

# C7790 Introduction to Molecular Modelling

## TSM Modelling Molecular Structures

### Lesson 8 Quantum Mechanics II

**PS/2020 Distant Form of Teaching: Rev1**

Petr Kulhánek

[kulhanek@chemi.muni.cz](mailto:kulhanek@chemi.muni.cz)

National Centre for Biomolecular Research, Faculty of Science  
Masaryk University, Kamenice 5, CZ-62500 Brno

# 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**) (!!!scalar value!!!)

Solutions to the SR equation are **pairs**:  $\psi_k$  and  $E_k$ .

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

# Hamiltonian of Chemical System

**Hamiltonian** of a chemical system, consisting of  $N$  nuclei of mass  $M$  and charge  $Z$  and  $n$  electrons of mass  $m$ , is given by:

kinetic energy operator

potential energy

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_i^2 - \frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 + \frac{1}{4\pi\epsilon_0} \left( \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i e}{r_{ij}} + \sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{r_{ij}} \right)$$

nuclei

electrons

core-core

electron-core

electron-electron

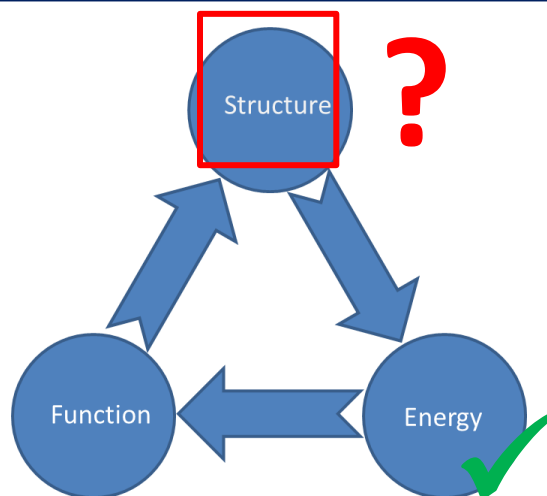
**motion**

**interactions**

**Potential energy** it is given by **electrostatic interaction** between charged particles:

Coulomb's law 
$$V = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

# Structure vs System State



Hypothetical exact solution of time-independent Schrödinger equation (ground state):

$\text{H}_2\text{O}$

**It describes too many properties such as:**

- electron density distribution
- distribution of nuclei due to translational, rotational and vibrational movements of the molecule
- and all their combinations

**This is too complicated for subsequent analyzes.**

# Born-Oppenheimer Approximation

# Born-Oppenheimer Approximation

$$\hat{H}\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

position of  
electrons

position of  
nuclei

WF provides a complicated description of the system state.

Real positions of nuclei and electrons are known only within the probabilistic description.

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_i^2}_{\text{Nuclei}} - \frac{1}{2m} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i}{r_{ij}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

The Born-Oppenheimer approximation **separates** motion of nuclei from electrons.

$$\psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$$

motion of nuclei

motion of electrons in the static field of  
nuclei

# Born-Oppenheimer Approximation

$$\hat{H} = \underbrace{-\frac{1}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_i^2}_{\text{electronic kinetic energy}} - \frac{1}{2m} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i}{r_{ij}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

$$\hat{H} \psi(\mathbf{r}, \mathbf{R}) = E \psi(\mathbf{r}, \mathbf{R})$$

$$\psi(\mathbf{r}, \mathbf{R}) = \Psi(\mathbf{r}, \mathbf{R}) \chi(\mathbf{R})$$

Born-Oppenheimer approximation

$$\hat{H}_e \Psi(\mathbf{r}, \mathbf{R}) = E_e(\mathbf{R}) \Psi(\mathbf{r}, \mathbf{R})$$

electronic properties of molecule

$$\hat{H}_R \chi(\mathbf{R}) = E_{VRT} \chi(\mathbf{R})$$

vibrational, rotational, translational motions of molecule

# Electronic Properties of System

$$\hat{H}_e = -\frac{1}{2m} \sum_{i=1}^n \nabla_i^2 + \sum_{i=1}^N \sum_{j>i}^N \frac{Z_i Z_j}{r_{ij}} - \sum_{i=1}^N \sum_{j=1}^n \frac{Z_i}{r_{ij}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{ij}}$$

$$\hat{H}_e \Psi(\mathbf{r}, \mathbf{R}) = E_e(\mathbf{R}) \Psi(\mathbf{r}, \mathbf{R})$$

The energy is a function of the position of nuclei (atoms).

$E(\mathbf{R})$

(function)

R - determines the configuration of nuclei (atoms) in space => structure for which we can determine the energy

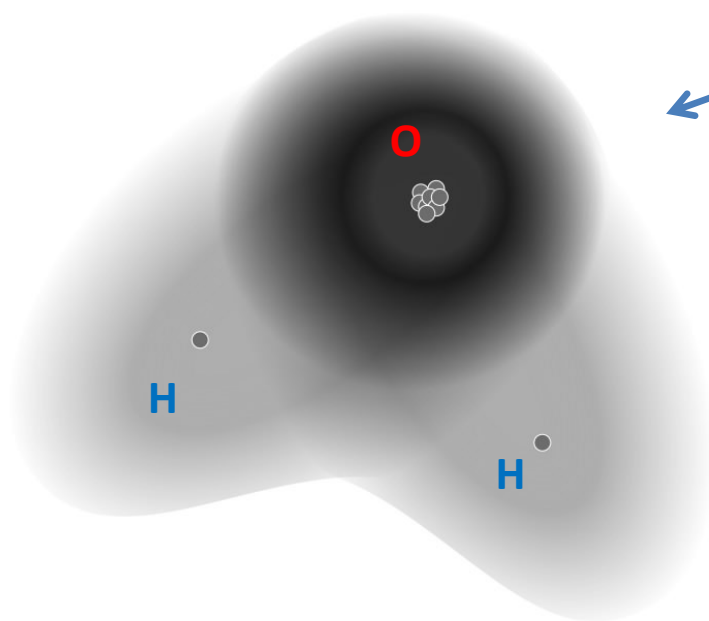
concept of potential energy surfaces



# Structure vs System State

$$\psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$$

Ground state of the water molecule (schematic):



distribution of electrons in the static field of nuclei

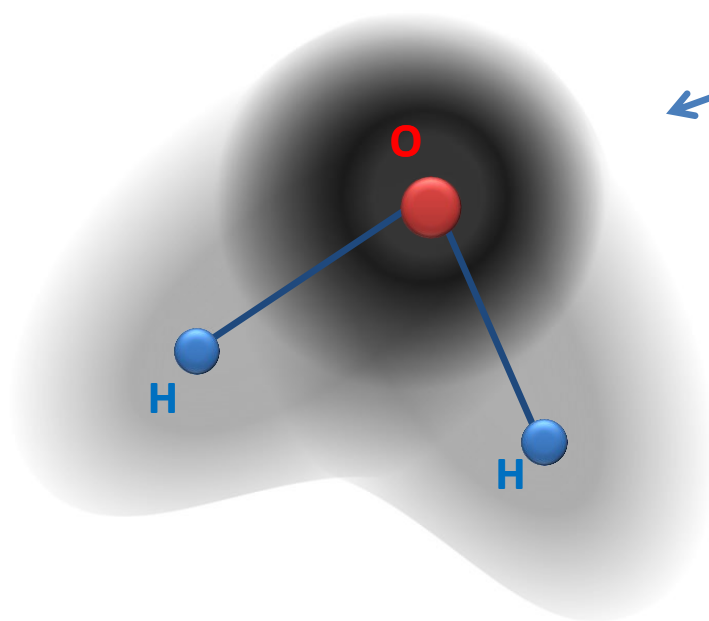
**it describes the overall state of the system partially**

<http://hypot.wordpress.com/2012/11/15/electron-density/>

# Structure vs System State

$$\psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$$

Ground state of the water molecule (schematic):



distribution of electrons in the static field of nuclei

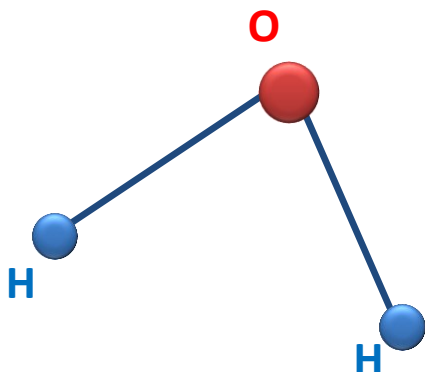
**it describes the overall state of the system partially**

<http://hypot.wordpress.com/2012/11/15/electron-density/>

# Structure vs System State

$$\psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$$

ground state of the water molecule (schematic):



distribution of electrons in the static field of nuclei

**it describes the overall state of the system partially**

schematic representation of the molecular structure - based on the distribution of electron density

<http://hypot.wordpress.com/2012/11/15/electron-density/>

# Nuclear Motions

$$\hat{H}_R = ?$$

the nuclei are affected by the potential

- electrostatic interaction of nuclei with each other
- effective potential of electrons in the field of nuclei

$$\hat{H}_R \chi(\mathbf{R}) = E_{VRT} \chi(\mathbf{R})$$

scalar value (not a function)

## Nuclei motions:

- vibrational
- rotational
- translational

it can be further approximated into individual motions and their contributions using approximations based on a similar principle as used in the BO approximation

# Nuclear Motions

the nuclei are affected by the potential

- a) electrostatic interaction of nuclei with each other
- b) effective potential of electrons in the field of nuclei

$$\hat{H}_R = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{M_i} \nabla_i^2 + E_e(R)$$

$$\hat{H}_R \chi(\mathbf{R}) = E_{VRT} \chi(\mathbf{R})$$

## Core movements:

- vibratory
- rotational
- translational

value (not function)

can be further approximated into individual movements and their contributions using approximations based on a similar principle as used in the BO approximation

# How accurate is BO approximation?

The BO approximation recognizes **the large difference between the electron mass and the masses of atomic nuclei**, and correspondingly the time scales of their motion.

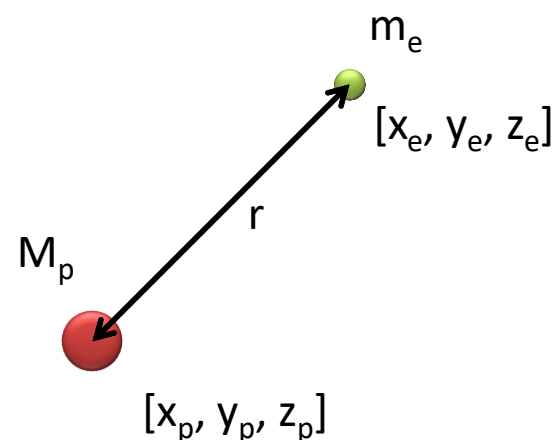
$$M_p = 1836 \text{ au}$$
$$m_e = 1 \text{ au}$$

## Atomic Units

### Constants used as units

Dimension	Symbol	Definition
action	$\hbar$	$\hbar$
electric charge	$e$	$e$
length	$a_0$	$4\pi\epsilon_0\hbar^2/(m_e e^2)$
mass	$m_e$	$m_e$
energy	$E_h$	$\hbar^2/(m_e a_0^2)$

### hydrogen atom



**difference is bigger for heavier elements**

[https://en.wikipedia.org/wiki/Hartree\\_atomic\\_units](https://en.wikipedia.org/wiki/Hartree_atomic_units)

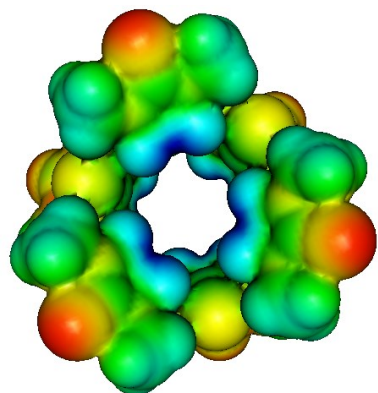
# Summary

- Born-Oppenheimer (BO) approximation is the most important approximation in molecular modelling
- It is rather accurate because of significant difference between electron and nuclei masses
- Electrons moves faster than nuclei (different time scales) and electrons can instantly update their distributions once the nuclei position changes.
- BO approximation is foundations for all calculation methods (model chemistry) used in molecular modelling

$$E(\mathbf{R}) \quad (\text{function})$$

concept of potential energy surfaces

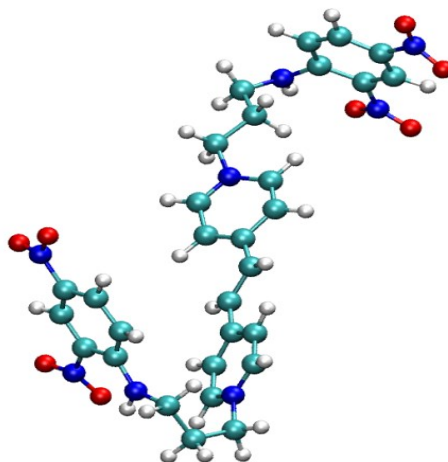
# Method overview (model chemistry)



QM (Quantum mechanics)

$$E(\mathbf{R})$$

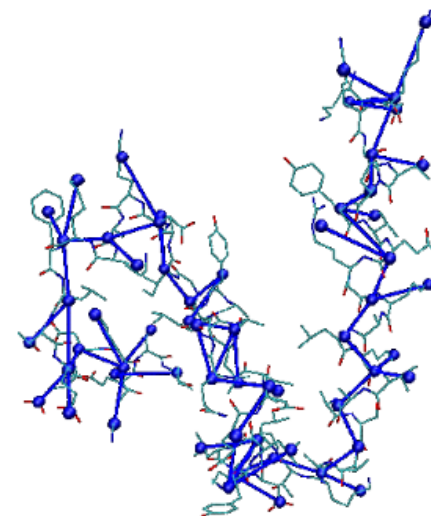
R - position of atom nuclei



MM (Molecular mechanics)

$$E(\mathbf{R})$$

R - position of atoms



CGM (Coarse-grained mechanics)

$$E(\mathbf{R})$$

R - position of beads