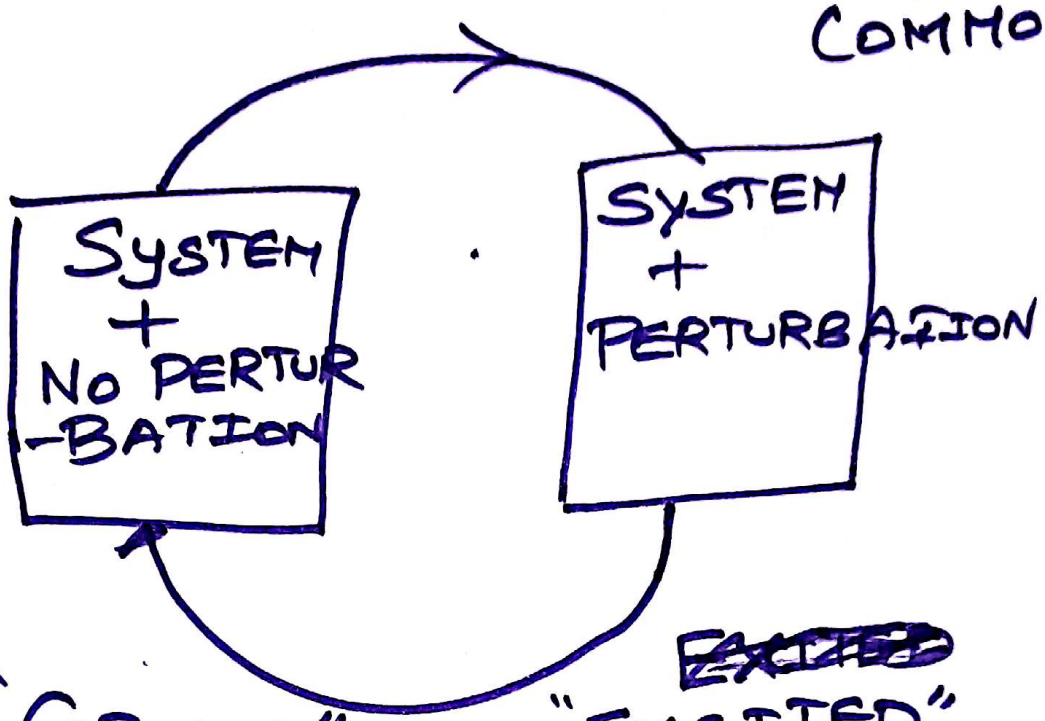
PERTURBATIONS

- P, V, T (THERMODYNAMICS)
- EXTERAL FIELDS (• ELECTRIC • MAGNETIC)
- ELECTROMAGNETIC WAVES (LIGHT) ⇓ MOST COMMON



"GROUND" ENERGY

"EXCITED" ENERGY + ΔE ⇐ EXTRA ENERGY

HAMILTONIAN: H_0

SMALL PERTURBATION } : $\Delta H \to 0$

LARGE PERTURBATION } : $\Delta H \gg 0$

$H_0 + \Delta H$ ⇓ $H_0 + H_p$ ⇐ PERTURBATIVE PART OF THE HAMILTONIAN

$H_p \equiv \Delta H$

MANY-BODY SYSTEMS

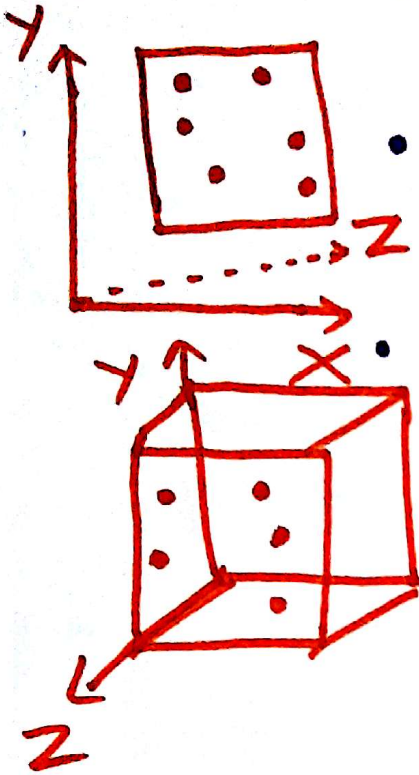
→ THERMODYNAMICS

- P, V, T, n; HERE n → NUMER OF MOLES
- FIXED n; $P = f(V, T)$ ⇓ EQUATION OF STATE
- ALL PROPERTIES CAN BE EXPRESSED AS FUNCTIONS OF P, V, T, n
- THE CONCEPTS OF ATOMS, MOLECULES, ELECTRONS ETC... ARE NOT NEEDED
- DIFFERENT ENERGY FUNCTIONS:
  - HEAT
  - WORK
  - ENTHALPY
  - INTERNAL ENERGY
  - ENTROPY
  - HELMHOLTZ FREE ENERGY
  - GIBBS FREE ENERGY
  - CHEMICAL POTENTIAL

MANY-BODY SYSTEMS

⇒ CLASSICAL STATISTICAL MECHANICS:

- SYSTEM CONSISTS of N PARTICLES



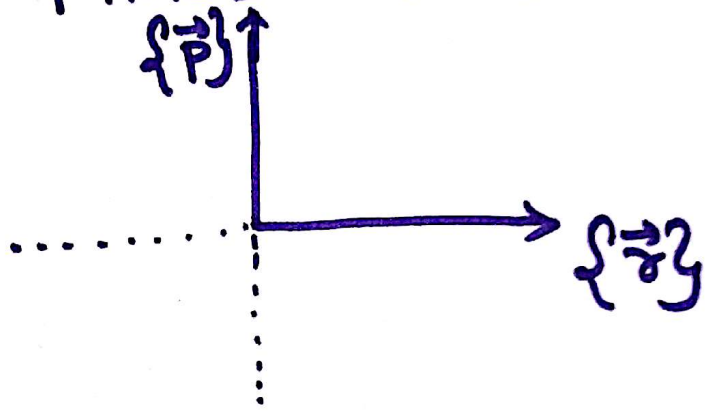
- $\{\vec{r}\} = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$

SET of POSITIONS

- $\{\vec{p}\} = (\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$

SET of MOMENTA

- PHASE SPACE



- DEFINE HAMILTONIAN

TOTAL ENERGY OF THE SYSTEM →

$$H(\{\vec{r}\}, \{\vec{p}\}) = U(\{\vec{r}\}) + K(\{\vec{p}\})$$

U: POTENTIAL ENERGY → INTERATOMIC INTERACTIONS

K: KINETIC ENERGY → THERMAL ENERGY

- $U(\{\vec{r}\})$ DEFINES THE POTENTIAL ENERGY SURFACE

- SOLVE HAMILTON'S EQUATIONS OF MOTION TO UNDERSTAND HOW $\{\vec{r}\}$ AND $\{\vec{P}\}$ VARY WITH TIME. (DYNAMICS)

$$\frac{d\vec{P}_i}{dt} = -\frac{\partial H}{\partial \vec{r}_i} = -\frac{\partial U}{\partial \vec{r}_i} \quad \forall i$$

FORCE ON ATOM i

HERE $\frac{\partial}{\partial \vec{r}_i} = \left(\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i}\right)$

GRADIENT

$$\frac{d\vec{r}_i}{dt} = \frac{\partial H}{\partial \vec{P}_i} \quad ; \forall i$$

- INITIAL CONDITIONS:

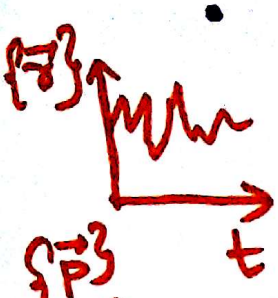
AT TIME $t=0$:

$\{\vec{r}(t=0)\}$ $\{\vec{P}(t=0)\}$

$\{\vec{r}(t=0)\}$: X-RAY DIFFRACTION, NMR, RANDOM

$\{\vec{P}(t=0)\}$: MAXWELL-BOLTZMANN DISTRIBUTION

• TIME EVOLUTION



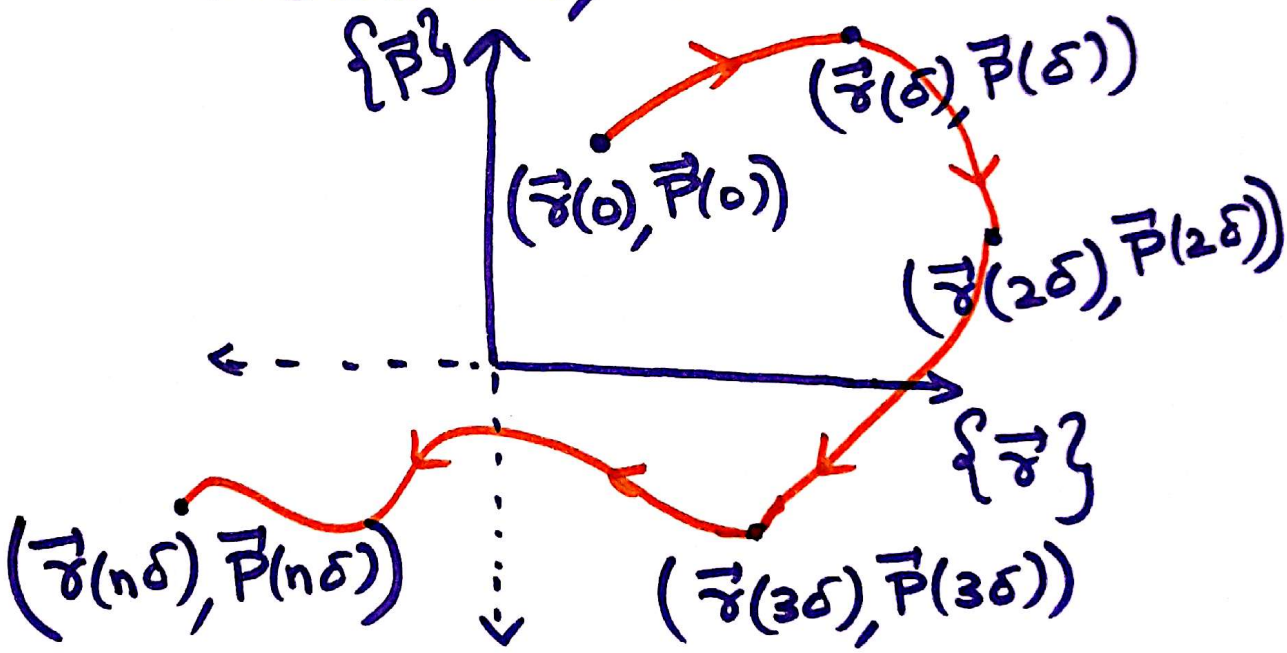
$$\{\vec{r}(t=0)\} \rightarrow \{\vec{r}(t=\delta)\} \rightarrow \{\vec{r}(t=2\delta)\} \rightarrow \{\vec{r}(t=3\delta)\} \rightarrow \{\vec{r}(t=4\delta)\} \cdots \{\vec{r}(t=n\delta)\}$$

HERE $\delta \Rightarrow$ TIME STEP

$n \Rightarrow$ A LARGE +VE INTEGER

$$\{\vec{p}(t=0)\} \rightarrow \{\vec{p}(t=\delta)\} \rightarrow \{\vec{p}(t=2\delta)\} \rightarrow \{\vec{p}(t=3\delta)\} \rightarrow \{\vec{p}(t=4\delta)\} \cdots \{\vec{p}(t=n\delta)\}$$

• TRAJECTORY ON PHASE SPACE



• ALL PROPERTIES CAN BE WRITTEN AS FUNCTIONS OF $\{\vec{r}\}$ AND $\{\vec{p}\}$

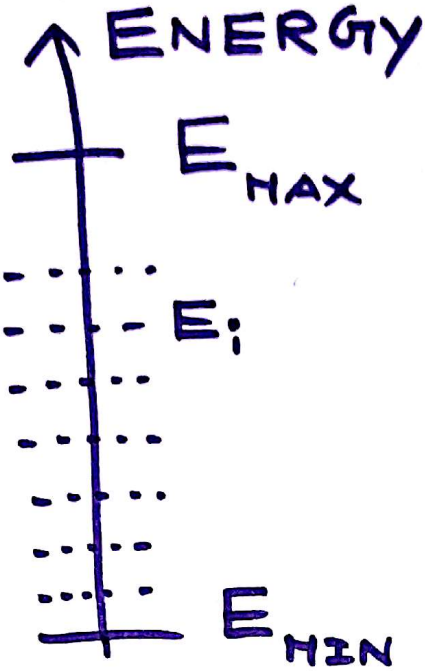
$$A(t) = A(\{\vec{r}(t)\}, \{\vec{p}(t)\})$$

TIME EVOLUTION OF "A" CAN BE STUDIED

ENERGY-LEVEL DIAGRAM

E_{MIN} → LOWEST ENERGY OF THE SYSTEM

E_{MAX} → HIGHEST ENERGY



$\Omega(E_i)$ ⇓ NUMBER OF MICROSTATES WITH ENERGY E_i

$\delta E \to 0$; $\delta E = 0$ CONTINUOUS ENERGY SPECTRUM (CLASSICAL SYSTEMS)

$\delta E \neq 0$ DISCRETE ENERGY LEVELS (QUANTUM SYSTEMS)

WHAT IF SOME EXTRA ENERGY E_p IS ADDED TO THE SYSTEM ?

→ $E_{MAX} - E_{MIN}$ CAN VARY

→ SYSTEM CAN TRANSIT BETWEEN DIFFERENT ENERGY LEVELS

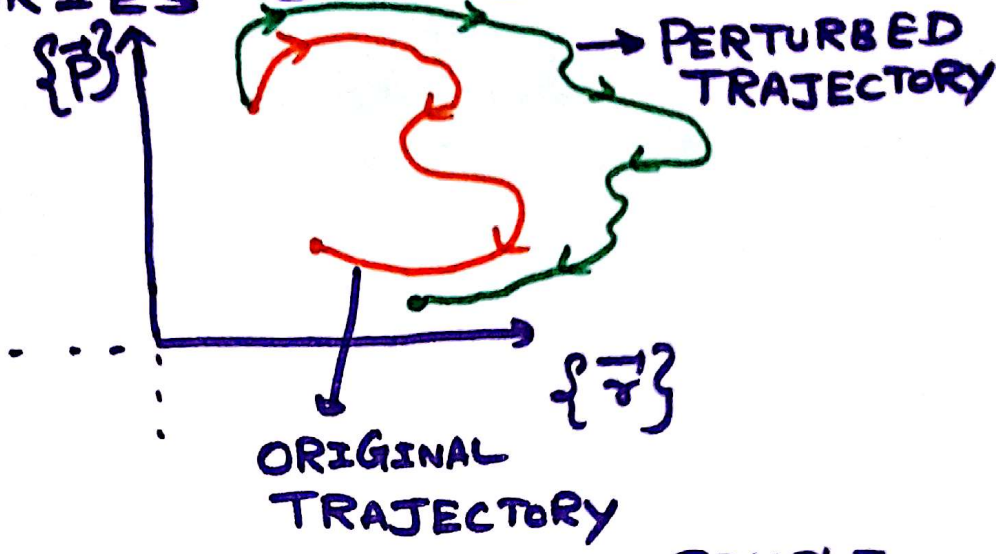
COMPARE ORIGINAL AND PERTURBED SYSTEMS

COMPARE ORIGINAL AND PERTURBED SYSTEMS

ORIGINAL SYSTEM: $H_0(\{\vec{r}\}, \{\vec{p}\})$

PERTURBED SYSTEM: $H_0(\{\vec{r}\}, \{\vec{p}\}) + H_p$

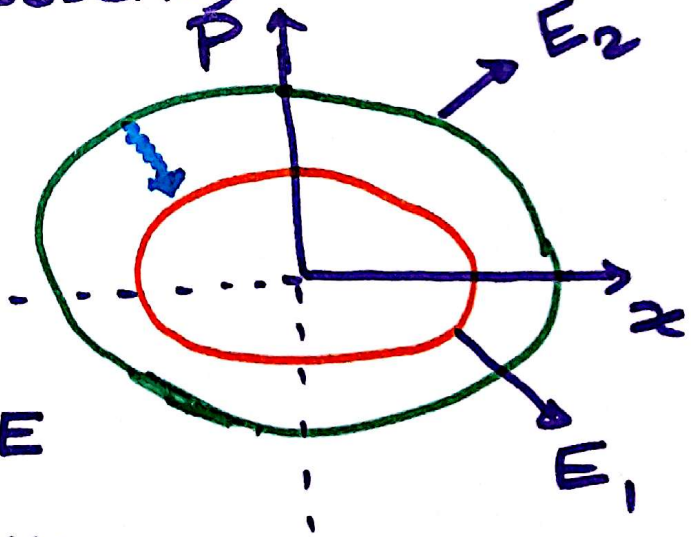
TRAJECTORIES CAN BE DIFFERENT



EXAMPLE: ONE-DIMENSIONAL SIMPLE HARMONIC OSCILLATOR (CLASSICAL)

REDUED MASS

$$\mu = \frac{Mm}{M+m} \simeq m$$



$$H_0(x, p) = \frac{p^2}{2m} + \frac{1}{2}kx^2 = E$$

SET $\boxed{H_0 = E}$ INITIALLY

$$\frac{x^2}{\left(\sqrt{\frac{2E}{k}}\right)^2} + \frac{p^2}{\left(\sqrt{2mE}\right)^2} = 1$$ ELLIPSE

$E_2 > E_1$

$$\boxed{E_2 = E_1 + E_p}$$