

- ① Phonons
- ② X-Ray
- ③ Electronic properties

RESPONSE FUNCTION → how ob measurements

P	R	F
X	X	S
✓	J	0
Ω	≡	
H	B	
Q	T	c_v

$$\xrightarrow{P} \boxed{\quad} \xrightarrow{R} R = F(P)$$

GOAL = what is F?

Builds a model
that give the
response

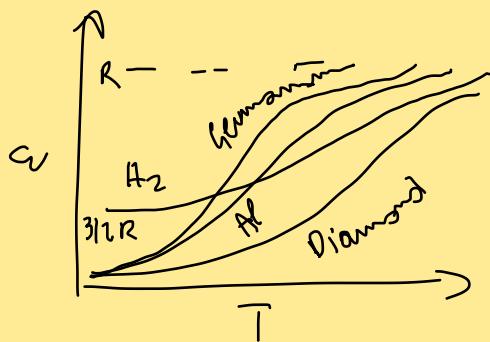
In principle we can do everything with quantum mechanics.
TASK → build models for $R = F(P) = A_P$ $A \approx \frac{R}{P}$ **LINEAR APPROXIMATION**

$c_v \xrightarrow{Q} \boxed{?} \xrightarrow{T}$ what is inside the box? Model

TERMODYNAMICS

- axiomatic theory
- not based on a model
- ergo phs law → connection the macroscopic behavior with the micro

WHAT IS THE CONNECTION BETWEEN Q-T?



ZERO PRINCIPLE

Something hot - something cold in contact → reach equilibrium

STATE → U, V, M, M_1, \dots, M_f

↓
internal energy
partial of chemical components

I need to make a choice = U or S, then the other variables are correlated

THE RUM CONTACT → two materials in contact exchange heat

THE RUM EQUILIBRIUM → The state does not change (dynamical eq.)

T → in Kelvin

$$\boxed{A} T_A \rightarrow \boxed{A} \boxed{B} T_{AB} \quad T_A \leq T_{AB} \leq T_B$$

FIRST PRINCIPLE

Perpetuum motion does not exist \rightarrow GENERALIZATION OF ENERGY CONSERVATION

$$\exists U: \alpha, \beta \text{ at equilibrium } E = U(\beta) - U(\alpha)$$

\uparrow

INTERNAL ENERGY

$$E = W + Q$$

W work done
 Q heat supplied

$$W + Q = \Delta U \text{ or } \Delta U = \Delta W + \Delta Q$$

e.g. $\Delta W = -P\Delta V \quad \Delta W = E \cdot \underline{\Delta P} \quad \Delta V = \underline{\Delta H}$

SECOND PRINCIPLE

heat flows spontaneously from high-T to low-T
it is not possible the opposite.

$\exists S$, ENTROPY, extensive variable

- showing arbitrary ADIABATIC process (no heat exchange)

$$Q_{\alpha \rightarrow \beta} = 0 \rightarrow S(\beta) \geq S(\alpha)$$

$$\Delta Q = 0 \rightarrow \Delta S \geq 0$$

$$\text{CANNOT occur } \Delta S \geq \frac{\Delta Q}{T}$$

$$\text{if transformation reversible } \Delta S = \frac{\Delta Q}{T}$$

THIRD PRINCIPLE

Related to QM

"The S of all perfect crystal at T=0 is always the same = a constant that we assume to be 0"

QUESTION = HOW TO CONNECT T WITH Q

$$\xrightarrow{\frac{\partial Q}{\partial T}} \boxed{?} \xrightarrow{\frac{T}{\Delta T}} \left(\frac{\Delta Q}{\Delta T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = C_V$$

$$\Delta Q + \Delta W = \Delta U$$

$$\Delta Q - P\Delta V = \Delta U$$

Principle of TD one at constant V?

STATE VARIABLE

REALITY \rightarrow not constant V
 $C_V \rightarrow C_P$

$$\text{e.g., } \Delta Q = I^2 R \Delta t$$

- $C_p \sim C_v$
 - CM phase space
 - SM Boltzmann
 - SM Equipartition
 - Duulang - Petit
- } Classical physics
-

$$\xrightarrow{P} \boxed{\quad} \xrightarrow{R} \left(\frac{dQ}{dT} \right)_{V,N} = C_{V,N}$$

$$F(P) = R \qquad dQ + dW = dU$$

LINEAR APPROXIMATION $dQ = TdS$

Let's be little bit more precise on the C_V definition: in principle I can also define $C_{P,N}$ and relates it with $C_{V,N}$

$$\left(\frac{dQ}{dT} \right)_{P,N} = C_{P,N}$$

$$C_{P,N} = C_{V,N} + \left(\frac{\partial V}{\partial T} \right)_{P,N} \left[\left(\frac{\partial U}{\partial V} \right)_{T,N} + \frac{P}{V} \right]$$

ISOTHERM. COMPRESSIBILITY $\kappa_{P,N} = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}$

Thermal expansivity $\alpha_{P,N} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N}$

We can combine all together and we obtain:

$$K_{T,N} (C_{P,N} - C_{V,N}) = TV \alpha_{P,N}^2 \rightarrow C_V \sim C_P$$

NB Water has very high specific heat = 'in' is the reason of life on earth
I feel cold when I touch metal because conduction is high

MODEL = Box full of particle

What we know for moving from mechanics (one system at the time) to statistical mechanics (average number of some systems)? Clarify the concept of phase space.

PHASE SPACE

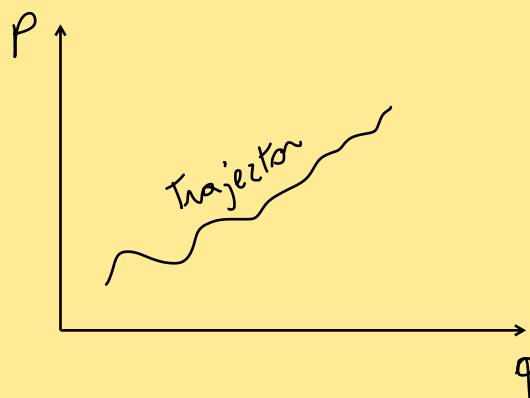
Hamiltonian mechanics allow to go from CLASSICAL to QUANTUM mechanics -

HM → position and momenta as INDEPENDENT VARIABLES

$$\begin{array}{l} \underbrace{\underline{x}_1, \underline{x}_2, \dots, \underline{x}_N}_{\text{POSITIONS}} \\ \underbrace{\underline{p}_1, \underline{p}_2, \dots, \underline{p}_N}_{\text{MOMENTA}} \end{array}$$

In HM I need only momenta = first order differential equation

$$(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_{3N}, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_{3N}) \rightarrow \text{PHASE SPACE}$$



$$\dim \Gamma = 2N_f \quad N_f \text{ degree of freedom}$$

Which equation do I have? No forces, ENERGY

$$H(\underline{q}_1, \underline{q}_2, \dots, \underline{q}_{3N}, \underline{p}_1, \underline{p}_2, \dots, \underline{p}_{3N}, t)$$

not all system

$$H = T + V$$

$$\begin{cases} \dot{\underline{q}}_i = \frac{\partial H}{\partial \underline{p}_i} \\ \dot{\underline{p}}_i = -\frac{\partial H}{\partial \underline{q}_i} \end{cases}$$

HAMILTON EQUATIONS

Kinetic energy is not related to the positions $\frac{1}{2}mv^2 = \frac{\underline{p}^2}{2m} = T$

$$\dot{\underline{p}}_i = -\frac{\partial H}{\partial \underline{q}_i} = -\frac{\partial V}{\partial \underline{q}_i} \rightarrow \text{Nothing less than the second law of Newton}$$

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

POISSON BRACKETS

I can use poisson brackets to rewrite the Hamilton equations

$$\dot{q}_i = \{q_i, H\}$$

$$\dot{p}_i = \{p_i, H\}$$

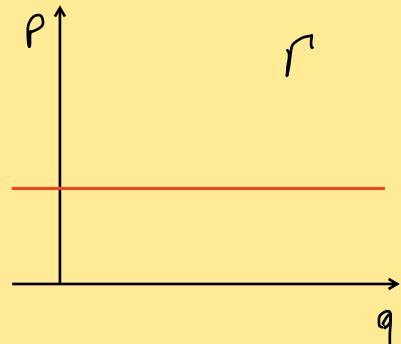
- useful when we will do harmonic oscillator
- quantization

Ex = FREE PARTICLE

$$H = \frac{p^2}{2m} = \frac{p_1^2 + p_2^2 + p_3^2}{2m}$$

$$N=1 \quad \text{dim } \Gamma = 6$$

$$(q_1, q_2, q_3, p_1, p_2, p_3)$$



$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{m} \rightarrow p_i = m \dot{q}_i \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} = 0 \rightarrow \text{Momentum is conserved: no forces!} \end{cases}$$

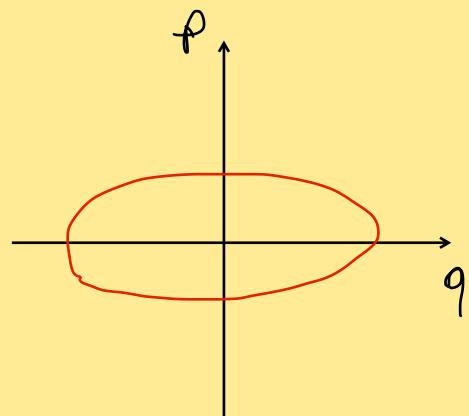
Ex = HARMONIC OSCILLATOR

$$H = \frac{p^2}{2m} + \frac{1}{2} \kappa q^2$$

$$\omega^2 = \frac{\kappa}{m}$$

$$\begin{cases} \dot{q}_i = \frac{\partial H}{\partial p_i} = \frac{p_i}{2m} \\ \dot{p}_i = -\frac{\partial H}{\partial q_i} = -\kappa q \end{cases} \rightarrow \begin{aligned} q &= q_0 \cos \omega t \\ p &= p_0 \sin \omega t \end{aligned}$$

choice free

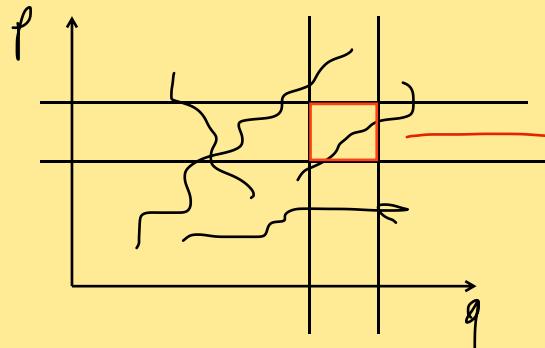


I have phase space now.

Now I have to introduce the concept of ENSEMBLE

ENSEMBLE \rightarrow each particle different initial conditions

To moving particle \rightarrow I need to consider averages



$$H(q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N})$$

N particles in total
 m_i particles in each cell

EQUILIBRIUM \rightarrow something that maximize the probability to find a particle

ONLY ONE
 CELL

$$\binom{N}{m_i} = \frac{N!}{m_i!(N-m_i)!}$$

ALL THE
 COMBINATION
 FOR ALL CELLS

$$P = \binom{N}{m_1} \binom{N-m_1}{m_2} \binom{N-m_1-m_2}{m_3} \dots = \frac{N!}{m_1! m_2! m_3! \dots}$$

I have to maximize P , if at EQUILIBRIUM

there is something missing:

- N remain the same $\sum_i m_i = N$ } TWO CONSTRAINT
- Energy conservation $\sum_i m_i \bar{E}_i = \bar{E}$ } TO IMPOSE

TRICK: I work on $\ln P$ instead of P

$$F[\{m_i\}, \alpha, \beta] = \ln P - \alpha (\sum_i m_i - N) - \beta (\sum_i m_i \bar{E}_i - \bar{E})$$

Lagrange
 mult.

I need to compute $\frac{\partial F}{\partial m_i} = 0$.

NB. $\ln P = \ln(N!) - \sum_i \ln(m_i!)$

$$\ln m! = \sum_1^m \ln m \sim \int_1^m \ln x dx =$$

$$\ln P = N \ln N - N - \sum_i (m_i \ln m_i - m_i)$$

STEARIAN
 APPROX.

$$\frac{\partial F}{\partial n_i} = 0 = -\ln m_i \nabla + \nabla - \alpha - \beta E_i; \quad \boxed{m_i = \exp(-\alpha - \beta E_i) \\ = A e^{-\beta E_i}}$$

This is a discrete formulation, I can do also the continuous formulation

$$dm = A e^{-\beta H(q, p)}$$

BOLTZMANN
DISTRIBUTION
FUNCTION

$$\int dm = N$$

$$A = \frac{1}{\int e^{\beta H} dp_1 dp_2 \dots dp_N dq_1 dq_2 \dots dq_N}$$

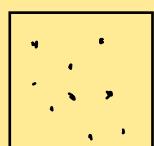
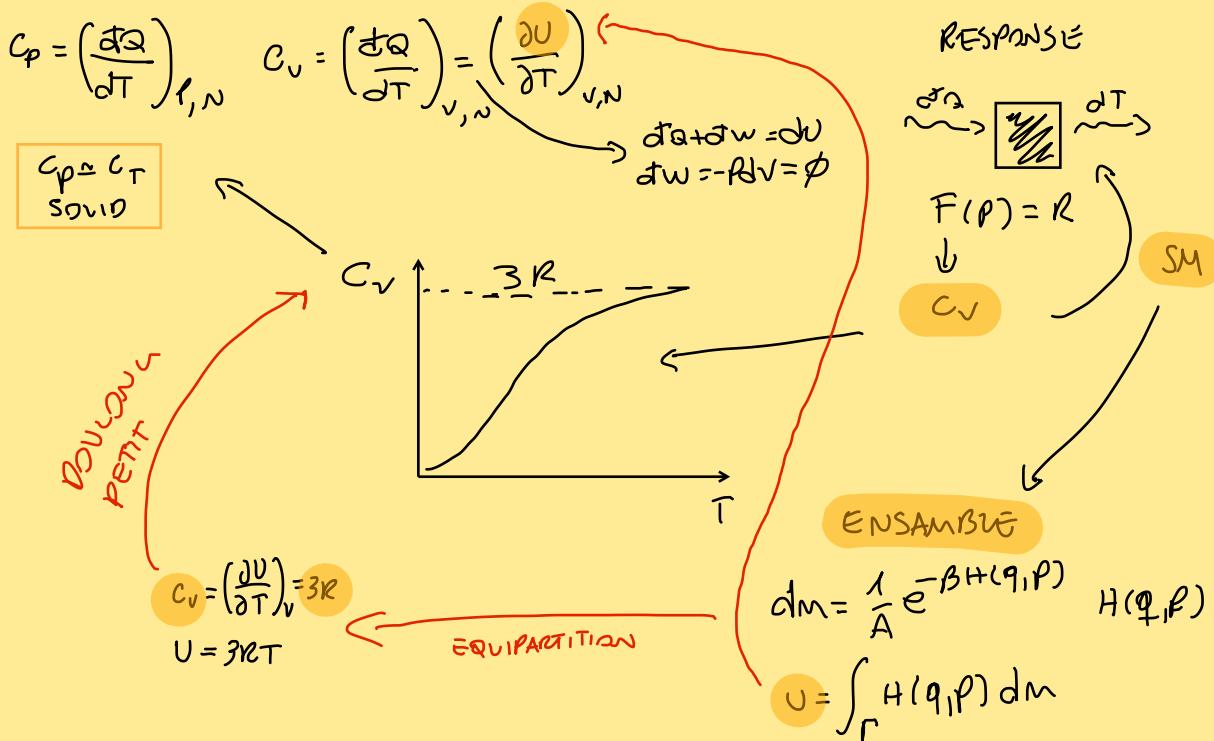
What is β ? $\beta = \frac{1}{k_B T}$, interpreted a posteriori

We need to count what happens to m_i when H is quadratic in T and V : we can derive the EQUIPARTITION THEOREM.

- CM
- CM + SM + TD
- Tutorial**
- Equipartition
- CM
- QM

Next

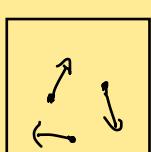
- QM Revision
- Article on Einstein



GAS

$$H = \frac{p^2}{m}$$

BOTH
QUADRATIC
HAMILTONIANS



SOLID

$$\sum_i \frac{p_i^2}{m} + \frac{1}{2} \sum_i q_i^2$$

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{3}{2} k_B T$$

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_i q_i^2 = 6N_A \frac{1}{2} k_B T = 3RT$$

$$H = H(q_1, q_2, q_3, \dots, p_1, p_2, \dots) = \sum_i (b_j p_j^2 + \alpha_j q_j^2)$$

$$U = \langle H \rangle \longrightarrow \frac{\int b_j p_j^2 dM}{\int dM} = \frac{\int b_j p_j^2 e^{-\beta H} dq_1 dq_2 \dots dp_1 dp_2 \dots}{\int e^{-\beta H} dq_1 dq_2 \dots dp_1 dp_2 \dots}$$

$$\text{NB } \prod_{k+j} \frac{\int e^{-\beta H} dp_k dp_{k+j}}{\int e^{-\beta H} dp_k p_{k+j}^2} = 1$$

$$\int e^{-(\alpha x)^2} x^3 dx = \frac{\sqrt{\pi}}{4\alpha^3}$$

$$\int e^{-(\alpha x)^2} dx = \frac{\sqrt{\pi}}{2\alpha}$$

$$= b_j \frac{1}{2\beta b_j} = \frac{1}{2\beta} = \frac{1}{2} k_B T$$

EQUIPARTITION
THEOREM
OF ENERGY

I can ob tens for every quadratic Hamiltonian that I know -

$$\frac{\int \alpha_j q_j^2 dM}{\int dM}$$

C_V is not a function of T ! PROBLEM!

I am not so off ... $T \rightarrow 0$, $C_V \rightarrow 3R$

For now the approximations one: quasistatic Hamiltonian

$$C_V = \left(\frac{\partial U}{\partial T} \right)_N = 3R \quad \text{DULONG - PETIT MODEL}$$

Classically we cannot explain the T dependence of C_V = we introduce QUANTUM MECHANICS.

1^o POSTULATE \rightarrow the wave function ψ describes the state of the system

$$\psi(r_1, r_2, \dots, r_f, t)$$

$$\psi^* \psi d\tau = \psi^* \psi dr_1 dr_2 \dots dr_f \rightarrow \int \psi^* \psi d\tau = 1$$

2^o POSTULATE \rightarrow From classical physics to quantum
classically we can always define an operator as function of positions and momenta.

ARE THE
SAME THING

$$\begin{cases} r_i \rightarrow \hat{r}_i \\ p_i \rightarrow i\hbar \frac{\partial}{\partial r_i} = -i\hbar \nabla_i \end{cases} \quad t_i = \frac{\hbar}{2m}$$

Ex. $H = \frac{p^2}{2m} \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$

$H = \frac{p^2}{2m} \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \nabla^2$

$\{f, g\} \rightarrow \frac{1}{i\hbar} [\hat{f}, \hat{g}]$

$$\{q, p\} = \frac{\partial q}{\partial \theta} \frac{\partial p}{\partial \theta} - \frac{\partial q}{\partial p} \frac{\partial p}{\partial \theta} = 1$$

$$[\hat{q}, \hat{p}] = i\hbar \quad (\hat{q}\hat{p} - \hat{p}\hat{q})\psi = \left(-x \left(i\hbar \frac{\partial}{\partial x} \right) - \left(-i\hbar \frac{\partial}{\partial x} \right)x \right) \psi$$

$$= -i\hbar x \frac{\partial \psi}{\partial x} + i\hbar \frac{\partial}{\partial x} (x\psi)$$

$$= -i\hbar \cancel{x} \frac{\partial \psi}{\cancel{\partial x}} + i\hbar \frac{\partial x}{\partial x} + i\hbar \cancel{\frac{\partial \psi}{\partial x}} = i\hbar$$

3^o POSTULATE → Eigenvalue problem

$$\hat{\mu} \psi = m \psi \quad m \text{ are the possible value that } \hat{\mu} \text{ can assume apply on } \psi$$

$$\hat{\mu} = \left(r; -i\hbar \frac{\partial}{\partial r}; t \right)$$

E4. $\hat{H} \psi = E \psi$ Schrödinger equation at the stationary state

4^o POSTULATE → The time evolution of the system is determined by the Schrödinger equation

$$\hat{H} \psi = i\hbar \frac{\partial}{\partial t} \psi$$

FREE-PARTICLE MODEL

$$H = \frac{p^2}{2m} \quad \hat{H} \psi = i\hbar \frac{\partial}{\partial t} \psi$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x, t)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t} \quad \psi(x, t) = \varphi(x)\phi(t)$$

Solved by separate the variable

$$-\frac{\hbar^2}{2m} \phi(t) \frac{\partial^2 \psi}{\partial x^2} = i\hbar \varphi(x) \frac{\partial \phi}{\partial t}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \phi}{\partial t} \quad \rightarrow \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E \psi \quad \psi(x) = B e^{ikx}$$

$$i\hbar \frac{\partial \phi}{\partial t} = E \phi \quad \phi(t) = A e^{-i\omega t}$$

$$\omega: i\hbar(-i\omega) = E$$

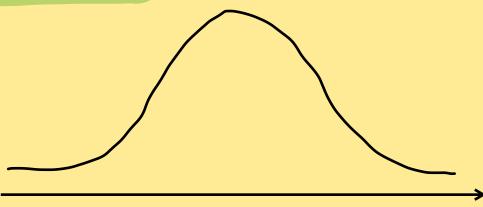
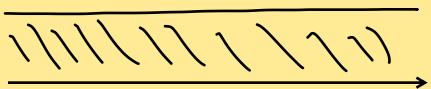
$$E = \hbar\omega = \frac{h}{8\pi} 8\pi v = h\nu \quad \text{EINSTEIN RELATION}$$

$$E = \frac{\hbar^2}{2m} k^2 \quad k = \frac{n\pi}{\lambda}$$

$$\hbar k = p = \frac{h}{8\pi} \frac{n\pi}{\lambda} = \frac{h}{\lambda} \rightarrow \frac{p\lambda}{\lambda} = \frac{h}{p}$$

PROBLEM Free-electron model gives a ψ that is NOT NORMALIZABLE

→ SOLUTION = WAVE-PACKETS



(D) \rightarrow +QM Einstein model

Coupled \rightarrow normal modes

TODAY

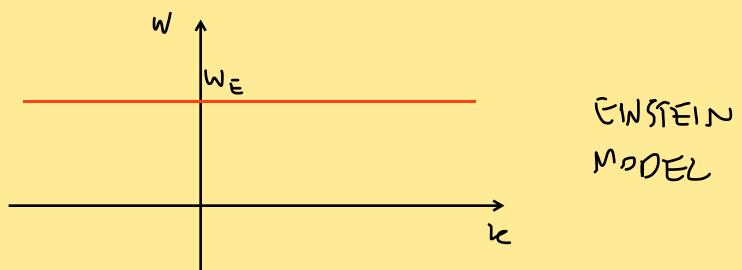
QM

Quasi particles

DOS

$$U = \hbar \omega_e \left(m_{BE} (\omega_1 T) + \frac{1}{2} \right) 3 N_A$$

↑
this point



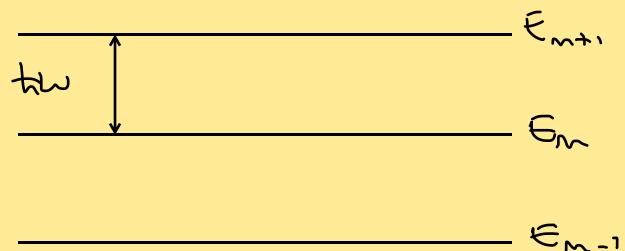
$$U = \sum_{m, \kappa} \hbar \omega_m(\kappa) \left(m_{BE} + \frac{1}{2} \right)$$

$$\psi_m(x, t) = |m\rangle \quad H|m\rangle = E_m |m\rangle \quad H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$[\hat{x}, \hat{p}] = i\hbar \quad [\hat{x}, \hat{H}] = \frac{i\hbar}{m} \hat{p}$$

$$\begin{cases} (E_m - E_n) \langle \kappa | \hat{x} | m \rangle = \frac{i\hbar}{m} \langle \kappa | \hat{p} | m \rangle \\ (E_m - E_n) \langle \kappa | \hat{p} | m \rangle = -im\hbar\omega^2 \langle \kappa | \hat{x} | m \rangle \end{cases}$$

$$E_n = \hbar\omega(n + c)$$



$$E_{m-1} \quad E_m \quad E_{m+1}$$

II QUANTIZATION

NB. In a non-relativistic regime, it does not add anything - it is only another notation -

$-im\omega$

$$\begin{cases} (\epsilon_m - \epsilon_n) \langle k | \hat{x} | m \rangle = \frac{i\hbar}{m} \langle k | \hat{p} | m \rangle \\ (\epsilon_m - \epsilon_n) \langle k | \hat{p} | m \rangle = -im\hbar\omega^2 \langle k | \hat{x} | m \rangle \end{cases} +$$

$$(-im\omega)(\epsilon_m - \epsilon_n) \langle k | \hat{x} | m \rangle + (\epsilon_m - \epsilon_n) \langle k | \hat{p} | m \rangle = (-im\omega) \frac{i\hbar}{m} \langle k | \hat{p} | m \rangle - im\hbar\omega^2 \langle k | \hat{x} | m \rangle$$

$$(\epsilon_m - \epsilon_n) \underbrace{\langle k | \hat{p} - im\omega x | m \rangle}_{\alpha} = \hbar\omega \underbrace{\langle k | \hat{p} - im\omega x | m \rangle}_{\alpha}$$

$\alpha \rightarrow$ electrons excitations (quasi particles)

$\alpha^+ \rightarrow$ odds excitations

$\left. \begin{array}{l} (\hat{p} - im\omega x)^* = (\hat{p} + im\omega x) \\ \alpha \neq \alpha^+ \rightarrow \text{not observable} \end{array} \right\}$ (2nd postulate QM)

Let's see some properties of α

$$\langle m-1 | \alpha | m \rangle = \lambda_m = \sqrt{m}$$

$$\alpha | m \rangle = \sqrt{m} | m-1 \rangle$$

LOWERING AND
RAISING OPERATORS

$$\langle m | \alpha^+ | m-1 \rangle = \lambda_m^* = \sqrt{m}$$

$$\alpha^+ | m-1 \rangle = \sqrt{m} | m \rangle$$

In II quantization each excitation corresponds to a quantum of energy -

Let's understand the ZERO-POINT ENERGY.

$$\langle 0 | 0 \rangle = \langle \hat{p} - im\omega x | 0 \rangle = 0 | 0 \rangle \xrightarrow{\text{by definition}} (\hat{p} + im\omega x)(\hat{p} - im\omega x) | 0 \rangle = (\hat{p}^2 + im\omega[\hat{x}, \hat{p}] + m^2\omega^2\hat{x}^2) | 0 \rangle$$

$$m\left(\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 - \frac{1}{2}\hbar\omega\right) | 0 \rangle = 0$$

$$H | 0 \rangle = \frac{1}{2}\hbar\omega | 0 \rangle$$

The absence of excitation have an energy because of indeterminism principle -

NB. $E_m = \hbar\omega \left(m + \frac{1}{2}\right)$

In order to simplify how we write it

$$(p - im\omega x) \frac{1}{\sqrt{2m\hbar\omega}} = \sqrt{\frac{m\omega}{2\hbar}} x + i \frac{p}{\sqrt{2m\hbar\omega}} = \alpha \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$(p + im\omega x) \frac{-i}{\sqrt{2m\hbar\omega}} = \sqrt{\frac{m\omega}{2\hbar}} x - i \frac{p}{\sqrt{2m\hbar\omega}} = \alpha^+ \quad \left. \begin{array}{l} \\ \end{array} \right\}$$

$$[\alpha, \alpha^+] = 1$$

$$H = (\alpha^\dagger \alpha + \frac{1}{2}) \hbar \omega$$

$\hat{N} = \alpha^\dagger \alpha \rightarrow$ how many excitations I have in the system

$$\hat{N}|M\rangle = \alpha^\dagger \alpha |M\rangle = M|M\rangle$$

$$\alpha = \begin{pmatrix} 0 & 1 & & & \\ 0 & 0 & \sqrt{2} & & \\ 0 & 0 & 0 & \sqrt{3} & \\ 0 & 0 & 0 & 0 & \sqrt{4} \\ \vdots & & & & \ddots \end{pmatrix} \quad \alpha^\dagger = \begin{pmatrix} 0 & & & & \\ 1 & 0 & & & \\ 0 & \sqrt{2} & 0 & & \\ 0 & 0 & \sqrt{3} & 0 & \\ 0 & 0 & 0 & \sqrt{4} & \\ \vdots & & & & \ddots \end{pmatrix} \quad N = \begin{pmatrix} 1 & 2 & 3 & 4 & & \\ & & & & \ddots & \\ & & & & & \ddots \end{pmatrix}$$

Now I want to write H for more than one oscillator = a family of oscillators

$$H = \sum_{m,k} \hbar \omega_{mk} (\alpha_{mk}^\dagger \alpha_{mk} + \frac{1}{2})$$

Now I have to count the particles differently

$$|M_1, M_2, M_3, \dots \rangle = \sum (a_1^\dagger)^{M_1} (a_2^\dagger)^{M_2} \dots |0\rangle \quad \text{FOCK SPACES} \rightarrow \text{direct product of H spaces}$$