

# Molecules

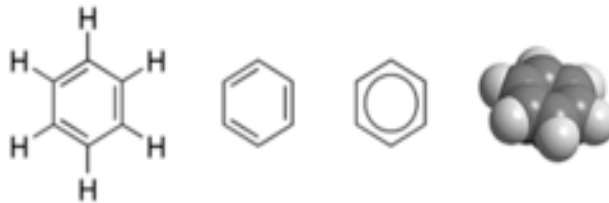
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# The full Hamiltonian of a molecule

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$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Everything you can know about the molecule is contained in the Hamiltonian.



This explains life, the universe, and everything!

# Born Oppenheimer approximation

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Fix the positions of the nuclei and consider the many electron Hamiltonian.

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

# Separation of variables (Trennung der Veränderlichen)

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$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

$$H_{elec\_red} = \sum_i \left( \frac{-\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} \right) = \sum_i H_{MO}$$

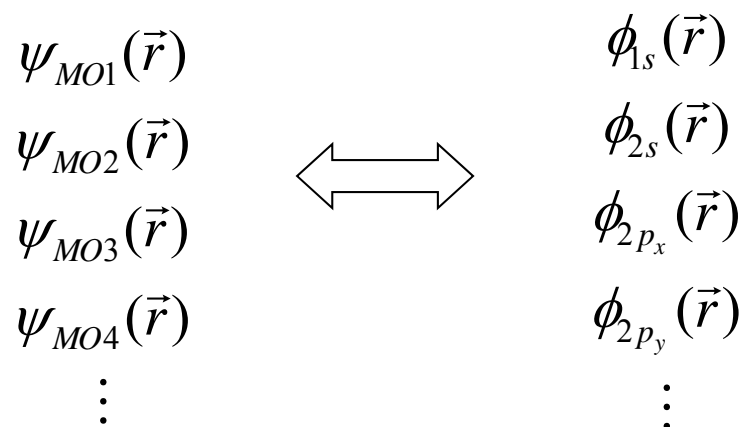
The Schrödinger equation can be solved by the separation of variables if the total Hamiltonian can be written as a sum of Hamiltonians each depending on only one variable.

$$H_t(r_1, r_2, \dots, r_n) = H_1(r_1) + H_2(r_2) + \dots + H_n(r_n)$$

# Molecular orbitals

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Molecular orbitals of a molecule are like the atomic orbitals of an atom.



You can put two electrons, spin up and spin down, in each molecular orbital.

# Molecular orbitals

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The first approximation for the many electron wave function of a molecule is an antisymmetrized product of molecular orbitals. The energy of this wave function should be evaluated using the electronic Hamiltonian.

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{MO1} \uparrow(\vec{r}_1) & \psi_{MO1} \downarrow(\vec{r}_1) & \dots & \psi_{MO,N} \uparrow(\vec{r}_1) \\ \psi_{MO1} \uparrow(\vec{r}_2) & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ \psi_{MO1} \uparrow(\vec{r}_N) & \dots & \dots & \psi_{MO,N} \uparrow(\vec{r}_N) \end{vmatrix}$$

# Linear Combination of Atomic Orbitals

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Look for a solution to the molecular orbital Hamiltonian,

$$H_{\text{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_A|}$$

of the form,

$$\psi_{\text{mo}} = \sum_n^N c_n \phi_n.$$

Here  $\phi_n$  are atomic orbitals with  $Z_{\text{eff}}$ .