

C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

C9087 Computational Chemistry for Structural Biology

Lesson 8

Quantum Mechanics II

JS/2022 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

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

nuclei

electrons

core-core

electron-core

electron-electron

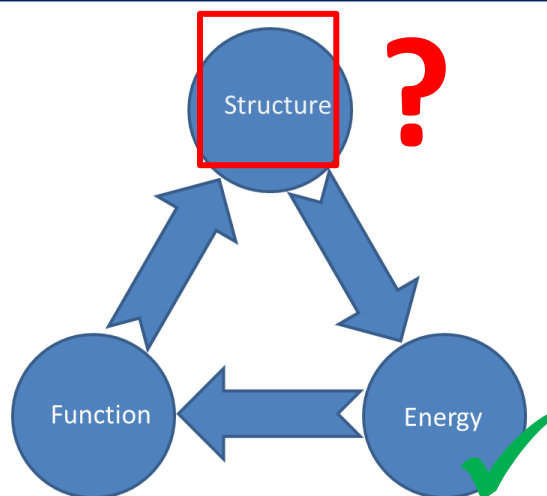
motion

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):

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

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

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)

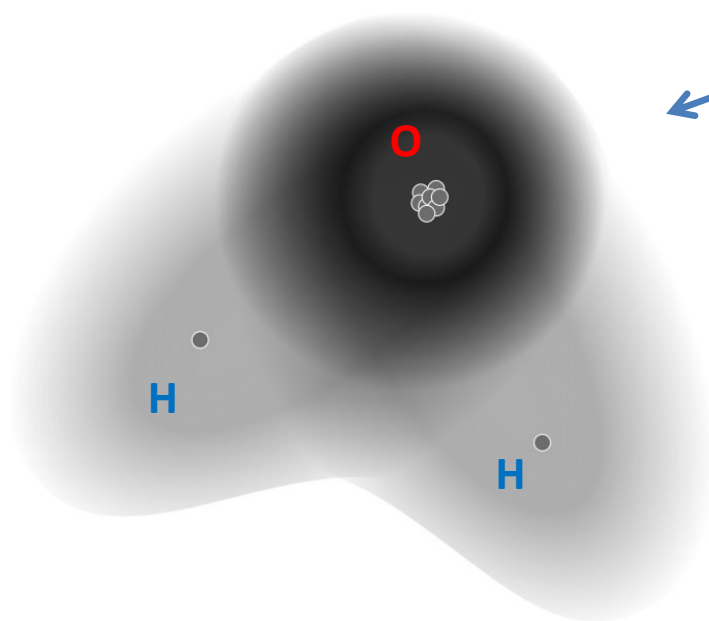
R - determines the configuration of nuclei (atoms) in space => structure for which we can determine the energy

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

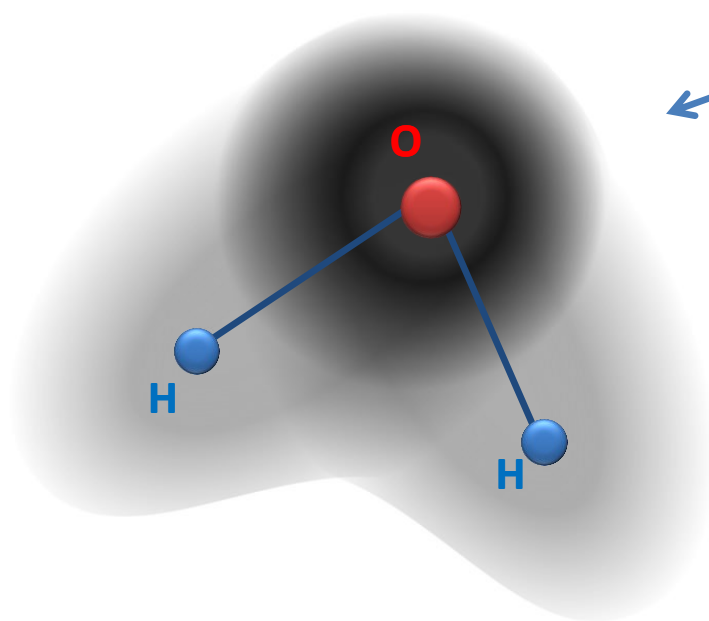
it describes the overall state of the system partially

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

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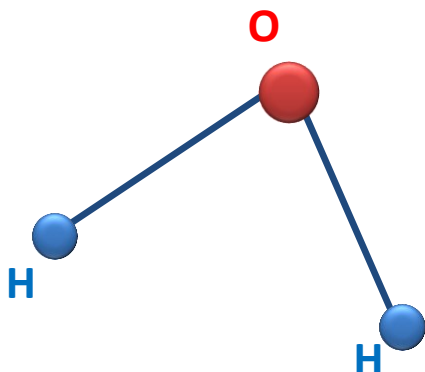
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ground state of the water molecule (schematic):



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

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

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

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.

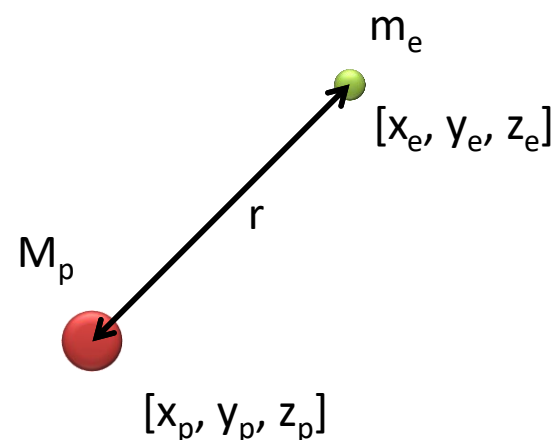
$$M_p = 1836 \text{ au}$$
$$m_e = 1 \text{ au}$$

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

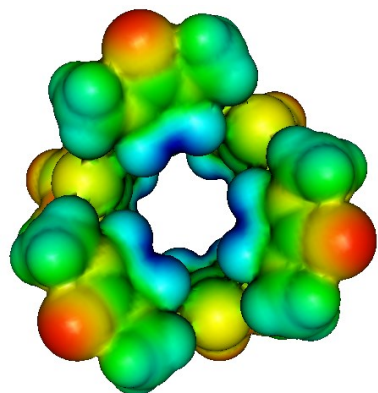
Summary

- 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

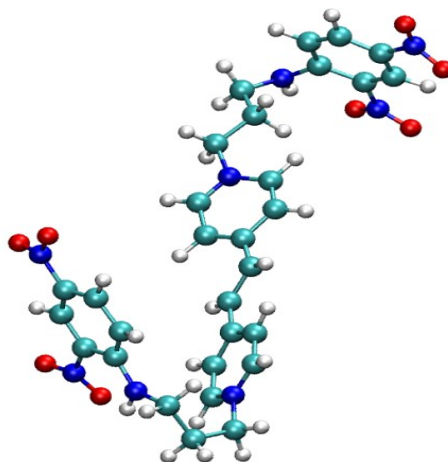
Method overview (model chemistry)



QM (Quantum mechanics)

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

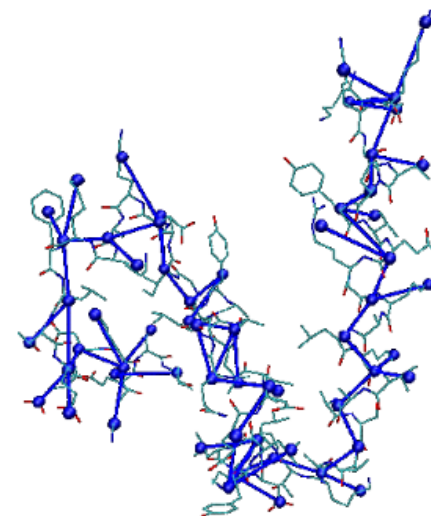
R - position of atom nuclei



MM (Molecular mechanics)

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

R - position of atoms



CGM (Coarse-grained mechanics)

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

R - position of beads