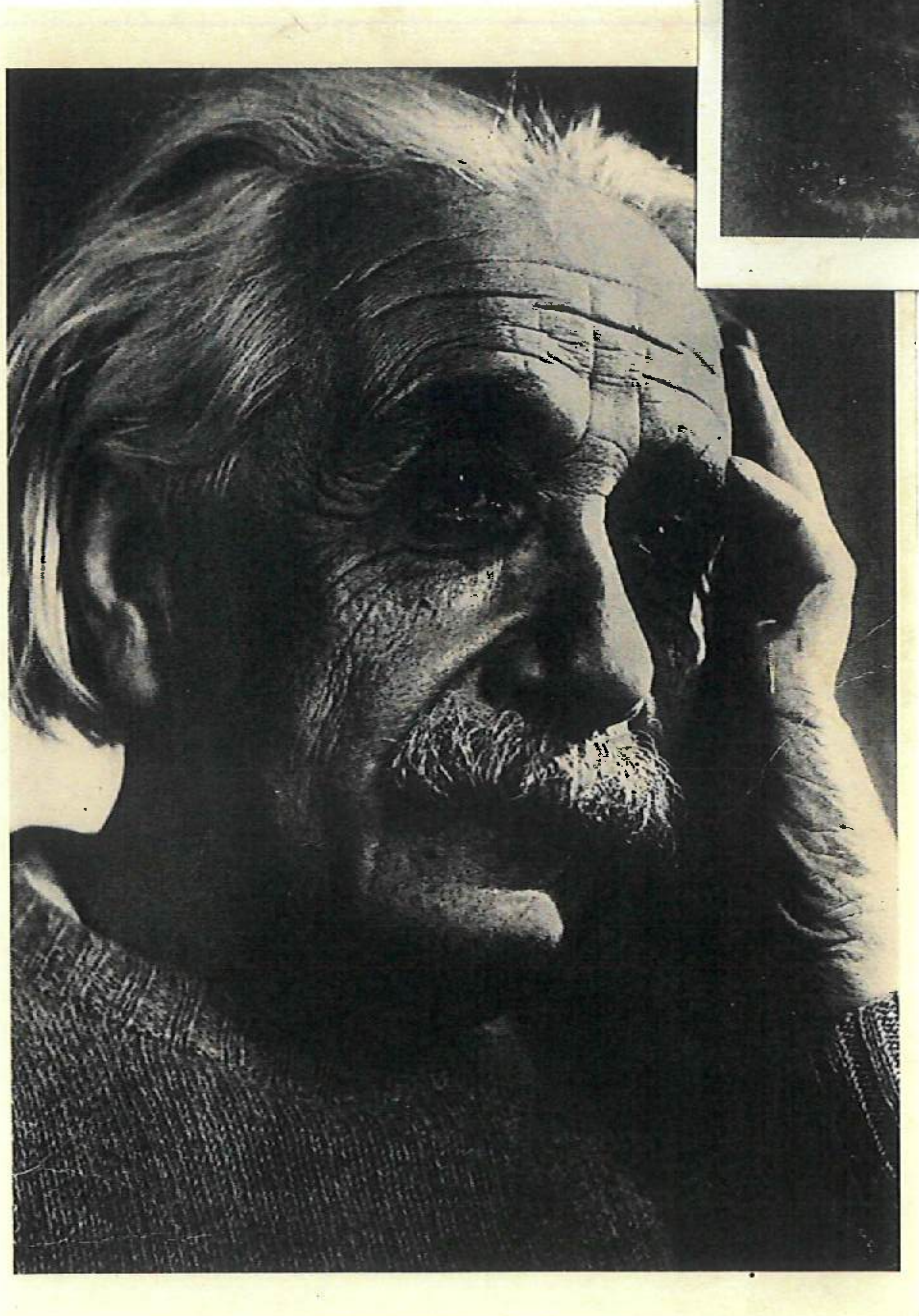
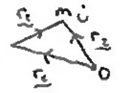
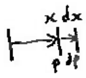
Russell Goyder





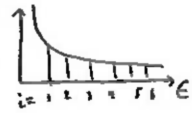
1A and 1B Physics.

Parallel axis	$I_o = I_c + M(r_c)^2$ $\longrightarrow$	 $I_o = \sum m_i (r_o)^2$
Perpendicular axis	$I_z = I_x + I_y$ $\longrightarrow$	$I_z = \sum m_i r_i^2$ — pythag.
Gyroscope	$\Omega = \dfrac{Mgr}{I\omega}$	$\Omega = \dfrac{d\theta}{dt} = \dfrac{d}{dt}\left(\dfrac{dL}{L}\right)$
Bragg Reflection	$n\lambda = 2d\sin\theta$	path diff.
Leonard-Jones 6-12 potential	$V(r) = \epsilon\left[\left(\dfrac{a_0}{r}\right)^{12} - 2\left(\dfrac{a_0}{r}\right)^6\right]$	
Joules Law	$dU = \left.\dfrac{\delta U}{\delta T}\right)_V dT + \left.\dfrac{\delta U}{\delta V}\right)_T dV$	$dU,\ dT = 0$ $dU \neq \therefore \left.\dfrac{\delta U}{\delta V}\right)_T = 0$
Kinetic theorey assumptions	normal + cunning $\longrightarrow$	(specular coll. / forces neg. / volume of molecule negl.
Solid angle. frac. of molecules within $\theta \to \theta + d\theta$	$\dfrac{\Omega}{4\pi} = \dfrac{1}{2}\sin\theta\, d\theta$	$\dfrac{\text{area}}{r^2}$
Flux	$N = \dfrac{1}{4} n \langle c \rangle \ (m^{-2})$	$\int$(angle frac.) (speed frac) $c\cos\theta \times n$.
Pressure	$p = \frac{1}{3} nm\langle c^2\rangle = \frac{1}{3}\rho\langle c^2\rangle$	$\int$ above $\times$ $\underbrace{2mc\cos\theta . c}$ momentum change.
Gas Law	$pV_m = \frac{1}{3} N_A m\langle c^2\rangle = \frac{1}{3} M_m \langle c^2\rangle = RT$ $\longrightarrow$	$KE_m = \dfrac{3RT}{2}$ equipartition.
microscopic gas Law	$p = nkT$	equipartition.
Dalton's Law of partial pressures	$p_T = \sum_i p_i \ / \ p_i = n_i kT$	(63)
Heat Capacities	$C_p - C_v = R$ (molar)	$dU = dQ - pdV \Rightarrow C_v dT = c_p dT - RdT$ if gas obeys Joules Law
Adiabatic ($dS = 0$)	$pV^\gamma = \text{const.}$ $\longrightarrow$	$dU = \cancel{dQ} + dW$ elim p, V, T using use $\Rightarrow \gamma = \dfrac{c_p}{c_v}$
Bulk modulus	$K = -V\left.\dfrac{\delta p}{\delta V}\right)_{S,T}$ (S adiabatic, T isothermal)	rate of change of p with fractional volume change K_T - gas law K_S - adiabatic.
Mean free path	$L = \dfrac{1}{\sqrt{2}\,\sigma n}$ where $\sigma = \pi d^2$	$L = $ mean speed / no. density $\times$ volume s^{-1}. ie distance (s^{-1})
Chance of different free paths.	$p(x) = e^{-x/L}$	 $p(x+dx) = p(x) + dp$ — change in p. also $= (\text{prob} \to x) \times (\text{prob} \to dx)$ $\left[\begin{array}{l} 1 - \text{prob of hit in } dx \\ = 1 - \alpha dx. \end{array}\right]$ $\langle x \rangle = \int_0^\infty x\, dp \Big/ \int_0^\infty dp$
Random walk	$x_{rms} = \sqrt{N}.L$ $\longrightarrow$	$x_n = x_{n-1} \pm L$ square, mean, root.
Transport Properties	– diff: $D = \frac{1}{3} L\langle c\rangle$ in $J_x = -\frac{\delta n}{\delta x}.D$	$\int$ physical prop. $\times$(angle frac)$\times$(speed frac) $c\cos\theta . n$
	– th. cond: $K = \frac{1}{3} L\langle c\rangle\rho c_v$ in $\dot{Q} = -K\frac{\delta T}{\delta x}$.	
	– visc: $\eta = \frac{1}{3} L\langle c\rangle\rho$ in $p_x = \eta\frac{\delta v_x}{\delta z}$	
Thermomolecular Pressure	$\dfrac{p_1}{p_2} = \sqrt{\dfrac{T_1}{T_2}}$	dynamic eq. when $J\rightarrow = J\leftarrow$ ie $n_1\langle c_1\rangle = n_2\langle c_2\rangle$ but $\langle c\rangle \propto \sqrt{T}$ $p \propto nT$
Equipartition	$\dfrac{1}{2} kT$	$\langle E\rangle = \int E(x) P(x)\, dx$ (normalised) $= \dfrac{\int\left(\frac{1}{2}kx^2\right) e^{\left(\frac{-\frac{1}{2}kx^2}{kT}\right)}}{\int e^{\left(\frac{-\frac{1}{2}kx^2}{kT}\right)}} = \frac{1}{2}kT$.

Isothermal atmos. pressure $\quad p = p_0 e^{-\left(\frac{mg}{kT}\right)z}$

$(p(z+dz) - p(z))A = -g \cdot / - nz$ but $p(z+dz) = p(z) + \frac{\delta p}{\delta z} dz \Rightarrow \int$

Boltzman factor $\quad \text{prob}_i \propto e^{-\epsilon_i/kT}$



isothermal atmosphere - special case.

Sedimentation $\quad n(h) = n_0 e^{-\frac{mgh}{kT}\left(\frac{\rho - \rho_L}{\rho}\right)}$

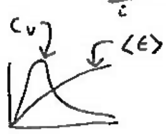
net grav. force $= gv(\rho - \rho_L)$ molecular density. turn into energy.

2 Level System $\quad p_1 = \left(1 + e^{-\Delta/kT}\right)^{-1}, \; p_2 = \left(1 + e^{\Delta/kT}\right)^{-1}$

$\overset{2}{\underset{1}{\uparrow\Delta}}$ g_2, g_1 assume $g_1 = g_2 = 1$ $\quad p_1 = e^{-\epsilon_1/kT} / \sum_i p_i$ ← normalise.

high, low Temp limits

2 Level Sys. - mean energy $\quad \langle\epsilon\rangle = \Delta / \left(1 + e^{\Delta/kT}\right)$ $\quad \sum_i \epsilon_i p_i / \sum p_i$



$U = N\langle\epsilon\rangle$ no. of systems.

$C_V = \frac{\delta}{\delta T}\left(N\langle\epsilon\rangle\right)\Big|_V$

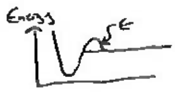
Schottky anomaly $\quad C_V = N\Delta^2 / \left(4kT^2 \cosh^2\left(\frac{\Delta}{2kT}\right)\right)$

Magnetic dipole moment $\quad M = N\mu \tanh\left(\mu B / kT\right)$

$\uparrow 2\mu B$: $\epsilon_1 = -\mu B$, $\epsilon_2 = \mu B$ $\quad M = N\langle m\rangle$

small x, $\tanh x \sim x$ $\Rightarrow \underline{B\chi = M}$ (const of prop)

Chem. reactions $\quad A + B \to C + D: \quad \dot{n}_C \propto n_A n_B e^{-\frac{\epsilon}{kT}}$



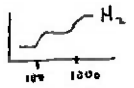
Arrhenius plot.....

Oscillator stats. $\quad \langle n\rangle = \frac{1}{e^{\hbar\omega/kT} - 1} \quad \langle\epsilon\rangle = \left(\langle n\rangle + \frac{1}{2}\right)\hbar\omega$

$\langle n\rangle = \sum_0^\infty n e^{\frac{\epsilon_n}{kT}} / \sum e^{\epsilon_n/kT}$ cancel 1/2 terms, $\frac{\sum n x^n}{\sum x^n} \to x \frac{d}{dx}\left[\ln \sum x^n\right]$ GP

Johnson noise $\quad \langle V^2\rangle = 4kTR\Delta f$ $\quad$ bollocks.

γ of Gases $\quad \gamma = \frac{c_p}{c_v} = 1 + \frac{2}{f}$ $\quad$ equipartition $+ C_{p_m} - C_{V_m} = R$



Maxwell-Boltzman Distribution. $\quad p(c) \propto c^2 e^{-\frac{mc^2}{2kT}}$

(velocity space) $p(c)\,dc = A e^{-\frac{mc^2}{2kT}} \cdot 4\pi c^2 dc \quad$ A - normalise.

$\left[\square \rightarrow p \propto v^3 e^{-\frac{mv^2}{2kT}}\right]$

Heat of Sublimation $\quad L_{sm} \sim \frac{z N_A \epsilon}{2}$ → relate to surface energy $\quad [\epsilon = \text{bond energy}]$

Surface energy $\quad \gamma \sim 2\epsilon n_s$ $\quad$ (n_s - no. density m^{-2})

zero creep method - equate energies then volumes const. cf ↗

Young Modulus $\quad E = \frac{1}{a_0}\left(\frac{\delta^2 U}{\delta r^2}\right)_{r = a_0}$.

Diffusion in solids $\quad D \propto \nu e^{-(\epsilon_V + \epsilon_D)/kT}$

Thermionic emission $\quad I \propto e^{\left(-\phi_0/kT\right)}$

Vapour pressure $\quad p_{vap} \propto T e^{-\frac{\epsilon}{kT}}$

Surface tension cf energy $\quad \gamma \sim 2\epsilon n_s$.

Pressure across liq (curved) surface $\quad \Delta p = \frac{2\gamma}{r}$ (spherical)

Vap. pressure over curved surface $\quad \Delta p_{vap} = \pm \frac{2\gamma}{r}\frac{\rho_v}{\rho_l}$

Liquid viscosity $\quad \eta = \eta_0 e^{\epsilon/kT}$

General Oscillation $x(t+T) = x(t) \,/\, \nu = \frac{1}{T} \,/\, \omega = 2\pi\nu$ o.k.

S.H.M. $\ddot{x} + \omega^2 x = 0$

solutions :
$$x = a\cos(\omega t + \phi)$$
$$x = A\cos\omega t + B\sin\omega t.$$
$$x = ae^{i\phi}e^{i\omega t} = Ae^{i\omega t}.$$

$A = a\cos\phi \quad B = -a\sin\phi.$
actually $z = Ae^{i\omega t}$, $x = \mathrm{Re}[z]$

energy
$$\frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 a^2$$
or $\frac{1}{2}\alpha\dot{x}^2 + \frac{1}{2}\alpha\omega^2 x^2 = \frac{1}{2}\alpha\omega^2 a^2$

α = inertial parameter, m, L.

or $E = \frac{1}{2}m\omega^2|A|^2$

Power $\bar{P} = \frac{1}{2}\mathrm{Re}[Fv^*] \longrightarrow$ care with multiplying complex no.s.

Kirchoff $\sum_i I_i = 0$ at node, $\sum ZI = \sum V$ round closed loop.

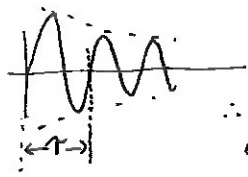
Damped SHM : $\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = 0$ $\quad 2\gamma = \frac{b}{m} \quad \omega_0^2 = \frac{k}{m}$ or $\frac{1}{LC}$.

overdamped : $x = e^{-\gamma t}(Ae^{qt} + Be^{-qt}) \rightarrow q^2 = \gamma^2 - \omega_0^2$

critically damped : $x = (A + Bt)e^{-\omega_0 t} \longrightarrow \gamma = \omega_0.$

underdamped : $x = e^{-\gamma t}(Ae^{i\omega_1 t} + Be^{i\omega_1 t})$ $\quad \omega_1^2 = \omega_0^2 - \gamma^2$

decrement $\frac{a_n}{a_{n+1}} = e^{\frac{2\pi\gamma}{\omega_1}} \longrightarrow$



$x_{max} = e^{-\gamma t}$
$\therefore \frac{a_n}{a_{n+1}} = \frac{e^{-\gamma t}}{e^{-\gamma(t+T)}}$

logarythmic decrement (natural) $\Delta = \frac{2\pi\gamma}{\omega_1}$

Forced (damped) SHM $m\ddot{x} + b\dot{x} + kx = F\cos(\omega t + \phi) = \mathrm{Re}[Fe^{i\omega t}]$

general equation $\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = \mathrm{Re}[Pe^{i\omega t}]$

solution : $z = \frac{Pe^{i\omega t}}{\omega_0^2 - \omega^2 + 2i\gamma\omega} \longrightarrow$ 2 arb const in P.
$x = \mathrm{Re}[z]$

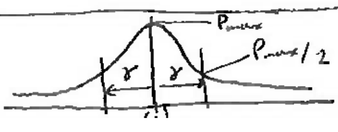
Impedance $Z = b + i\left(\omega m + \frac{k}{\omega}\right) \longrightarrow$ compare elec / mech
inertial term, - m L
restorative term, k, $\frac{1}{C}$
damping term. - b, R.

or $Z = 2\gamma + i\left(\frac{\omega^2 - \omega_0^2}{\omega}\right)$

Power (absorbed/disapated) $\langle P\rangle(\bar{W}) = \frac{b|F|^2}{2|Z|^2} \longrightarrow$ use impedence $v^* = \frac{F^*}{Z^*}$

Max power $\bar{W}_{max} = \frac{|F|^2}{2b} \longrightarrow$ equate this with $\frac{\text{this}}{2}$ to get $\omega_+ \omega_-$

Power bandwidth $= 2\gamma \; \left(= \frac{b}{m}\right)$



Quality Factor $\quad Q = \frac{\omega_0}{2\gamma}$

For good Q : no. of rads for energy to decay be e^{-1}

Q : $\frac{2\pi(\text{energy stored})}{(\text{energy lost per cycle})}$

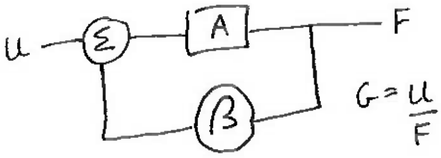
Q : π/Δ

Q : $\frac{\text{velocity resonance freq.}}{\text{bandwidth.}}$

Q : $\frac{\text{amplitude at } \omega_0}{\text{amplitude at } \omega = 0}$ } same $|F|$

Feedback
- gain

$$G = \frac{A}{1 - A\beta}$$

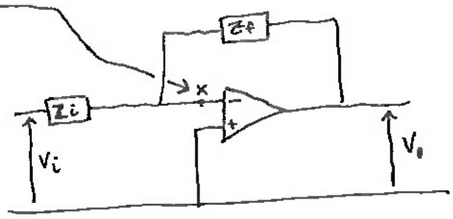


Inverting amplifiers:

virtual earth at -ve input

$\Sigma I_i = 0$

$G = -Z_f / Z_i$



Coupled Oscillations

$$|\underline{A} - \omega^2 \underline{I}| = 0$$

Normal modes

$$\sum_{n=1}^{N} E_n = E_T$$

Energy in normal mode n. N total modes. - no energy interchange between modes.

Newtons Law of Gravity

$$\underline{f} = -\frac{GM}{r^2}\underline{i}_r$$

Work done

$$\int_A^B \underline{f} \cdot \underline{dl} = -(\phi_B - \phi_A)$$

Conservation of energy

$$\frac{1}{2}mv^2 + \phi = 0$$

$$\int_A^B \frac{d}{dt}(m\underline{v}) \cdot dl = \frac{m}{2}\int_A^B \frac{d\, v \cdot v}{dt}\, dt = \phi_B - \phi_A.$$

Work done - differential form:

$$\underline{f} = -\nabla\phi$$

(conservative fields).

Keplers Laws

1 ellipse, sun-foc. 2 equal area equal time 3 $T \propto r^{3/2}$

Potential

$$\phi = -\frac{GM}{r}$$

Gauss's Law

$$\int_S \underline{f} \cdot \underline{dA} = -4\pi GM$$

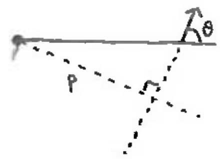
$$\int_S \underline{f} \cdot \underline{dA} = -GM \int_{\text{Sphere}} d\Omega$$

Angular momentum

$$\underline{L} = m(\underline{r} \times \underline{v})$$

$L = mrv\sin\theta$.

Collision Parameter $p = r\sin\theta$



Kepler no. 3 $T\left(=\frac{2\pi r}{v_\phi}\right) = \frac{2\pi}{\sqrt{GM}} r^{3/2}$ $\rightarrow$ $\frac{v_\phi^2}{r} = \frac{GM}{r^2}$

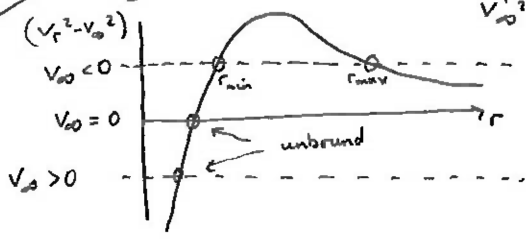
centrip. = grav. (circular orbits $\rightarrow L = mv_\phi r$ const)

Energies $T_{(KE)} + U_{(PE)} = -\frac{1}{2}\frac{GMm}{r}$

$KE = \frac{1}{2} PE.$

Specific angular momentum $h = vp = vr\sin\phi.$

General Orbits $v_r^2 - v_\infty^2 = \frac{2GM}{r} - \frac{h^2}{r^2}$ $\rightarrow$ $\frac{1}{2}m(v_\phi^2 + v_r^2) + m\phi = \text{cons}$ $\uparrow v_\infty^2$



Electric field strength $\underset{\sim}{E} = \frac{q}{4\pi\varepsilon_0 r^2}\underset{\sim}{i_r}$

Electric potential $\underset{\sim}{E} = -\nabla V$

$V = \frac{q}{4\pi\varepsilon_0 r}$

Gauss's Law $\int_S \underset{\sim}{E}\cdot d\underset{\sim}{A} = \frac{q}{\varepsilon_0}$ $\rightarrow$ $\int_S \underset{\sim}{E}\cdot d\underset{\sim}{A} = \frac{\int_S q\, d\Omega}{4\pi\varepsilon_0}$

Elec. f. strength of - wire length λ $E_r = \frac{\lambda}{2\pi\varepsilon_0 r}$ $\rightarrow$ (or coulombs $m^{-1} = \lambda$)

- charged conducting plane $E_\perp = \frac{\sigma}{\varepsilon_0}$ $\rightarrow$ (σ Cm^{-2})

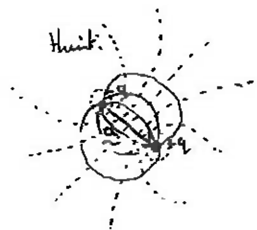
Capacitance of sphere $C = 4\pi\varepsilon_0 R$

$\int_\infty^R \underset{\sim}{E}\cdot dr = -(V_R - V_\infty)$ and $Q = CV.$

-of coaxial cable $C = \frac{2\pi\varepsilon_0}{\ln(b/a)}$

(earth b) (λ (cm^{-1}) get E then use $\underset{\sim}{E} = -\underset{\sim}{\nabla} V$.

-of parallel plate cap. $C = \frac{\varepsilon_0 A}{d}$



Electric dipole moment $\underset{\sim}{p} = \sum_i q\underset{\sim}{r_i}$ $\underset{\sim}{p} = q\underset{\sim}{a}$

Electrostatic potential energy $W = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}QV = \frac{1}{2}CV^2$

Energy Density $u = \frac{1}{2}\varepsilon_0 E^2$

energy (Volume)$^{-1}$

$w = \frac{1}{2}\frac{Q^2}{C} \rightarrow V = Ed$, $Q = CV$, $C = \frac{\varepsilon_0 A}{d.} \rightarrow u.$

Magnetic flux density $\underset{\sim}{B} = \frac{\mu_0 P}{4\pi r^2}\underset{\sim}{i_r}$

Magnetostatic Potential $\quad \underset{\sim}{B} = -\mu_0 \nabla V_m$

[Magnetic field strength $\quad \underset{\sim}{H} = -\nabla V_m$]

Integral form $\quad V_m = \int_{\infty}^{r} -\frac{1}{\mu_0} \cdot \underset{\sim}{B} \cdot \underset{\sim}{dl}$.

Gauss's Law $\quad \int_S \underset{\sim}{B} \cdot d\underset{\sim}{A} = 0 \longrightarrow$ no free poles. differential form $\underset{\sim}{\nabla} \cdot \underset{\sim}{B} = 0$.

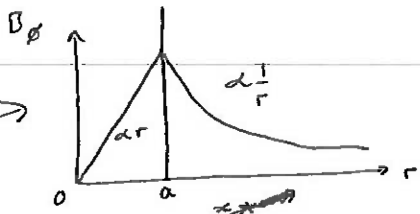
Magnetic dipole moment : $\quad \underset{\sim}{m} = p\underset{\sim}{a}$

Couple on dipole in field : $\quad \underset{\sim}{G} = \underset{\sim}{m} \times \underset{\sim}{B}$

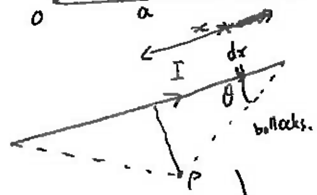
$$\underset{\sim}{G} = \underset{\sim}{r} \times \underset{\sim}{f} = \underset{\sim}{a} \times p\underset{\sim}{B} = p\underset{\sim}{a} \times \underset{\sim}{B}.$$
cf. $F = Eq$

magnetic dip. moment $\quad \underset{\sim}{m} = I\, d\underset{\sim}{A}$ $\quad$ current flowing in current loop of area $d\underset{\sim}{A}$. dir - corkscrew rule.

Ampères circuital theorem : $\quad \oint \underset{\sim}{B} \cdot \underset{\sim}{ds} = \mu_0 I_{enclosed}$.



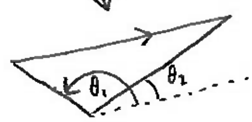
Mag. field - long wire : $\quad B_\phi = \frac{\mu_0 I r}{2\pi a^2}$



Biot-Savart Law : $\quad d\underset{\sim}{B} = \frac{\mu_0 I}{4\pi} \frac{\underset{\sim}{ds} \times \underset{\sim}{r}}{r^3}$

Mag field - finite wire : $\quad \underset{\sim}{B} = \frac{\mu I}{4\pi} \left(\frac{\cos\theta_2 - \cos\theta_1}{a} \right)$

- infinite solenoid : $\quad B_i = \mu_0 N I \longrightarrow$ Ampere.



- on axis of current loop : $\quad B_{\parallel} = \frac{\mu_0 I}{2} \frac{a^2}{(x^2+a^2)^{3/2}}$

- toroid $\quad B_\phi = \frac{a}{r} \mu_0 N I$

- finite solenoid on axis $\quad B_{\parallel} = \frac{\mu_0 I N}{2} (\cos\theta_2 - \cos\theta_1)$

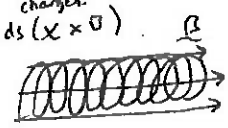
Force on current element in mag. field. $\quad \underset{\sim}{f} = I(\underset{\sim}{ds} \times \underset{\sim}{B})$

$$f_p = p\,dB = \frac{\mu_0 I p}{4\pi} \frac{\underset{\sim}{ds} \times \underset{\sim}{r}}{r^3}$$
$$\therefore f_I = -f_p \quad \underset{\sim}{B} = \frac{\mu_0 p}{4\pi}\left(-\frac{\underset{\sim}{r}}{r^3}\right)$$

Force on charged particle moving in mag. field. $\quad f = q(\underset{\sim}{v} \times \underset{\sim}{B})$

$$\therefore \underset{\sim}{f} = q\, \underset{\text{no. density of charges.}}{\underline{N_q}}\, v\,(\underset{\sim}{ds} \times B) = qN_q\,ds\,(\underset{\sim}{v} \times B)$$

+ elec. field .... $\quad f = q(\underset{\sim}{v} \times \underset{\sim}{B} + \underset{\sim}{E})$



cyclotron frequency $\downarrow$ (gyrofrequency) $\quad \nu_g = \frac{1}{2\pi} \frac{qB}{m} \longrightarrow T = \frac{2\pi r_g}{V_\perp} = \frac{2\pi}{V_\perp} \frac{m V_\perp}{qB}$

Radius (gyroradius) $\quad r_g = \frac{m V_\perp}{qB} = \text{const.}$

Lorentz transformations

$$x' = \gamma(x - Vt)$$
$$y' = y$$
$$z' = z$$
$$t' = \gamma\left(t - \frac{Vx}{c^2}\right)$$

$$\gamma = \left(1 - \frac{V^2}{c^2}\right)^{-\frac{1}{2}}$$

Time difference $$t_2' - t_1' = -\frac{\gamma V}{c^2}(x_2 - x_1)$$

for events simult. in S.

Time dilation $$t = \frac{t'}{\gamma}$$ sub x' in t'.

Interval $$\Delta s^2 = c^2\Delta t^2 - \Delta x^2 - \Delta y^2 - \Delta z^2.$$ invariant.

Proper time $$\Delta\tau = \frac{\Delta s}{c}$$

Proper length $$L_0$$

Length contraction $$L = \frac{L_0}{\gamma}$$

Velocity addition:

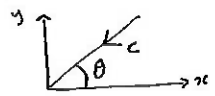
$$u_x' = \frac{u_x - V}{1 - \frac{Vu_x}{c^2}}$$

momentum four vector
$$\underset{\sim}{U} = (\gamma u_x, \gamma u_y, \gamma u_z, \gamma)$$
Lorentz transformations

$$u_y' = \frac{u_y}{\gamma\left(1 - \frac{Vu_x}{c^2}\right)}$$

$$u_z' = \frac{u_z}{\gamma\left(1 - \frac{Vu_x}{c^2}\right)}$$

Transforming light. $$\cos\theta' = \frac{\frac{V}{c} + \cos\theta}{1 + \frac{V}{c}\cos\theta}$$



Doppler effect $$\nu_{obs} = \frac{\nu_0}{\gamma\left(1 + \frac{u}{c}\cos\theta\right)}$$

ok.

Doppler effect - radially away from obs. $$\nu_{obs} = \sqrt{\frac{c-u}{c+u}}\,\nu_0$$

Minowski metric $$ds^2 = c^2dt^2 - dx^2 - dy^2 - dz^2.$$

momentum $$p = \gamma m\underset{\sim}{u}.$$

velocity four vector $$\underset{\sim}{U} = [\gamma u_x, \gamma u_y, \gamma u_z, \gamma]$$

momentum four vector $$\underset{\sim}{P} = [\gamma m u_x, \gamma m u_y, \gamma m u_z, m\gamma]$$

$m\int \frac{d\gamma u}{dt} \cdot dx \qquad dx = u\,dt.$

Energy

$\Downarrow$

$$\int \underset{\sim}{f} \cdot d\underset{\sim}{x} = mc^2(\gamma_2 - \gamma_1)$$

Total energy $\quad E = \gamma mc^2$

Rest mass energy $\quad E_0 = mc^2.$

Kinetic energy $\quad = E - E_0 = (\gamma - 1)mc^2.$

Energy / momentum $\quad E^2 - p^2c^2 = (mc^2)^2$ → equate norms of four vectors (mom.) in own + ref. frame.

momentum $\quad p^2 = (\gamma^2 - 1)m^2c^2 \quad \leftarrow \quad E = \gamma mc$

Force $\quad \underset{\sim}{f} = \frac{\gamma^3 m}{c^2}\left(\frac{d\underset{\sim}{u}}{dt} \cdot \underset{\sim}{u}\right)\underset{\sim}{u} + \gamma m \frac{d\underset{\sim}{u}}{dt}.$

$$\gamma = \left(1 - \frac{\underset{\sim}{u} \cdot \underset{\sim}{u}}{c^2}\right)^{-1/2}$$

$$\underset{\sim}{f} = \frac{d}{dt}\gamma m\underset{\sim}{x}$$

charged particles on moving in $\underset{\sim}{B}$ or $\underset{\sim}{E}$.

$\underset{\sim}{E}$: $\quad u = \dfrac{eEt/m}{\left(1 + \dfrac{e^2E^2t^2}{m^2c^2}\right)^{1/2}}$

$\underset{\sim}{B}$: $\quad r_g = \dfrac{\gamma m u_\perp}{eB}$

$$\underset{\sim}{f} = q(\underset{\sim}{u} \times \underset{\sim}{B} + \underset{\sim}{E})$$

Kirchoffs Law $\left.\frac{\delta \Delta_r H}{\delta T}\right)_p = \Delta_r C_p$ (diff. $\Delta_r H = \nu_L H_L + \nu_M H_M + \ldots - \nu_A H_A - $)

where $\Delta_r C_p = \nu_L C_p^{(L)} + \nu_M C_p^{(M)} + \ldots - \nu_A C_p^{(A)} - \nu_B C_p^{(B)}$

Work done on system $dw = -p_{ext}\, dV$

piston.

rev $\therefore p_{int} = p_{ext} = \frac{nRT}{V} \Longrightarrow \int$

In a reversible process $w' = nRT \ln\left(\frac{V_f}{V_i}\right)$ (rev max)

G, as f(p) $G(p) = G^\circ + nRT \ln\left(\frac{p}{p^\circ}\right)$ — master eq'n ③ $\left.V = \frac{\delta G}{\delta p}\right)_T$ $\uparrow$ $\frac{nRT}{p}$

Gibbs-Helmholtz eq'n $\frac{\delta}{\delta T}\left(\frac{G}{T}\right)_p = -\frac{H}{T^2}$ $\longrightarrow$ $\frac{d}{dT}(GT^{-1}) = \frac{-G}{T^2} + T^{-1}\frac{dG}{dt}$. $= \frac{-(H-TS)}{T^2} + \frac{1}{T}(-S)$

$= \frac{-H}{T^2}$

[ok for $\Delta_r H$, $\Delta_r G$]

Chemical potential + G at const p, T — sod this one. $\longrightarrow$ $G(p, T, n_A, n_B)$ chain rule.

Chemical potential $\mu_A = \mu_A^\circ + RT \ln\left(\frac{p_A}{p^\circ}\right)$ $\longrightarrow$ μ_A dep. on p_A in same way as G. $\left.V = \frac{\delta G}{\delta p}\right)_T$.

$\Delta_r G^\circ$ and eq. kp.

$\Delta_r G^\circ = -RT \ln K_p$ $\longrightarrow$ ① $d\xi\, \nu_A = dn_A$ ② $\frac{dG}{d\xi} = 0$ eq. ③ $\mu_i(p_i)$ ④ define $\Delta_r G$ as $\nu\mu^\circ_{prod} - \nu\mu^\circ_{react}$.

Van't Hoff Isochore - temp dep. of Kp $\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ(T)}{RT^2}$ $\longrightarrow$ from Gibb Helmholtz and $\Delta_r G = -RT \ln K_p$.

eq. $\therefore G_m^\alpha = G_m^\beta$ = $Vdp - SdT$

Clapeyron eq'n $\frac{dp}{dT} = \frac{\Delta H_m}{T\Delta V_m}$ $\longrightarrow$  $\longrightarrow$ $T\Delta S_{phase\ change} = \Delta H_{phase\ change}$. $\int$ assume $\Delta_r H$ const.

Electrode potentials $\Delta G_{cell} = -nFE$ $\longrightarrow$ $\nu_A A + \nu_B B \rightarrow \nu_{prod}$ prod. involves n electrons. dG = add rev work = $n d\xi FE$

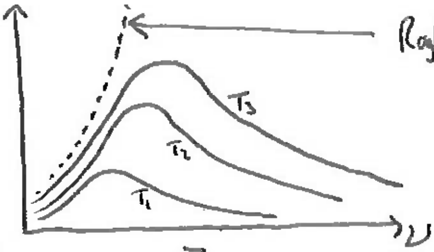
Nernst Eq'n. $E = E^\circ - \frac{RT}{nF} \ln\left[\frac{a_L^{\nu_L} a_M^{\nu_M}}{a_A^{\nu_A} a_B^{\nu_B}}\right]$ $\longrightarrow$ after $d\xi$, $dn_A = \nu_A d\xi$ $dG = \mu_i dn_i$

$dG = -nFEd\xi$

$\mu_i = \mu_0 + RT \ln a_i$

Evidence for quantisation : I

Black body radiation :



Rayleigh – Jeans Law – $dU = \rho d\lambda$

$$\boxed{\rho = \frac{8\pi kT}{\lambda^4}}$$

but when λ is small ..... ?

ultraviolet catastrophe !

Stephan's Law

$I \propto T^4$

Wien's displacement Law $[\nu I_{max} \propto T]$

$\nu_{max} \propto T$

$E = h\nu$ – photon

so, Planck : $dU = \rho d\lambda$

$$\rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right)$$

No U.V. catastrophe with Planck.

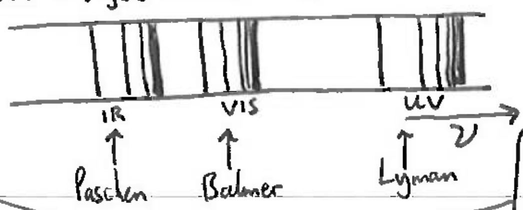
Photoelectric effect – UV light incident on metal $\Longrightarrow$ ejection of e^-

Obs: ① Threshold ν for emission indep of I
② KE of e^- $\propto \nu$ alone.
③ Even for very low I, get emission

$$\frac{1}{2}m_e v^2 = h\nu + \varnothing$$

Explain: ① Threshold $h\nu > \varnothing$ – work function.
② KE is $\propto \nu$
③ Low I – no prob. only need $h\nu \times 1$.

Hydrogen Spectra



Rhdberg : $\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ trans from $n_2 \longrightarrow n_1$.

Bohr explaination : Three main postulates
① e^- move in circular orbits around nucleus
② Only fixed orbits allowed – no emission when in orbit.
③ One orbit $\rightarrow$ another $\Rightarrow$ photon emission.

good cos quantitative

but still a fudge until ..... Einstein + Schrodinger.

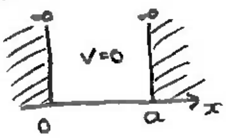
– de Broglie – $p = h/\lambda$ (1923)   Heisenberg (1926) – $\Delta p \Delta x \geq \frac{\hbar}{2}$ ✱ with Bohr picture – we have improved !

WAVE MECHANICS : Schrödinger Eq'n :

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0.}$$

$\psi^*\psi dx$ – prob of $x \longrightarrow x + dx$ (Born postulate)

Particle in box :



S.E. in 1D : $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$. Set $V = \infty$ outside $V = 0$ inside

$\therefore \frac{d^2\psi}{dx^2}\left(-\frac{\hbar^2}{2m}\right) = E\psi$

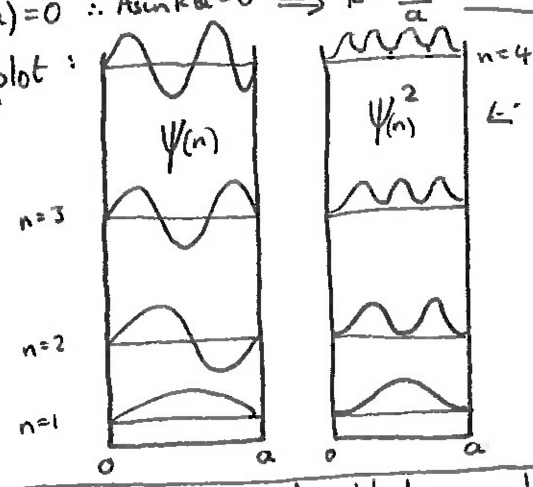
SHM eq'n – try $\psi = A\sin kx + B\cos kx$.

Boundary conds $\psi(0) = 0 \therefore B = 0$, $\psi(a) = 0 \therefore A\sin ka = 0 \Longrightarrow k = \frac{n\pi}{a}$

$$\psi = A\sin\left(\frac{n\pi x}{a}\right)$$

(subst) $E = \frac{n^2 h^2}{8ma^2}$

Normalise $\int_0^a \psi^*\psi dx = 1 \therefore A = \sqrt{\frac{2}{a}}$ plot :



– energy quantised
– $P(x)$ – nodes
– $n = 0$, $\psi = 0$
$n = 1$ – lowest poss n
$\Rightarrow$ zero point energy
– spacing $\propto \frac{1}{m} \propto \frac{1}{a}$
$\therefore$ small situations, noticed

2D – solve SE for box, get

$$\psi = \frac{2}{a}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{a}\right)$$

$$E = (n_x^2 + n_y^2)\frac{h^2}{8ma^2}$$

$\Longrightarrow$ for some sets of q. no's eg 2,1 1,2

same E, diff. $\psi_{2,1}$ $\psi_{1,2}$

– DEGENERACY.

3D get :

$(n_x^2 + n_y^2 + n_z^2)$		Degeneracy
12	222	1
11	311, 131, 113	3
9	221, 212, 122	3
6	211, 121, 112	3
3	111	1

Solving S.E. for the Hydrogen atom :

Turn SE. $\longrightarrow$ sph. polars , get $R(r)$ and $Y(\theta, \varnothing)$. when seperate variables $\psi = R(r).\theta(\theta)\Phi(\varnothing)$.
– get 3 o.d.e's in $\theta, \varnothing, r$.

get n principal $n = 1, 2$
l asimuthal/orb. $l = 0 \rightarrow (n-1)$
m_l magnetic $m_l = 0 \rightarrow -l \rightarrow +l$.
(m_s – $\pm\frac{1}{2}$ spin)

restrictions result from need for ψ – well behaved

$$\psi(n, l, m_l) = R(n, l)\,Y(l, m_l)$$

Get : $\psi_{1s} = Const_{1s}\, e^{-r/a_0}$
$\psi_{2s} = -Const_{2s}\, r e^{-r/2a_0}$

sph. symm.
– get Bohr rad.

$\psi_{2p_x} = Const_{2p_x} \cdot r e^{-r/2a_0} \sin\theta\cos\varnothing$

ang. dependence

$$E_n = \left(\frac{-\hbar^2}{2ma_0^2}\right)\frac{1}{n^2}$$

From Na spectrum, get selection rule - $\Delta L = \pm 1$ $\Delta m_L = -1, 0, +1$ on anything, for atoms.

n determines total no. of nodes ie $(n-1)$

" " " no. of orbitals - n^2

" " " energy

L azimuthal from $R(L)\,Y(L)$

orbital degeneracy $(2L+1)$.

determines orbital angular momentum : $M^2 = L(L+1)\hbar^2$

m_L - determines orientation of orbital.

quantised angular mom? think wave on a ring :

$2\pi r = n\lambda$

$M = mvr$, $\lambda = \frac{h}{mv}$

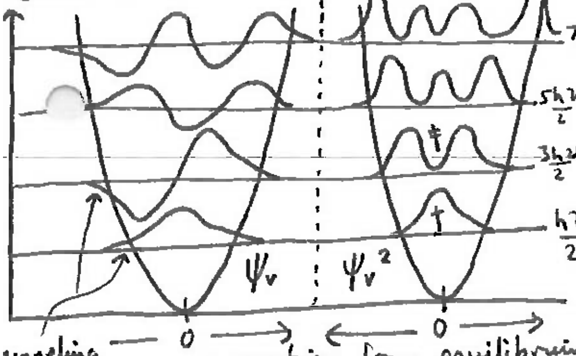
2D gives $M = L\hbar$ 3D ⇒ residual M zero point energy

MOLECULAR SPECTRA - already done atomic spectra - use S.E. again :

- Vibration : S.H.O. model - $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\mu = \frac{m_A m_B}{m_A + m_B}$ Pot. energy $= \frac{1}{2}kx^2$.

S.E. : $\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}(E - \frac{1}{2}kx^2)\psi = 0$ try $\psi = Ae^{-\alpha^2 x^2/2}$ ⟶ $\underbrace{\left(\frac{2\mu E_0}{\hbar^2} - \alpha^2\right)}_{=0} + x^2\underbrace{\left(\alpha^4 - \frac{\mu k}{\hbar^2}\right)}_{=0} = 0$

elim α ⇒ $E = \frac{1}{2}h\nu_0$ or $E = (v+\frac{1}{2})h\nu_0$ (3D) ⇒ vib. energy levels are equally spaced.



$\frac{7h\nu_0}{2}$ $\frac{5h\nu_0}{2}$ $\frac{3h\nu_0}{2}$ $\frac{h\nu_0}{2}$

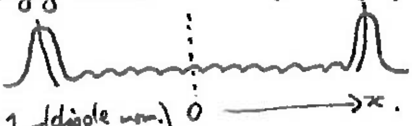
ψ_v ψ_v^2

tunneling 0 seperation from equilibrium

† - opposite of classical prediction.

‡ - never at eq'm position.

classical limit ⟶



Selection rule : $\Delta v = \pm 1$ (dipole mom. necessary)

$\psi = Ae^{-\alpha^2 x^2/2}$ sol'n for $v=0$.

for $v>0$, $\psi_v = N_v H_v(\alpha^{1/2}x)e^{-\alpha^2 x^2/2}$

N_v - normalisation

$H_v \alpha^{1/2} x$ - Hermite polynomials.

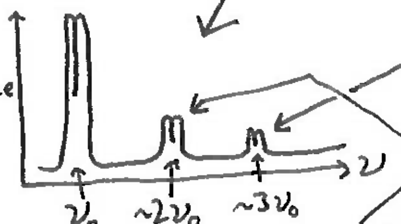
("modified sine wave".)

! - only get spectrum if there is a dipole moment

A∿∿∿B - nothing if A = B ok if A ≠ B.

In real life ..... Anharmonic model

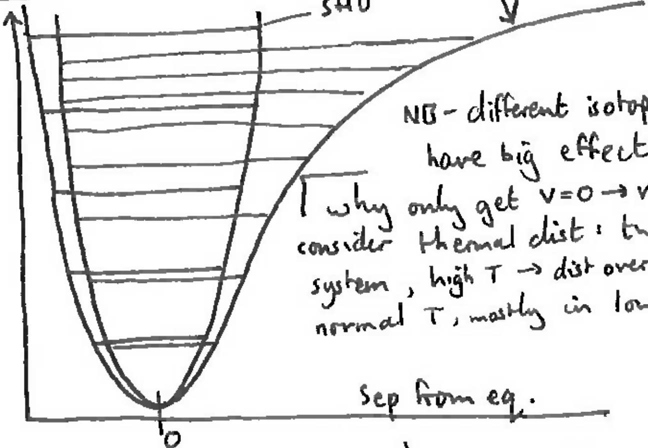
Also get



absorbance ν

ν_0 $\sim 2\nu_0$ $\sim 3\nu_0$

- overtones - changes of $\Delta v = \pm 2, \pm 3$ etc.
- get progressively weaker.
- doublets. - approx integer multiples of ν_0.



E SHO 0 Sep from eq.

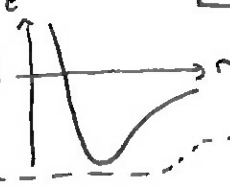
NB - different isotopes eg HCl DCl have big effect on ν_0

why only get $v=0 \rightarrow v$ trans'ns ?

consider thermal dist : two level system, high T → dist over states normal T, mostly in lower state

The last straw : MORSE POTENTIAL

use in S.E. instead of $\frac{1}{2}kx^2$



E r

⟶ get ⟶

v = 2 1 0

$E_v = (v+\frac{1}{2})h\nu_e - (v+\frac{1}{2})^2 h\nu_e x_e$

Anharmonicity const

- Rotation - rigid rotator model.

two axes. $E_{rot} = \frac{1}{2}I\omega_x^2 + \frac{1}{2}I\omega_z^2$

$I = \mu r_{AB}^2$

2D - Q mech :

r_{AB} A B

$\pi r_{AB} = J\lambda = \frac{Jh}{mv}$ ∴ $M = \frac{mvr_{AB}}{2} = \frac{Jh}{2\pi} = J\hbar$

rot. q. n. $\left[E = \frac{1}{2}I\omega^2\right]$

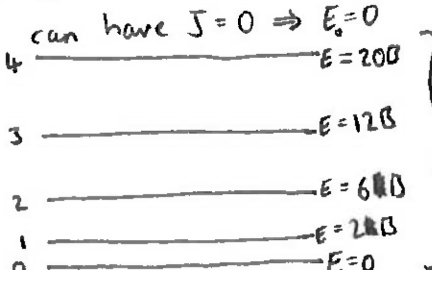
$\boxed{\text{Two fold degeneracy - clockwise/anticlockwise}}$

3D get $M^2 = J(J+1)\hbar$ (again) and $E_{rot} = \frac{\hbar^2}{2I}J(J+1)$

2D 3D

$\boxed{\text{degeneracy} = 2J+1}$

can have $J=0 \Rightarrow E_0 = 0$



J = 4 $E = 20B$

3 $E = 12B$

2 $E = 6B$

1 $E = 2B$

0 $E = 0$

microwave spectrum.

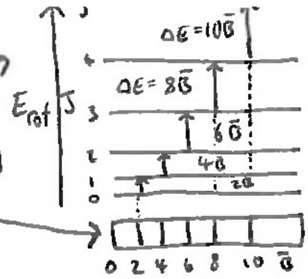
Selection rules : ① Molecule must have dipole moment for pure rotational spectra - not H_2 etc.

② $\Delta J = \pm 1$

B - rotational const. $\bar{B}$ in $cm^{-1} = \frac{h}{8\pi^2 I c}$

Consider transition $J = J' \rightarrow J = J'+1$

$\Delta E/_J = 2B(J'+1)$

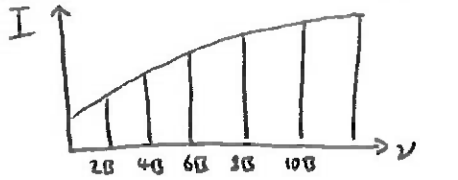


even spacing

incidentally..... spacings $\rightarrow B \rightarrow I \rightarrow r_{AB}^{\circ}$ quick + accurate.

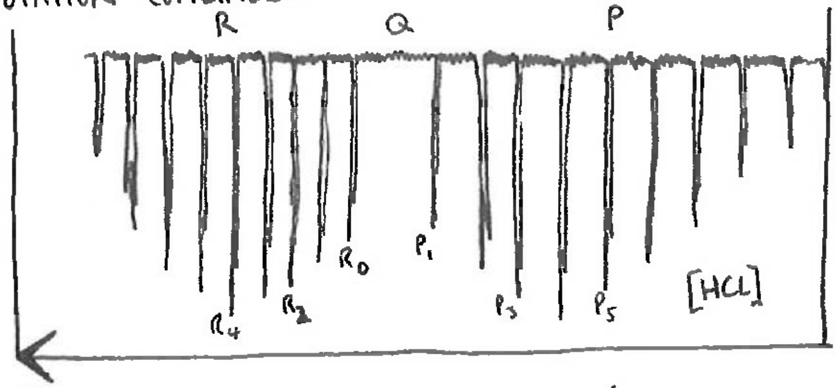
Intensity: rot levels close tog. ∴ low ↓ results in distrib. over levels (boltzmann)

spectrum ∴ max no. of transitions for J = 5 − 11



VIBRATION AND ROTATION COMBINED:

transmittance

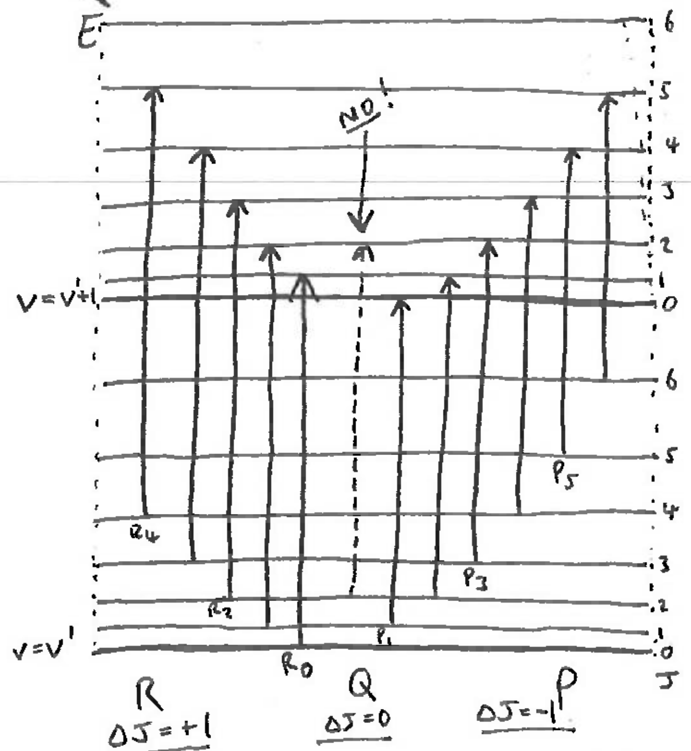


all associated with $\Delta V = 1$

Selection Rules together:

$\Delta V = \pm 1$
$\Delta J = \pm 1$] both!

– origin of double peak in overtone spectrum.



– intensity of absorbtion ∝ ~~deg~~ number of molecules making transition
  – ie ∝ degeneracy of particular set of Q Nos.
  – ∝ to thermal effects – Boltzman.

— split peaks – $H^{35}Cl$ and $H^{37}Cl$.

– spacing between peaks – 2B but B decreases with higher V (ie with inc. energy) $B = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu r_{AB}^2}$

more vib, inc in this

– $\Delta E = \Sigma \Delta E_{vib}, \Delta E_{rot}$

KINETICS. – Stoichiometric coeffs $\nu_A + \nu_B \rightarrow \nu_L L + \nu_M M$ $\quad \nu_{A,B}$ −ve $\quad \nu_{L,M}$ +ve

time independent stoichiometric reaction – no change of ν_i with time

For $aA + bB \rightarrow yY + zZ$, rate (prod/consump.) $= -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{y}\frac{d[Y]}{dt} = \frac{1}{z}\frac{d[Z]}{dt}$

Rate of cons/prod not same for all species. ⟶ rate of reaction $= r = \frac{1}{V}\frac{d\xi}{dt}$ where $\xi = \frac{n - n^{\circ}}{\nu}$

ξ – always same. – careful how define though. volume of system. n° – initial amount, ν – st. coeff.] for a species

For some reactions r can be written (empirically)

as $r_A = k_A [A]^{\alpha}[B]^{\beta}$ $\quad \frac{k_A}{-\nu_A} = k$ $\quad$ eg for $A + 2B \rightarrow 3Z$ $\quad$ [Rate Law – rate (conc) fixed temp]

rate of cons. A $\quad$ rate const w.r.t. k $\quad$ rate const/coeff $\quad k = k_A = \frac{k_B}{-2} = \frac{k_Z}{3}$

Elementary reactions – one occuring with no intermediates.

What order is reaction? ① rate $= k[A]^{\alpha}$ plot $\ln r \leftrightarrow \ln[A]$ get the necessaries (differential method)

② 1st order? Check: $\text{rate}_A = -\frac{d[A]}{dt} = k_A[A]$ $\quad \int \longrightarrow \ln\left(\frac{[A]_t}{[A]_0}\right) = -k_A t$

plot: this against this

③ 2nd Order? $2[A] \longrightarrow$ prods. $r_A = -\frac{d[A]}{dt} = k_A [A]^2 \int\longrightarrow \frac{1}{[A]_t} - \frac{1}{[A]_0} = k_A t$ plot $\frac{1}{[A]_t}$ vs t.

General - measure $[A]$ as $f(t)$.
└ see which method ①, ②, ③ gives best fit.

½ Life 1st order $t_{1/2} = \frac{\ln 2}{k_A}$ 2nd order $t_{1/2} = \frac{1}{k_A[A]_0}$ dep. on starting conc.

Reactions with >1 reactant: $aA + bB \longrightarrow$ prods. $r_A = -\frac{1}{a}\frac{d[A]}{dt} = k[A][B]$

if $\frac{[B]_0}{[A]_0} = \frac{b}{a}$ then $\frac{1}{[A]_t} - \frac{1}{[A_0]_0} = kbt$

Isolation method: Keep all but one under study in excess ∴ [ ] ~ const.

Slow Reactions - look at initial rates - inspection of data.

Temperature dependence: Arrhenius: $k = Ae^{-E_{act}/RT}$ two temps: $\boxed{\ln\left(\frac{k_{T_2}}{k_{T_1}}\right) = -\frac{E_{act}}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]}$

Obtaining Kinetic data: titration, light absorption ($\ln[Ab] \propto$ conc) elec. potentials, conductivity, pressure changes, (Nernst eq'n)

Collision Theorey: no. of collisions of A with Bs (s^{-1}) $Z_B = N_B \pi d_{AB}^2 \langle u \rangle$ with A molecules m^{-3}....

.... $Z_{AB} = N_A N_B \pi d_{AB}^2 \langle u \rangle$ but $\langle u \rangle = \sqrt{\frac{8kT}{\pi\mu}}$ ∴ $Z_{AB} = N_A N_B d_{AB}^2 \sqrt{\frac{8\pi kT}{\mu}}$ $\mu = \frac{m_A m_B}{m_A + m_B}$.

(collisions between A, B molecules s^{-1} and m^{-3})

So for $A + B \xrightarrow{k}$ prod.

$k = -\frac{dN_A}{dt} = Z_{AB}\, e^{-E/kT}$

in terms of conc.... $Z'_{AB} = \frac{Z_{AB}}{L[A][B]}$ (6×10^{23})

steric factor p - to fit data ie a fix - fudge factor.

Three atom system: PE surface:

Steady State Approx: Get elemental reactions. Assume $\frac{d[\text{Intermediate}]}{dt} = 0$ subst for [Intermediates], get rate expression.

Eg $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Mech: $N_2O_5 \longrightarrow NO_2 + NO_3\cdot$ $r_1 = k_1[N_2O_5]$

$NO_2 + NO_3\cdot \longrightarrow N_2O_5$ $r_{-1} = k_{-1}[NO_2][NO_3\cdot]$

$NO_2 + NO_3\cdot \longrightarrow NO_2 + O_2 + NO$ $r_2 = k_2[NO_2][NO_3\cdot]$

$NO + NO_3\cdot \longrightarrow 2NO_2$ $r_3 = k_3[NO][NO_3\cdot]$

get $\frac{d[NO_3\cdot]}{dt}$ put $= 0$ same for $[NO]$

Unimolecular - $A \longrightarrow B + C$

often obs: 1st order, become 2nd order as reaction proceeds.

Lindemann Mech: $A + A \rightarrow A^* + A$ k_2 (activated)

$A^* + A \rightarrow A + A$ k_{-2}

$A^* \xrightarrow{k_1}$

Steady State approx on $[A^*]$

Thermal decomposition of H_2, Br_2 - Linear Chain r.

Initiation - $Br_2 + M \rightarrow 2Br\cdot + M$
Prop. $Br\cdot + H_2 \rightarrow HBr + H\cdot$
Prop. $H\cdot + Br_2 \rightarrow HBr + Br\cdot$
Inhib. $H\cdot + HBr \rightarrow Br\cdot + HBr$
Term $Br\cdot + Br\cdot + M \rightarrow Br_2 + M$

steady state approx for $Br\cdot$, $H\cdot$ then HBr (subst)

why not.... $H_2 + M \longrightarrow 2H\cdot + M$ - coz H_2 bond strong
.... $Br\cdot + HBr \rightarrow Br_2 + H\cdot$ coz $H{-}Br > Br_2$ bond strength.

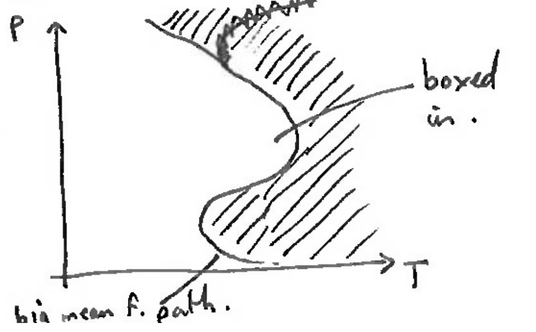
For Cl: $H\cdot + HCl \rightarrow H_2 + Cl\cdot$ ✗

I: $I\cdot + H_2 \rightarrow HI + H\cdot$

Photochemical - $Br_2 + h\nu \rightarrow 2Br\cdot$ $r = 2I_a$ (no. of ok ν photons $m^{-3}s^{-1}$).

Branched Chain reactions

Init $H_2 + O_2 \longrightarrow 2OH\cdot$ coll. with wall.
Prop. $OH\cdot + H_2 \longrightarrow H_2O + H\cdot$
Branch. $H\cdot + O_2 \rightarrow OH\cdot + O\cdot\cdot$
Branch $O\cdot\cdot + H_2 \rightarrow OH\cdot + H\cdot$
} 1 rad → 2 rads.
Term $H\cdot \longrightarrow$ wall.



Periodic Table:

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge			Br	Kr
Rb	Sr									Ag		In	Sn			I	Xe
Cs	Ba									Au	Hg	Tl	Pb			At	Rn

why 4s lower than 3d? Penetration.

d block contraction – d electrons do not shield each other – degenerate.

Ionisation energy: Molar ΔU for $M_{(g)} \rightarrow M^+_{(g)} + e^-_{(g)}$.

Down group – IE: decrease – two factors – Z_{eff}, size of e^- cloud.

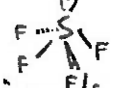
Across period – IE increase – Z_{eff}.

Electron Affinity: Energy released $M \rightarrow M^-_{(g)}$ – signs careful.

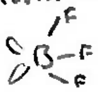
Electronegativity: (flattening – d-block contraction) – Oxidation state, atoms bonded to, state of hybridisation state.

Covalent radius: dep. on environment
ie hybridisation, double/single bonds, ox. state, coord number, ionicity, geometry

VSEPR special cases: SF_4



$ICl_2^{\ominus}$ – linear. BF_3



Bent T.

bond angles of more electroneg. ligands are < than for unelectroneg. ligands.

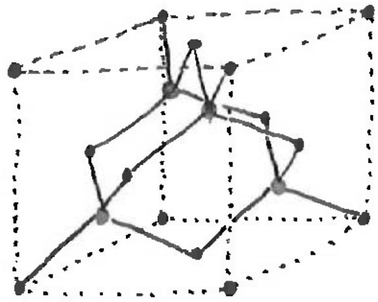
down group, bond angle decreases – size / dec. electroneg. (same thing really)

N_2:

Polyatomics – don't hybridise.... use ligand group orbitals.

Complexes ... hybridisation? NO! Electrostatic bonds.

ZnS



Born-Lande: $U_{lat.} = \frac{Z_+ Z_- e^2}{4\pi\varepsilon r} . N_A . A\left(1 - \frac{1}{n}\right)$

A – Madelung const. (structure) – geometry.

n – Born exponent (repulsion on ions)

take out Madelung get Kapustinskii.

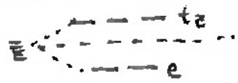
Remember – hard-hard soft-soft ☺ chelating effect.

Crystal field theory – explains high/low spin complexes. competition between pairing energy and Δ_o.

Spectrochemical series: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < en < bipy < phen. < CN^-$

I^- gives low Δ_o. (generally dep on M–L length).

Tetrahedral Δ_{tet}.



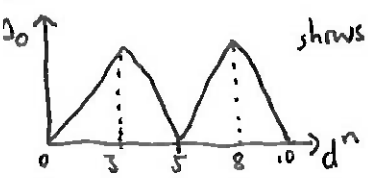
only get High/Low spin ambiguities for $d^4 - d^7$ configs.

d_{z^2} $d_{x^2-y^2}$ point between ligands

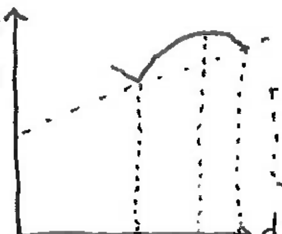
d_{xy} d_{xz} d_{yz} point closer to ligands.

$\Delta_o > \Delta_t$ $\Delta_t < P$ ∴ high spin

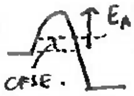
Lattice enthalpies:



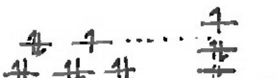
shows up in:



part of E_A



Jahn-Teller



xy plane? or zx/zy planes?

fix theory to fit data.

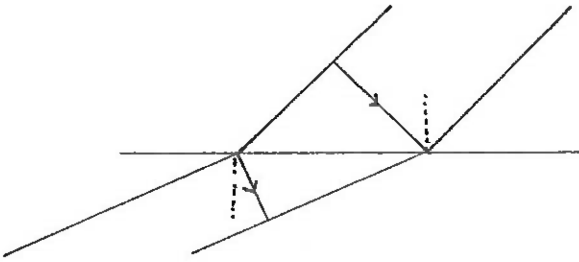
1B

WAVES:

Snell's Law

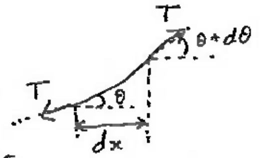
$$n_1 \sin\theta_1 = n_2 \sin\theta_2$$

where $\dfrac{n_1}{n_2} = \dfrac{c_2}{c_1}$



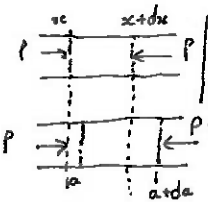
Wave equation for string

$$\frac{\partial^2 y}{\partial x^2} = \frac{\rho}{T}\frac{\partial^2 y}{\partial t^2}$$



Wave equation for sound in gas

$$\frac{\partial^2 a}{\partial x^2} = \frac{\rho}{\gamma P}\frac{\partial^2 a}{\partial t^2}$$



$PV^\gamma = k \Rightarrow \dfrac{dp}{p} = -\gamma \dfrac{dV}{V} = -\gamma \dfrac{da}{dx}$ then diff.

net force $= -\dfrac{\partial P}{\partial x}\, dx\, dS$

$= \underbrace{\rho\, dx\, dS}_{\text{mass}} \underbrace{\dfrac{\partial^2 a}{\partial x^2}}_{\text{acc'n}}$.

DYNAMICS.

Acceleration

$$\ddot{\underset{\sim}{r}} = \underset{\sim}{a} = (\ddot{r} - r\dot{\theta}^2)\hat{\underset{\sim}{r}} + (2\dot{r}\dot{\theta} + r\ddot{\theta})\hat{\underset{\sim}{\theta}}$$

$\underset{\sim}{r} = r\hat{\underset{\sim}{r}}$
$\dot{\underset{\sim}{r}} = \dot{r}\hat{\underset{\sim}{r}} + r\dot{\hat{\underset{\sim}{r}}}$
$\ddot{\underset{\sim}{r}} = \ldots\ldots$

$\dot{\hat{\underset{\sim}{r}}} = \dot{\theta}\hat{\underset{\sim}{\theta}}$
$\dot{\hat{\underset{\sim}{\theta}}} = -\dot{\theta}\hat{\underset{\sim}{r}}$.

Rotating frames

$$\left.\frac{d}{dt}\right|_S = \left.\frac{d}{dt}\right|_{S'} + \underset{\sim}{\omega}\times$$

$\underset{\sim}{u} = u_x'\hat{\underset{\sim}{x}} + u_y'\hat{\underset{\sim}{y}} + u_z\hat{\underset{\sim}{z}}$
$\dot{\underset{\sim}{u}} = \ldots\ldots$

do twice on $\underset{\sim}{r}$.

Fictitious forces

$$m\left.\ddot{\underset{\sim}{r}}\right|_{S'(\text{in rot. frame})} = m\left.\ddot{\underset{\sim}{r}}\right|_{S(\text{true force})} \underbrace{- 2m\underset{\sim}{\omega}\times\dot{\underset{\sim}{r}}\Big|_{S'}}_{\text{coriolis}} \underbrace{- m\underset{\sim}{\omega}\times(\underset{\sim}{\omega}\times\underset{\sim}{r})}_{\text{cent.}}$$

Centrifugal force

$$\underset{\sim}{F}_{cent} = r\dot{\theta}\hat{\underset{\sim}{r}}$$

write $\underset{\sim}{r}$, $\underset{\sim}{\omega}$ in cyl. polars.

Coriolis force

$$\underset{\sim}{F}_{cor} = -2m(\underset{\sim}{\omega}\times\underset{\sim}{v})$$

above

[Orbits]

Effective Potential

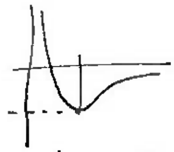
$$U'(r) = U(r) + \frac{J^2}{2mr^2}$$

$E = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\theta}^2 + U(r)$
$J = mr^2\dot{\theta}$

Circular Orbit radius and Energy

$$\underbrace{r_0 = \frac{J^2}{mA}}_{\text{semi latus rectum.}} \qquad E_0 = -\frac{mA^2}{2J^2}$$

diff. $U'(r)$



(Energy) Orbits Equation

$$\frac{dr}{d\theta} = r^2\sqrt{\frac{e^2}{r_0^2} - \left(\frac{1}{r} - \frac{1}{r_0}\right)^2}$$

- Energy, elim A with r_0, E_0
- complete square, define $e = \sqrt{1 - \frac{E}{E_0}}$
- get θ dep from $J = mr^2\dot{\theta}$.

(Force) Orbits Equation

$$\frac{d^2u}{d\theta^2} = \frac{Am}{J^2} - u \qquad \left(\text{sol'n: } u = \frac{Am}{J^2} + A\cos\theta\right)$$

- radial bit of p. polars acc'n.
- $\ddot{r} \to \dfrac{d\theta}{dt}\dfrac{d}{d\theta}\left(\dfrac{d\theta}{dt}\dfrac{dr}{d\theta}\right)$
- subst. $r = u^{-1}$

Ellipse bits:

same $\underline{E}$ same $\underline{a}$ / same J same r_0

from $r = \dfrac{r_0}{1 + e\cos\theta}$.

Kepler's Laws

1. Planets move in ellipses with sun at one focus
2. Radius vector sweeps out equal areas in equal times

$dS = \frac{1}{2}r^2 d\theta$

$\dfrac{dS}{dt} = \dfrac{1}{2}r^2\dot{\theta}$
$= \dfrac{J}{2m}$
$=$ const.

(Kepler)

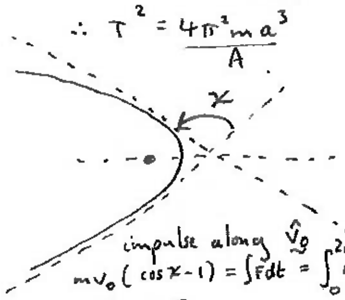
③ (Orbital period)$^2 \propto$ (major axis)^3

$T^2 \propto a^3$

$T = \dfrac{\pi ab}{\frac{dS}{dt}} = \dfrac{2\pi abm}{J}$

$b^2 = a r_0 = a\dfrac{J^2}{mA}$

$\therefore T^2 = \dfrac{4\pi^2 m a^3}{A}$



Unbound Orbits

- Parabola $\quad r = r_0 - r\cos\theta \quad \left(\lim_{e\to 1}\right)$

- Hyperbola $\quad r = \dfrac{r_0}{1+e\cos\theta} \quad e > 1.$

- Scattering angle $\quad \cot\left(\dfrac{\chi}{2}\right) = \dfrac{m v_0^2 B}{A} \quad B$ = impact parameter $\quad v_0|_\infty$.

impulse along $\hat{v}_0$

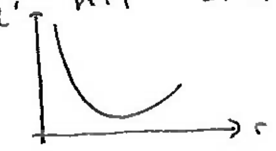
$m v_0(\cos\chi - 1) = \int F dt = \int_0^{2\pi-\chi} \dfrac{A\cos\theta}{r^2}\dfrac{dt}{d\theta}d\theta$

$J = m v_0 B$

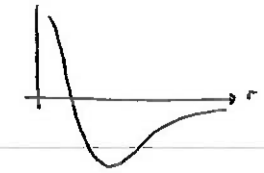
$F = -A r^n \hat{r}$

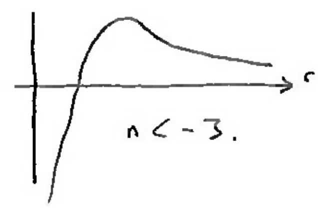
- General Central force field. $\quad U'(r) = \dfrac{A r^{n+1}}{n+1} + \dfrac{J^2}{2mr^2}$

: Bound, Stable $\quad n > 1$



Unbound + B, stable $\quad -1 > n > -3$





$n < -3.$

Unbound, unstable, bound.

$U' = U_0 + \frac{1}{2}(r-r_0)^2 \dfrac{d^2U'}{dr^2}\Big|_{r=r_0}$

Nearly circular orbits $\quad \omega = \sqrt{n+3}\,\Omega$ (orbit frequency)

$[\Omega_p = \Omega - \omega]$

try $r = r_0 + a\cos\omega t$
coeffs must be same if E const.

[RIGID BODY DYNAMICS]

System of particles $\quad \sum_i \underset{\sim}{F_i} = \underset{\sim}{F_0}$ and $\sum_i \underset{\sim}{r_i}\times \underset{\sim}{p_i} = \underset{\sim}{G_0}$

$\sum_{ij} r_i \times F_{ij} = 0$

$= \frac{1}{2}\sum_{ij}(r_i \times F_{ij} - r_j \times F_{ji})$

$= \frac{1}{2}\sum_{ij}(r_i - r_j)\times F_{ij} = 0$ coz $\parallel$.

Definition of ω $\quad \underset{\sim}{V_i} = \underset{\sim}{\omega} \times \underset{\sim}{r_i}$

Inertia Tensor $\quad \underline{\underline{I}} = \begin{pmatrix} r_i^2 - x_i^2 & -x_i y_i & -x_i z_i \\ -x_i y_i & r_i^2 - y_i^2 & -y_i z_i \\ -x_i z_i & -y_i z_i & r_i^2 - z_i^2 \end{pmatrix}$

$\underset{\sim}{J} = I\underset{\sim}{\omega} = \sum_i m_i \underset{\sim}{r_i} \times (\underset{\sim}{\omega} \times \underset{\sim}{r_i})$

Rotational Kinetic energy $\quad T = \frac{1}{2}\underset{\sim}{\omega}\cdot \underline{\underline{I}}\,\underset{\sim}{\omega}$

$T = \frac{1}{2}\sum_i m_i(\underset{\sim}{\omega}\times \underset{\sim}{r_i})(\underset{\sim}{\omega}\times\underset{\sim}{r_i})$
scalar trip. prod.

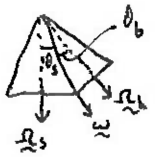
Euler equations $\quad G_1 = I_1\dot{\omega}_1 + \omega_2\omega_3(I_3 - I_2)$ and 4 (cyclic perms)

rotating frames on $\underset{\sim}{J}$.

Body freq. (symm. top) $\quad \Omega_b = \dfrac{I_1 - I_3}{I_1}\omega_3$

Euler eq'ns.

Space freq. (symm. top) $\quad \Omega_s = \dfrac{J}{I_1}$ around $\underset{\sim}{J}$.



$\Omega_s \omega\sin\theta_s = \Omega_b\omega\sin\theta_b$

$\to$ ($\times$ product) $\underset{\sim}{\Omega_s} = \dfrac{\Omega_s}{J}\underset{\sim}{J}$

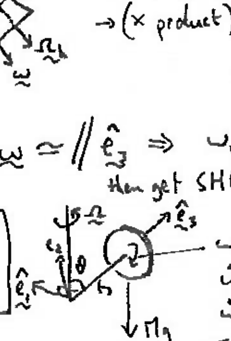
$\underset{\sim}{\Omega_b} = \Omega_b(0,0,1)$

$\underset{\sim}{\omega} = (\omega_1, \omega_2, \omega_3)$

Body freq (asymmetric top) $\quad \Omega_b^2 = \dfrac{\omega_3^2(I_3 - I_1)(I_3 - I_2)}{I_1 I_2}$

let $\underset{\sim}{\omega} \simeq \parallel \hat{\underset{\sim}{e}}_3 \Rightarrow \omega_1, \omega_2 \ll \omega_3$
then get SHM Euler eq'ns.

Gyroscope $\quad \Omega = \dfrac{I_3\omega_s}{2(I_1 - I_3)\cos\theta}\left[1 \pm \sqrt{1 - \dfrac{4Mgh(I_1 - I_3)\cos\theta}{I_3^2\omega_s^2}}\right]$



$\underset{\sim}{\omega} = (0, \Omega\sin\theta, \Omega\cos\theta + \omega_s)$

$\dot{\omega}_2 = 0$

$\dot{\omega}_1 = \omega_s\omega_2$

Euler(1st) eq'n.

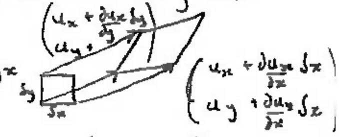
[elasticity]

Young's Modulus $\tau = Ye$ $\qquad \tau = \frac{F}{A} \quad e = \frac{\delta L}{L}$

Poisson's Ratio $\frac{\delta w}{w} = -\sigma \frac{\delta L}{L}$ $\qquad$ for pull ∴ shrink.

Stress tensor $\underset{\sim}{F} = \underset{\approx}{\tau}\,\underset{\sim}{A}$ $\qquad \tau_{ij}$ - force per unit area in i dir due to area in j dir.

Strain tensor $\underline{e}$ stretch : $e_{xx} = \frac{\partial u_x}{\partial x} \quad e_{xy} = \frac{1}{2}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) = e_{yx}$

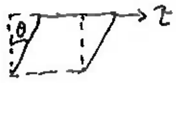


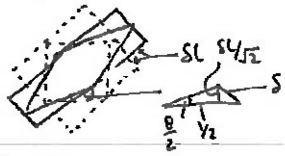
strain(stress) $\underline{\underline{e}} = \frac{1}{Y}\left[(1+\sigma)\underline{\underline{\tau}} - \sigma \,\mathrm{Tr}(\underline{\underline{\tau}})\cdot \mathbb{1}\right]$ $\qquad e_1 = \frac{1}{Y}\left[\tau_1 - \sigma(\tau_2 + \tau_3)\right]$ isotropic material.

stress(strain) $\underline{\underline{\tau}} = \frac{Y}{1+\sigma}\left[\underline{\underline{e}} + \frac{\sigma}{1-2\sigma}\mathrm{Tr}(\underline{\underline{e}})\cdot\mathbb{1}\right]$ $\qquad$ take trace then subst back in.

Bulk modulus $B = \frac{Y}{3(1-2\sigma)}$ $\qquad$ unit cube $\frac{\delta V}{V} = -\frac{P}{B}$

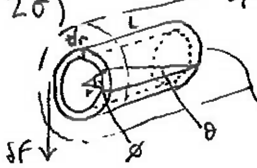
Shear modulus $n = \frac{\tau}{\theta} = \frac{Y}{2(1+\sigma)}$





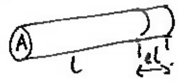
Longitudinal modulus $M_L = B + \frac{4n}{3} = \frac{Y(1-\sigma)}{(1+\sigma)(1-2\sigma)}$ $\qquad e_1 = \frac{\delta x}{x} \quad e_2 = e_3 = 0 \quad \tau_1 = M_L e_1 \quad e_1 = \frac{\tau_1}{Y} - \sigma\frac{\tau_2}{Y} - \sigma\frac{\tau_3}{Y}$

Torsion of Cylinder $G = \frac{\pi a^4 n \phi}{2L}$



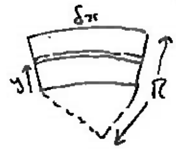
$n = \frac{\delta F}{\delta A}/\theta \quad \delta A = 2\pi r dr \quad \int dr.$

Elastic energy $U = \frac{1}{2}\mathrm{Tr}(\underline{\underline{\tau}}\,\underline{\underline{e}})$ per unit vol.



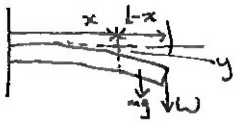
$\Delta E = \int_0^{eL} \frac{YA\,x}{L}\,dx \quad (eL = x)$

Bending moment $BR = YI$

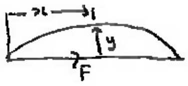


$e = \frac{y}{R} \quad$ total torque $= B = \int \frac{Yy^2}{R} dA \quad I = \int y^2 dA.$

Cantilever $YIy = \frac{1}{6}W(L-x)^3 + \frac{1}{24}w(L-x)^4 + Cx + D.$ $\qquad \frac{1}{R} = \left(\frac{d^2y}{dx^2}\right)$



Bowed Beam. $F_c = \frac{YI\pi^2}{L^2}$ Euler force



$B(x) = -Fy \simeq YI\frac{d^2y}{dx^2}$ ∴ SHM eq'n. $k^2 = \frac{F}{YI} = \frac{\pi^2}{L^2}.$

[normal modes]

normal mode frequencies (+ ratio of max amplitudes) $\omega^2 \underline{\underline{M}}\,\underset{\sim}{x} = \underline{\underline{k}}\,\underset{\sim}{x}$

$\Rightarrow \left|\underline{\underline{k}}\,\underline{\underline{M}}^{-1} - \omega^2\mathbb{1}\right| = 0$

$T = \frac{1}{2}\dot{\underset{\sim}{x}}\cdot\underline{\underline{M}}\,\dot{\underset{\sim}{x}} \quad U = \frac{1}{2}\underset{\sim}{x}\cdot\underline{\underline{K}}\,\underset{\sim}{x}$

$\underset{\sim}{x} = X^{(n)}\cos(\omega_n t + \phi_n)\,\underset{\sim}{e_n}$

$\dot{x} =$ etc....

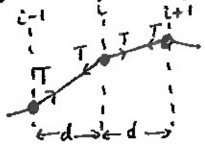
use $(\underline{\underline{K}} - \omega_n^2\underline{\underline{M}})\underset{\sim}{e_n} = 0$

Energy in normal modes $E = \frac{1}{2}X^{(n)2}\underset{\sim}{e_n}\cdot\underline{\underline{K}}\,\underset{\sim}{e_n} = \frac{1}{2}X^{(n)2}\omega_n^2\,\underset{\sim}{e_n}\cdot\underline{\underline{M}}\,\underset{\sim}{e_n}$

- remains const. in each mode $U = \sum_n U_n \quad T = \sum_n T_n$

equal mass case $\underline{\underline{M}}\,\underset{\sim}{e_n} = m\,\underset{\sim}{e_n}$

limit of many particles $\frac{\partial^2 y}{\partial t^2} = \frac{T}{\rho}\frac{\partial^2 y}{\partial x^2} \quad \rho = \frac{m}{d}$

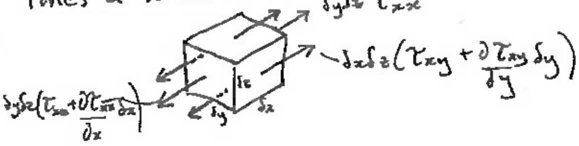


Vibrational modes of N atom molecule $3N - 6$ $\qquad$ 3 translational, 3 rotational — zero frequency modes.

[elastic waves]

x direction eq'n of motion for element $\quad \rho \ddot{u}_x = \frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} + \frac{\partial \tau_{xz}}{\partial z}$

Forces in x dir:

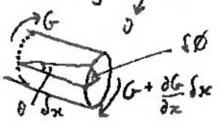


Pressure (longitudinal) waves $\quad \rho \ddot{u}_x = \frac{\partial \tau_{xx}}{\partial x}$ $\quad$ shear stresses = 0.

Pressure waves in a rod $\quad V_p = \sqrt{\frac{Y}{\rho}}$ $\quad \tau_{xx} = Y e_{xx} \quad e_{xx} = \frac{\partial u_x}{\partial x}$.

Pressure waves in a solid bulk medium $\quad V_p = \sqrt{\frac{M_L}{\rho}}$ $\quad \tau_{xx} = M_L e_{xx}$ $\quad$ rod: $\tau_{yy} = \tau_{zz} = 0$ $\quad$ bulk: $e_{yy} = e_{zz} = 0$.

Shear (transverse) waves $\quad V_s = \sqrt{\frac{n}{\rho}}$ $\quad e_{xy} = \frac{1}{2}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) \quad u_y = 0$ $\quad \tau_{xy} = \frac{Y}{1+\sigma} e_{xy} = 2n e_{xy} \quad \rho \ddot{u}_x = \frac{\partial \tau_{xy}}{\partial y}$



Torsional waves in rod $\quad V_t = \sqrt{\frac{n}{\rho}}$ $\quad I\ddot{\phi} = \frac{\partial G}{\partial x}\delta x \quad G = \frac{1}{2}\pi n a^4 \frac{\delta \phi}{\delta x}$ $\quad I = \frac{1}{2}a^2 \pi a^2 \rho \delta x$

Pressure waves in fluid (no S waves) $\quad V_p = \sqrt{\frac{B}{\rho}}$ $\quad n = 0 \quad M_L = B + \frac{4n}{3}$

Pressure waves in gas $\quad V_p = \sqrt{\frac{\gamma P}{\rho}}$ $\quad pV^{\gamma} = k \quad \therefore \frac{\delta p}{p} = -\gamma \frac{\delta V}{V} \quad \therefore B = \gamma P$.

Impedance: Pressure waves $\quad Z_p = \sqrt{M_L \rho}$ or $\sqrt{Y\rho}$ or $\sqrt{B\rho}$ $\quad Z_p = \frac{\text{"Force"}}{\text{"vel"}} = \frac{\tau_{xx}}{\frac{\partial u_x}{\partial t}} = \frac{M_L \frac{\partial u_x}{\partial x}}{} \rightarrow u_x = u_x(x \pm V_p t)$

: Shear waves $\quad Z_s = \sqrt{n\rho}$ $\quad Z_s = \frac{\tau_{xy}}{\dot{u}_x} = \frac{n\, \partial u_x/\partial y}{\frac{\partial u_x}{\partial x}}$. $\quad u_x = u_x(y \pm V_s t)$

: Torsional waves $\quad Z_T = \frac{1}{2}\pi a^4 \sqrt{n\rho}$ $\quad Z_T = \frac{G}{\dot{\phi}} = \frac{1}{2}\pi a^4 n \frac{\partial \phi/\partial x}{\partial \phi/\partial t}$. $\quad \phi = \phi(x \pm V_t t)$

Energy in elastic waves $\quad E = T + U = 2T = 2U$ $\quad U = \frac{1}{2}\rho \dot{u}_x^2 + \frac{1}{2}\tau_{xx} e_{xx}$ for pressure wave per unit vol. $\quad \tau_{xx} = M_L e_{xx} \quad e_{xx} = \frac{\partial u_x}{\delta x} \quad u_x = f(x \pm V_p t)$

Rate of energy flow $\quad P = U V_p$.

ELECTROMAGNETISM

Maxwell's Equations

$$\operatorname{div} \underset{\sim}{D} = \rho_{free}$$

$\int_S \underset{\sim}{E} \cdot d\underset{\sim}{S} = \frac{Q}{\varepsilon_0} = \int_V \frac{\rho}{\varepsilon_0} d\tau$ div. theorem $\quad \rho = \rho_p + \rho_f$

$$\operatorname{curl} \underset{\sim}{E} = -\frac{\partial \underset{\sim}{B}}{\partial t}$$

emf $= \oint \underset{\sim}{B} \cdot \underset{\sim}{v} \times d\underset{\sim}{l} = \int_S -\frac{\partial}{\partial t}\underset{\sim}{B} \cdot d\underset{\sim}{S} = \oint \underset{\sim}{E} \cdot d\underset{\sim}{l}$

$$\operatorname{div} \underset{\sim}{B} = 0$$

$$\operatorname{curl} \underset{\sim}{H} = \underset{\sim}{J} + \frac{\partial \underset{\sim}{D}}{\partial t}$$

Ampere, bcret $\quad i = \frac{\partial q}{\partial t} = \partial\left(\frac{\varepsilon \varepsilon_0 A}{d} V\right) = A \frac{\partial \underset{\sim}{D}}{\partial t}$.

Lorentz force $\quad \underset{\sim}{F} = q(\underset{\sim}{E} + \underset{\sim}{v} \times \underset{\sim}{B})$ $\quad$ from def'n of $\underset{\sim}{E}$ and $d\underset{\sim}{F}$ i.e. $= I d\underset{\sim}{l} \times \underset{\sim}{B}$

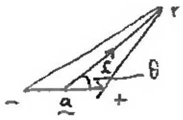
Definition of $\underset{\sim}{E}$ $\quad \underset{\sim}{F} = q\underset{\sim}{E}$

Definition of V $\quad dV = -\underset{\sim}{E} \cdot d\underset{\sim}{r} = \underset{\sim}{\nabla} V \cdot d\underset{\sim}{r}$ $\quad \underset{\sim}{E} = \underset{\sim}{F}$ on unit charge.

Field near surface of charged conductor $\quad \underset{\sim}{E} = \frac{\sigma}{\varepsilon_0} \underset{\sim}{n}$ $\quad$ Gauss.

Field near uniform line charge $\quad \underset{\sim}{E} = \frac{\lambda \hat{r}}{2\pi \varepsilon_0 r}$ $\quad$ Gauss.

Far field due to electric dipole (potential) $V = \dfrac{\underset{\sim}{p} \cdot \hat{r}}{4\pi\varepsilon_0 r^2}$



$V = \dfrac{1}{4\pi\varepsilon_0}\left[\dfrac{q}{r - \frac{a}{2}\cos\theta} - \dfrac{q}{r + \frac{a}{2}\cos\theta}\right]$ cancel $\frac{a^2}{4}\cos^2\theta$.

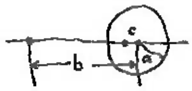
Couple on dipole in uniform field $\underset{\sim}{G} = \underset{\sim}{p} \times \underset{\sim}{E}$ — $G = qEa\sin\theta$

Force on dipole in non un. field. $\underset{\sim}{F} = (\underset{\sim}{p} \cdot \underset{\sim}{\nabla})\underset{\sim}{E}$ — ok.

Potential energy of dipole $U_{dip} = \underset{\sim}{p} \cdot \underset{\sim}{E}$ — consider const. $|\underset{\sim}{p}|$

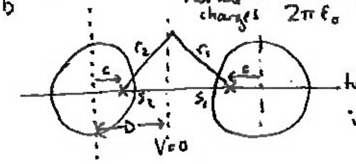
Conducting sphere in uniform field $V_{sph.} = \left(\dfrac{a^3}{r^3} - 1\right)E_0 r\cos\theta$ — dipole + uniform. $V = 0$ on $r = a$. polarisability $p = \alpha E_0$ $\alpha = 4\pi\varepsilon_0 a^3 E_0$ $\left(E = \frac{\sigma}{\varepsilon_0}\right)$

Point charge near cond. sphere strength $\alpha = \frac{a}{b}$ pos'n $c = \frac{a^2}{b}$ — $V = 0$ on $r = a$.



line charge near cond. cylinder strength $= 1$ pos'n $c = \frac{a^2}{b}$ — $V_{\text{two line charges}} = \dfrac{\lambda}{2\pi\varepsilon_0}\log\dfrac{r_2}{r_1}$ equipotentials have $\frac{r_2}{r_1}$ const.

Cap. of pair of cond. cylinders $C = \dfrac{\pi\varepsilon_0}{\log_e\left(\dfrac{a}{D - \sqrt{D^2 - a^2}}\right)}$



S_1, S_2 two easy points to apply ratio r_1/r_2; if $a \ll D$, $C = \dfrac{\pi\varepsilon_0}{\ln\left(\frac{2D}{a}\right)}$

Electrostatic energy $U = \dfrac{1}{2}\sum_{i=1}^{N} V_i q_i$ — ith charge goes $0 \to \alpha q_i$, in pot. αV_i $dW = \sum_{i=1}^{N} \alpha V_i \, d\alpha q_i$ $\therefore U = \Sigma V_i q_i \int_0^1 \alpha \, d\alpha$

- for continuous distribution $U = \dfrac{1}{2}\int_V \rho V \, d\tau$ — $q_i \to \rho \, d\tau$. $\Sigma \to \int$.

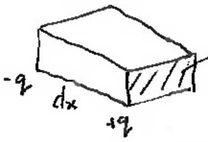
$U_c = \frac{1}{2}CV^2 = \frac{\varepsilon_0 A d}{2} \cdot \frac{V^2}{d^2} = \frac{1}{2}\varepsilon_0 \tau E^2$

Electric field energy (mark 1) $U = \frac{1}{2}\varepsilon_0 E^2$ per unit vol.

Force on surface of charged. cond. $F = \dfrac{\sigma^2}{2\varepsilon_0}$ — move surface dx, reduce e. field energy work done $= F dx$.

Polarisation (dip. mom. per unit vol) $\underset{\sim}{P} = N\underset{\sim}{p}$

Polarisation surface charge density $\sigma = \underset{\sim}{P}_\perp$



$p_{element} = q\,dx = P_x \, d\tau$, $\sigma = \dfrac{q}{dy\,dz}$

Polarisation charge density $\rho_{pol} = -\operatorname{div}\underset{\sim}{P}$ — only in non uniform $\underset{\sim}{E}$ — two elements

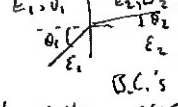
Displacement Current $\underset{\sim}{D} = \varepsilon_0\underset{\sim}{E} + \underset{\sim}{P}$ — from proof of $\operatorname{div}\underset{\sim}{D} = \rho_{free}$.

Permitivity (Dielectric const) $\underset{\sim}{D} = \varepsilon\varepsilon_0\underset{\sim}{E}$ — in isotropic medium $\underset{\sim}{D} \parallel \underset{\sim}{P}$.

Susceptability (electric) $\underset{\sim}{P} = \chi\varepsilon_0\underset{\sim}{E}_{inside.}$ $(\varepsilon = 1 + \chi)$ — χ dimensionless.

Boundary Conditions for $\underset{\sim}{D}$ $D_\perp$ continuous — Gauss, no free surface charges

Boundary Conditions for $\underset{\sim}{E}$ $E_\parallel$ continuous — Work argument.



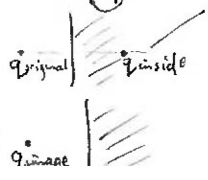
Electrostatic Snell $\varepsilon\cot\theta = \text{constant}$

Relationship between $\underset{\sim}{P}$ and applied field $\underset{\sim}{P} = \left(\dfrac{\chi}{1 + n\chi}\right)\varepsilon_0\underset{\sim}{E}_0$ — field uniform inside, dipole outside — B.C.'s potential continuous across boundary; $\perp$ comp. D continuous also

Depolarisation Factor, n thin slab $= 1$ sphere $= \frac{1}{3}$ cylinder $= \frac{1}{2}$ rod $\parallel E_0 = 0$

Point Charge in semi-infinite dielectric $q_{outside} = \dfrac{2q}{1 - \varepsilon_0}$ — E_{out} due to $q_{original}$, q_{inside} — image

$q_{inside} = -\left(\dfrac{\varepsilon - 1}{\ldots}\right)q$ — E_{in} due to q_{image}



remember! Field on axis along axis due to charge ring $= \frac{Q\cos\theta}{4\pi\varepsilon_0 r^2}$.

Clausius - Mossotti. $\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\alpha}{3\varepsilon_0}$

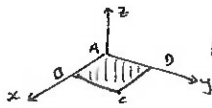
Electric field energy density (mark 2). $U = \frac{1}{2}\underset{\sim}{D}\cdot\underset{\sim}{E}$ $\quad u = \frac{1}{2}\int_V \rho_f V\,d\tau$ but $\operatorname{div} D = \rho_{free}$

Force on Current Element. $d\underset{\sim}{F} = I\,d\underset{\sim}{l}\times\underset{\sim}{B}$ def'n.

Biot - Savart. $d\underset{\sim}{B} = \frac{\mu_0 I}{4\pi}\frac{d\underset{\sim}{l}\times\underset{\sim}{r}}{r^3}$

Force between two currents: $d\underset{\sim}{F}_{21} = \frac{\mu_0 I_1 I_2}{4\pi r^3} d\underset{\sim}{l}_2 \times (d\underset{\sim}{l}_1 \times \underset{\sim}{r})$ force on 2 due to 1.

Couple on dipole in uniform $\underset{\sim}{B}$. $d\underset{\sim}{G} = d\underset{\sim}{m}\times\underset{\sim}{B}$



force on AB, BC etc. $\underset{\sim}{m} := I\,d\underset{\sim}{S}$.

Couple on finite loop. $\underset{\sim}{G} = \underset{\sim}{m}\times\underset{\sim}{B}$ mini loops cancel inside.

Magnetic Scalar Potential. $\underset{\sim}{B} = -\mu_0\nabla\phi_m$ def'n.

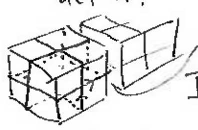
Scalar Potential of current loop. $\phi_m = \frac{I\Omega}{4\pi}$ $\quad \int_S \frac{\underset{\sim}{r}\cdot d\underset{\sim}{S}}{r^3} = \delta\Omega$ $\quad \underset{\sim}{B}\cdot d\underset{\sim}{r}$, scalar triple product

Potential of small dipole $\phi_m = \frac{\underset{\sim}{m}\cdot\underset{\sim}{r}}{4\pi r^3}$ $\quad d\underset{\sim}{m} = I\,d\underset{\sim}{S}$ $\quad d\underset{\sim}{m}\cdot\underset{\sim}{r} = I\Omega r^3$ $\quad \phi = \frac{I\Omega}{4\pi}$.

Ampères Circuital Theorem $\oint\underset{\sim}{B}\cdot d\underset{\sim}{r} = \mu_0 I$ solid angle arguments with loop $\phi_m = \frac{I\Omega}{4\pi}$

Magnetic Vector Potential $\underset{\sim}{B} = \operatorname{curl}\underset{\sim}{A}$ def'n.

Magnetisation current density $\underset{\sim}{J}_m = \operatorname{curl}\underset{\sim}{M}$



net flow at interface = ? $\quad I\,dx\,dy = M_z\,d\tau$.

Magnetic field strength $\underset{\sim}{H} = \frac{1}{\mu_0}(\underset{\sim}{B} - \mu_0\underset{\sim}{M})$ include $\underset{\sim}{J}_m$ in differential form of Ampere's theorem.

Susceptibility $\underset{\sim}{M} = \chi_m\underset{\sim}{H}$ $\quad \underset{\sim}{M}\propto\underset{\sim}{H}$ Isotropic medium.

Permeability $\mu_r = 1 + \chi_m$ $\quad \underset{\sim}{B} = \mu_0\mu_r\underset{\sim}{H}$. $\quad \underset{\sim}{H} = \frac{1}{\mu_0}(\underset{\sim}{B} - \mu_0\underset{\sim}{M})$

Boundary Conditions for $\underset{\sim}{B}$ $\quad B_\perp$ continuous Gauss.

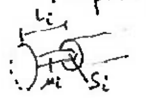
Boundary Conditions for $\underset{\sim}{H}$ $\quad \underset{\sim}{H}_{/\!/}$ continuous Ampere (no surface current)

Field on axis in short solenoid $H_p = \frac{nI}{2}(\cos\theta_1 - \cos\theta_2)$ Biot Savart for one loop then integrate

[Relationship between $\underset{\sim}{M}$ and applied field] Magnetisable sphere in uniform field. $\underset{\sim}{M} = \left(\frac{3(\mu_1 - 1)\mu_2}{2\mu_2 + \mu_1}\right)\underset{\sim}{H}_0$ $\quad \phi_m$ continuous on $r = a$ $\quad B_\perp$ continuous on $r = a$.

Electromagnet (field in gap) $B_{gap} \simeq \frac{\mu_0 N I}{l}$ Ampere around solenoid $B_i = B_g$ $\quad \mu\mu_0 H_i = \mu_0 H_g$ $\quad \mu l \gg 2\pi r$.

Magnetomotive force $NI = \oint\underset{\sim}{H}\cdot d\underset{\sim}{l}$ Ampere.



Φ const $= \mu\mu_0 HS (= SB)$ subst into mag. force (current $\equiv$ flux)

Reluctance $Rel. = \sum_i \frac{l_i}{\mu_i\mu_0 S_i}$

Diamagnetic Susceptibility $\chi_{dia.} = -\frac{ne^2\langle r_0^2\rangle\mu_0}{6m}$

$m r_0\omega_0^2$ = elec + Lorentz
subst $r = r_0 + \delta r$ $\quad \omega = \omega_0 + \delta\omega$
get Larmor freq. $\omega_L = \frac{eB}{2m}$
extra dip. mom = area $\times\,\Delta I$
average over all orientations of Δm.

Paramagnetic Susceptability $\chi_H = \dfrac{\mu_0 n m_0^2}{3kT}$ $\quad Y(\theta)d\theta \propto e^{\frac{m_0 B\cos\theta}{kT}} \cdot \frac{1}{2}\sin\theta\, d\theta.$ $\quad \propto -e^{zx}dz \quad x = \frac{m_0 B}{kT}, \; z = \cos\theta.$ $\quad \langle m_{//}\rangle = ?$

Curie-Wiess Law $\chi_f = \dfrac{n m_0^2 \mu_0}{3k(T-T_c)}$ $\quad T_c = \lambda A$ (curie const.)

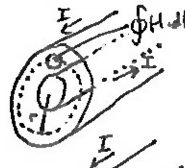
Faraday's Law $V = -L\dfrac{\partial I}{\partial t}$ $\left(\dfrac{\partial \Phi}{\partial t}\right)$ $\quad \Phi = LI$. L const if circuit rigid.

self Inductance of:

- long solenoid $\left(\dfrac{L}{l}\right) = \dfrac{\mu_0 N^2 S}{l^2}$

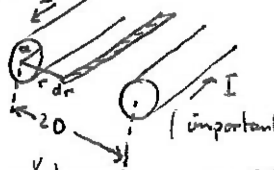
$\oint H.dl = I \quad \Phi = B_i S$ $\quad \dfrac{\text{total flux}}{I} = \dfrac{N\Phi}{I} \; \ldots\ldots$

- coaxial cylinders $\left(\dfrac{L}{l}\right) = \dfrac{\mu_0}{2\pi}\log_e\left(\dfrac{b}{a}\right)$



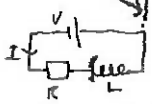
$\oint H dl = I$ $\quad$ radial slice, dr by L $\quad \Phi = B(r) L dr \;\therefore\; \int_a^b \dfrac{\mu_0 L I}{2\pi}\dfrac{dr}{r}$

- parallel cylinders $\left(\dfrac{L}{l}\right) = \dfrac{\mu_0}{\pi}\log_e\left(\dfrac{2D}{a}\right)$



$a \ll D.$ $\quad LI = 2\dfrac{\mu_0 I L}{2\pi}\displaystyle\int_a^{2D-a}\dfrac{dr}{r} = \ldots$ (important!)

Energy in Inductance $U_{Ind.} = \frac{1}{2}\Phi I = \frac{1}{2}LI^2$



$V = IR + I\dfrac{\partial L}{\partial t}$ $\quad$ multiply by I.

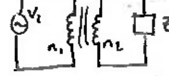
Mutual Inductance $\Phi_2 = M I_1$ $\quad$ (def'n) $\Phi_2 = L_2 I_2 + M I_1$

Coupling Coeff. $M = k\sqrt{L_1 L_2} \quad 0 \le k \le 1$

coupled eq'ns $\times I$ then add. U_m total $\ge 0 \;\therefore\; M \le \sqrt{L_1 L_2}$ $\quad$ consider two wires one solenoid.

Ideal Transformer $\dfrac{L_1}{L_2} = \left(\dfrac{n_1}{n_2}\right)^{1/2}$ $k=1$ $\quad V_{1,2} = -n_{1,2}\dfrac{\partial \Phi}{\partial t}$ $\quad L \propto n^2.$

Reflected Impedance "see" $j\omega L_1 \,/\!/\, Z_2\left(\dfrac{n_1}{n_2}\right)^2$ $\quad$ equiv. circuit:



$M = \sqrt{L_1 L_2}$ $\quad \dfrac{L_1}{L_2} = \left(\dfrac{n_1}{n_2}\right)^2.$

Magnetic energy density $U_m = \frac{1}{2}\underset{\sim}{H}\cdot\underset{\sim}{B}$ $\quad W_{TOT} = \frac{1}{2}\displaystyle\sum_{k=1}^{N}\left(\oint A I dl\right)_k$ $\quad I dl = J d\tau \quad J = \nabla\times H$ $\quad$ div $A\times H \ldots$

EM Waves - free space $c = \dfrac{1}{\sqrt{\varepsilon_0 \mu_0}}$ $\quad \underset{\sim}{\text{curl}}\,[M3]$

Impedance of free space $Z_0 = \sqrt{\dfrac{\mu_0}{\varepsilon_0}}$ $\quad$ plane wave solutions, $\dfrac{E_x}{H_y}$ real $\therefore$ in phase. (also $E_x = B_y c$

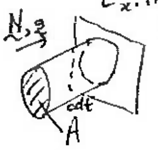
Rate of change of energy $P = -\displaystyle\int_V \underset{\sim}{J}\cdot\underset{\sim}{E}\, d\tau$ $\quad$ Work done to move q by $dl = -q\underset{\sim}{E}\cdot\underset{\sim}{dl}$.

M4, M2 subst.

Poynting's theorem $W = \dfrac{\partial}{\partial t}\displaystyle\int_V \frac{1}{2}(\underset{\sim}{E}\cdot\underset{\sim}{D} + \underset{\sim}{H}\cdot\underset{\sim}{B})\,d\tau + \int_S(\underset{\sim}{E}\times\underset{\sim}{H})\cdot\underset{\sim}{dS}$

Poynting Vector $\underset{\sim}{N} = \underset{\sim}{E}\times\underset{\sim}{H}$ $\quad$ rate of energy flow through unit area [energy flow density]

$|\underset{\sim}{N}| = U.c$ $\quad E_x.H_y = \dfrac{E_x^2}{Z_0}$ etc.



ok. $\quad$ Force $= \dfrac{dp}{dt} = \dfrac{A\,cdt\,g}{dt}$

Radiation Pressure $\underset{\sim}{R} = cg(1+r)$

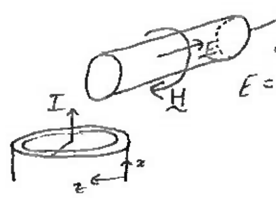
$R = \dfrac{\underset{\sim}{N}}{c}$ $\quad E^2 - p^2c^2 = m^2c^4$ $\quad \underset{\sim}{N} = E$ per area per time. $\quad \therefore E_{vol\,el.} = c\langle|N|\rangle A\,dt$ $\quad p = \dfrac{E}{c}$ $\quad R = g c$.

EM Waves - in insulating media $c' = \dfrac{c}{\sqrt{\varepsilon\mu}}$ $\quad n_i = \dfrac{c}{c'} = \sqrt{\varepsilon\mu} \simeq \sqrt{\varepsilon}$ $\quad Z = 377\sqrt{\dfrac{\mu}{\varepsilon}}\,\Omega.$

- in plasmas $n_p = \sqrt{1 - \dfrac{\omega_p^2}{\omega^2}}$ $\quad \omega_p^2 = \dfrac{Ne^2}{\varepsilon_0 m}$ $\quad$ take mean displacement of e^- plane wave solution get ε from $1+\chi$ $(\underset{\sim}{P} = Ne\underset{\sim}{r})$

- in conducting media $n_c = \pm(1+j)\sqrt{\dfrac{\mu\sigma}{2\omega\varepsilon_0}}$ $\quad$ M4 $\rightarrow$ effective permittivity. $\quad n = \sqrt{\mu\varepsilon'}$

Skin depth $\quad \delta = \dfrac{1}{ak_0} \left(= \dfrac{\lambda_0}{2\pi a} \right)$



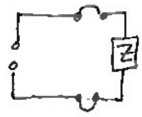
wave into wire $E = E_0 e^{j(ak_0 z - \omega t)} e^{(-ak_0 z)}$

Resistance of Wire at High freq. $\quad = \dfrac{1}{2\pi r \delta . \sigma}$

Transmission Line: speed: $\quad v = \dfrac{1}{\sqrt{LC}}$

Impedance (characteristic) $\quad Z = \pm \sqrt{\dfrac{L}{C}}$

equivalent circuit.



of coaxial lines $\quad Z_{coax.} = \sqrt{\dfrac{\mu_0}{\varepsilon\varepsilon_0}} \dfrac{\log_e(b/a)}{2\pi}$ $\quad C = \dfrac{2\pi\varepsilon\varepsilon_0}{\log_e(b/a)}$; $L = \dfrac{\mu_0}{2\pi}\log_e\left(\dfrac{b}{a}\right)$ $\quad v = \dfrac{1}{\sqrt{\mu_0\varepsilon\varepsilon_0}}$

of parallel lines $\quad Z_{/\!/ \text{lines}} = \sqrt{\dfrac{\mu_0}{\varepsilon_0}} . \dfrac{\log_e \frac{2d}{a}}{\pi}$ $\quad C = \dfrac{\pi\varepsilon_0}{\log_e\left(\frac{2d}{a}\right)}$; $L = \dfrac{\mu_0}{\pi}\log_e\left(\dfrac{2d}{a}\right)$ $\quad v = \dfrac{1}{\sqrt{\mu_0\varepsilon_0}} = c$

of parallel strips $\quad Z_{\text{stripline}} = \sqrt{\dfrac{\mu_0}{\varepsilon_0}} . \dfrac{d}{a}$ $\quad C = \dfrac{\varepsilon_0 a}{d}$; $L = \dfrac{\mu_0 d}{a}$ $\quad v = \dfrac{1}{\sqrt{\mu_0\varepsilon_0}} = c.$

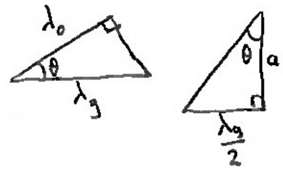
of short terminated line $\quad \dfrac{Z_{in}}{Z} = \dfrac{Z_T \cos ka - j Z \sin ka}{Z \cos ka - j Z_T \sin ka}$ $\quad$ superpose incident + reflected waves.

– open circuit $\quad \dfrac{Z_{in}}{Z} = j\cot(ka)$ $\quad 0 < ka < \frac{\pi}{2}$ cap. $\quad \frac{\pi}{2} < ka < \pi$ ind. $\quad Z_T = \infty$.

– short circuit $\quad \dfrac{Z_{in}}{Z} = -j\tan ka$ $\quad 0 < ka < \frac{\pi}{2}$ ind. $\quad \frac{\pi}{2} < ka < \pi$ cap. $\quad Z_T = 0$.

– Quarter wave trans. $\quad \dfrac{Z_{in}}{Z} = \dfrac{-jZ}{-jZ_T}$ $\quad \therefore \quad Z^2 = Z_{in} Z_T$ $\quad$ caps.

Wave guide equation (Dispersion relation) $\quad k_{guide}^2 = k_{freespace}^2 - \left(\dfrac{m^2\pi^2}{a^2} + \dfrac{n^2\pi^2}{b^2} \right)$



elim θ.

Cut off frequency $\quad k_{cut\,off} = \sqrt{\dfrac{m^2\pi^2}{a^2} + \dfrac{n^2\pi^2}{b^2}}$

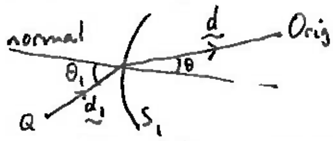
Impedance for waves in guide $\quad Z_{waveguide} = \dfrac{k_0}{k_g} Z_0$ $\quad Z_0 = 377\Omega$ $\quad \dfrac{E_x}{H_y}$ $\quad \text{curl } \underline{E} = -\mu_0 \dfrac{\partial \underline{H}}{\partial t}$

Wave speeds: $\quad V_{ph} V_{group} = c^2$ $\quad \dfrac{\omega^2}{c^2} = k_g^2 + k_c^2$ $\quad v_g = \dfrac{\partial \omega}{\partial k_g}$.

<u>OPTICS</u> lensmakers formula $\quad \dfrac{1}{u} + \dfrac{1}{v} = \dfrac{1}{f}$ $\quad \dfrac{1}{f} = (n-1)\left(\dfrac{1}{R_1} - \dfrac{1}{R_2} \right)$ $\quad (1 \rightarrow 2)$

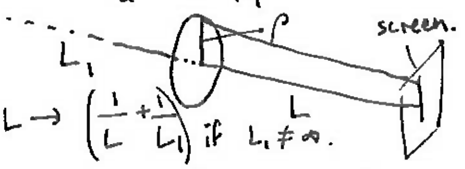
Magnification $\quad \dfrac{h_{image}}{h_{object}} = \dfrac{-v}{u}$ $\quad$ draw lens diagram $h_0 > f$

Kirchoff Diffraction Integral (point source) $\quad \psi_0 = \dfrac{ik}{2\pi} \displaystyle\int_{S_1} \dfrac{e^{ik(d+d_1)}}{dd_1} \left(\dfrac{\cos\theta + \cos\theta_1}{2} \right) dS$



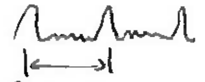
Fraunhofer regime if: $\quad \rho^2 \ll \lambda L$

Fresnel regime if: $\quad \rho^2 \geq \lambda L$



$L \rightarrow \left(\dfrac{1}{L} + \dfrac{1}{L_1} \right)$ if $L_1 \neq \infty$.

Interference condition: $\quad (\omega_1 - \omega_2) T \ll 1$ $\quad (\underset{\sim}{k_1} - \underset{\sim}{k_2}) . r \sim \text{const}$ $\quad (\phi_1 - \phi_2) \sim \text{konst}$ $\quad \psi_i = A_i e^{i(\underset{\sim}{k_i} . \underset{\sim}{r} - \omega_i t + \phi_i)}$ $\quad$ intensity = ?

Diffraction Grating model $h(y) = \sum_{m=0}^{N-1} \delta(y - mD)$ F.T. is G.P.  $\frac{qD}{2} = m\pi$.

N slits.

Fraunhofer circular aperture $\frac{\psi(\theta)}{\psi_0} = \frac{\pi d^2}{2} \frac{J_1\left(\frac{kd}{2}\sin\theta\right)}{\left(\frac{kd}{2}\sin\theta\right)}$ d-diameter.

Babinet's Principle — Complementary apertures - same except bright spot at origin. π out of phase

$\psi_a = \int_a e^{-i(px+qy)} dA$

$\psi = \int_{\mathbb{R}^2} dA - \int_a dA = \delta - \psi_a$

Bragg's Law $n\lambda = 2d\sin\theta$.

nth Fresnel zone $\sqrt{(n-1)\lambda R} < \rho_n \leq \sqrt{n\lambda R}$ $\phi = \frac{\pi s}{\lambda R}$. on axis. R = aperture screen distance.

Cornuspiral $u = x\sqrt{\frac{2}{\lambda R}}$ $v = y\sqrt{\frac{2}{\lambda R}}$.

Parabolic reflector $x = ky^2$ $f = \frac{1}{4k}$.

Resolution limit of microscope $\theta_{min} = \frac{1.22\lambda}{D}$ $d_{min} = \frac{\lambda}{\sin\alpha}$.

Resolution limit of telescope $\theta_{min} = \frac{1.22\lambda}{D}$

Resolution limit of diff. grating : $R_d = \frac{\lambda}{\Delta\lambda_{min}} = Nm$ m th order. N lines.

Michleson Interferometer $I = A^2\cos^2\left(\frac{\pi\Delta p}{\lambda}\right)$

- resolving power of $R_{m\text{-}m} = \Delta$

Resolving power of Fabry-P Etalon: $R_{f\text{-}p} = \frac{\lambda}{\Delta\lambda} = \frac{\pi n d}{\lambda}\sqrt{F}$ $F = \frac{4r^2}{(1-r^2)^2}$

THERMODYNAMICS.

Boyle's Law $pV = f(T)$

Ideal gas def'n of temp. $T = pV/R$.

1st Law $dU = dq + dW$. $d(\text{heat input}) = dU + \text{work done by gas}$
$= dU + pdV$
$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV + pdV$

Heat Capacities $c_p = c_v + R$ (ideal gases)

Adiabatic expansion $pV^\gamma = \text{const}$ $pdV = -dU = -C_v dT = -C_v d\left(\frac{pV}{R}\right)$ get $\frac{\gamma dV}{V} = -\frac{dp}{p}$.

Efficiency of heat engine $\eta = \frac{W}{Q_H}$

Efficiency of heat pump $\eta_{hp} = \frac{Q_H}{W}$.

Heat engine $W = Q_h - Q_c$

Thermodynamic temp. $\eta_{rev} = \frac{\tau_H - \tau_c}{\tau_H}$

Heat engine again $\frac{Q_h}{Q_c} = \frac{\tau_h}{\tau_c}$

Isothermal expansion of gas $Q_h = R T_h \ln\left(\frac{V_B}{V_A}\right)$

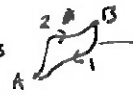
Thermod / Ideal Gas temperatures $\tau = T$ — put ideal gas through Carnot cycl

Clausius - Clapeyron equation $\dfrac{dp}{dT} = \dfrac{L}{T(V_{vap} - V_{liq})}$ — put cylinder with liq + vap in eq through carnot cycle.

Clausius' Theorem $\oint \dfrac{dQ}{T} \leq 0$ for anything — use heat from Carnot engine to drive Carnot cycle

Entropy def'n $S = \displaystyle\int_{\text{standard state}}^{\text{present state}} \dfrac{dQ_{rev}}{T}$ — from Clausius f(state) - also from Clausius.

Adiabatic change $dS = 0$ — adiabatic = Isentropic

Clausius  connect brand X.

Increasing entropy $\Delta S_{A\ \text{universe}}^{B} \geq 0$

Entropy of Joule exp. $\Delta S = R \ln\left(\dfrac{V_f}{V_i}\right)$

Maxwell Relation $\left.\dfrac{\partial S}{\partial p}\right|_T = \left.\dfrac{\partial V}{\partial T}\right|_p$ — $F = U - TS$ $G = H - TS$ $H = U + pV$ dG

Joule-Kelvin Expansion $\left.\dfrac{\partial T}{\partial p}\right|_H = \dfrac{T}{C_p}\left[\left.\dfrac{\partial V}{\partial T}\right|_p - \dfrac{V}{T}\right]$

Total no. of states of two systems $g_1(E_1)g_2(E_2)$

Statistical temperature $\dfrac{d \ln g_i}{dE_i} = \beta = \dfrac{1}{kT}$ — want to maximise $g_1 g_2$, $E = E_1 + E_2$.

Boltzman distribution $p_i = \dfrac{e^{-\frac{\varepsilon_i}{kT}}}{\sum_i e^{-\varepsilon_j/kT}}$

Partition function $Z = \sum_j e^{-\frac{\varepsilon_j}{kT}}$

waves in a box (sides a) (quantum states of gas atom) $K = \dfrac{\pi}{a}\sqrt{n^2 + m^2 + l^2}$ — $\psi(\underline{r}) = A \sin\left(\dfrac{l\pi x}{a}\right)\sin\left(\dfrac{m\pi y}{a}\right)\sin($

Number of states with energy < E $g(\varepsilon) = \dfrac{1}{8}\,\dfrac{4\pi}{3}\left(\dfrac{2ma^2}{\pi^2\hbar^2}\varepsilon\right)^{3/2}$ — $\varepsilon_{lmn} = \dfrac{(\hbar k)^2}{2m}$

Pressure of ideal (mon) gas $p = \dfrac{2u}{3}$ — energy density. — expand box by F → change energy of lmn th state, $F = 1 + \delta_{\text{small}}$ = work done against wall

Pressure of photon gas $p = \dfrac{u}{3}$ — energy ∝ momentum not squared.

Entropy (mark 1) $S = k \ln g(E)$ — $g(E)$ really $g(E)\delta E$ δE small. $d \ln g = \dfrac{dE}{kT}$ $\dfrac{dE}{T} = S$.

Changing system's heat $dQ = \sum_i \varepsilon_i dn_i$ — more systems to higher energy states.

~~Chan~~ Doing work on system $dW = \sum_i n_i d\varepsilon_i$ eg expanding box — $E = \sum_i n_i \varepsilon_i$, $dE = ?$

Maxwell-Boltzman dist. $p(c)\,dc = \left(\dfrac{m}{2\pi kT}\right)^{3/2} 4\pi c^2 dc\, e^{-\frac{mc^2}{2kT}}$ — const. from normalisation, velocity space, energy from momentum

Diatomic molecule q. states : $\varepsilon = \frac{\pi^2\hbar^2}{2ma^2}(l^2+m^2+n^2) + \frac{\hbar^2}{2I}J(J+1) + Nh\nu$ actually $(N+1/2)h\nu$

Prob. J (eg) $P(J) = \frac{(2J+1)e^{\frac{\hbar^2 J(J+1)}{2IkT}}}{\sum_J (2J+1)e^{\hbar^2 J(J+1)/2IkT}}$ sum over all l m n N - cancels with normalisation factors.

Equipartition $\frac{kT}{2}$ per d.o.f. calculate $\langle\varepsilon\rangle(l,m,n,J,N)$

$\langle E \rangle$ mean energy $\langle E \rangle = -\frac{d\ln Z}{d\beta}$

Planck's Law $u(\nu)d\nu = \frac{8\pi h\nu^3 d\nu}{c^3(e^{\frac{h\nu}{kT}}-1)}$

$\varepsilon_{lmn} = \frac{\hbar c\pi}{a}\sqrt{l^2+m^2+n^2}$.
mean ε in mode $\sum p_i(n)\, n\varepsilon_i$
$\langle\varepsilon_i\rangle = \frac{\varepsilon_i}{e^{\varepsilon_i/kT}-1}$
$\times$ no. of modes with energy ε_i.

Rayleigh - Jeans Law $u(\nu)d\nu = \frac{8\pi kT\nu^2 d\nu}{c^3}$ limit of $h\nu \ll kT$.

Wien's Law position of max energy $\propto$ Temp.

Particle escape rate density $N = \frac{1}{4}n\langle c\rangle$ per unit area per sec.

Power from B-B : $P = \frac{1}{4}cu(\nu) = \frac{2\pi\nu^3}{c^2(e^{h\nu/kT}-1)}$

Total energy density of B-B $U_{tot} = \frac{\pi^2k^4T^4}{15\hbar^3c^3}$ $\int_0^\infty u(\nu)d\nu$ $\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}$

Dulong and Petit $c = 3k$ per molecule. equipartition.

Mean energy of quantum osc. $\langle\varepsilon\rangle = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1}$ prob. having n quanta of $h\nu$ $= \frac{e^{-nh\nu/kT}}{Z}$ $Z = \frac{1}{(1-e^{-\frac{h\nu}{kT}})}$

Internal energy of solid due to lattice vibrations $U = \int_0^\infty \frac{h\nu\, g(\nu)d\nu}{e^{\frac{h\nu}{kT}}-1}$ $U = \sum_{\text{all modes}} \langle \text{energy per mode} \rangle$
$g(\nu)d\nu$ number of modes in $d\nu$

No. of longitudinal vibrational modes of lattice $g_{long}(\nu)d\nu = \frac{4\pi\nu^2}{c_{long}^3}a^3 d\nu$

Phonon energy $\varepsilon_{lmn} = h\nu = \hbar k c_{long}$
no. of modes $< h\nu = \frac{1}{8}\frac{4\pi}{3}(l^2+m^2+n^2)^{\frac{3}{2}}$

Total energy of solid $U = 4\pi a^3 h\left(\frac{1}{c_{long}^3} + \frac{2}{c_{trans}^3}\right)\int_0^{\nu_{max}} \frac{\nu^3 d\nu}{e^{\beta h\nu}-1}$ — low and high temp limits!

for two transverse pol.s

for N particles.

Debye's Prescription $\frac{4\pi}{3}a^3\nu_{max}^3\left(\frac{1}{c_{long}^3} + \frac{2}{c_{trans}^3}\right) = 3N$

Debye T^3 law (low temp) $C_V = \frac{\pi^2k^4}{30\hbar^3}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)a^3 4T^3$ $\left(\frac{dU}{dT}\right)$ replace ν_{max} by ∞ $\int = \frac{\pi^4}{15}$ $h\nu_{max} \ll kT$.

Debye Temperature $\Theta_D = \frac{h\nu_{max}}{k}$

$h\nu_{max} = kT$
above, Dulong petit
below, Debye T^3.

Internal energy of solid as $f(\Theta_D)$ $U = 3NkT\left[3\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1}\,dx\right]$

(assumes: c indep of λ
continuous energy level distribution)

Rubber band tension (per molecule) $F = \frac{kTr}{aN}$ $r \ll N$.

2N links / stretch molecule to $2ar$ / link length a
$S \approx k \ln\left({}^{2N}C_{N+r}\right)$
stretch more by dr W.D. = F 2adr
U indep of pattern: $T = TdS$ (ie dG

Third Law of thermod. $S \to 0$ as $T \to 0$

glasses still are in random state.

Gibbs Entropy $S = -k \sum_i p_i \ln p_i$

def'n.

QUANTUM MECHANICS

Photoelectric effect $E_{max} = h\nu - W$

- no e^- if $E < W$
- number emitted $\propto$ intensity.
- E_{max} indep of intensity
- emission begins immediately.

Compton effect $\lambda' - \lambda_0 = \frac{h}{m_e c}(1 - \cos\theta)$

$E^2 = p^2c^2 + m^2c^4$ for electron.
energy conserved $E + m_e c^2 = E' + \gamma m_e c^2$
momentum cons: x $p = p'\cos\theta + p_e \cos\phi$
y $-p'\sin\theta = p_e \sin\phi$.

de Broglie Hypothesis $p = \frac{h}{\lambda}$ for particles

Wave packet $\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)}\,dk$ where $g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx}\,dx$

[$g(k) = \text{FT}\,\Psi(x,0)$]

Heisenberg Uncertainty Principle $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

Group (Particle) Velocity $\frac{\Delta\omega}{\Delta k} = \left.\frac{d\omega}{dk}\right|_{k_0} + \frac{1}{2}\left.\frac{d^2\omega}{dk^2}\right|_{k_0} \Delta k$

subst
$k = k_0 + \Delta k$
$\omega = \omega_0 + \Delta\omega$
into wavepacket.

Width of w.packet after time t $W = \sqrt{(\Delta x)^2 + \frac{\hbar^2 t^2}{4m^2(\Delta x)^2}}$

$\Delta v_x = \frac{1}{2}\frac{d^2\omega}{dk^2}\Delta k$ dispersive velocity
$E = \hbar\omega$ $p = \hbar k$

Momentum representation $\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x,t) e^{\frac{-ipx}{\hbar}}\,dx$

$k = \frac{p}{\hbar}$ $g(k) \to g\left(\frac{p}{\hbar}\right)$.

Gaussian Wave packet $\Psi(x,t) = A e^{\frac{-x^2}{4\alpha}} e^{\frac{ip_0 x}{\hbar}} e^{-i\omega_0 t}$

standard Gaussian: $e^{-(x-x_0)^2/2\sigma^2}$ $\sigma = \Delta x = \sqrt{\alpha}$

$\phi(p,t) = \frac{e^{-i\omega_0 t}}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A e^{\frac{-x^2}{4\alpha}} e^{\frac{ip_0 x}{\hbar}} e^{\frac{ipx}{\hbar}}\,dx$

complete square in exponent c.f. standard Gaussian

Definition of uncertainty $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

$\Delta x^2 = \langle (x - \langle x \rangle)^2 \rangle$

Stationary states $\Psi(x,t) = \Psi(x) e^{i\omega t}$

$|\Psi|^2$ indep of time.

Momentum operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

def'n.

Position operator $\hat{x} = x$

def'n.

(Non-rel) Kinetic energy operator $\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\hbar}{2mi}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial\Psi}{\partial x}$

Hamiltonian (for $V(x)$) $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$

Eigenfunctions of Hamiltonian $\hat{H}\Psi = E_i\Psi$

Average value of obs. corres. to $\hat{A}$ $\quad \langle \hat{A} \rangle = \int_{-\infty}^{\infty} \psi^*(x)\,\hat{A}\,\psi(x)\,dx$ $\quad$ def'n.

Hermitian Conjugate $\quad \int_{-\infty}^{\infty} \phi^* A \psi \, dx = \int_{-\infty}^{\infty} \psi \left[A^\dagger \phi\right]^* dx$ $\quad$ def'n.

Hermiticity $\quad A = A^\dagger$ $\quad$ def'n.

Commutator of $\hat{A}$ and $\hat{B}$ $\quad [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. $\quad$ def'n.

Making Hermitian operator $\quad \hat{C} = \hat{A}\hat{B} + \hat{B}\hat{A} = \hat{C}^\dagger$

Hermitian commutator $\quad i[\hat{A}, \hat{B}]$ $\quad \left(i[A,B]\right)^\dagger = -i[B,A]$
$= i[A,B]$.

Beam of Particles $\quad \psi = A e^{i(kx - \omega t)}$ $\quad |A|^2$ = no. of particles per unit length.

(One dim.) Probability density current $\quad j(x) = \mathrm{Re}\left[\psi^* \frac{\hat{p}}{m} \psi\right]$ $\quad \frac{\partial P}{\partial t} = \frac{\partial}{\partial t} \int_{-\infty}^{\infty} \psi^* \psi \, dx = j(a) - j(b)$. $\quad \dot{\psi}^* \psi + \dot{\psi}^* \psi$

S.E. + c.c. subst. $\int$ valid $\forall a$,

Wave number $\quad k = \sqrt{\frac{2m(E-V)}{\hbar^2}}$ $\quad$ subst. $\psi = Ae^{ikx}$ into S.E.

B.C.'s for finite ΔV $\quad \psi$ and $\frac{\partial \psi}{\partial x}$ continuous. $\quad \psi$ cont, single valued
SE $\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2}(E-V)\psi$

B.C.'s for infinite ΔV $\quad \psi$ continuous $\frac{\partial \psi}{\partial x}$ finite discont'y $\quad \frac{\partial \psi}{\partial x} = -\frac{2m}{\hbar^2} \int^x (E-V)\psi \, dx$

Reflected amplitude at $\_\!\!\sqcap$ $\quad r = \frac{k_1 - k_2}{k_1 + k_2}$

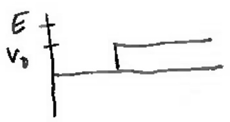
Transmitted amplitude at $\_\!\!\sqcap$ $\quad t = \frac{2k_1}{k_1 + k_2}$ $\quad t = 1 - r$.

Reflection Coefficient $\quad R = |r|^2$ $\quad$ reflected flux = ?

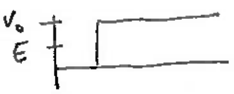
Transmission Coefficient $\quad T = \frac{k_2}{k_1}|t|^2$ $\quad R + T = 1$ $\quad$ transmitted flux = ? use $j(x) = \mathrm{Re}\left[\psi^* \frac{\hat{p}}{m} \psi\right]$

reflection with phase change of π

from $k = \sqrt{\frac{2m}{\hbar^2}(E-V)}$



reflection with no phase change



evanescence. $\quad k = iq$.

Square barrier $E > V_0$

solve system.
peaks are from destructive interference from first and second interfaces.

Square barrier $0 < E < V_0$

Weak tunnelling through square barrier ($q_2 a$ large) $\quad \left(\frac{k_1 T}{k_2} = \right)|t|^2 = \frac{16 k_1^2 q_2^2 e^{-2q_2 a}}{(k_1^2 + q_2^2)^2}$

$t = \frac{4k_1 k_2}{(k_1+k_2)^2 e^{-ik_2 a} - (k_1 - k_2)^2 e^{ik_2 a}}$

$= \frac{4ik_1 k_2}{(k_1^2 - q_2^2)(e^{q_2 a} - e^{-q_2 a}) + 2ik_1 q_2 (e + e}$

$|t|^2 = \frac{4k_1^2 q_2^2}{(k_1^2 - q_2^2)^2 \sinh^2 q_2 a + 4k_1^2 q_2^2 \cosh^2 q_2 a}$

Finite square well

$+ve\ E$ - infinite number of unbound states

$-ve\ E$ - finite no. of bound states $\Rightarrow$ values of E also finite.

Type 1 solutions (symmetric) $q = k\tan(ka)$

let $ka = x$ solve system.

$qa = y$

$x^2 + y^2 = ?f(E)$ solve system.

Type 2 solutions (antisym.) $-q = k\cot(ka)$

1-D Harmonic oscillator potential $V = \frac{1}{2}m\omega^2 x^2$

Hermite's Equation $\frac{d^2H}{dq^2} - 2q\frac{dH}{dq} + (\varepsilon - 1)H = 0$

subst $q = x\sqrt{\frac{m\omega}{\hbar}}$ $\varepsilon = \frac{2E}{\hbar\omega}$ into SE try $\psi = H(q)\exp(-\frac{q^2}{2})$

rec. rel $\frac{a_{n+2}}{a_n} = -\frac{(\varepsilon - 1 - 2n)}{(n+2)(n+1)} \rightarrow = 0$ $\varepsilon(E) = 2n+$

Energy levels $E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$

Dirac notation $\langle\phi|\psi\rangle = \int_{-\infty}^{\infty} \phi^* \psi \, dx$ def'n.

state vector $|\psi\rangle$ def'n.

Average value of observable $\hat{A}$ $\langle\psi|\hat{A}|\psi\rangle = \langle\hat{A}\rangle$ (expectation value).

State corres. to observable $\hat{A}|\psi\rangle = a|\psi\rangle$ $|\psi\rangle$ eigenstate $a = \langle\hat{A}\rangle$.

Time dependent S.E. $\hat{H}|\psi\rangle = i\hbar\frac{\partial\psi}{\partial t}.$

This $\rightarrow \langle\phi_1|A|\phi_2\rangle = a\langle\phi_1|\phi_2\rangle$

equals

that $\rightarrow \langle\phi_1|A|\phi_2\rangle^\dagger = a^*\langle\phi_1|\phi_2\rangle$

Orthogonality of state vectors $\langle\phi_1|\phi_2\rangle = 0$

Reality of eigenvalues $a = a^*$ put $\phi_1 = \phi_2 = \phi$

Postulates of Q.M.

1. $|\psi\rangle$ contains most info that we can know about system.
2. For every obs. A $\exists$ Hermitian op. $\hat{A}$. Measure A get a.
3. If get a from $|\phi\rangle$ then prob (a) when in $|\psi\rangle$ is $|\langle\phi|\psi\rangle|^2$.
4. If get a from $|\psi\rangle$ then system changed to $|\phi\rangle$. (collapse of wave func.)
5. Between measurements, system evolves as $i\hbar\frac{\partial|\psi\rangle}{\partial t} = \hat{H}|\psi\rangle$.

Eigenfunctions span space $\psi = \sum_i c_i\phi_i = c_i\phi_i$ (sum. conv.) where $c_i = \langle\phi_i|\psi\rangle$

Prob$(a) \propto |c_i|^2$ $\langle\hat{A}\rangle = a_i|c_i|^2$ (is weighted average) $\langle\psi|A|\psi\rangle = \langle\psi|A|\sum c_i\phi_i$ $A\phi_i = a\phi_i$.

Linear comb. of deg. e-states that is orthogonal. $\langle\phi_1|\phi\rangle = 0$ if $\frac{\alpha}{\beta} = -\frac{\langle\phi_1|\phi_2\rangle}{\langle\phi_1|\phi_1\rangle}$ where $|\phi\rangle = \alpha|\phi_1\rangle + \beta|\phi_2$

Commuting Observables (compatable) $\hat{A}|\phi_i\rangle = a_i|\phi_i\rangle$ and $\hat{B}|\phi_i\rangle = b_i|\phi_i\rangle$ consider $\hat{A}\hat{B}|\phi_i$

Non-commuting Observables (incompatable) $[\hat{A}, \hat{B}] \neq 0$

$\hat{A}_d = \hat{A} - \bar{A} \Rightarrow \delta A^2 = \langle\hat{A}_d^2\rangle$

$|\phi\rangle = (\hat{A}_d + i\lambda\hat{B}_d)|\psi\rangle$

$\langle\phi|\phi\rangle \geq 0 \Rightarrow$ discrim. ≤ 0

$[A_d, B_d] = [A, B]$

General Uncertainty relations $\Delta\hat{A}\Delta\hat{B} \geq \frac{1}{2}|\langle i[A, B]\rangle|$

Minimum Uncertainty State $\Delta\hat{A}\Delta\hat{B} = 0 \Rightarrow$ differential eq'n eg $p_x, x \rightarrow$ Gaussian

Harmonic Potential Ladders Ops: $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} + \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}$ def'n. (lowering)

Hermitian Conjugate of ladder op.: $\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x} - \frac{i\hat{p}}{\sqrt{2m\hbar\omega}}$ (raising).

Hamiltonian In terms of ladder Operators: $\hat{H} = \hbar\omega\left(\hat{a}\hat{a}^\dagger - \frac{1}{2}\right)$ use $aa^\dagger - a^\dagger a = 1 \to$ subst into $aa^\dagger + a^\dagger a = \frac{2\hat{H}}{\hbar\omega}$

Ground State criterion: $\hat{a}|\phi_0\rangle = 0 \Rightarrow E_0 = \frac{1}{2}\hbar\omega$ $\quad \hat{H}|\phi_0\rangle = \hbar\omega(aa^\dagger - \frac{1}{2})|\phi_0\rangle \ldots$

Ground state eigenfunction $\hat{a}|\phi_0\rangle = 0$ in terms of $\hat{x}, \hat{p} \Longrightarrow \phi_0(x) = C_0 e^{-\frac{m\omega x^2}{2\hbar}}$ $C_0 = \sqrt{\frac{m\omega}{\pi\hbar}}$

Excited states: $|\phi_n\rangle \propto (\hat{a}^\dagger)^n |\phi_0\rangle$ in terms of $\hat{x}, \hat{p}$.

Time dependence of wave function: $\Psi(x,t) = \sum_k c_k(0) e^{\frac{-iE_k t}{\hbar}} \phi_k(x)$ $\quad c_k(0) = \langle \phi_k(x) | \Psi(x,0)\rangle$, $\hat{H}|\phi_k\rangle = E_k|\phi_k\rangle$

Stationary State $\phi_k(x)$ - $\underline{|\Psi|^2 = |c_k(0)|^2 |\phi_k|^2}$ $\quad$ time dep. goes with mod. stat state is ϕ_k.

Time dependence of expectation values: $\frac{d}{dt}\langle A\rangle = \frac{1}{\hbar}\langle i[\hat{H},\hat{A}]\rangle$ $\quad \frac{d}{dt}\langle A\rangle = \int \frac{\partial\Psi^*}{\partial t} A\Psi + \Psi^* A \frac{\partial\Psi}{\partial t}\, dx$ subst $\hat{H}$ ....

Expectation Values at time t : $\langle\hat{A}\rangle\Big|_t = \sum_{jk} c_j^* c_k e^{\frac{i(E_j - E_k)t}{\hbar}} \cdot \int_{-\infty}^{\infty} \phi_j^* \hat{A} \phi_k\, dx$ $\quad c_k = \langle\phi_k|\Psi(0)\rangle$, $\Psi(x,0)$.

Ehrenfest's Theorem: when $\hbar$ negligible, $\langle A\rangle$ obeys classical eq'ns of motion (equivalence!)

Time-energy uncertainty $\Delta E \Delta t \geq \frac{\hbar}{2}$ $\quad$ eg. - width of spectral lines - mass limit for short-lived particles.

Parity operator $\hat{P}\Psi(x) = \Psi(-x)$ $\quad$ symmetry operators exist for every conserved quantity that commute with Hamiltonian

Translation operator $\hat{D}_\varepsilon \Psi(x,t) = \Psi(x,t) + \varepsilon\frac{\partial\Psi}{\partial x}$ $\quad \Psi(x,t) \to \Psi(x+\varepsilon, t) = \varepsilon\frac{\partial\Psi}{\partial x} + \Psi$. (linear mom. cons.)

Orbital Angular Momentum operators $L_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, $L_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$, $L_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$ $\quad \underline{L} = \underline{r} \times \underline{p}$ classically.

Commutation Relations $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$ + perms. $\quad y[p_z, z]p_x + p_y[z,p_z]x = i\hbar(xp_y - yp_x)$

Total Orbital Ang. Mom. $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

- commutation relations $[\hat{L}^2, L_x] = 0$ + cyclic perms.

Ang. Mom. Ladder Operators $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$, $\hat{L}_- = \hat{L}_x - i\hat{L}_y$ $\quad$ change evalues of L_z. $\hat{L}_+ = \hat{L}_-^\dagger$.

Eigenstate of L_z $\quad L_z|\phi_m\rangle = m\hbar|\phi_m\rangle$

Eigenstate of L^2 $\quad L^2|\phi_m\rangle = \Lambda\hbar^2|\phi_m\rangle$ $\quad \langle\hat{L}_z^2\rangle \leq \langle\hat{L}^2\rangle$. l = max value of m. number of states $2l+1$.

L^2 in terms of ladder ops $\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hbar\hat{L}_z + \hat{L}_z^2$ $\quad$ apply to $|\phi_l\rangle \to \Lambda = l(l+1)$.

State with evals $l(l+1)\hbar^2$, $m\hbar$: (l,m)th Spherical Harmonic $Y_{lm}(\theta,\phi)$.

Ladder ops. on sph. harmonics $L_+ Y_{lm}(\theta,\phi) = D_{lm} Y_{l\,m+1}(\theta,\phi)$ $\quad$ sim'ly for L_-, $\to C_{lm}$

Coefficient of $\quad D_{lm} = \hbar\sqrt{l(l+1) - m(m+1)}$ $\quad \langle L_+ Y_{lm}|L_+ Y_{lm}\rangle = C_{lm}^2$

Ladder ops in sph. polars $\hat{L}_\pm = \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\frac{\partial}{\partial\phi}\right)$ $\quad$ write in cartesians then convert.

$\hat{L}_z$ in sph. polars $\quad L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$ $\quad$ same.

ϕ dependence $\quad Y_{lm}(\theta,\phi) = F_{lm}(\theta)e^{im\phi}$ $\quad$ apply L_z to $|Y_{lm}\rangle$

COMPLEX VARIABLES (1B Maths Summary)

Laurent Series

For f'ns analytic at all but finite no. of points,

$$\boxed{f(z) = \sum_{n=-\infty}^{\infty} a_n (z-z_0)^n}$$

Zeros

f has a zero of order N at z_0 if $\boxed{a_N}$ is the first coeff not to $=0$

$f = a_N (z-z_0)^N + a_{N+1}(z-z_0)^{N+1} + \ldots\ldots (\infty)$ (for $N>0$, $n<N$)

Poles

f has a pole of order N at z_0 if $\boxed{a_{-N}}$ is the first coeff not to $=0$

$f = a_{-N}(z-z_0)^{-N} + a_{-N+1}(z-z_0)^{-N+1} + \ldots$

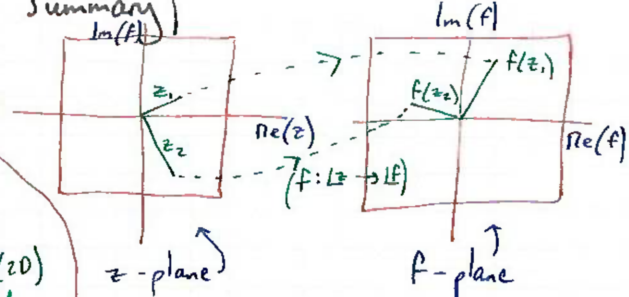
- can be removed by $\times (z-z_0)^N$!

f has an essential singularity if $N=\infty$ in the above:

eg: $e^{\frac{1}{(z-z_0)}}$ at z_0.

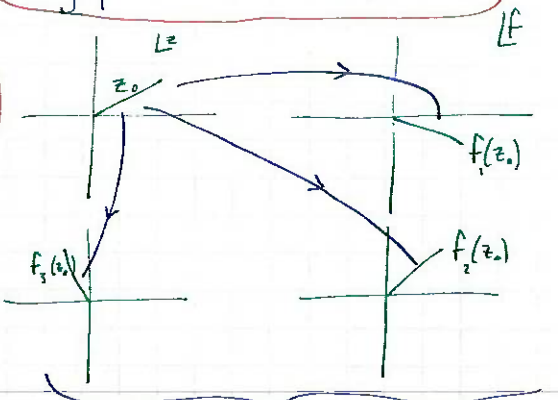
Multivaluedness and Branch Cuts.

- Can write variation of $f(z)$ with x on same diagram (2D) but with complex f'ns, need 4-D as z and f both have 2 d.o.f. So need to draw:



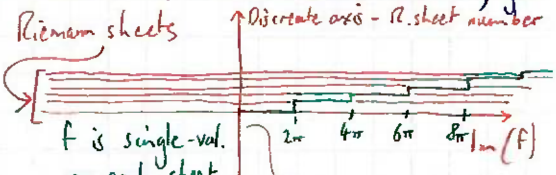
So can trace path to represent a continuous variation of z - get corresponding path in $\mathbb{L}f$. (f plane).

BUT Some times the map from $\mathbb{L}z \to \mathbb{L}f$ is one to many or many to one - then can do this:



3 (of many poss.) Rieman sheets.

Imagine them foliating 3D space, then when $f(z) = \ln(z)$ and $z = 1.e^{i\theta}$, get:



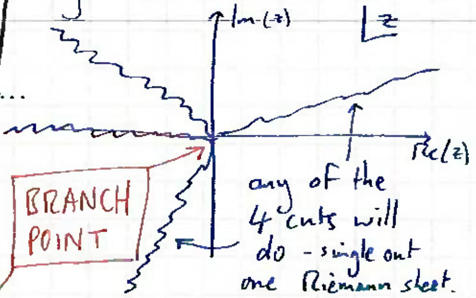
f is single-val. on each sheet (each complex plane)

R(f) out of page

or can use Branch Cuts:

ie. put a line in $\mathbb{L}z$ that can't cross, then don't get multivalues.

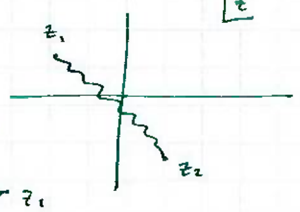
eg $f(z) = \ln(z)$:



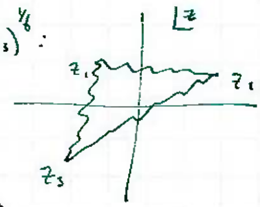
ie point in z-plane which when circled causes $f(z)$ to be multivalued.

FINITE BRANCH CUTS

- need powers of $f(z)$ at the (two) or more branch points to sum to an integer, eg: $f(z) = (z-z_1)^{1/2}(z-z_2)^{1/2}$:

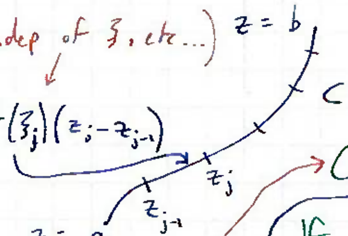


also: $f(z) = (z-z_1)^{1/3}(z-z_2)^{1/2}(z-z_3)^{1/6}$:



Contour Integration

Def'n: $\displaystyle\int_C f(z)\,dz = \lim_{\substack{n\to\infty \\ \text{and } |z_j - z_{j-1}|\to 0}} \sum_{j=0}^{n} f(\xi_j)(z_j - z_{j-1})$ (indep of ξ, etc...)



So just add up values of $f(z)$ as z changes from $a \to b$ in some way ie. along some path!

Can use PARAMETERS: let $z = z(t)$

then: $\displaystyle\int_C f(z)\,dz = \int_{t_0}^{t_1} f[z(t)]\frac{dz}{dt}\,dt$

$\underbrace{\hphantom{xxxxxxxxxxxxxxxx}}_{\text{Real Integral (of complex f'n)}}$

Now $\oint (z-z_0)^n\,dz = 2\pi i$ if $n=-1$
$= 0$ otherwise.

eg. unit circle

CAUCHY'S THEOREM:

If f is analytic in a simply connected domain then for every closed curve, (not nec. reversible)

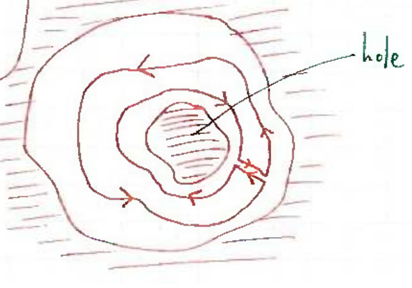
$$\boxed{\oint f(z)\,dz = 0}$$

To prove, use 2-D divergence theorem then C-R relations.

$\Rightarrow$ PATH INDEPENDENCE

So can deform paths to more convenient ones!

if multiply connected, can do this:



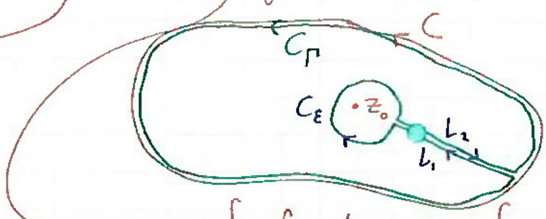
COMPLEX VARIABLES (cont'd)

Cauchy's Integral Formula

$$\boxed{\oint \frac{f(z)}{(z-z_0)}\,dz = 2\pi i f(z_0)}$$

for analytic f, s.c. D etc...

use Cauchy's Theorem to prove:



says: $\displaystyle\int_{C_\Gamma} \frac{f}{(z-z_0)}\,dz = 0 = \int_{C+L_1+L_2+C_\varepsilon}$

Parametrise C_ε as $z = z_0 + \varepsilon e^{i\theta}$

So $\displaystyle\int_{C_\varepsilon} = \int_0^{2\pi} \frac{[f(z_0)+O(\varepsilon)]\, i\varepsilon e^{i\theta}\,d\theta}{\varepsilon e^{i\theta}} = -2\pi i$

$$= \int_C + \underbrace{\int_{L_1} + \int_{L_2}}_{\text{cancel}} + \int_{C_\varepsilon}$$

$$\Rightarrow \int_C = -\int_{C_\varepsilon} = 2\pi i f(z_0) \quad \text{as } \varepsilon \to 0$$

Derivatives

use: + first princ. differentiation

$$f(z_0) = \frac{1}{2\pi i}\oint \frac{f(z)}{(z-z_0)}\,dz \Rightarrow \left.\frac{d^n f}{dz^n}\right|_{z_0} = \frac{n!}{2\pi i}\oint \frac{f(z)}{(z-z_0)^{n+1}}\,dz$$

Liouville's Theorem

If an analytic f'n deviates from a constant value anywhere on the orange, then it is singular somewhere!

Calculus Of Residues

Near a singular point, z_0, can write $f(z) = \sum_{n=-\infty}^{\infty} a_n (z-z_0)^n$

where a_n is nonzero up to a certain $n (<0)$.

Now: $\oint (z-z_0)^n\,dz = 0 \quad n \neq -1$
$\qquad\qquad\qquad = 2\pi i \quad n = -1$

$$\Rightarrow \boxed{\oint f(z)\,dz = 2\pi i\, a_{-1}}$$

TP3 ①

Electrostatic Analogy

(i is $90°$ anticlock. rotation operator)

$$f^* g \equiv \underline{f}\cdot\underline{g} + i\,|\underline{f}\times\underline{g}|$$

let $\nabla = \frac{\partial}{\partial x} + i\frac{\partial}{\partial y}$

then $\nabla^* g = \text{div}\, g + i\,|\text{curl}\, g|$

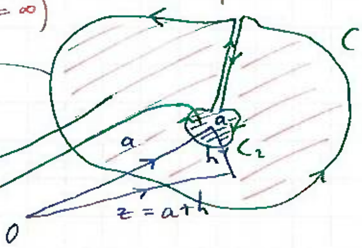
let $E^* = u + iv$ then max. eq'ns $\text{div}\,\underline{E} = 0$, $\text{curl}\,\underline{E} = 0$ are

$$\boxed{\nabla E^* = 0} \Leftrightarrow \text{C.R. conditions.}$$

More complex analysis - Laurent Series

If have singular function, can expand about the singularity: $(f(a) = \infty)$

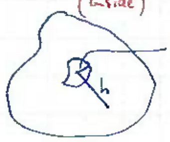
total contour does not include singularity



So: $\displaystyle f(a+h) = \frac{1}{2\pi i}\oint_{C_1} \frac{f(z)}{z-(a+h)}\,dz + \frac{1}{2\pi i}\oint_{C_2} \frac{f(z)}{z-(a+h)}\,dz$

C_1: outside C_2 $\qquad$ C_2: (inside)

$z - a \gg h$ on contour C_1



$z - a \ll h$ on contour C_2

So $\displaystyle\frac{1}{z-(a+h)} = \sum_{n=0}^{\infty} \frac{h^n}{(z-a)^{n+1}}$ $\qquad$ So $\displaystyle\frac{1}{z-(a+h)} = \sum_{n=1}^{\infty} \frac{(z-a)^{n-1}}{h^n}$

$$\Rightarrow f(a+h) = \sum_{n=-\infty}^{\infty} a_n h^n$$

where $\displaystyle a_n = \frac{1}{2\pi i}\oint_{C_1} \frac{f(z)}{(z-a)^{n+1}}\,dz$ for $n \geq 0$

and $\displaystyle a_n = \frac{1}{2\pi i}\oint_{C_2} \frac{f(z)}{(z-a)^{n+1}}\,dz$ for $n < 0$

Kramers - Kronig Relations

If have a causal function, can always write as $f(t) = \Theta(t)\,g(t)$.

if then find F.T., need to know F.T. of Θ: it is divergent ∴ include $e^{-\lambda t}$

So $\displaystyle \Theta_\omega = \frac{\lambda}{\omega^2 - \lambda^2} - i\frac{\omega}{\omega^2 + \lambda^2}$

$\displaystyle \to \pi\delta(\omega) - \frac{i}{\omega}$ as $\lambda \to 0$

now F.T. of product = conv:

$\displaystyle f_\omega = \int \Theta_\omega(\omega - \omega_1)\, g(\omega_1)\,\frac{d\omega_1}{2\pi}$

So $\displaystyle f_\omega = \frac{1}{2}\int f(\omega-\omega_1)\, g(\omega_1)\,d\omega_1 - \frac{i}{2\pi}\int \frac{g(\omega_1)}{\omega-\omega_1}\,d\omega_1$

now for simplicity choose $g(t)$ antisym, real. Then g_ω is real.

$$f_\omega = \underbrace{\frac{1}{2} g_\omega}_{\text{real}} - \frac{i}{2\pi}\underbrace{\int \frac{g_\omega(\omega_1)\,d\omega_1}{\omega-\omega_1}}_{\text{real}} \quad \text{so } \text{Re}(f_\omega) = \frac{g_\omega}{2} \quad \text{Im}(f_\omega) = \frac{-1}{2\pi}\int \frac{g_\omega\,d\omega_1}{\omega-\omega_1}$$

$$\Rightarrow \boxed{\text{Im}(f_\omega) = \int \frac{\text{Re}(f_\omega)\,d\omega'}{(\omega-\omega')\,\pi}}$$

if let $g(t)$ be real, get g_ω is imaginary, then reverse integral