C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 8
Quantum Mechanics II

PS/2021 Present Form of Teaching: Rev1

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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**: ψ_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

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{M_i}\nabla_i^2 - \frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla_i^2 + \frac{1}{4\pi\varepsilon_0}\left(\sum_{i=1}^{N}\sum_{j>i}^{N}\frac{Z_iZ_j}{r_{ij}} - \sum_{i=1}^{N}\sum_{j=1}^{n}\frac{Z_ie}{r_{ij}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{e^2}{r_{ij}}\right)$$

nuclei   electrons   core-core   electron-core   electron-electron
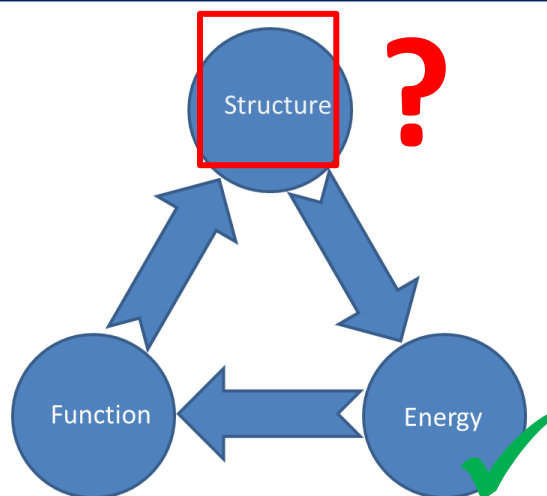
motion   **interactions**

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

Coulomb's law $V = \dfrac{1}{4\pi\varepsilon_0}\dfrac{q_iq_j}{r_{ij}}$

Structure *vs* System State

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

H_2O

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

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

WF provides a complicated description of the system state.
Real positions of nuclei and electrons are known only within the probabilistic description.

position of electrons

position of nuclei

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

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

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

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

Born-Oppenheimer approximation

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

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

electronic properties of molecule

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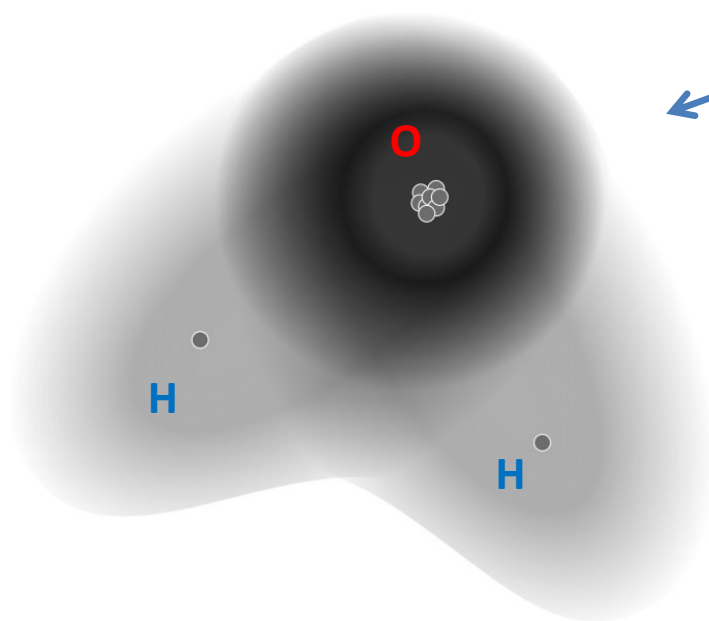
$$E(\mathbf{R})$$ (function)

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):

O
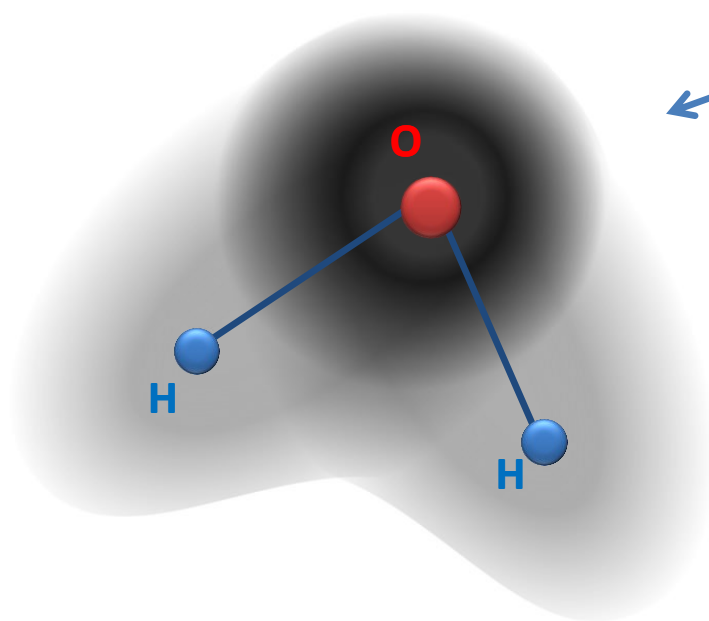
H

H

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

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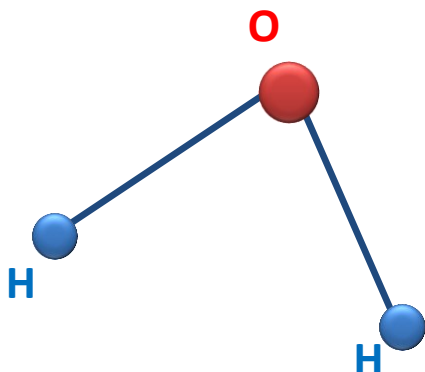distribution of electrons in the static field of nuclei

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O

H

H

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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

a) electrostatic interaction of nuclei with each other
b) 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

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

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

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.
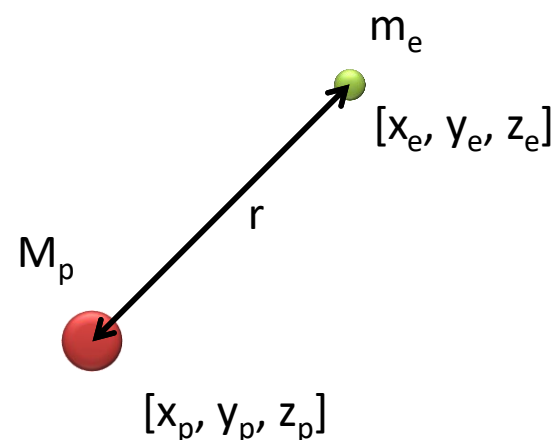
hydrogen atom

M_p = 1836 au
m_e = 1 au

m_e

$[x_e, y_e, z_e]$

r

M_p

$[x_p, y_p, z_p]$

difference is bigger for heavier elements

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	$\hbar^2/(m_e a_0^2)$

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

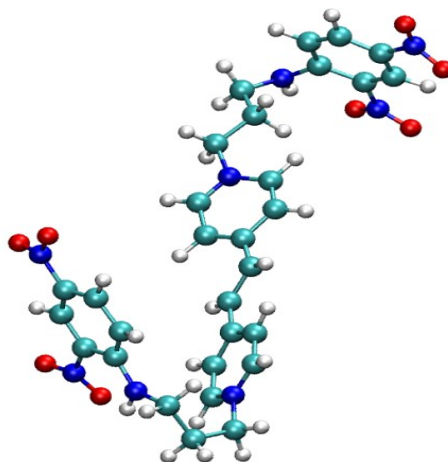$$E(\mathbf{R})$$ (function)

concept of potential energy surfaces

Method overview (model chemistry)
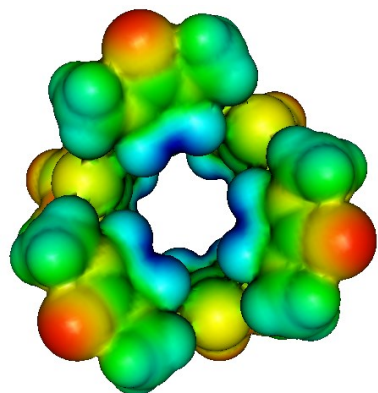
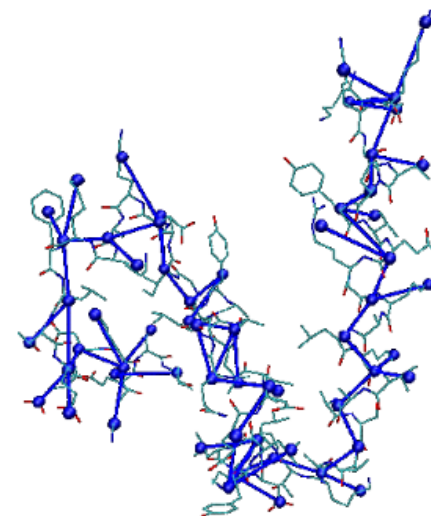| QM (Quantum mechanics)	MM (Molecular mechanics)	CGM (Coarse-grained mechanics)
$E(\mathbf{R})$	$E(\mathbf{R})$	$E(\mathbf{R})$
R - position of atom nuclei	R - position of atoms	R - position of beads