

C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

Lesson 11 Quantum Mechanics III

PS/2021 Present Form of Teaching: Rev2

Petr Kulhánek

kulhanek@chemi.muni.cz

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

Context

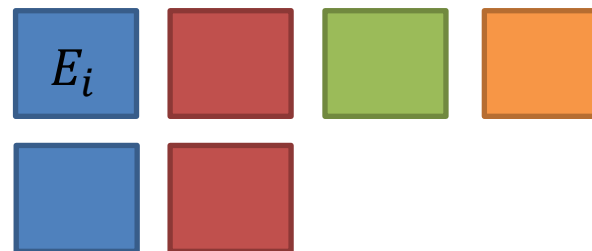
Phenomenological thermodynamics

equilibrium (binding affinities)
kinetics

Thermodynamic properties:
H, S, G, ...

Time average:

Ensemble average:



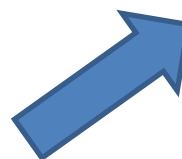
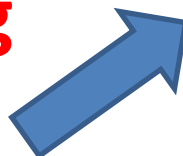
Molecular Dynamics

Statistical thermodynamics
Monte Carlo simulations

Mechanical properties:
 E_i

Molecular modelling

How to describe interactions?

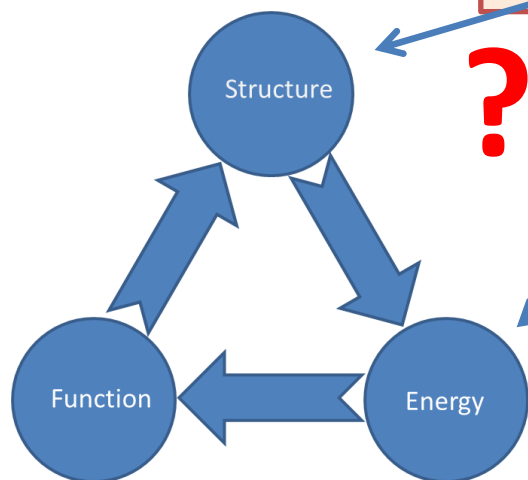


Context

Quantum Mechanics

- It can properly describe systems composed of atoms, which are further composed from electrons and atom nuclei (dual character - particle/wave).
- Microstate energies are solution of time-independent Schrödinger equation.

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



- **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)**
- **Analytically solvable for simple systems**

QM Description of Simple Systems

- hydrogen atom
 - harmonic oscillator
 - rigid rotator
 - particle in potential well
- hydrogen molecule

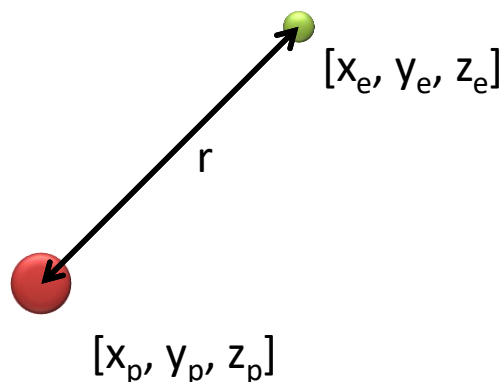
approximate description for

- vibrational
- rotational
- translational

motions

Hydrogen Atom

Hydrogen atom



Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_p^2 - \frac{\hbar^2}{2m} \nabla_e^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

operator describing
proton motion

operator describing
electron motion

electrostatic interaction
between proton and electron

Motion of **two bodies** can be described by motion of **one body** with a **reduced weight**:

$$\mu = \frac{Mm}{M + m}$$

What is the reduced mass of hydrogen atom (proton/electron)?

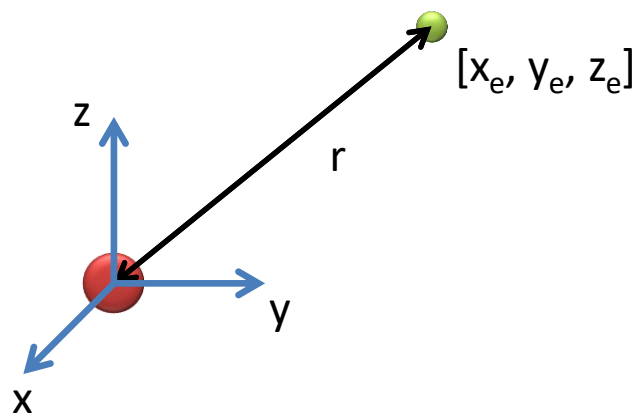
$$M = 1836 \text{ au}$$

$$m = 1 \text{ au}$$

$$\mu = 0.99945 \text{ au}$$

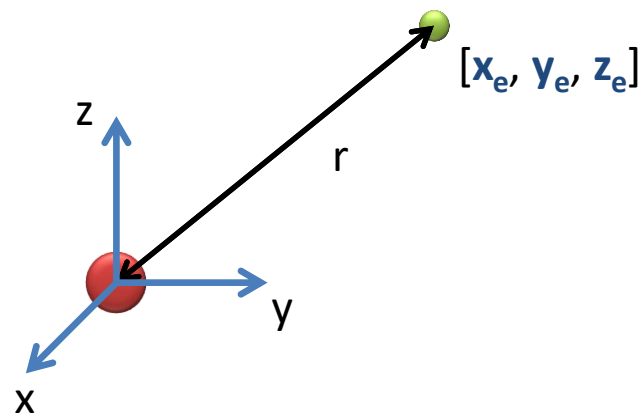
practically the same weight

Hydrogen atom

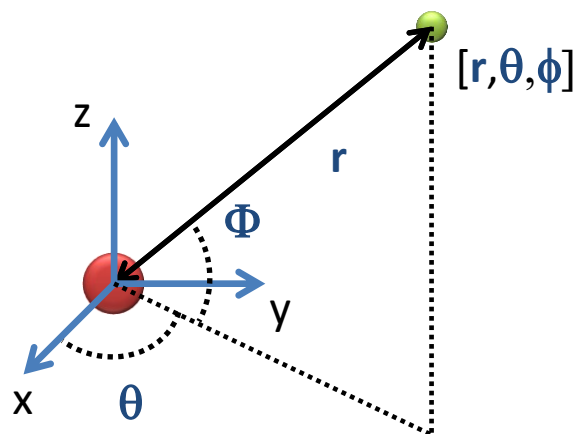


$$\mu = \frac{Mm}{M+m} \approx m \quad \hat{H} \approx -\frac{\hbar^2}{2m} \nabla_e^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

Cartesian vs spherical coordinates



$$r = \sqrt{x_e^2 + y_e^2 + z_e^2}$$



$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Hydrogen atom - solution

$$\hat{H}\psi_k(r, \theta, \phi) = E_k\psi_k(r, \theta, \phi)$$

Solution:

$$\psi_k(r, \theta, \phi) = R_{n,l}(r)Y_{l,m}(\theta, \phi)$$

$$E_k = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}$$

angular (angular) part of the wave function (WF)
radial part of the wave function

quantum numbers:

n - principal quantum number (1,2,3 ...)

l - angular quantum number (0, ..., n-1 = s, p, d, f, g,...)

m - magnetic quantum number (-l, ..., 0, ..., l)

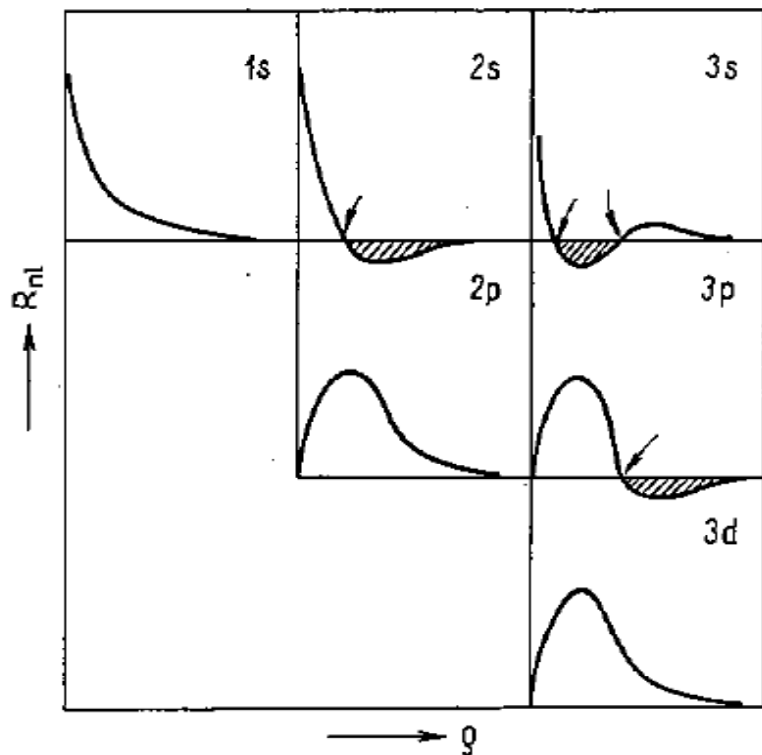
in atomic units:

$$E_k = -\frac{1}{2n^2}$$

Z - proton number ϵ_0 - vacuum permittivity

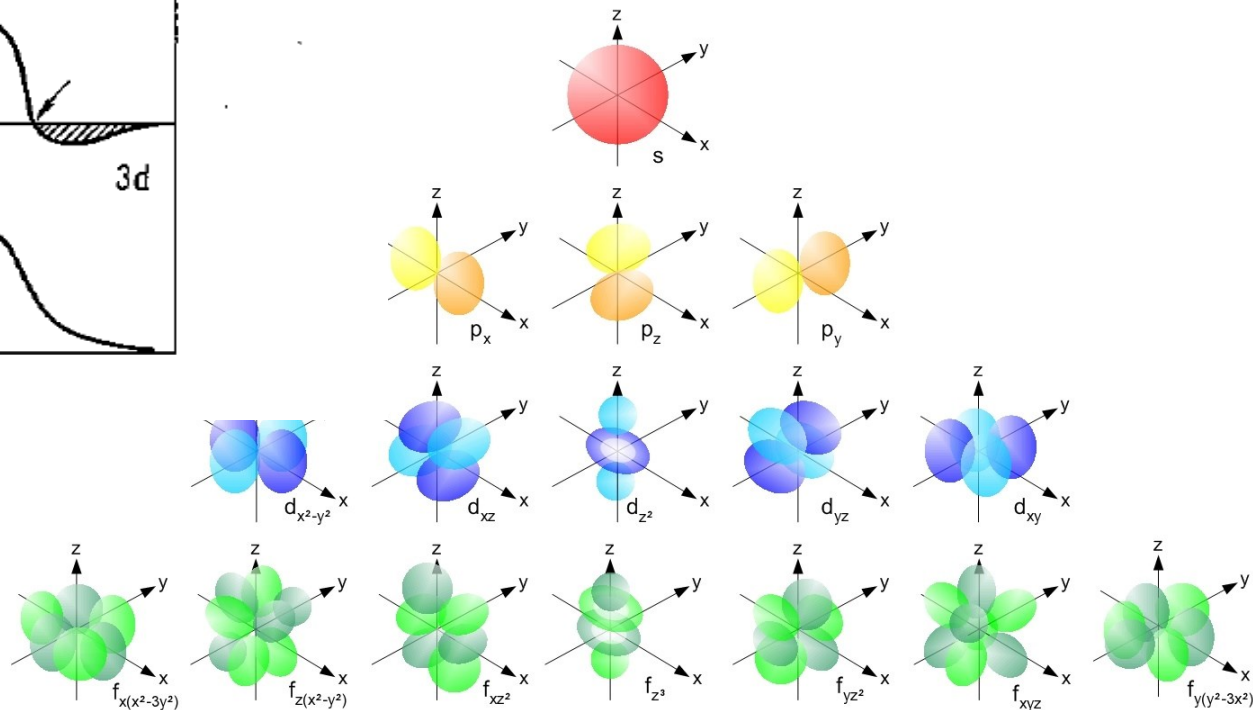
e - electron charge a_0 - Bohr radius

Hydrogen atom - solution



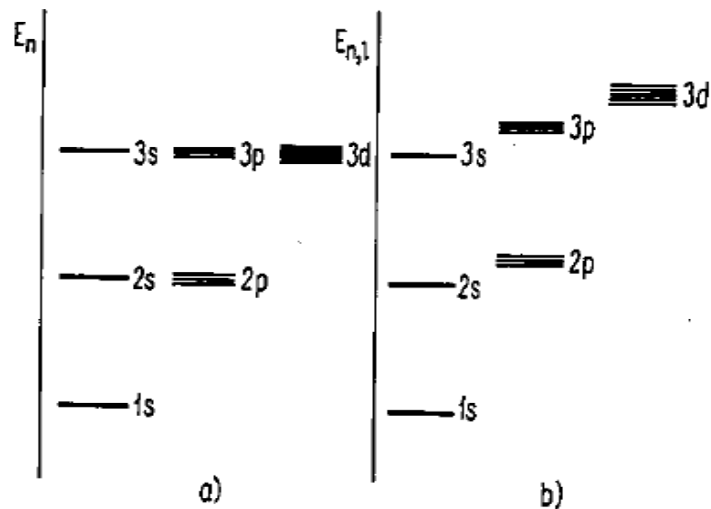
radial component of the wave function

angular component of the wave function



Summary

- Hydrogen atom and hydrogen like atoms (atom cations with one electron) are only chemical systems, whose SE is solvable analytically.
- Allowed energy is discretized (quantized) and dependent only on the principal quantum number.
- Hydrogen atom WF is a foundation for atomic orbitals employed by quantum chemistry methods.



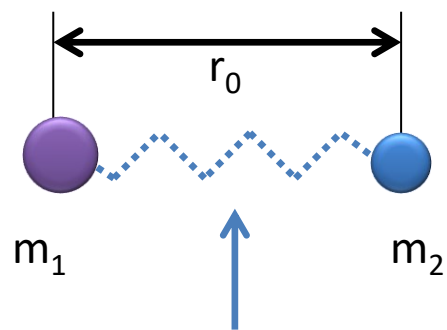
- The hydrogen atom has degenerate states, i.e., states with the same n have the same energy.
- Atoms with more electrons.

SR solution for simple systems

- hydrogen atom
 - harmonic oscillator
 - rigid rotator
 - particles in potential well
- approximate description for
- vibratory
 - rotational
 - translational
- motions

Harmonic Oscillator

Harmonic oscillator



spring with stiffness K

$$F(r) = K(r - r_0)$$



$$V(r) = \frac{1}{2} K(r - r_0)^2$$

the force is proportional to the deviation from the equilibrium position

Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r)$$

Simplification:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r)$$

$$V(r) = \frac{1}{2} K(r - r_0)^2$$

Harmonic oscillator - solution

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

Solution:

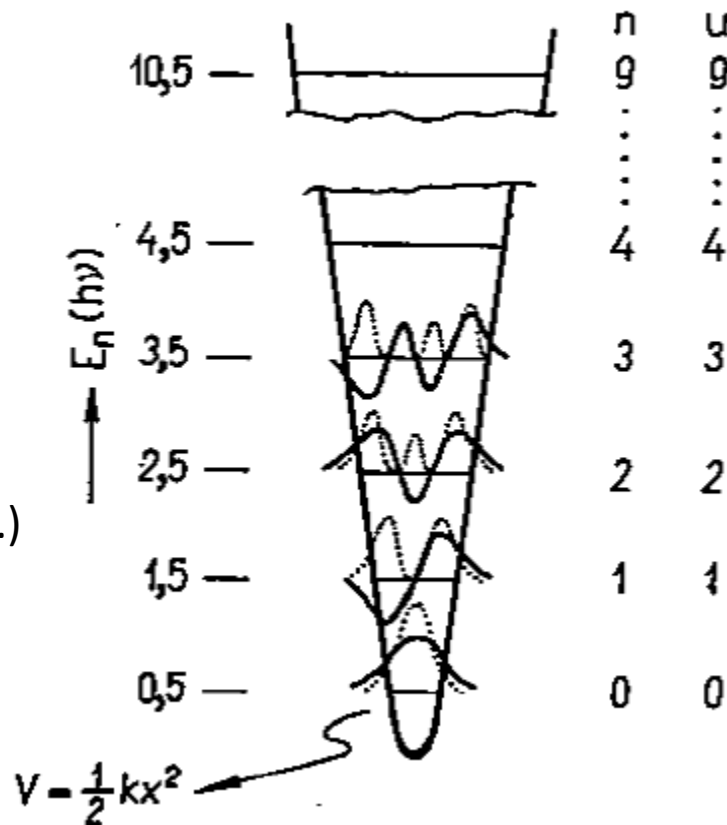
$$\psi_k(r) = \Xi_v(r)$$

$$E_k = \left(v + \frac{1}{2} \right) \hbar \omega$$

quantum numbers:

v - vibrational quantum number (0,1,2,3 ...)

$$\text{angular frequency } \omega = \sqrt{\frac{K}{\mu}}$$



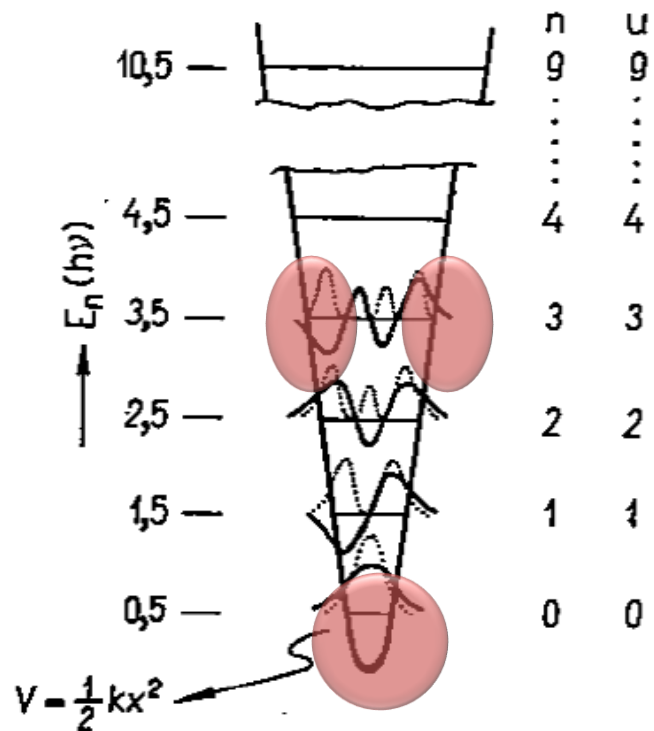
Summary

- **Quantum harmonic oscillator cannot have zero energy in the ground state.**
- This intrinsic behaviour can be explained by uncertainty principle.
- For low vibrational numbers, the highest probability for particle finding is at equilibrium distance (this is opposite to the classical harmonic oscillator behavior).
- Energies are equidistant.

position/momentum

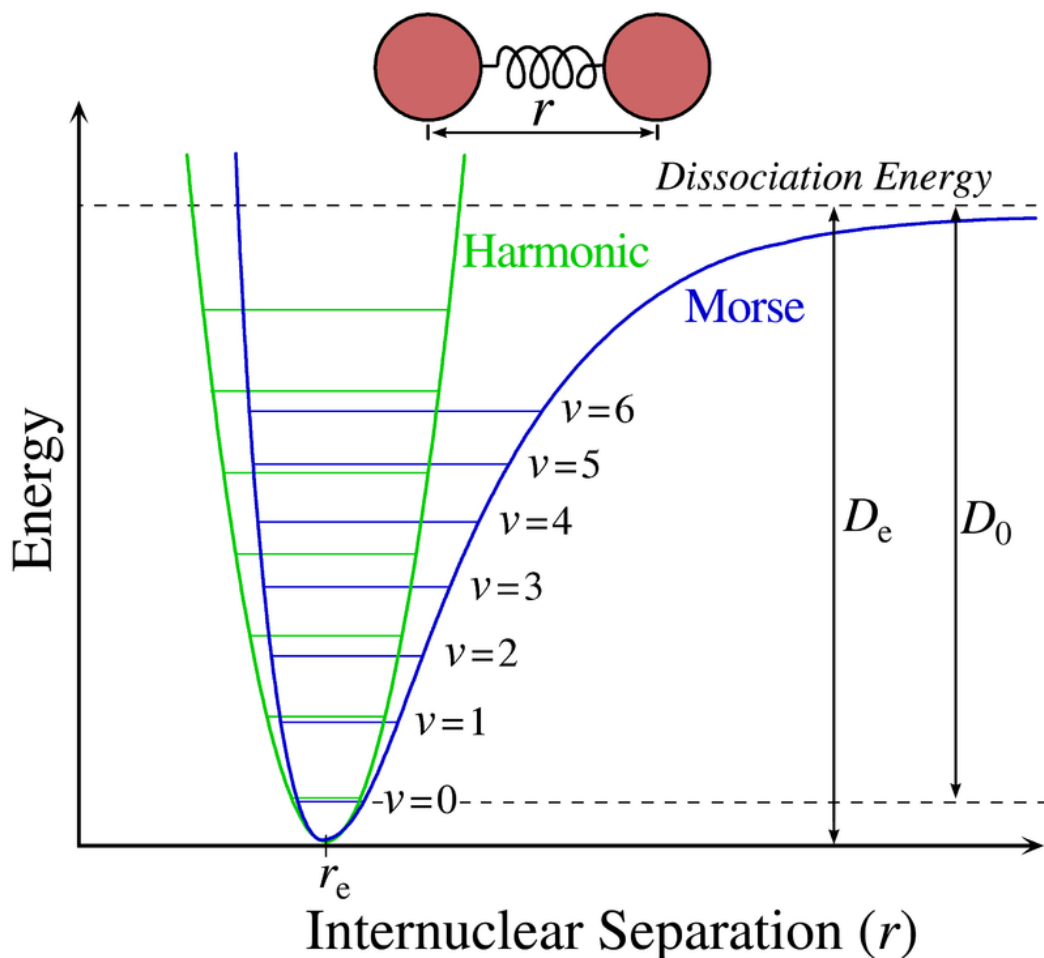
$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

- no motion (exact momentum)
- position at potential bottom (exact position)



Harmonic vs anharmonic oscillator

Simplified description of vibrational motion. A more accurate empirical description is given by Morse's potential.



Morse potential

$$V(r) = D_e \left(1 - e^{-a(r-r_0)}\right)^2$$

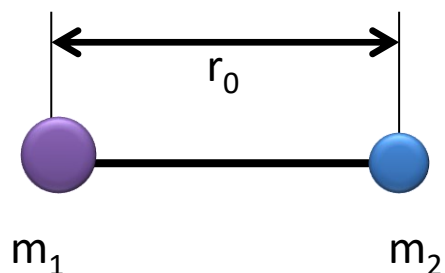
Harmonic potential

$$V(r) = \frac{1}{2} K (r - r_0)^2$$

$$K = \sqrt{\frac{a}{2D_e}}$$

Rigid Rotor

Rigid rotor



Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2$$

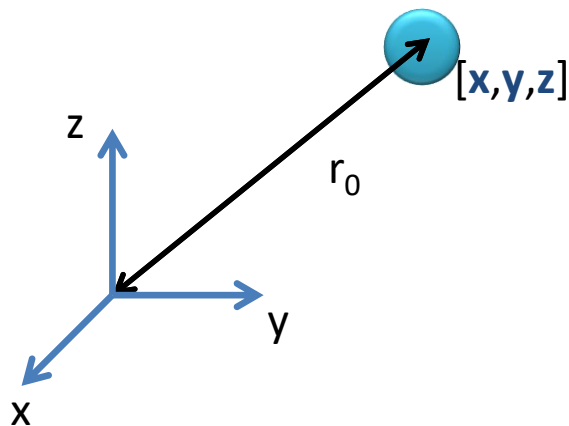
with constraint $r = r_0$

Simplification:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2$$

with constraint $r = r_0$



Rigid Rotor - solution

$$\hat{H}\psi_k(\theta, \varphi) = E_k\psi_k(\theta, \varphi)$$

Solution:

$$\psi_k(\theta, \varphi) = Y_{l,m}(\theta, \phi)$$



angular part of the wave function

$$E_l = \frac{\hbar^2}{2I}l(l+1)$$

quantum numbers:

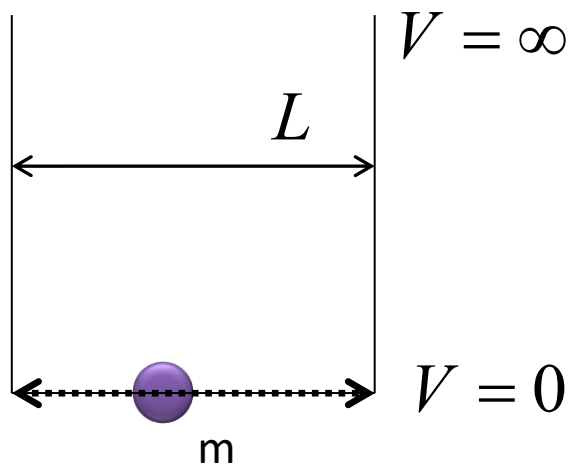
l - angular quantum number (0,1,2, ...)

m - magnetic quantum number (-l,...,0,...,l)

moment of inertia $I = \mu r_0^2$

Particle in a Box

Particle in a box



1D potential box (the infinite potential well) is infinitely deep, so the probability of particle finding outside the box is zero.

Hamiltonian

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

with constraint

$$\psi(r) = 0$$

for $r > L$ and $r < 0$

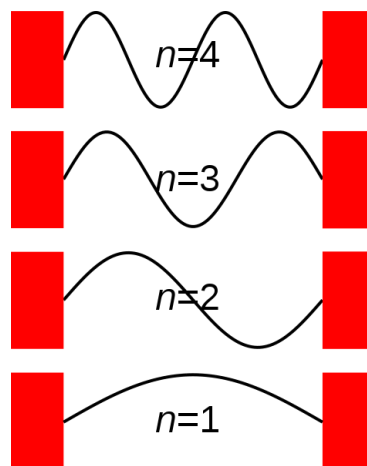
Solution:

$$\psi_n = A \sin\left(\frac{n\pi}{L} x\right)$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

quantum numbers:

n - quantum number (1,2, ...)



standing waves

For a multi-dimensional potential box (3D), the dimensions can be replaced by the box volume.

Hydrogen Molecule

- Many electron atoms (He, Li, ...)
 - Born-Oppenheimer approximation
 - One-electron approximation
 - ...
- Many atom (=many electron) molecules
 - Born-Oppenheimer approximation
 - One-electron approximation
 - ...

Revision

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

časově závislá Schrödingerova rovnice

Revision

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

time-dependent Schrödinger equation

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

time-independent Schrödinger equation

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

system can exist in several quantum states described by wavefunction ψ_k and energy E_k

Revision

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

time-dependent Schrödinger equation

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

time-independent Schrödinger equation

Born- Oppenheimer approximation

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

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

$$\hat{H}_e\Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R})\Psi_m(\mathbf{r}, \mathbf{R})$$

electron motion in the static field of nuclei
electronic properties

$$\hat{H}_R\chi_l(\mathbf{R}) = E_{VRT,l}\chi_l(\mathbf{R})$$

nuclei motion in effective field of electrons
vibration, rotation, translation

Revision

$$\hat{H}_e \Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \Psi_m(\mathbf{r}, \mathbf{R})$$

electron motion in the static field of nuclei
electronic properties

$$\hat{H}_R \chi_l(\mathbf{R}) = E_{VRT,l} \chi_l(\mathbf{R})$$

nuclei motion in effective field of electrons
vibration, rotation, translation

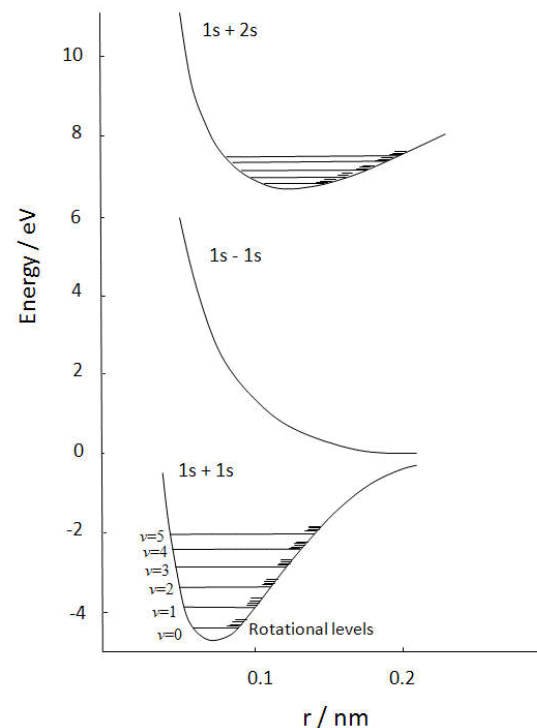
electronic energy part

vibration, rotation,
translation energy part

$$E_k = E_m(R_{opt,m}) + E_{VRT,l}$$

total energy of the state

optimal geometry, at
which E_m is minimal



Revision

$$\hat{H}_e \Psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \Psi_m(\mathbf{r}, \mathbf{R})$$

electron motion in the static field of nuclei
electronic properties

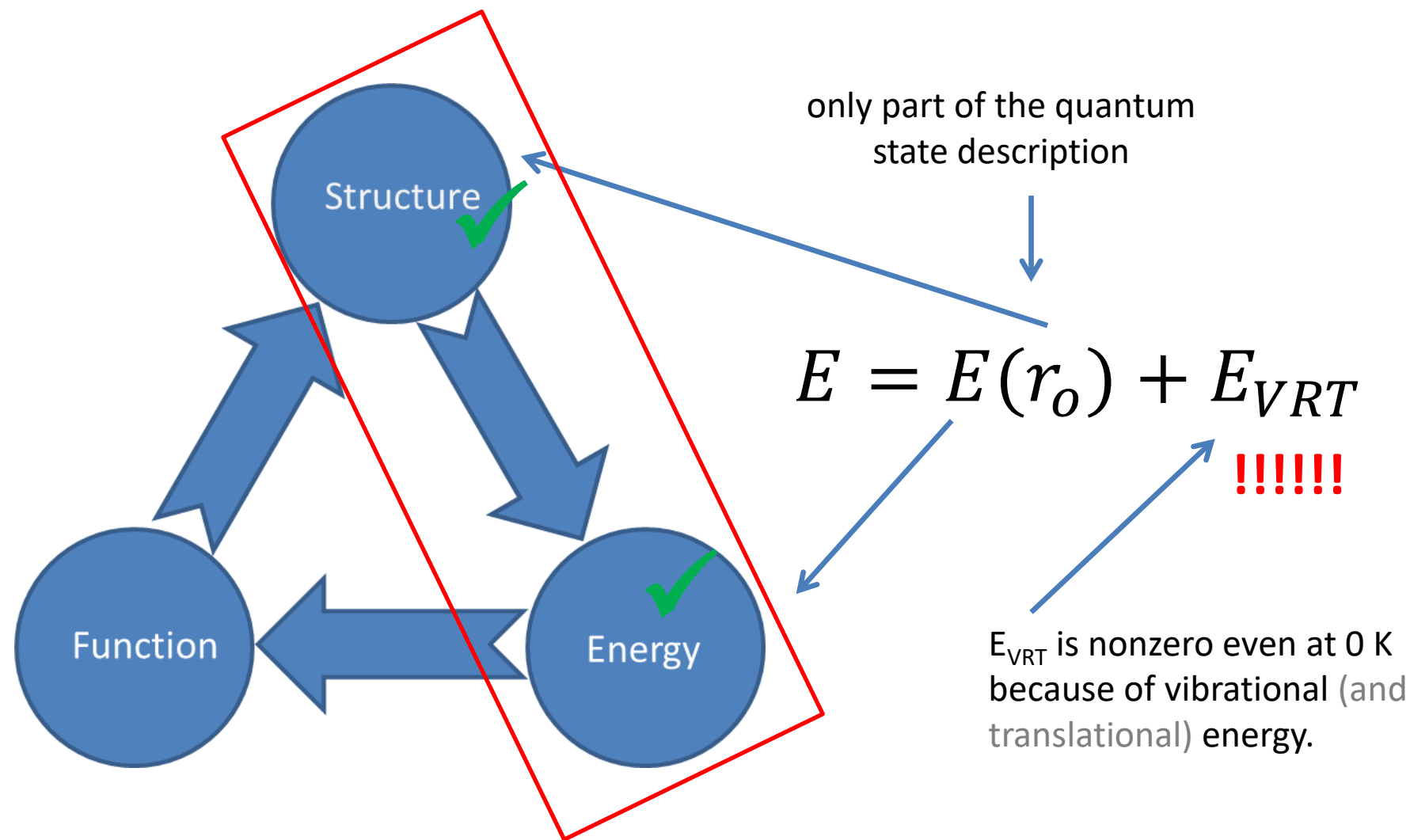
$$\hat{H}_R \chi_l(\mathbf{R}) = E_{VRT,l} \chi_l(\mathbf{R})$$

nuclei motion in effective field of electrons
vibration, rotation, translation

je možné obdobným
způsobem dále rozdělit na
samostatné příspěvky
vibrační, rotační a translační

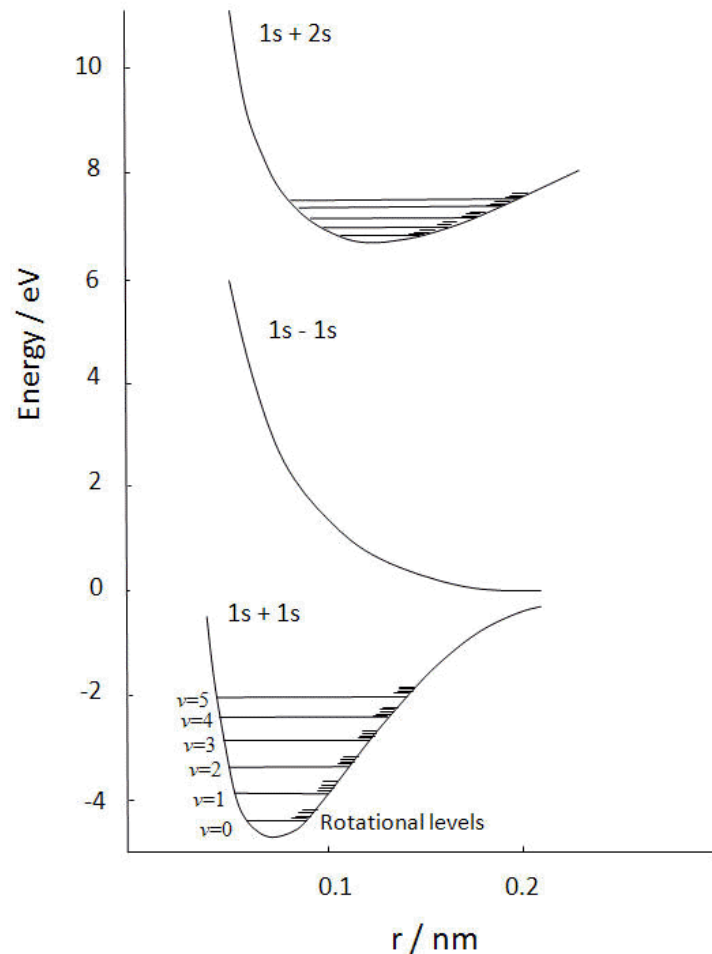
$$E_{VRT,l} = E_{V,i} + E_{R,j} + E_{T,k}$$

Structure vs system state



Homework

1. What is the order of the dissociation energies of H_2 (hydrogen molecule), D_2 (deuterium molecule), and T_2 (tritium molecule)?



Focus on the ground state ($1s+1s$) only:

Help:

- vibrations are quantized

$$E_V = \left(v + \frac{1}{2} \right) h\nu \quad \text{vibrational quantum number } 0, 1, 2, \dots$$

- neglect rotation and translation (why?)

Total energy of the ground state:

$$E = E(r_o) + E_V(v = 0)$$