Born-Oppenheimer approximation & Electronic Schrödinger equation

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Born-Oppenheimer (BO) approximation

-Motivation

- Nuclei are much heavier than electrons:

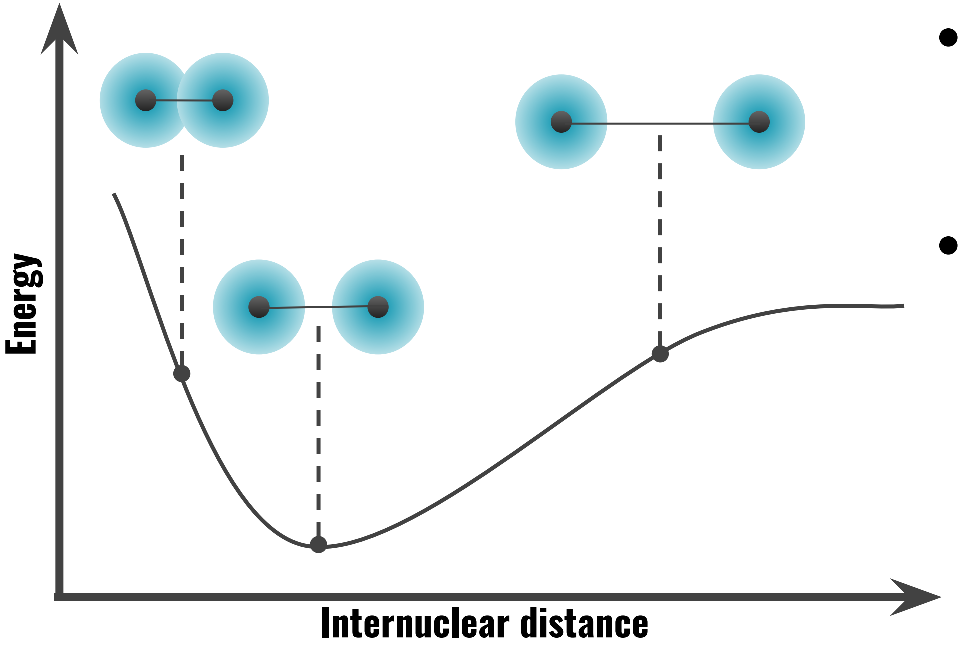
$$\frac{m_Z}{m_e} \geq 1836$$

- Effectively, electrons adjust themselves instantaneously to nuclear configurations.

- Electron and nuclear motions are uncoupled, thus the energies of the two are separable.

Born-Oppenheimer (BO) approximation

-Implication



- For a given nuclear configuration, there is an unique electronic energy.
- As nuclei move continuously, the points of electronic energy join to form a potential energy surface on which nuclei move.

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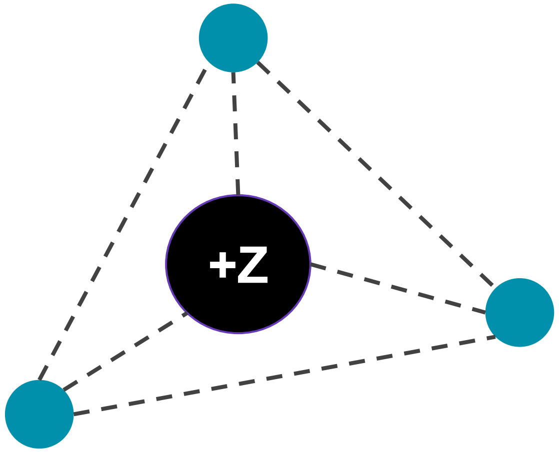
The hamiltonian

-Definition



The Hamiltonian of a quantum system collects the operators of all relevant energy contributions to the system.

Under the Born-Oppenheimer approximation these are:

- Kinetic energy of the electrons.
- Coulomb attraction between the electrons and nucleus.
- Coulomb repulsion between electrons.

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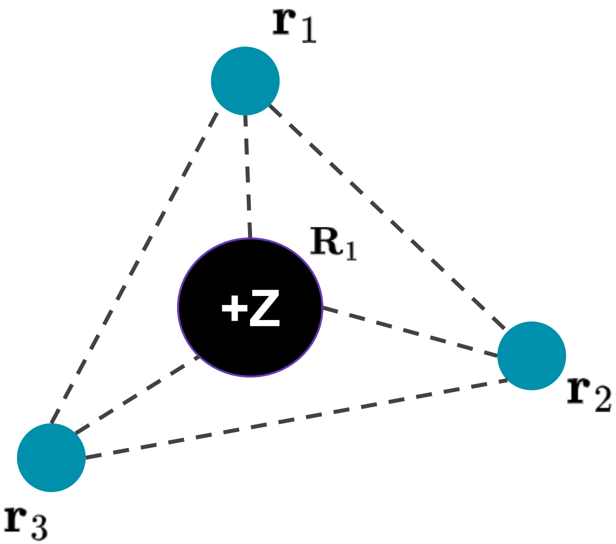
The hamiltonian

-Mathematical formulation



Hamiltonian operator:

$$\widehat{H} = \widehat{T}_e + \widehat{V}_{Ne} + \widehat{V}_{ee}$$

Kinetic energy operator (N electrons):

$$\widehat{T}_e = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2$$

Nuclear attraction operator (N electrons, M nuclei):

$$\widehat{V}_{Ne} = -\sum_{j=1}^{M}\sum_{i=1}^{N} \frac{Z_j}{|\mathbf{R}_\mathrm{j} - \mathbf{r}_\mathrm{i}|}$$

Electron repulsion operator (N electrons):

$$\widehat{V}_{ee} = \sum_{j=1}^{N}\sum_{i=1}^{N} \frac{1}{|\mathbf{r}_\mathrm{j} - \mathbf{r}_\mathrm{i}|}$$

R and **r** refer to the positions of nuclei and electrons, respectively.

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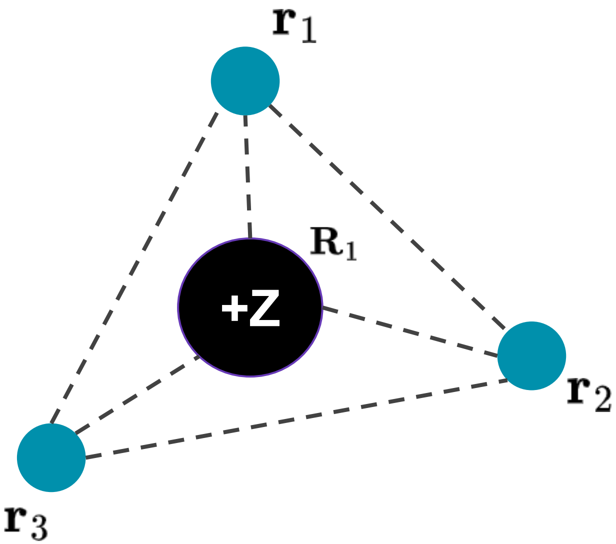
The electronic Schrödinger equation



$$\hat{H}\Psi = E\Psi$$

- The solution to the electronic Schrödinger equation provide us with the wavefunction that contain all information of our system.

- It can only be solved for very simple cases, for systems with less than a handful of electrons.

- It is the basis for electronic structure calculation techniques like Hartree-Fock and Density Functional Theory.

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Summary

- The *Born-Oppenheimer approximation* allow us to separate the motion of electrons and nuclei.
- Thus, for a given nuclear configuration, there is an unique electronic energy.
- We only need to consider the electrons quantum-mechanically.
- The *Hamiltonian* of a quantum system collects the operators of all relevant energy contributions to the system, these are:
  - Kinetic energy of the electrons.
  - Coulomb attraction between the electrons and nucleus.
  - Coulomb repulsion between electrons.
- Using the Hamiltonian, the electronic Schrödinger equation can be used to describe the motions of the electrons.

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