C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 11
Quantum Mechanics III

PS/2020 Distant Form of Teaching: Rev1

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:

Molecular Dynamics

Ensemble average:

Mechanical properties:
E_i

Statistical thermodynamics
Monte Carlo simulations

Molecular modelling

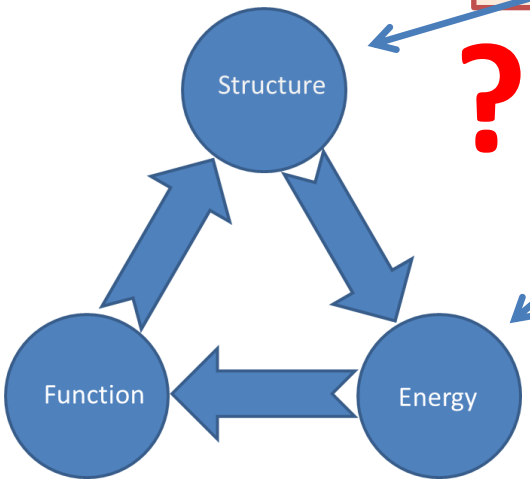
How to describe interactions?

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

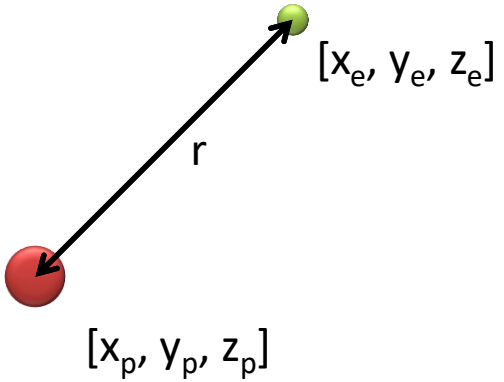
- hydrogen atom
  - harmonic oscillator
  - rigid rotator
  - particle in potential well
- hydrogen molecule

approximate description for
- vibrational
- rotational
- translational

motions

Hydrogen Atom

Hydrogen atom



Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_p^2 - \frac{\hbar^2}{2m}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

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)?

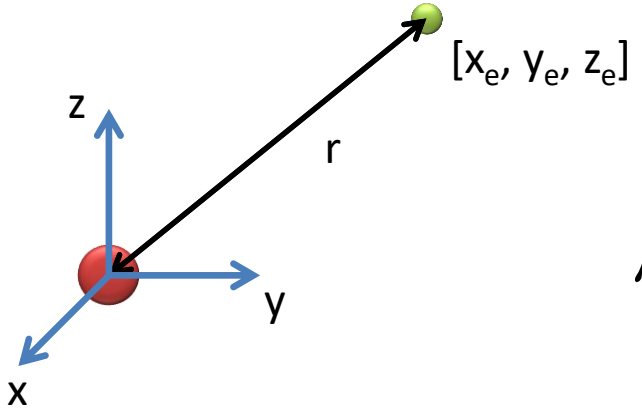
M = 1836 au

m = 1 au

μ = 0.99945 au

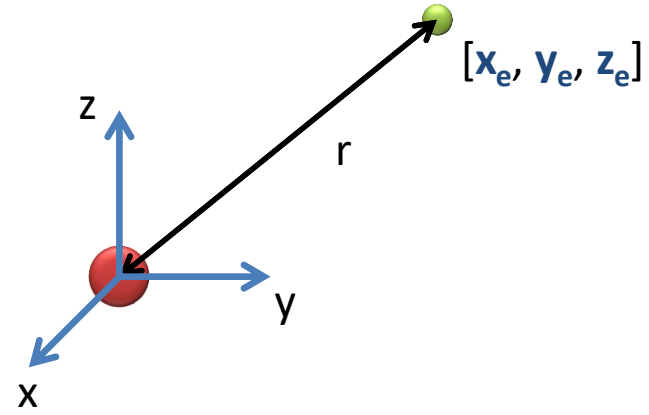
practically the same weight

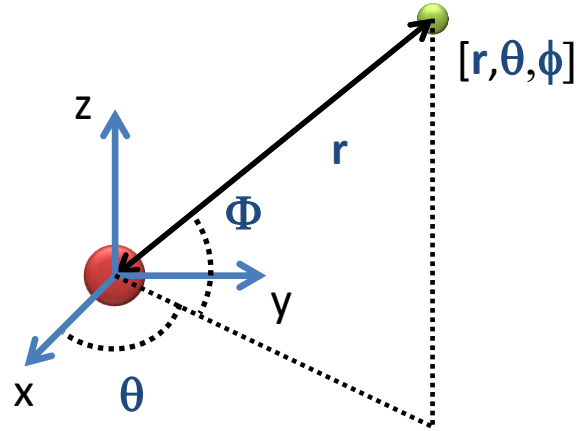
Hydrogen atom



$$\mu = \frac{Mm}{M+m} \approx m \qquad \hat{H} \approx -\frac{\hbar^2}{2m}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

Cartesian vs spherical coordinates





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

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

Hydrogen atom - solution

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

Solution:

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

$$E_k = -\frac{Z^2e^2}{8\pi\varepsilon_0 a_0 n^2}$$

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:

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

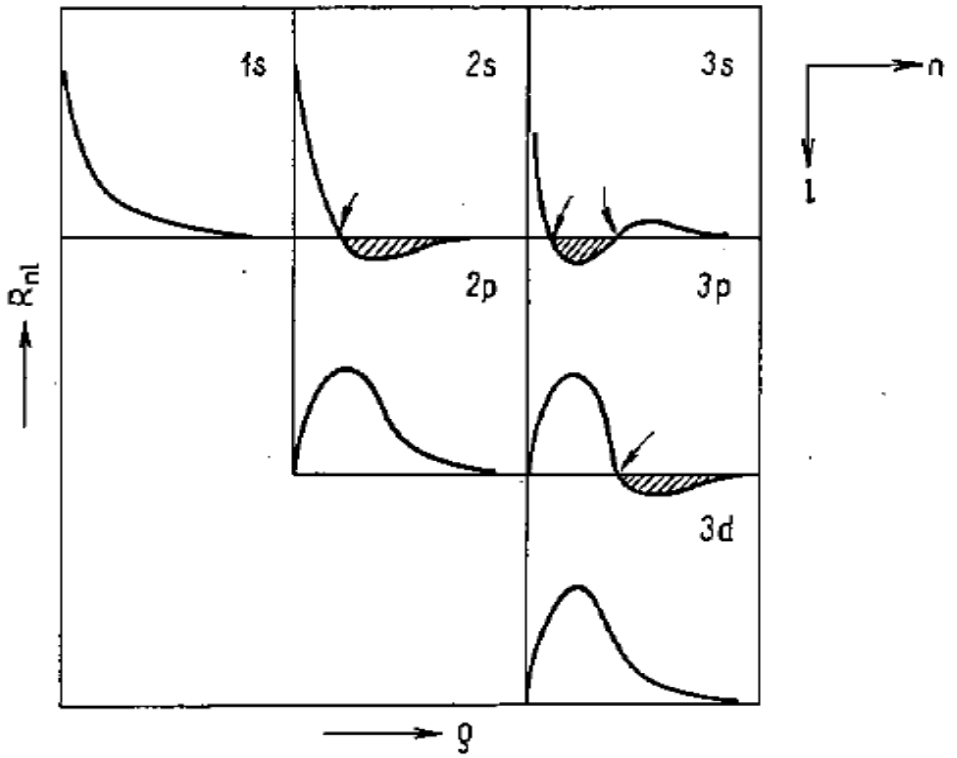
Z - proton number

e - electron charge

ε_0 - vacuum permittivity

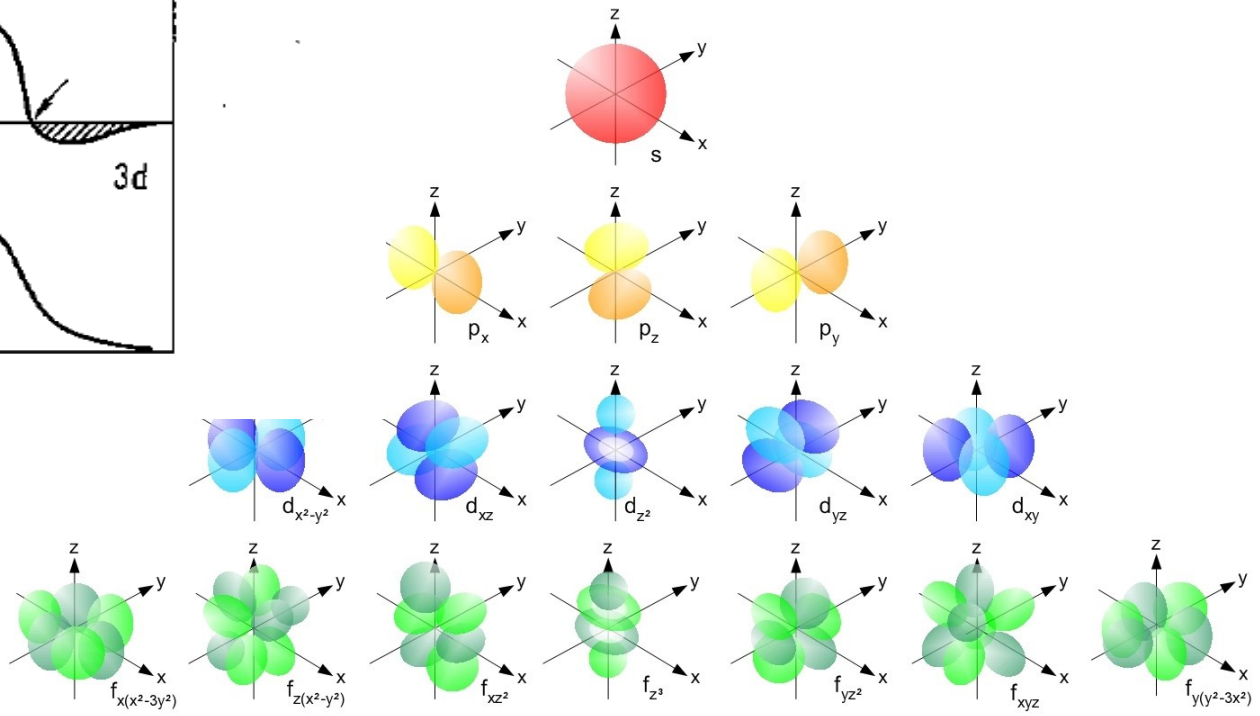
a_0 - Bohr radius

Hydrogen atom - solution



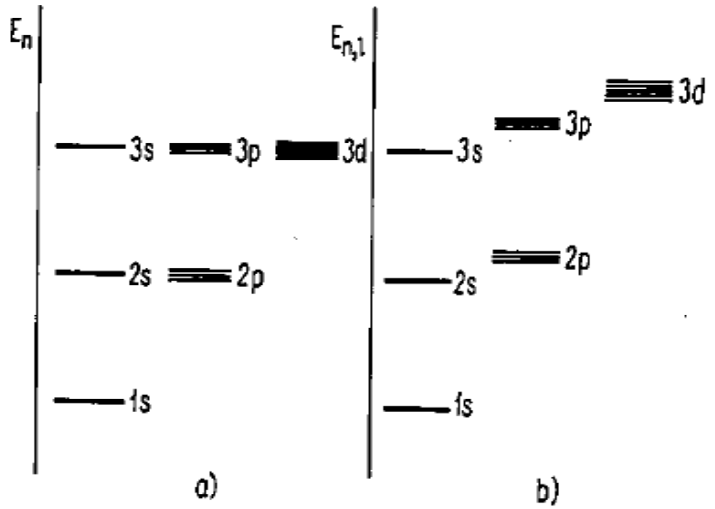
radial component of the wave function

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.



a) The hydrogen atom has degenerate states, i.e., states with the same *n* have the same energy.
b) Atoms with more electrons.

SR solution for simple systems

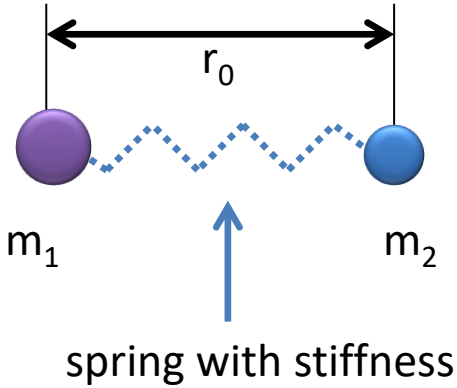
- hydrogen atom
  - harmonic oscillator
  - rigid rotator
  - particles in potential well

approximate description for
- vibratory
- rotational
- translational

motions

Harmonic Oscilator

Harmonic oscillator



Hamiltonian

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

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

the force is proportional to the deviation from the equilibrium position

Simplification:

$$\mu = \frac{m_1 m_2}{m_2 + m_2} \qquad \hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V(r) \qquad V(r) = \frac{1}{2}K(r - r_0)^2$$

Harmonic oscillator - solution

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

Solution:

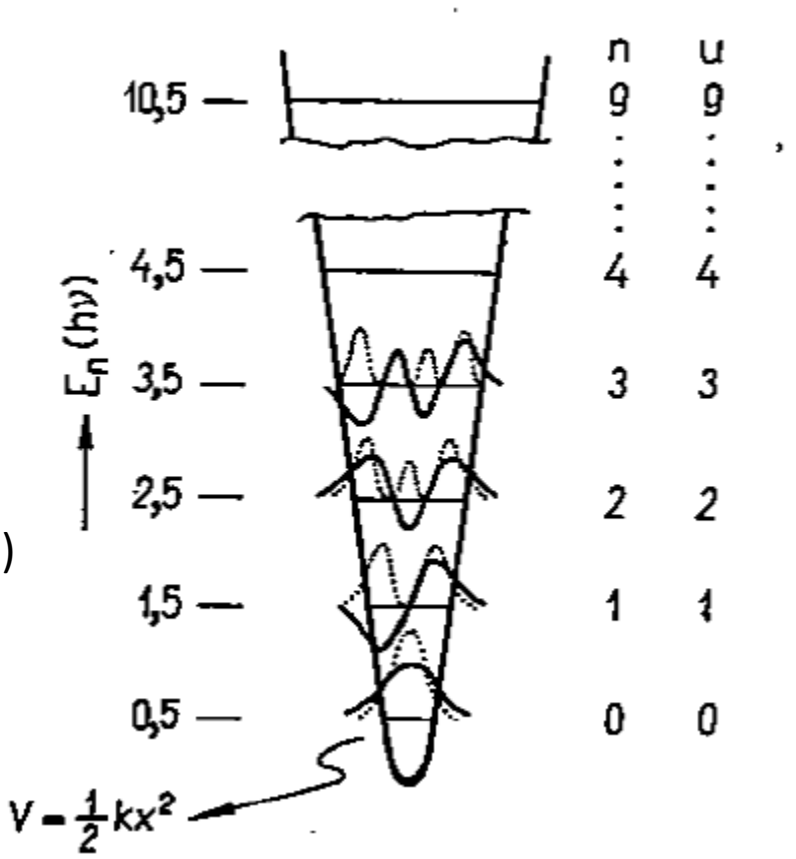
$$\psi_k(r) = \Xi_v(r)$$

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

quantum numbers:

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

angular frequency $\varpi = \sqrt{\frac{K}{\mu}}$



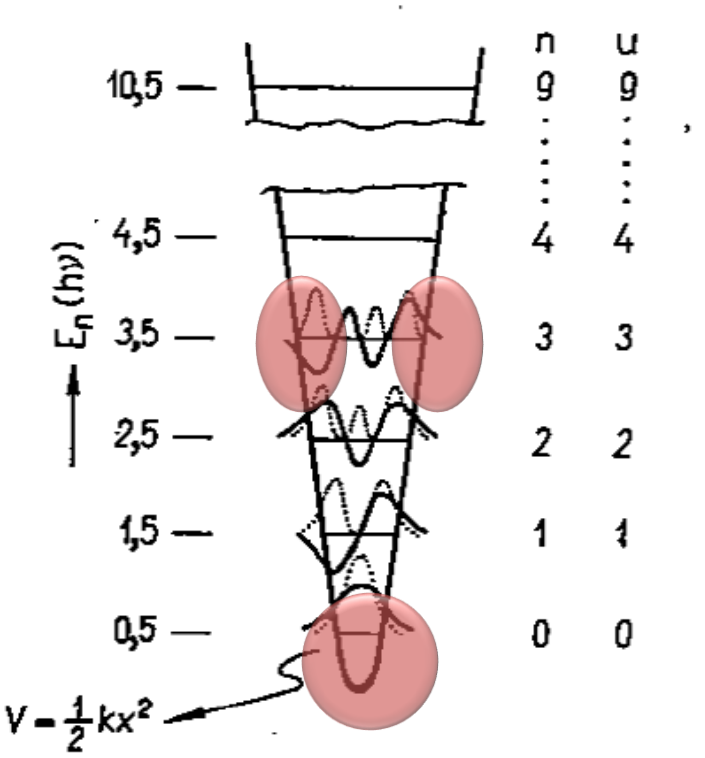
Summary

- **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

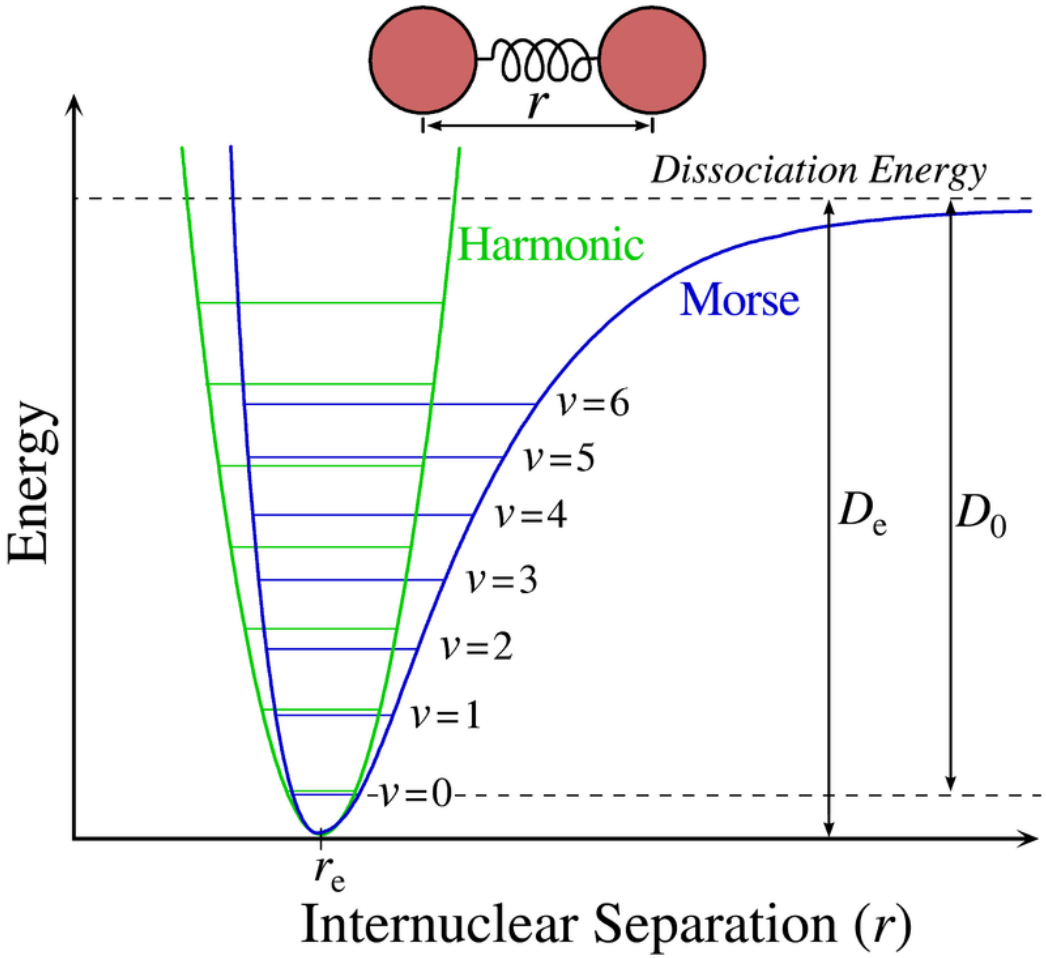
$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

- 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

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

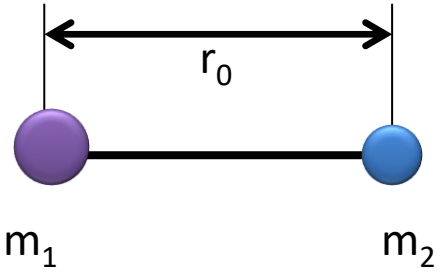
Harmonic potential

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

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

Rigid Rotor

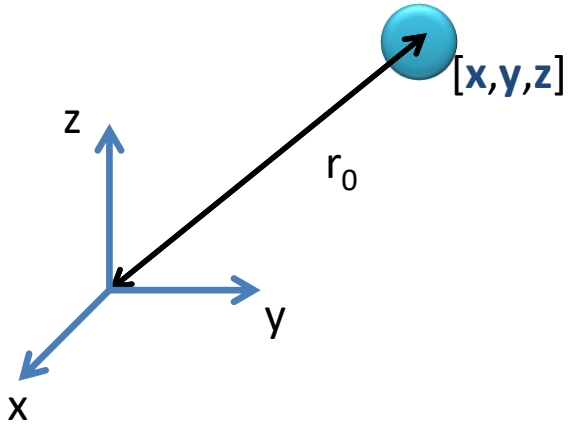
Rigid rotor



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:

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

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

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:

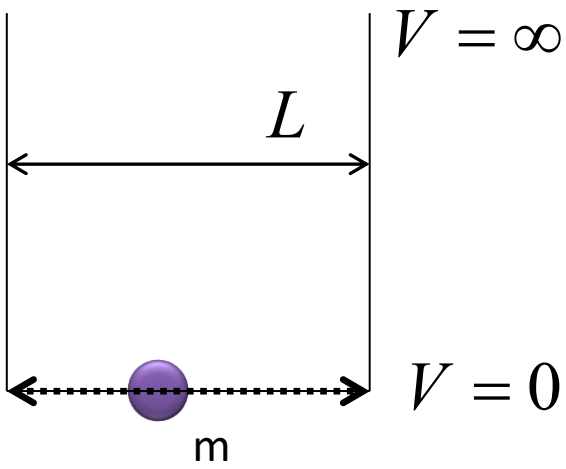
l - angular quantum number (0,1,2, ...)

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

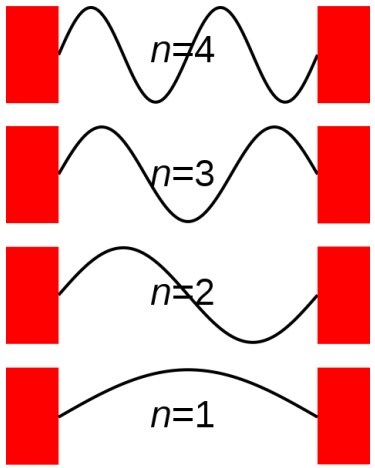
$$\psi(r) = 0$$

for r > L and r < 0

Solution:

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

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



standing waves

quantum numbers:

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

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

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

Born- Oppenheimer approximation

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

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

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

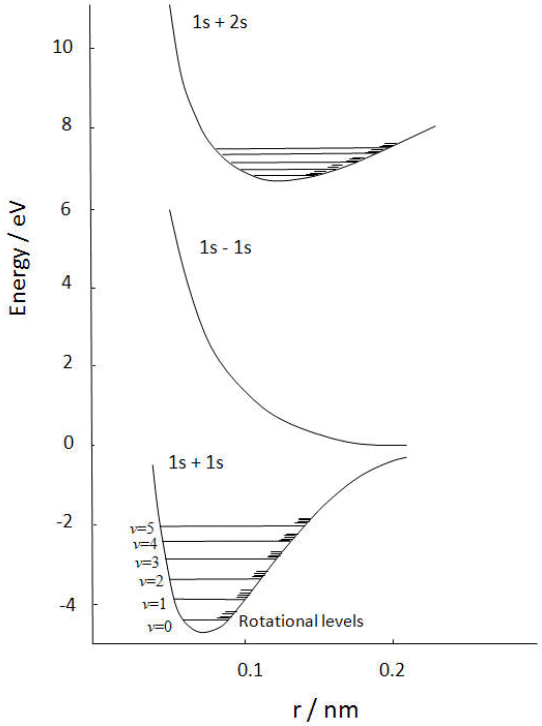
electronic energy part

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

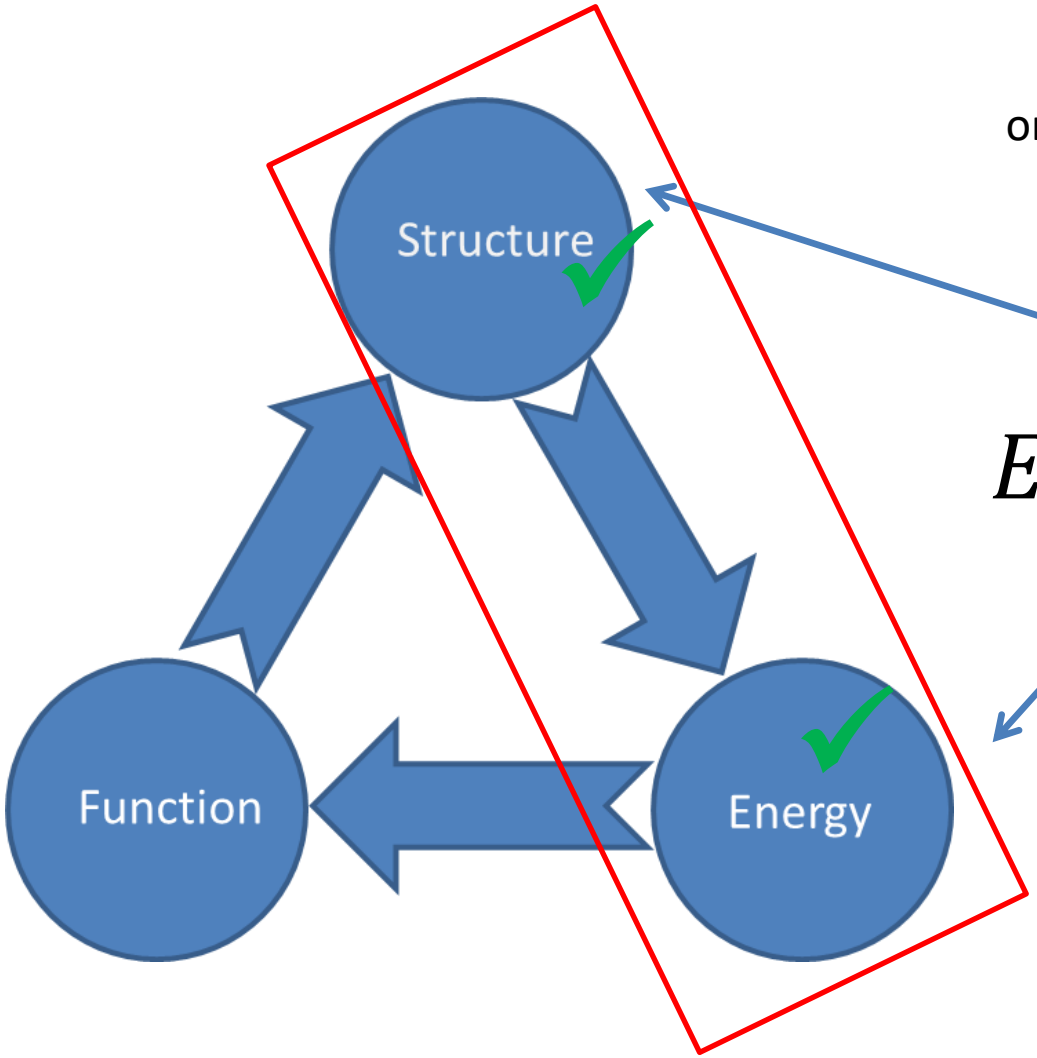
$$\hat{H}_R \chi_l(\mathbf{R}) = E_{VRT,l}\chi_l(\mathbf{R})$$

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



only part of the quantum state description

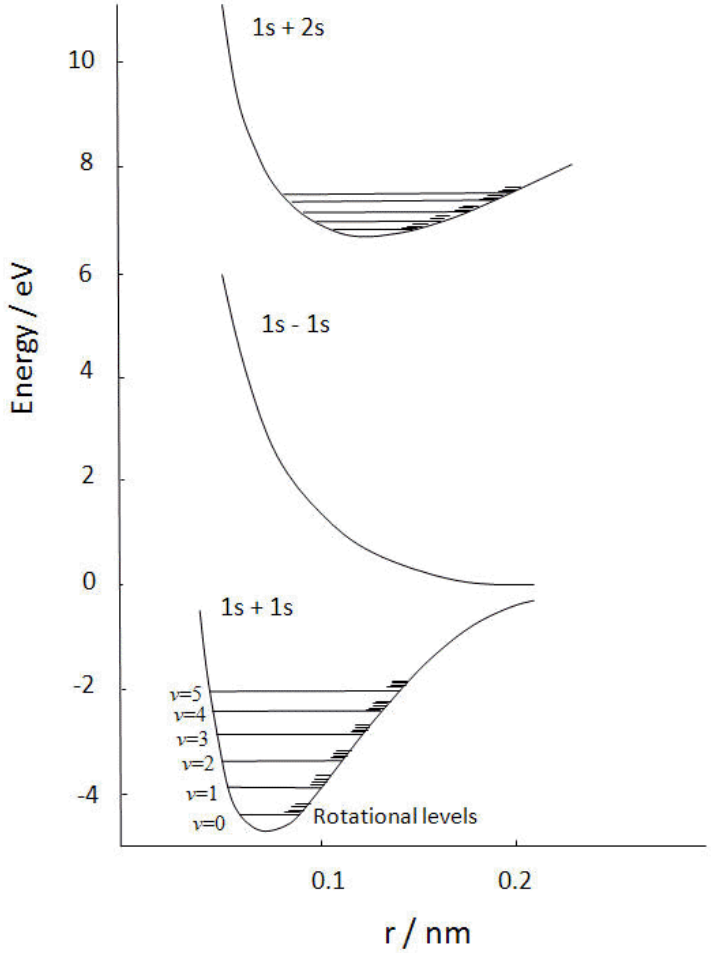
$$E = E(r_o) + E_{VRT}$$

!!!!!!

E_{VRT} is nonzero even at 0 K because of vibrational (and translational) energy.

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

$$E_V = \left(v + \frac{1}{2}\right) h\upsilon$$

vibrational quantum number 0,1,2,...

- neglect rotation and translation (why?)

Total energy of the ground state:

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