C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 7
Quantum Mechanics I

PS/2020 Distant Form of Teaching: Rev1

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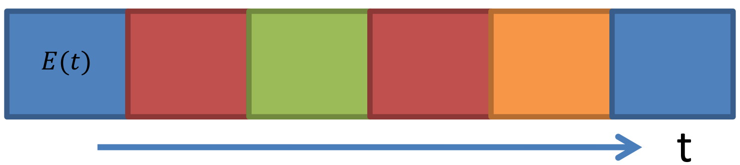
Context

Phenomenological thermodynamics

equilibrium (binding affinities)
kinetics

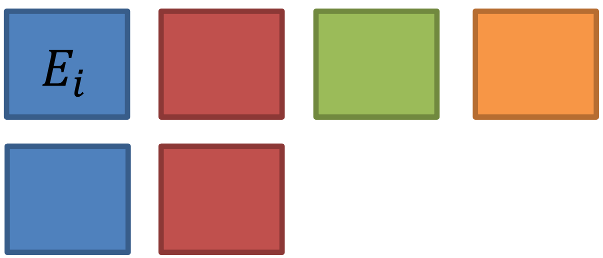
Thermodynamic properties:
H, S, G, …

Time average:



Molecular Dynamics

Ensemble average:



Statistical thermodynamics
Monte Carlo simulations

Mechanical properties:
E_i

Molecular modelling

How to describe interactions?

Quantum mechanics

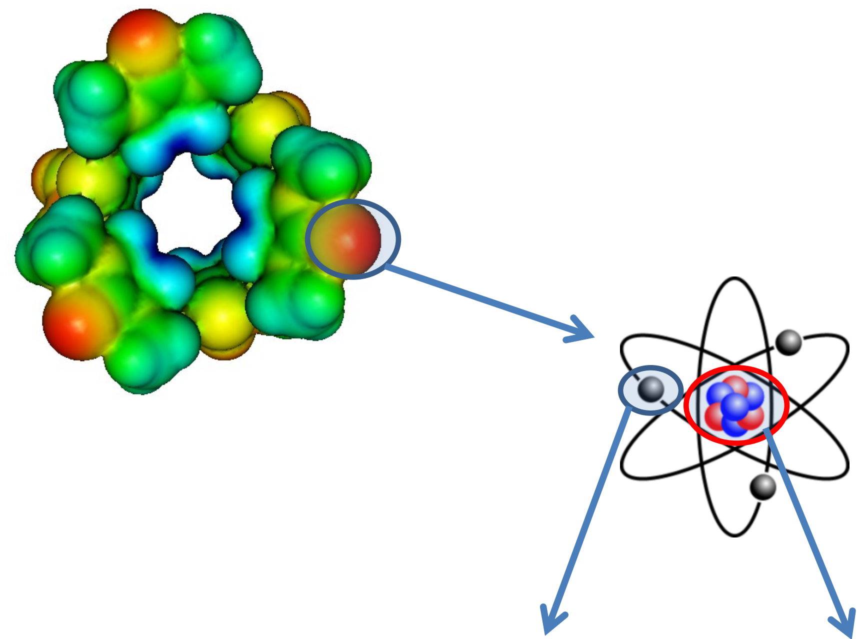
Chemical system

chemistry

physics

macrosystem
↓
molecule
↓
atom
↓
electrons | nuclei
↓
protons, neutrons

wave character



In chemistry, a nucleus is considered to be a mass object with a positive charge equal to a proton number. Thus, nuclear structure is not taken into account.

Complication in description

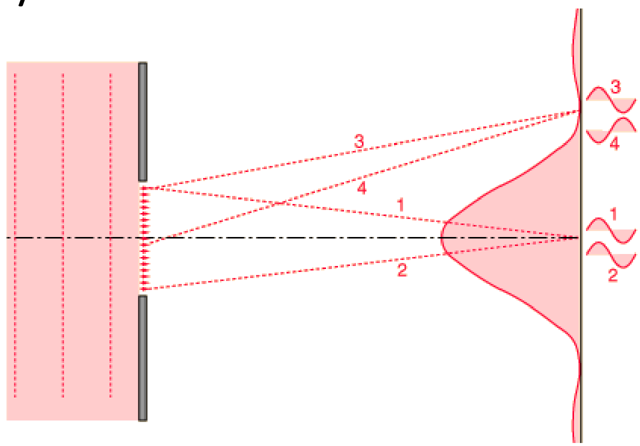
Elementary particles and objects composed of them (nuclei) do not obey classical physics laws. **Particles exhibits a dual character.** A particle with a momentum *p* also behaves like a wave with the wavelength λ.

$$\lambda = \frac{h}{p} = \frac{h}{m_0 v}\sqrt{1-\frac{v^2}{c^2}}$$

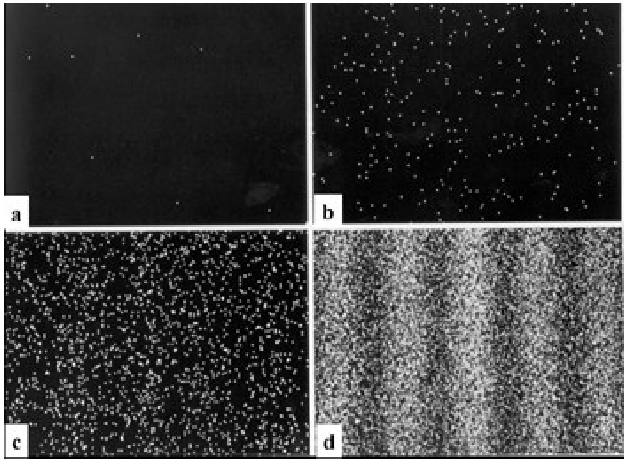
de Broglie hypothesis

1923

Confirmed by numerous experiments, such as the passage of electrons through single/double slits.



diffraction on one slit



passage of electrons through two slits.

Foundation of Quantum Mechanics

Wave character of particles require special approaches to describe their behaviors.

Schrödinger equation (SR) is a foundation of quantum mechanics (QM).

$$\hat{H}\phi(\mathbf{r},t) = i\hbar \frac{\partial \phi(\mathbf{r},t)}{\partial t}$$

time-dependent Schrödinger equation

Hamiltonian (operator)
(it defines the **system**, i.e., the number of particles and how they interact with each other, or how they interact with their surroundings)

wave function
(it defines a **state** of the system)

Legend:

r - position vector of particles, t - time
i - imaginary unit, h - Planck constant,
ħ - reduced Planck constant

$$\hbar = \frac{h}{2\pi}$$

Hamiltonian

Hamiltonian (operator of the total energy):

It describes particle motions and interactions.

$$\hat{H} = \sum_i \hat{T}_i + \widehat{V}$$

kinetic energy operator for particle *i*

potential energy operator

Kinetic energy operator:
(particle movement)

$$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Laplacian in Cartesian coordinates

Potential energy operator:
(interaction between particles)

$$\widehat{V} = V(\mathbf{r}, t)$$

potential energy itself

Wave function

- it describe a **state** of the system
- it can be a complex function
- physical interpretation is difficult
- square value of the wave function is related to **probability density**

probability density

$$\psi_k^*(\mathbf{r})\psi_k(\mathbf{r})d\tau$$

probability

the probability to find the system in the configuration **r** in a volume element $d\tau$

$$\int_{\mathbf{\Omega}} \psi_k^*(\mathbf{r})\psi_k(\mathbf{r})d\tau = 1$$

The probability that we will find particles in the entire space is 100 %.

Interpretation of QM

4.1 Classification adopted by Einstein
4.2 The Copenhagen interpretation (Copenhagen Convention)
4.3 Many worlds
4.4 Consistent histories
4.5 Ensemble interpretation, or statistical interpretation
4.6 de Broglie–Bohm theory
4.7 Relational quantum mechanics
4.8 Transactional interpretation
4.9 Stochastic mechanics
4.10 Objective collapse theories
4.11 von Neumann / Wigner interpretation: consciousness causes the collapse
4.12 Many minds
4.13 Quantum logic
4.14 Quantum information theories
4.15 Modal interpretations of quantum theory
4.16 Time-symmetric theories
4.17 Branching space-time theories
4.18 Other interpretations

www.wikipedia.com

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Copenhagen interpretation* is an interpretation of quantum mechanics that is most prevalent among physicists. According to this interpretation, **probabilistic nature of** quantum mechanical predictions **cannot be explained** in some other way, such as unknown (hidden) **deterministic theory**.

Quantum mechanics provides probabilistic results because the universe itself is probabilistic rather than deterministic.

*mainly due to theoretical physics Niels Bohr

www.wikipedia.com

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Fundamental problems:

- Is it apparatus of quantum mechanics (particles) also applicable to macrosystems?
  - Paradoxes:
    - Schrödinger's cat
    - Wigner's friend

Castelvecchi, D. Reimagining of Schrödinger's Cat Breaks Quantum Mechanics - and Stumps Physicists. *Nature* **2018**, *561* (7724), 446–447.

Uncertainty principle

Heisenberg's uncertainty principle (also uncertainty relation) is a mathematical property of two complementary quantities. Heisenberg's principle says that the more accurately we determine one of the complementary properties, the less accurately we can determine the other - no matter how accurate instruments are.

The most common relations:

uncertainty in determining the momentum (velocity) of a particle

uncertainty in particle positioning

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

position/momentum

uncertainty in determining time at which we measured the energy

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

energy/time

uncertainty in determining the energy of the system

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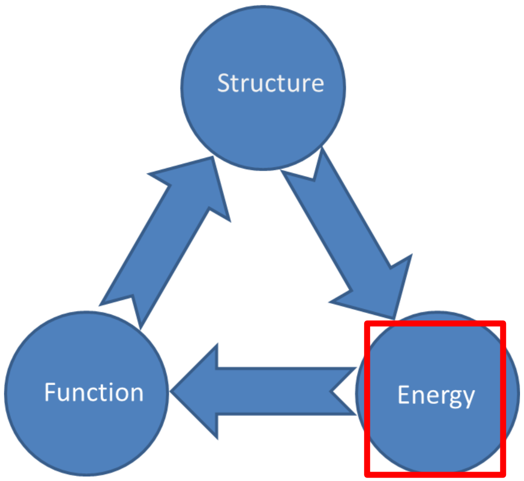
energy/time

uncertainty in determining the energy of the system

Heisenberg is stopped by the traffic police. The policeman asks him, "Do you know how fast you drove?" Heisenberg replies, "No, but I know where I am."

System energy



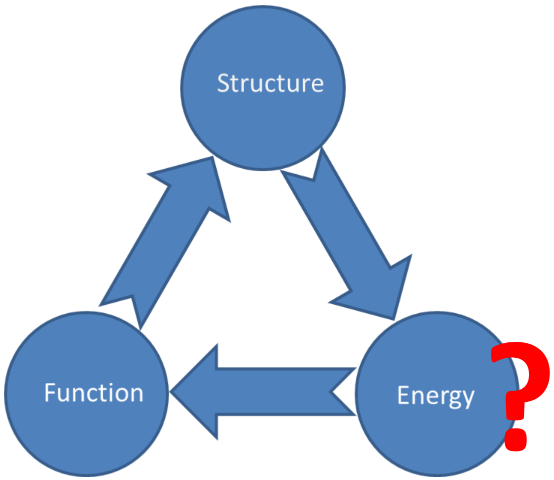
Thermodynamic properties:
H, S, G, …

Ensemble average:

Mechanical properties:
E_i

Statistical thermodynamics
Monte Carlo simulations

System energy



time-dependent Schrödinger equation

$$\hat{H}\phi(\mathbf{r},t) = i\hbar \frac{\partial \phi(\mathbf{r},t)}{\partial t}$$

the system state described by the wave function is known at the **exact moment in time**

Heisenberg's uncertainty principle

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

energy of the system cannot be determined

Schrödinger equation

$$\hat{H}\phi(\mathbf{r},t) = i\hbar \frac{\partial \phi(\mathbf{r},t)}{\partial t}$$

time-dependent Schrödinger equation

time separation

$$\phi(\mathbf{r},t) = \psi(\mathbf{r}) f(t)$$

time (t) and configuration (r) are set independent of each other

$$\hat{H}\psi_k(\mathbf{r}) = E_k \psi_k(\mathbf{r})$$

$$i\hbar \frac{df(t)}{dt} = Ef(t)$$

time independent Schrödinger equation

Time independence

$$\phi(\mathbf{r},t)=\psi(\mathbf{r})f(t)$$

Time (t) and particle configuration (**r**) are considered as independent variables. Consequently, the state description is also independent to time and configuration.

The following applies to independent events:

$$P(A\cap B)=P(A)P(B)$$

the join probability of A and B events

probability of event A

probability of event B

A similar approximation is used for:

- Born-Oppenheimer approximation
- separation of translational, rotational, and vibrational movements
- one-electron approximations (Hartree-Fock method)

Schrödinger equation

time independent Schrödinger equation

$$\hat{H}\psi_k(\mathbf{r}) = E_k\psi_k(\mathbf{r})$$

Hamiltonian (operator)
(it defines a **system**, i.e., number of particles and how they interact with each other)

wave function + **energy of state** k
(it defines a **state** k)

Solutions to the SR equation are **pairs**: ψ_k and E_k.

Each pair represent possible realization of the system (a microstate) and its energy.

System vs State (inaccurate example)

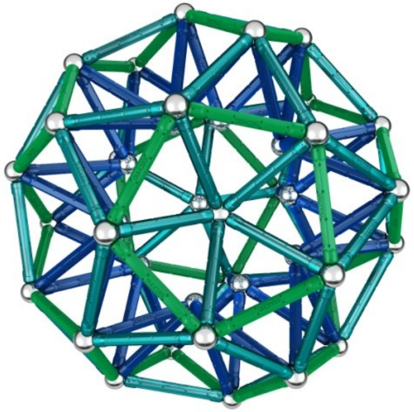
! Very rough comparison not taking into account the probabilistic behavior of quantum systems !

System definition:
The Hamiltonian indicates the number of spheres and connectors (particles) and their mutual interaction.

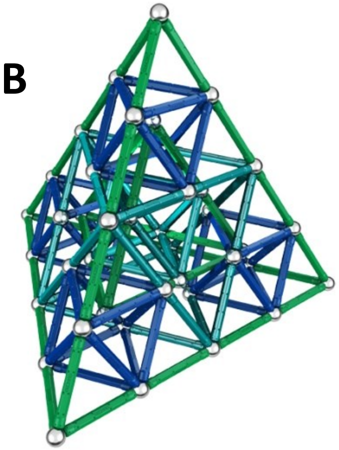
geomag

System status:
Determined by the wave function, which indicates the actual arrangement of balls and connectors in space.

state A



state B

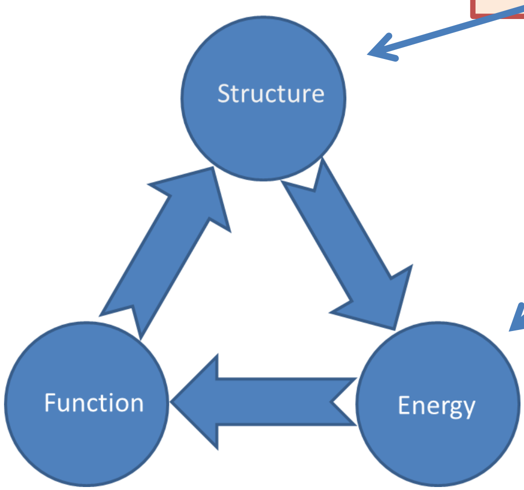


http://www.magnetickysvet.cz

Summary

- Molecules are composed from atoms. Atoms are composed from electrons and nuclei.
- Electrons, nuclei, and atoms (and molecules) are small and exhibit dual character (wave/particle).
- Behavior of particles and their assemblies can be described by time-independent Schrodinger equation.
- Solution of Schrödinger equation provides all possible microstates and their energies.

$$\hat{H}\psi_k(\mathbf{r}) = E_k\psi_k(\mathbf{r})$$



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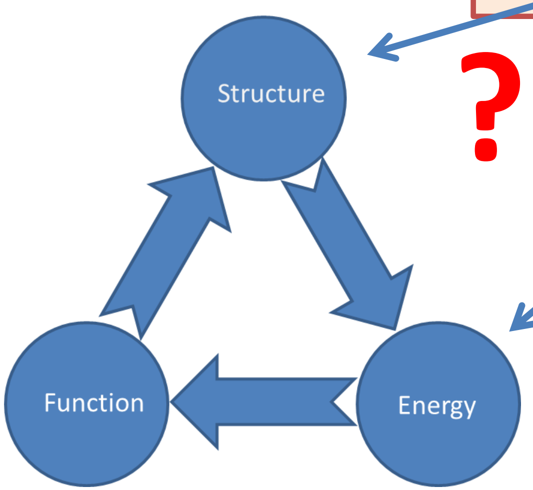

- **Probabilistic description of the structure in the given state**
- **Unsolvable for microstates of macrosystems (> 10^{23} atoms)**
- **Practically impossible to solve even for small chemical systems (hydrogen molecule)**