Finite Ring Geometries and Role of Coupling in Molecular Dynamics and Chemistry

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FINITE PROJECTIVE RING GEOMETRIES

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Outline of the talk

Changes (evolution in time) – quantitative / **qualitative**

Examples of **qualitative** approximations in elementary physical models – implications (constraints) for space and time

Qualitative changes – implications for space and time
$\Rightarrow$ hierarchic build-up principles

Static vs. dynamic approach

Conventional approach in physics / chemistry –
certain combination of a **static** and **dynamic** approaches

Static ~ existence of elementary building blocks primarily assumed (in **space** - 3D, phase space, …)

Dynamic ~ interaction by forces (electromagnetic, gravitational) derived from properties of matter (charge, mass)

Motion in **time**

Laws of physics – laws of conservation, formulated in the context of infinitesimal calculus (continuous space and time) and closed systems

$\Rightarrow$ qualitative change $\rightarrow$ quantitative change

Qualitative change

In such a setup – a conceptual problem with describing any **qualitative** change (~ formation of a system of bound particles)

Difficulties with the notion of **time**
'Evolution' according to physical laws ~ reversible time, describes only quantitative changes, absence of qualitative changes

Qualitative change ~ **arrow** of time

?

Such change of the nature of **time**
⇓
Change of concept of **space**

Qualitative change

? Can a **qualitative** change be described within a **continuous** concept

Qualitative change – emergence of new properties
atoms → molecule : center of mass, moment of inertia, vibrational frequency

? Can a **qualitative** change be described within a concept of a **closed system**

Should be perhaps considered together with the continuous / discrete issue

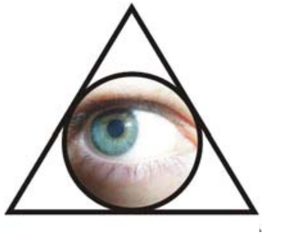
Characteristics of living systems

Where is the boundary between living systems (LS) and lifeless nature?

Analyzing the assembly of complex (living) systems to the simplest constituents $\rightarrow$ self-assembly

The role of **information** in living systems ?

Do we need some higher-level ‘principle’ for the initial step ?



Different Concept of Space and Time

Self-assembly of bound systems

Extension of the model to complex systems with properties attributed to ‘living systems’

Modification of the concept of **space** and **time** in the sense that these do not exist independently from bodies, their building blocks, and fields that make them mutually interact, but are inseparable, emergent

Space, Time, and Numbers

- ? Is not the main obstacle to consistent description of quantitative and qualitative changes on one common footing the continuous character of space and time?

- ? Some principle of ‘least possible’ change in the concept of finite geometries that would imply a least possible change in time and space in the sense that :

- ➢ **Both space and time** only **emerge** at a certain level of complexity of finite geometry objects

- ➢ **All fundamental physical quantities** only **emerge** at a certain level of complexity of finite geometry objects

Space, Time, and Information

- Existence of objects and their interactions would not have to be assumed as primary, but they would also emerge together with **space** and **time**

- Finite geometry approach – a fundamental concept for representing **information** on a common footing with physical objects and interactions?

- Finite geometry – potential language of emergence?

Bond in the QM context

Bond between two hydrogen atoms

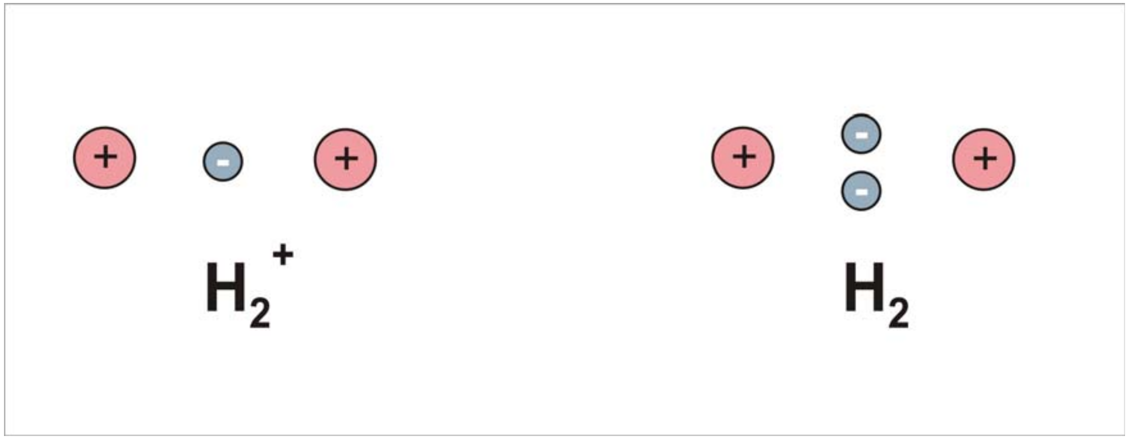
Hydrogen atom – system of one proton and one electron, **exactly solvable** in the framework of quantum mechanics

In fact a system of an electron in a central Coulomb field
Spherical symmetry, electron orbitals classified by irreducible representations of the spherical group

Also the system of two proton and one electron (H_2^+), **exactly solvable,** however a problem arises for a system with two electrons (H_2)

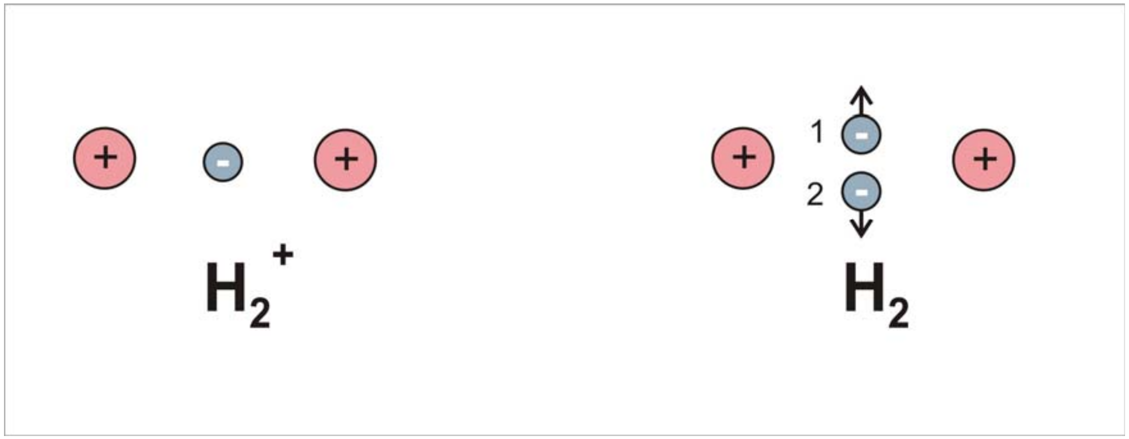
Bond in the QM context

Bond between two protons



Intuitively – the system with two electrons features stronger repulsion than that with one electron ⇒ unstable

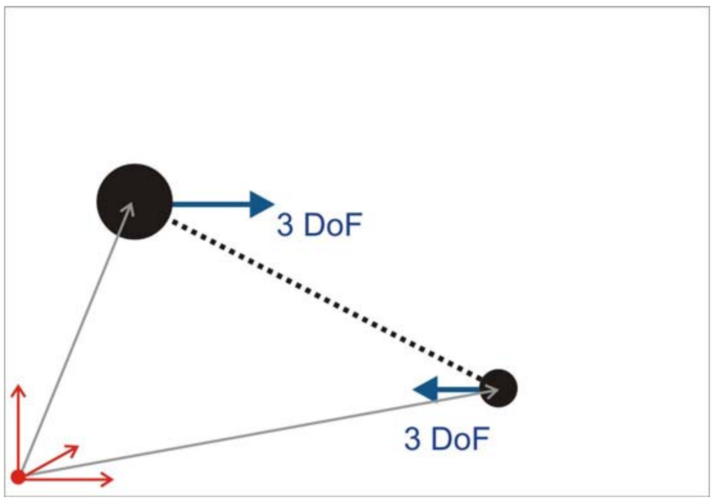
Bond in the QM context

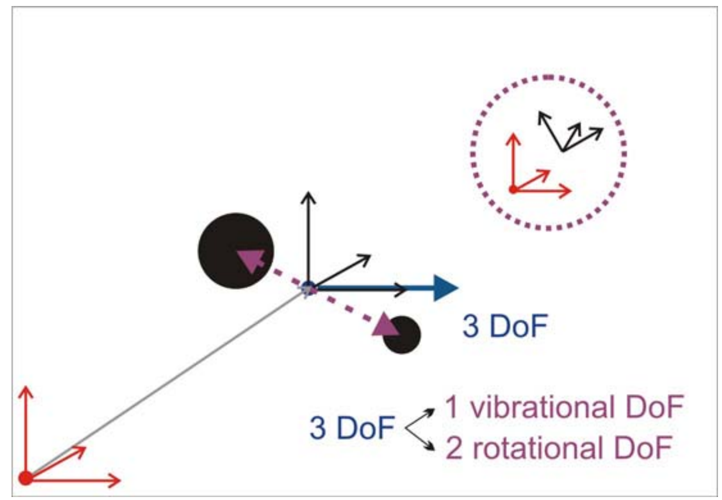


Only the additional assumption of the electron spin and the Pauli exclusion principle leads to a bound H_2 molecule

Free / bound particles

Idealized point particles (interacting, with no internal structure, no dimensions)

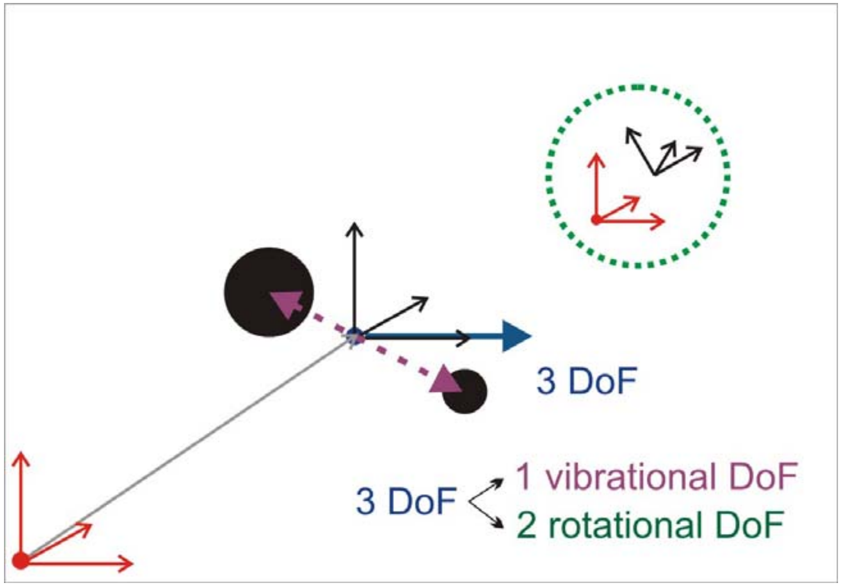




Classical problem of two bodies interacting by gravitation – cannot treat the change unbound ↔ bound

Conservation of total energy $E_{tot} = E_{kin} + E_{pot}$

Free → bound particles



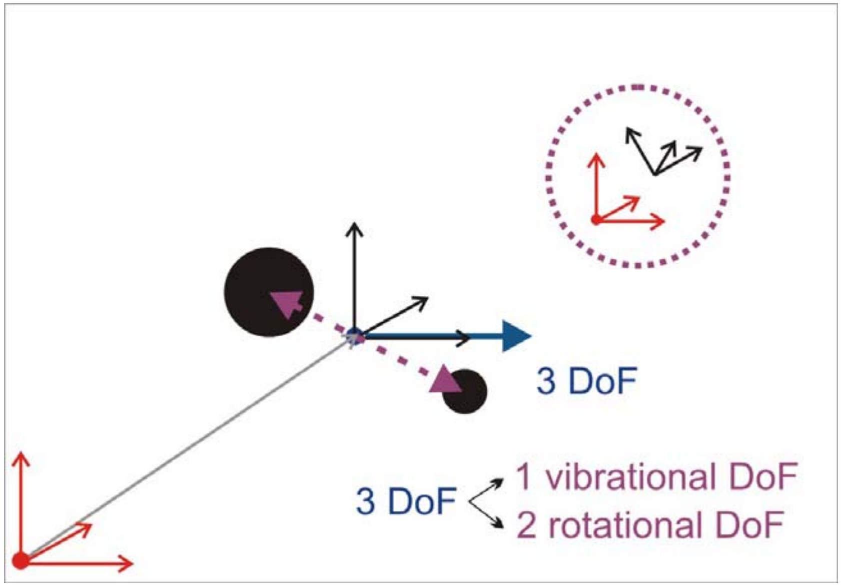
Admitting the change of the total energy
$E_{tot} = E_{kin} + E_{pot}$

$E_{tot} > 0 \rightarrow E_{tot} < 0$

Qualitative change – 3 degrees of freedom (**DoF**) with no periodicity change to periodic DoF which carry the property of defining a cyclic time (emerging with the creation of a bond)

Vibrational and rotational DoF are qualitatively different !
~ Different symmetry

Free → bound particles

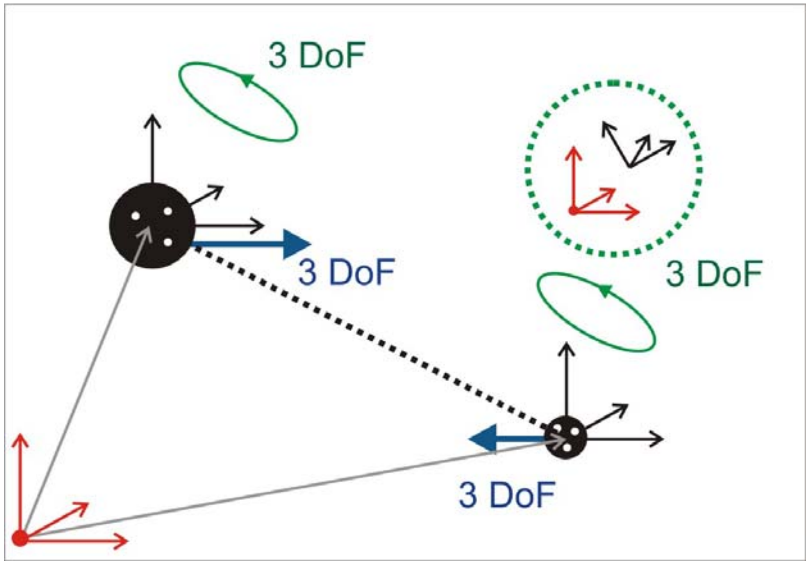


Admitting dissipation of the total energy

$$E_{tot} > 0 \rightarrow E_{tot} < 0$$

Qualitative change – exchange of energy with the **environment** or **internal DoF**

Free → bound objects



Object composed from
N particles (N>2)
3N degrees of freedom

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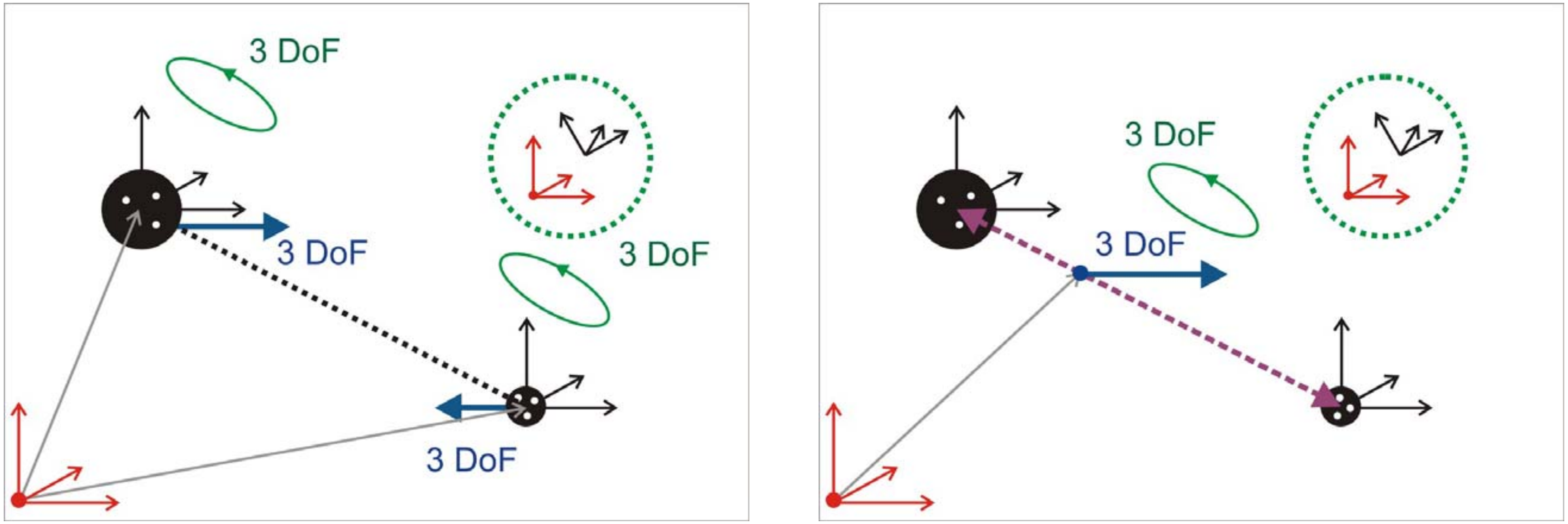
3 translation
3 rotation
3N-6 vibration (internal DoF)

Objects with internal DoF – the total energy can be in principle redistributed into these internal DoF in such a manner that it cannot be reversibly recovered, because of qualitatively different types of motion and different timescales → hierarchic nature

Free → bound objects

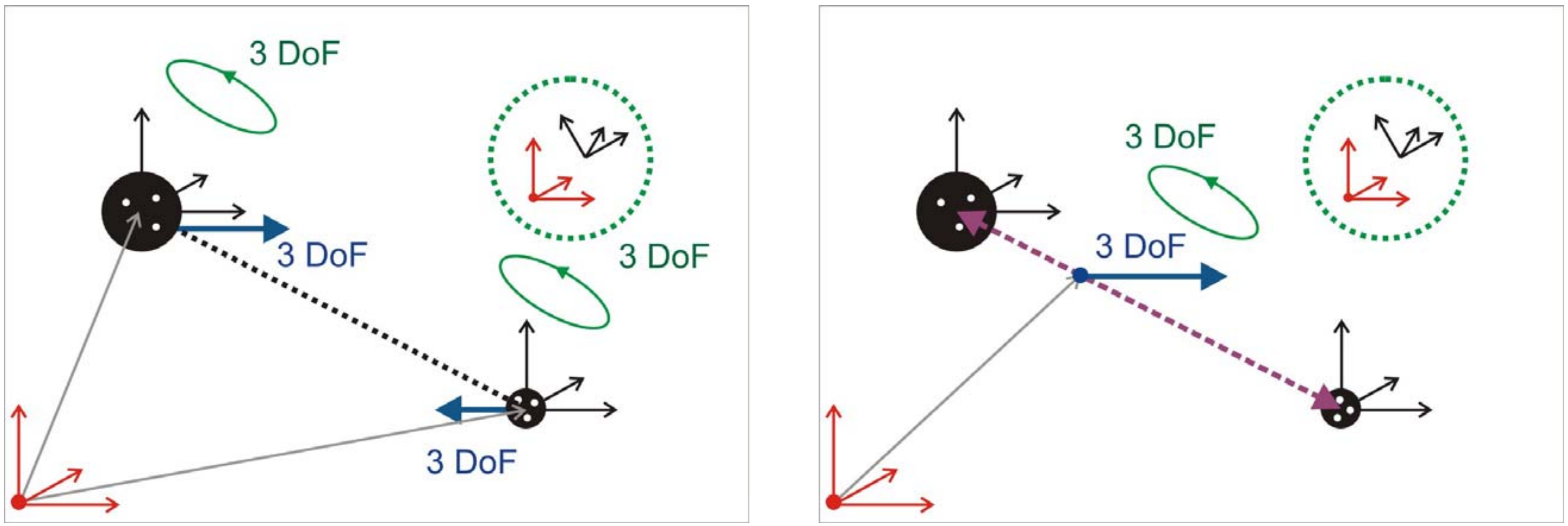


Bond between two objects with internal DoF

3 translation DoF + **3** rotation DoF ⇒ **6** vibration DoF

i.e. $(3N_1-6) + (3N_2-6) = 3(N_1+N_2-6) + \mathbf{6}$

Hierarchy in chemical bonding



The process of creation of a new (chemical) bond has **hierarchic** features – spatial and temporal
Due to existence of two quite distinct types of particles – heavy nuclei and light electrons

Hierarchic principles in molecules

Mass ratio - electrons / nuclei

$$m_e / m_H \approx 1/1836$$

$\Leftrightarrow$ Born-Oppenheimer (adiabatic) approximation

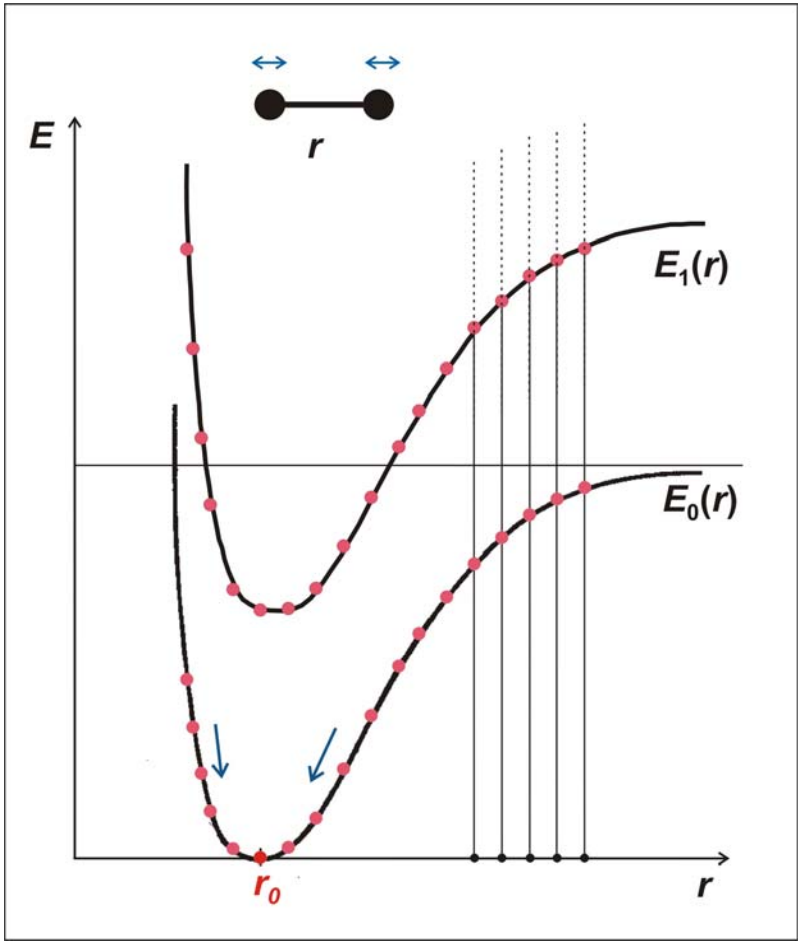
~ lighter electrons react more rapidly to motion of slower nuclei $\Rightarrow$ provide an averaged **electrostatic potential** for the motion of nuclei (molecular vibrations)

Hierarchic principles in molecules

The equilibrium structure of a molecule (***r_0***) – stable point of the dynamics on the molecular potential surface

When nuclei are displaced from equilibrium – a return force pulls them back and makes them oscillate

Quantum system – no state of rest at equilibrium (r_0)



Hierarchic principles in molecules

The third dynamical level in the game – overall rotation of the molecule

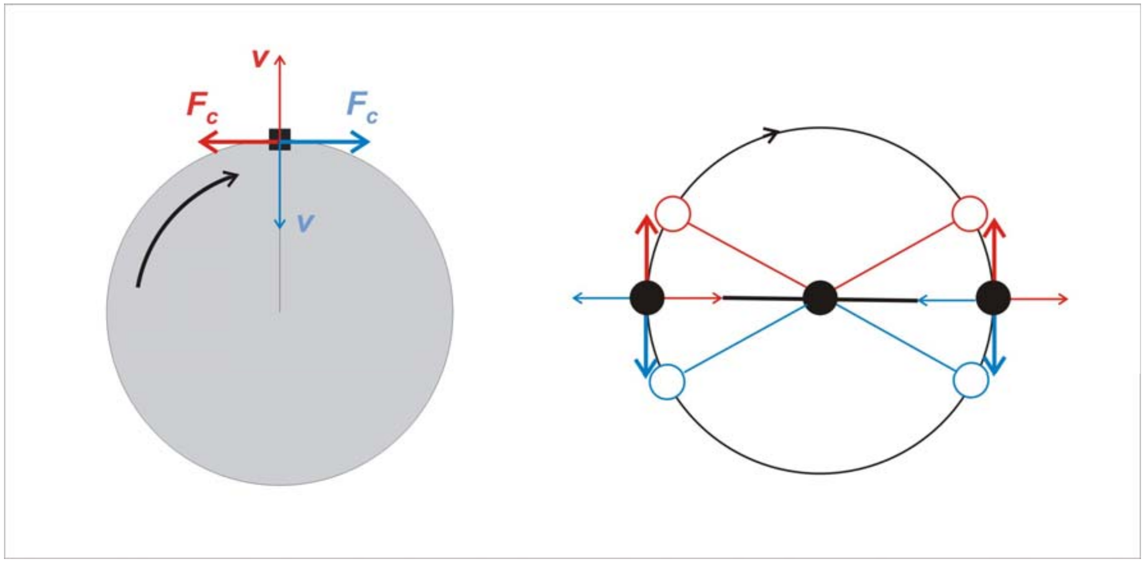
Slower than the electronic and nuclear (vibrational) motions $\Rightarrow$ the rotational chracteristics (moments of inertia) correspond to **averaged vibrational stucture**

However – the rotating molecular frame is not inertial

$\Rightarrow$ **Coriolis forces** in polyatomic molecules couple the internal molecular vibrational motions – in both the spatial and temporal domains

Coriolis force in a polyatomic molecule

Object moving in a rotating frame to a place with a different tangential velocity – subject to a virtual Coriolis force



$$\vec{F}_{cor} = -2m\left[\vec{\omega}\times\vec{v}\right]$$

Asymmetric stretching ⇒ Coriolis force bends the molecule
~ coupling of vibrational modes (dependent on rotation)

Hierarchic principles in molecules

Regarding molecules as hierarchic dynamical systems

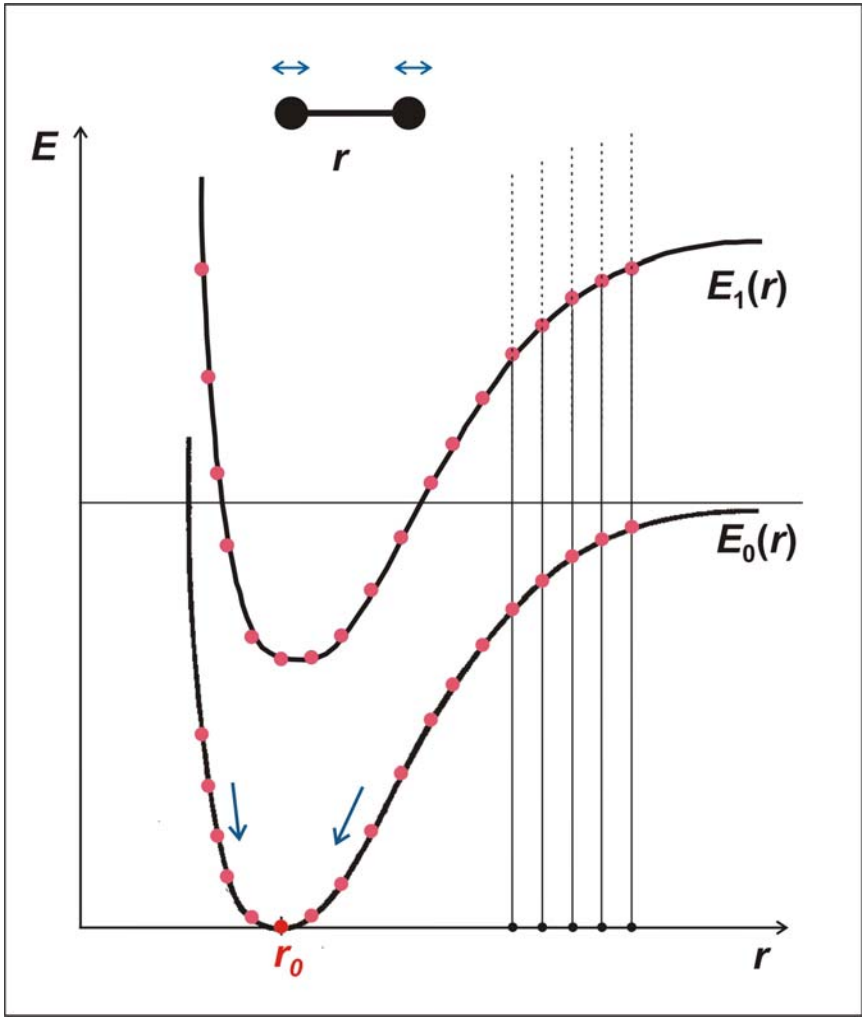
Attributing some symmetry to an object (molecule) assumes implicitly that the object has some ‘stable’ configuration $\Leftrightarrow$ minimum of the potential function of the hierarchically higher (electronic) system

Instantaneous configurations of the lower system need not conserve the symmetry of the higher, but averaged over periods of their motion they do

Hierarchic principles in molecules

Concept of molecular structure and its symmetry is a rigid constraint in the context of chemical changes

Chemical reactions violate the hierarchies of molecular motions



Hierarchic principles in DS

Different timescales $\Leftrightarrow$ hierarchic structure

What can change dramatically the timescales **?**

Resonance in the hierarchically higher system

~ coupled oscillators (*symmetry considerations*)

~ exchange of energy between its parts

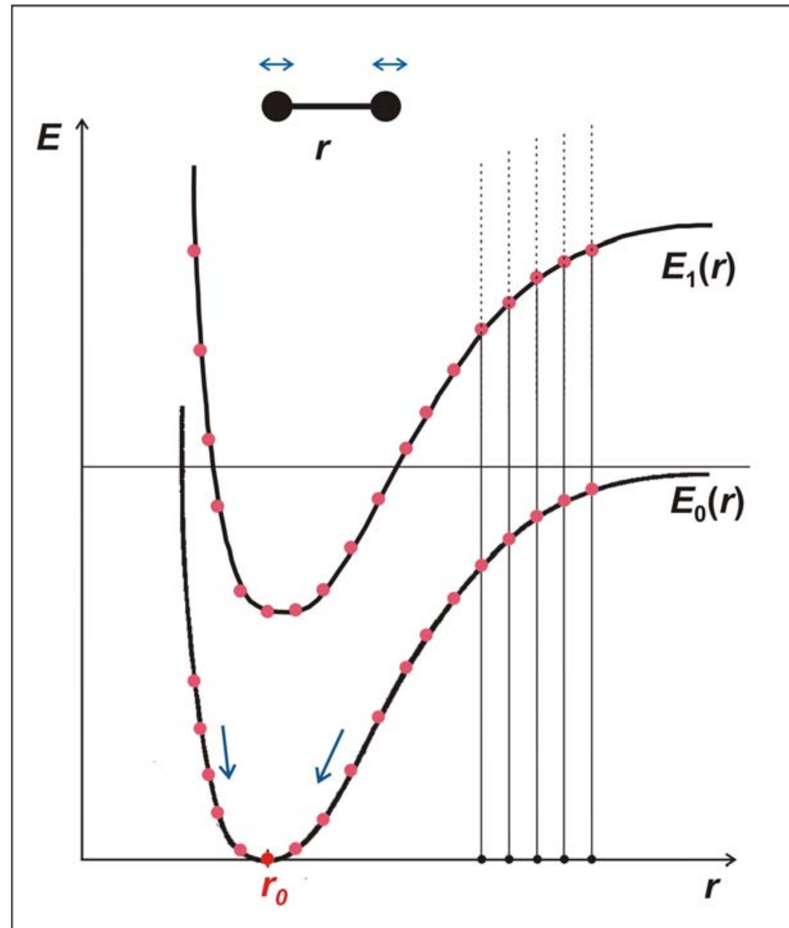
Conservation laws on different levels of hierarchy and between different hierarchic levels

Hierarchic principles in molecules

Concept of equilibrium structure of a molecule – molecular potential surface and dynamics of nuclei on it

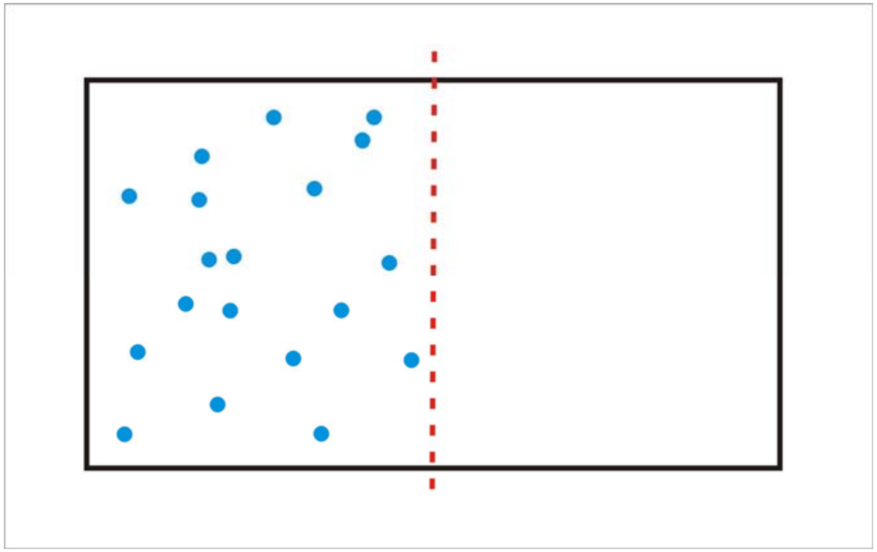
$$m_e / m_H \approx 1/1836$$

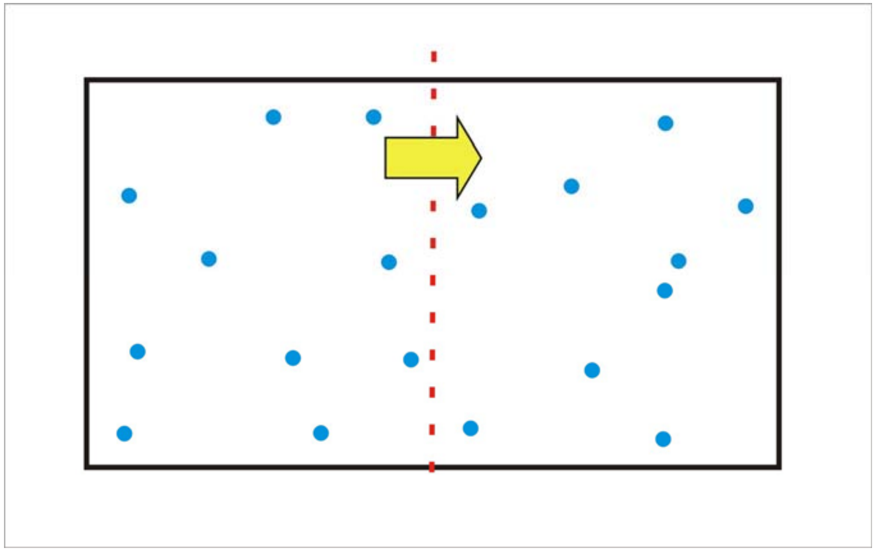
Lower limit for time in averaging the motion of electrons ~ **uncertainty of energy**



Irreversible process with arrow of time

Classical manifestation of the second law of thermodynamics





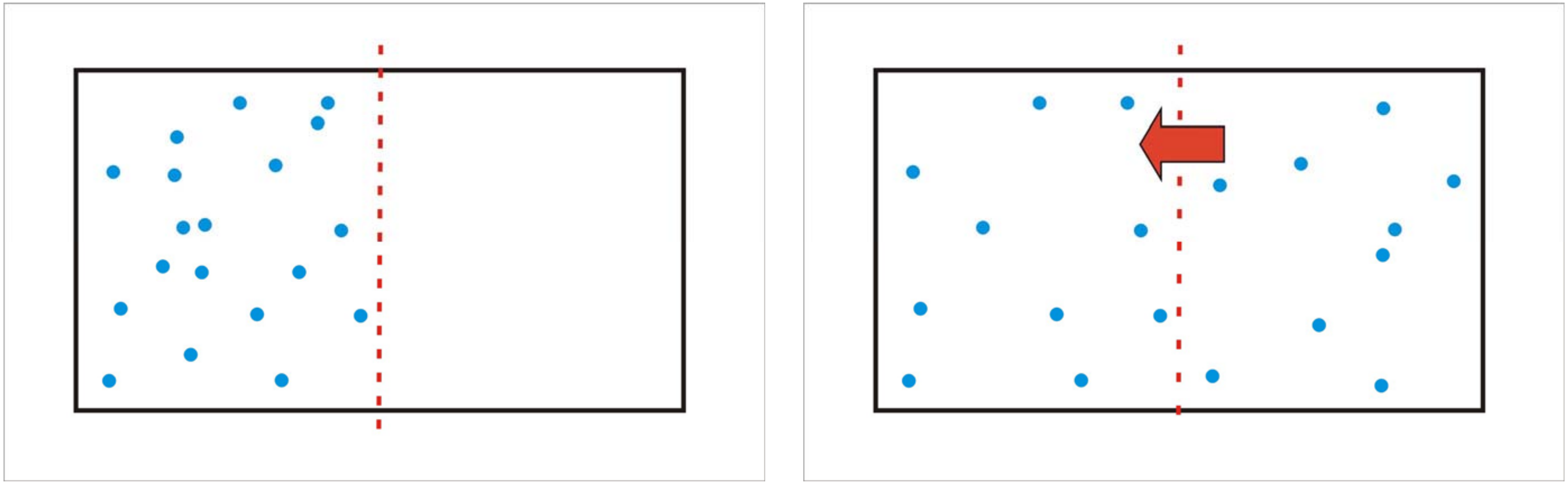
‘Spontaneous’, requires some finite time

Measure of the difference – entropy S

$$dS > 0$$

Irreversible process with arrow of time

Classical manifestation of the second law of thermodynamics



‘spontaneous’, $dS > 0$, requires some (finite) time

‘exceptional’, $dS < 0$,   requires exceedingly more (∞) time

Statistical approach to entropy

Relation of the microscopic states of a system to the properties of the system

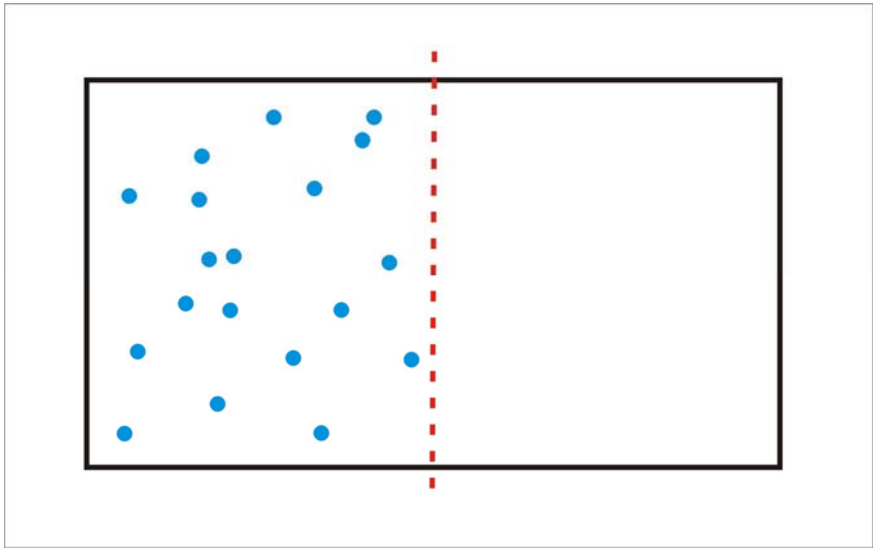
Entropy is a measure of the number of microstates W of the system compatible with a certain property

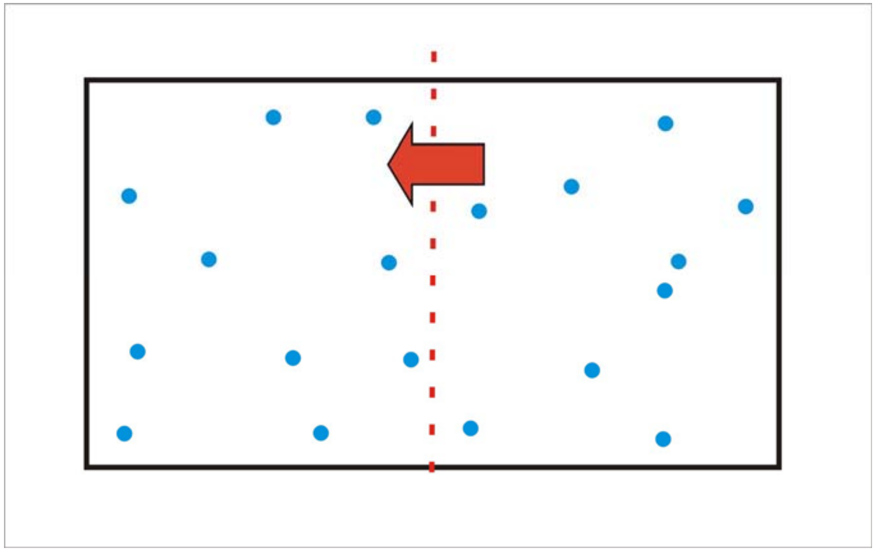
$$S = k_B \ln W$$

Example – gas in a container, microstates are the possible positions and momenta of its particles

Evolution of the system towards equilibrium - a state with the highest probability $\Rightarrow$ reaching a maximum of entropy

Examples of probabilities



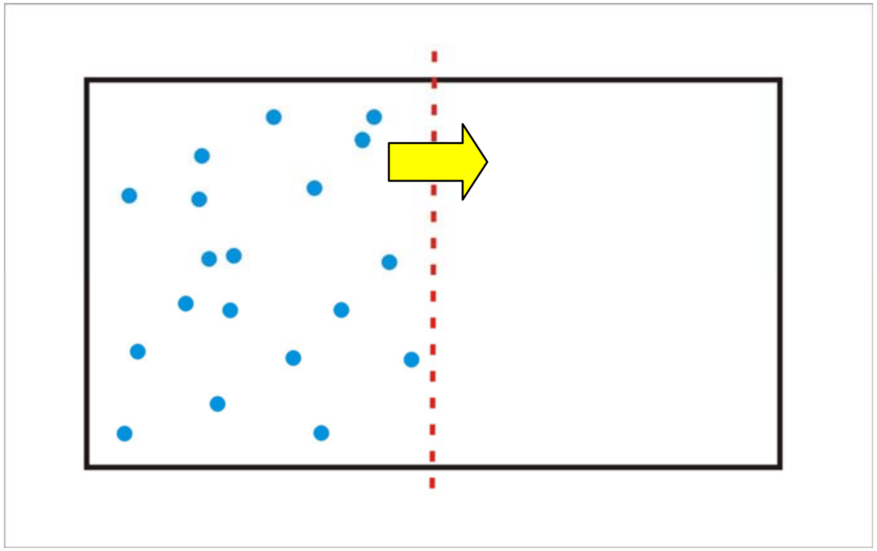


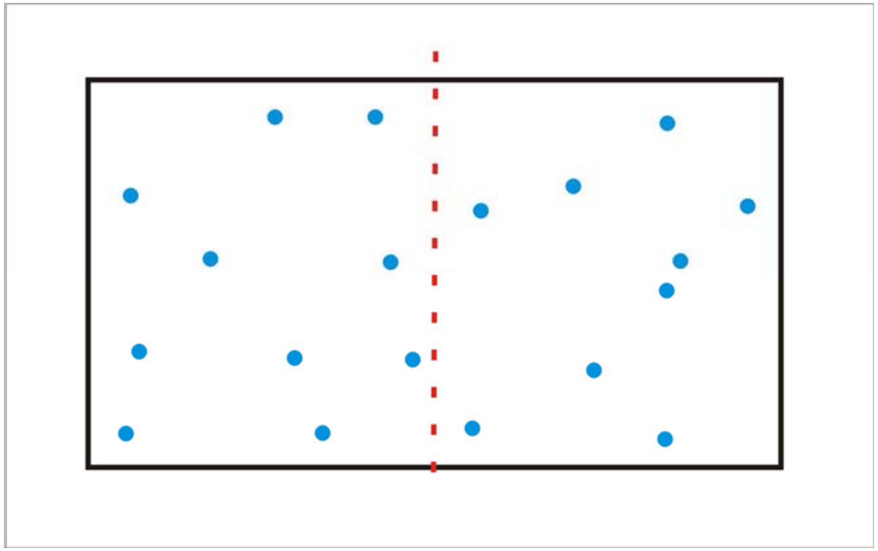
Case of 100 coins being tossed – heads / tails

- Macrostate of all being the same – 1 microstate out of 2^{100}
- Most probable macrostate – 50 heads 50 tails – still ~ 10^{29} microstates

Implicit hierarchic arrangement

Slightly different approach !



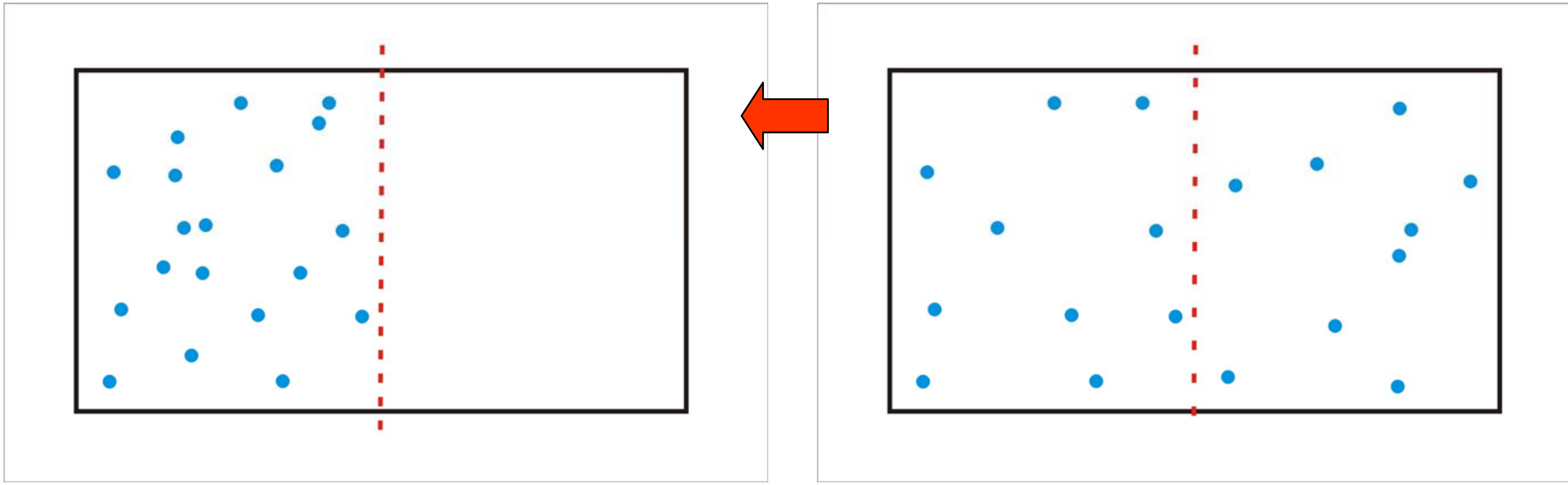


The free volume (surroundings) has a different property from the space among the particles

To be able to state it in this manner – requires introducing the notion of a **hierarchic** view

⇨ Process requiring finite amount of time

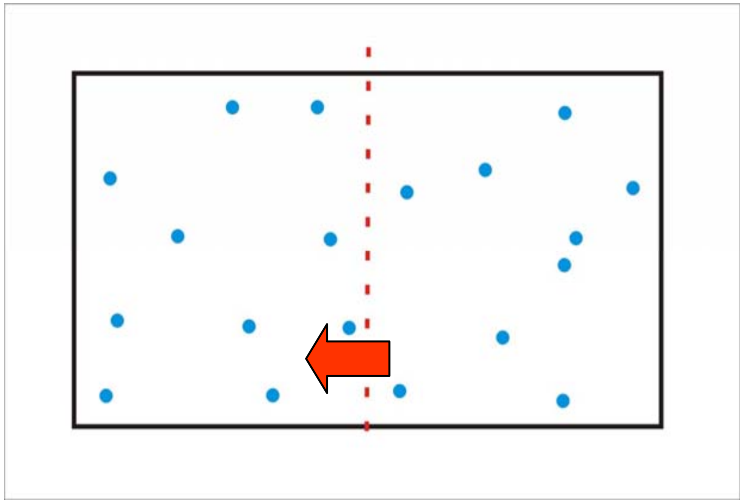
Implicit hierarchic arrangement



Restoring the original arrangement – is in principle possible

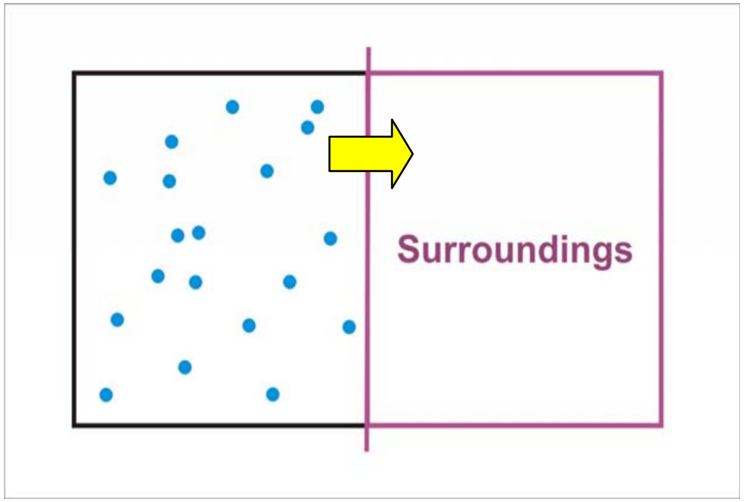
BUT it requires a different hierarchic setup

Different hierarchic arrangements



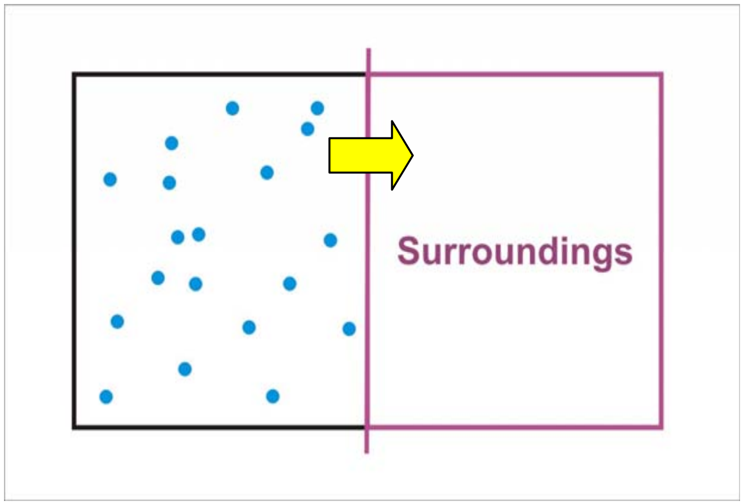
Driven process – requires existence of some independent system (with proper structure) that can accomplish

From the hierarchic point of view a **hierarchically higher** system



Spontaneous process requires existence of some surroundings that can be regarded as a **hierarchically lower** system

Different hierarchic arrangements

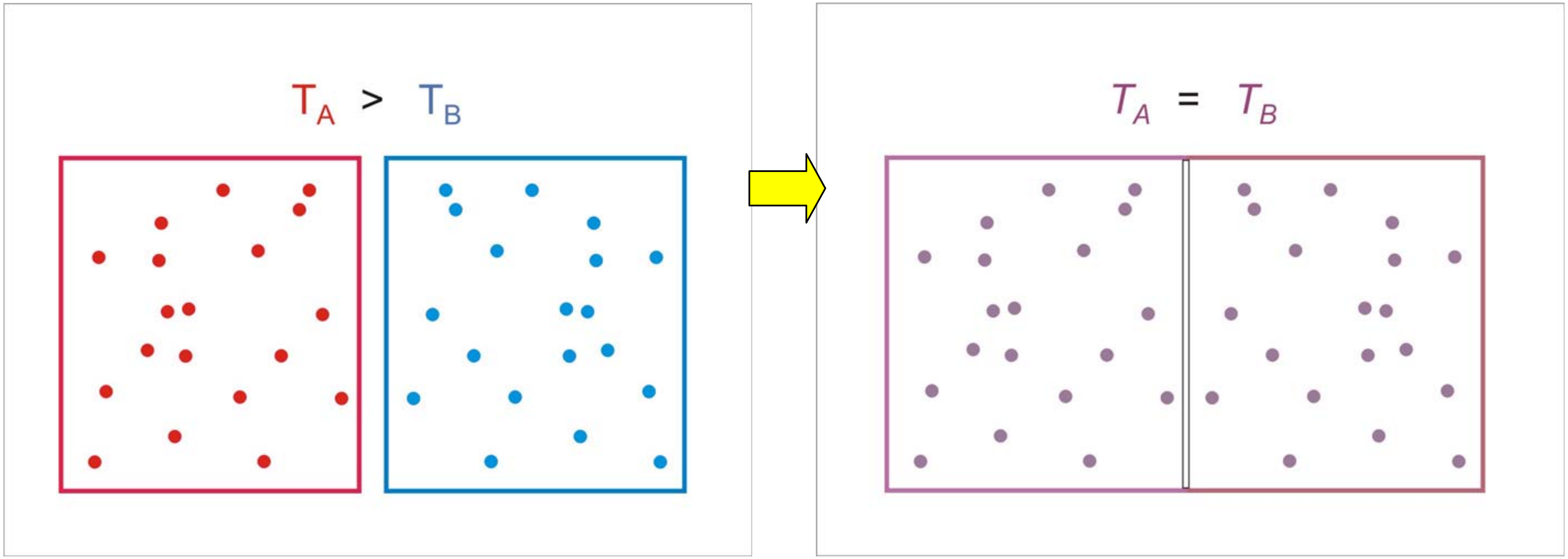


Existence of a hierarchically lower system

☹ ? Free space ~ hierarchically lower system

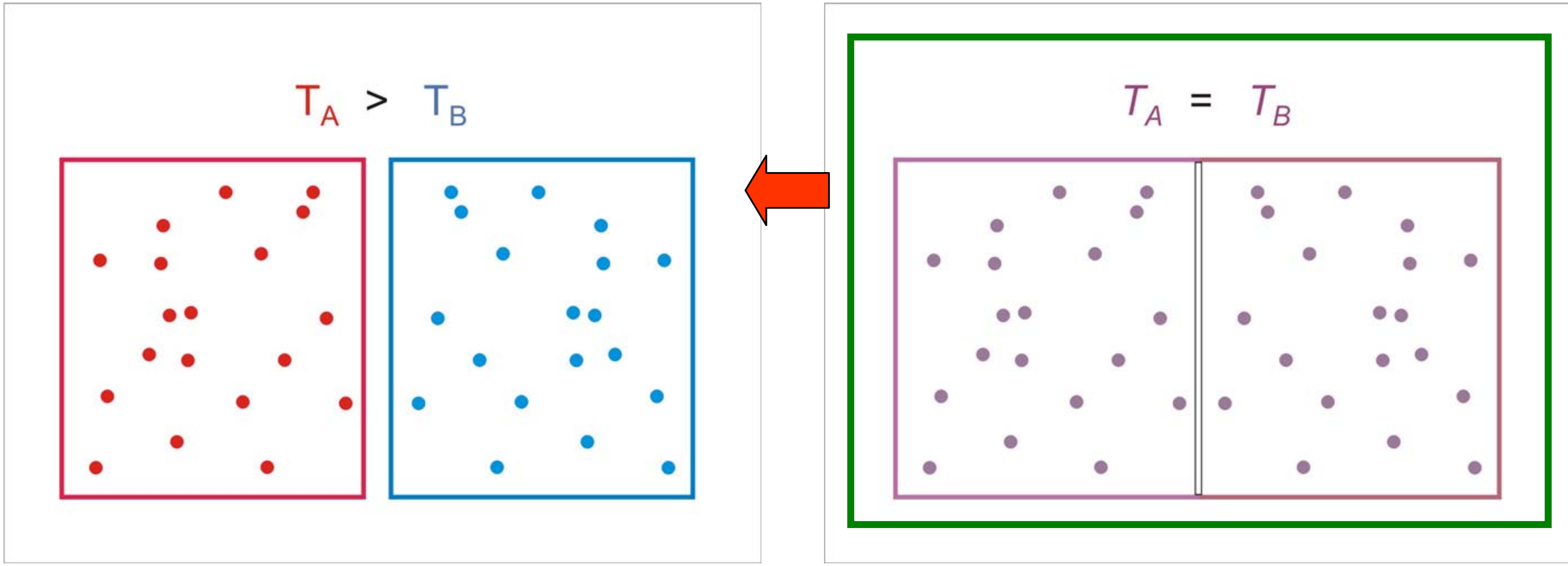
☺ Not difficult to conceive a hierarchically lower system in case of assuming e.g. heat exchange (transfer) between a hot and cold subsystem

Different hierarchic arrangements



Spontaneous equilibration of temperature – *T* is a measure of hierarchic order

Different hierarchic arrangements



Driven – we need a **third** system enclosing the two subsystems

A heat pump – requiring some energy input for decreasing the entropy inside the gas

Examples of probabilities

Case of 100 coins being tossed – heads / tails

- Macrostate of all being the same – 1 microstate out of 2^{100}
- Most probable macrostate – 50 heads 50 tails – still ~ 10^{29} microstates

Biological model systems (proteins) have typically chains of ~ 100 building blocks (aminoacids) and the rareness of configurations used in living systems is enormous

Examples of probabilities

Proteins chains of typical length of 100 aminoacids made of ~ 20 types of aminoacids

~ throwing 100 dice, each with 20 faces (when order matters and each object can appear more than once)

The total number of possible combinations

$$\boxed{20^{100} \sim 1.26 \times 10^{130}}$$

The Nature is using only a very exceptional fraction of all conceivable combinations of aminoacids in proteins

Living systems

- All functions of living systems (metabolism, reproduction) - amazing process, which creates (in the sense of statistical thermodynamics) a state with an extremely low number of microscopic configurations ~ low entropy

- Contradictory to the ‘statistical force’ of the 2nd law of thermodynamics ~ evolution of the system towards the most probable configuration

- Could we solve the seeming paradox by hierarchization of such complex systems and assuming processes in lower systems to be driven by higher systems and proceed in **parallel** and **not sequential** times

Final question

Is such principle typical for ‘living’ systems or is it in some sense a general principle of the nature?

Free

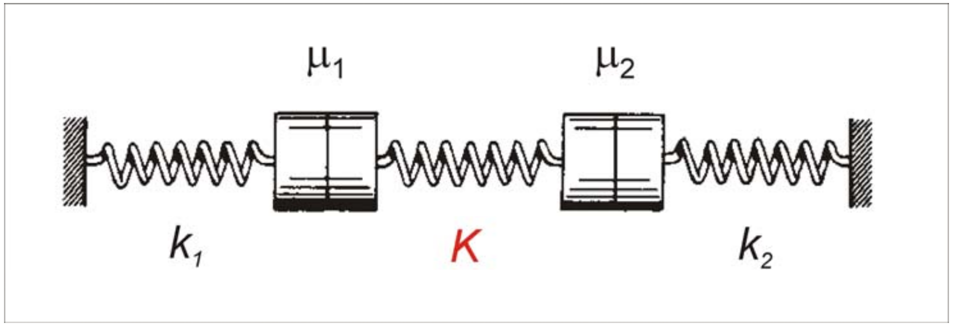
Coupled Harmonic Oscillators

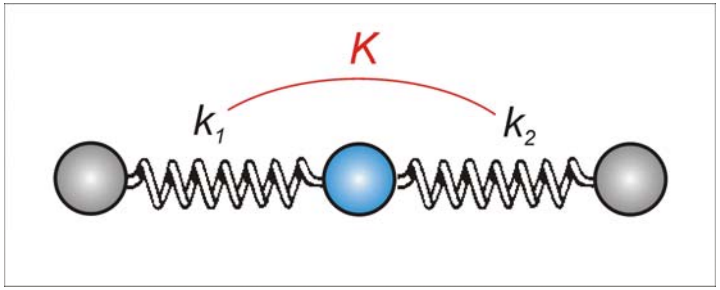
Simplest approximation

- two identical harmonic oscillators
- with weak coupling

$$\mu_1 = \mu_2 \quad k_1 = k_2 = k$$

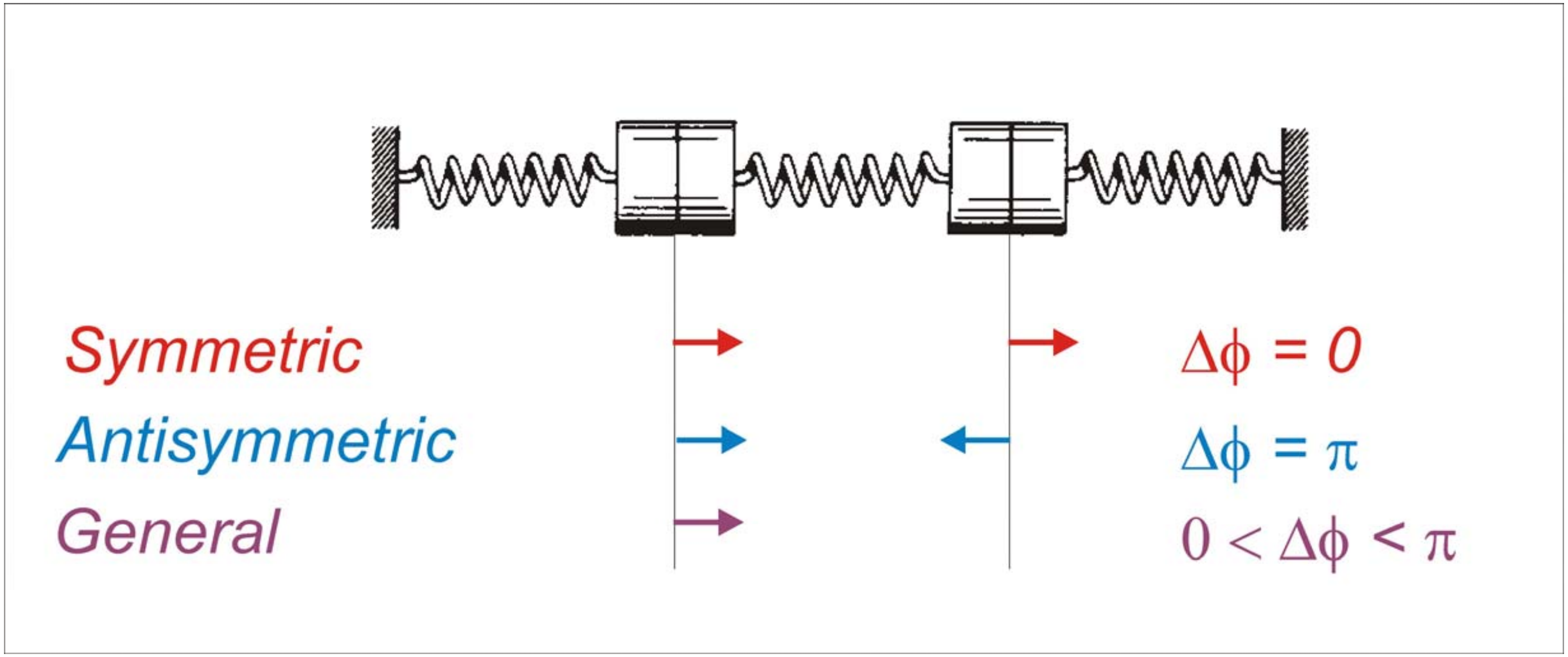
$$K << k$$





Coupled Harmonic Oscillators

- Modes of coupled oscillators – symmetric / antisymmetric / general
- $\Leftrightarrow$ Initial conditions (amplitudes, velocities)



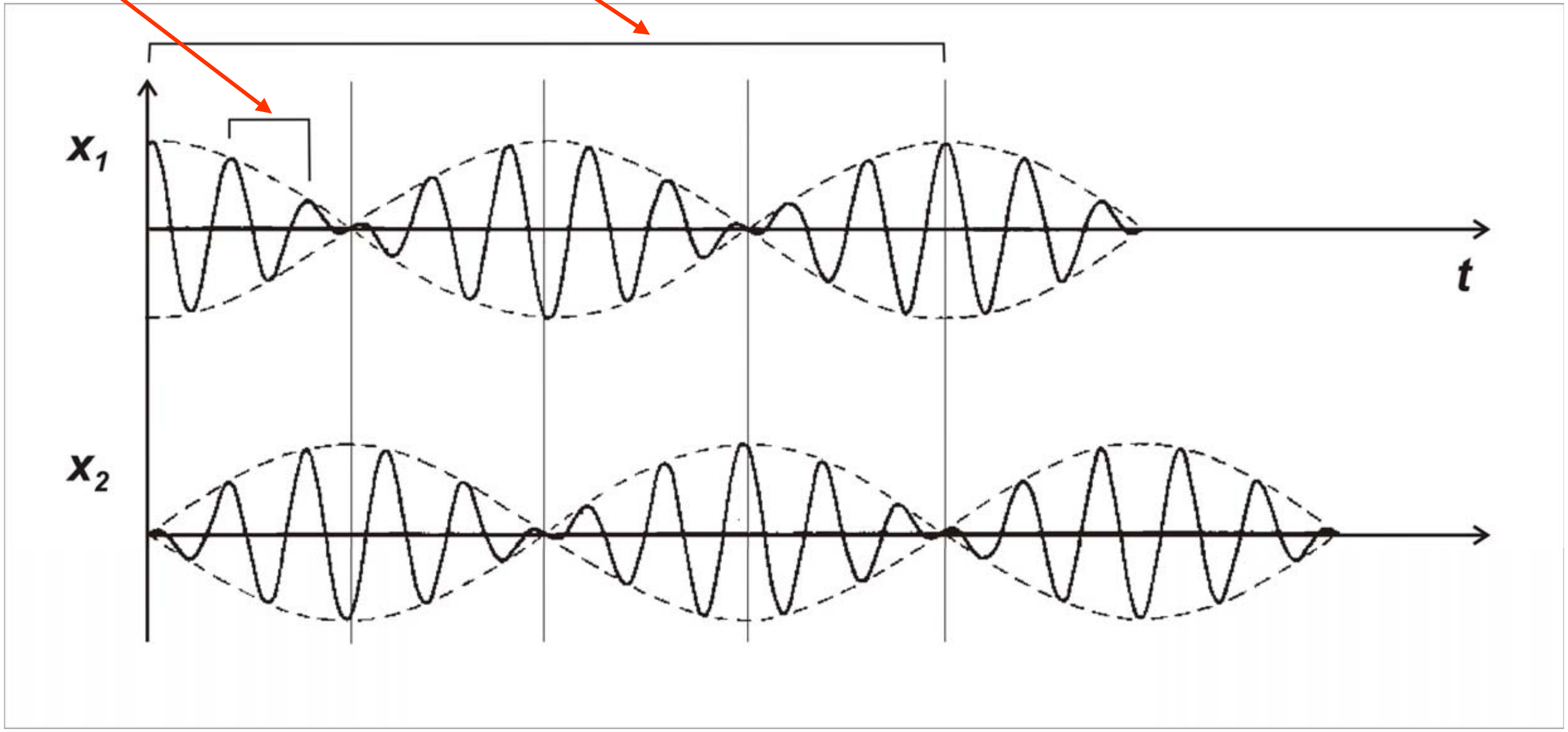
$$\omega_{sym} = (k/\mu)^{1/2}$$

$$\omega_{anti} = [(k+2K)/\mu]^{1/2}$$

Amplitudes of coupled oscillators

$$x_1 = A_0 \cos(\Omega_- t)\cos(\Omega_+ t) \qquad x_2 = A_0 \sin(\Omega_- t)\sin(\Omega_+ t)$$

$$\Omega_+ = \tfrac{1}{2}\left(\omega_{sym} + \omega_{anti}\right) \quad \Omega_- = \tfrac{1}{2}\left(\omega_{anti} - \omega_{sym}\right) \quad \omega_{sym} = \left(k/\mu\right)^{1/2} \qquad \omega_{anti} = \left[\left(k + 2K\right)/\mu\right]^{1/2}$$



Coupled Harmonic Oscillators

Symmetry of internal motions in a realistic dynamical system - regarded as both spatial and temporal (S/T)

$\Rightarrow$ S/T asymmetry - periodic exchange of roles of the coupled oscillators - exciting $\leftrightarrow$ excited, this asymmetry is related to the weak interactions (multipole)

$\Rightarrow$ dramatic change of period of energy exchange between the coupled oscillators