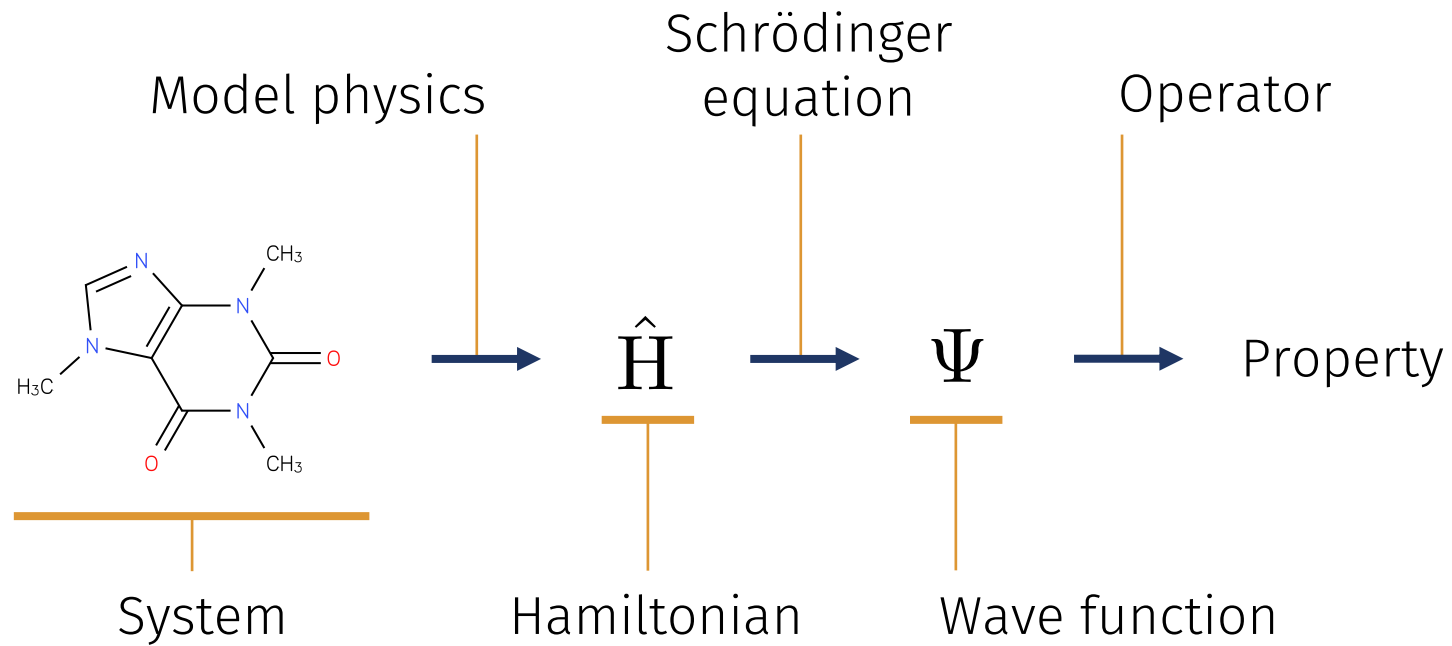
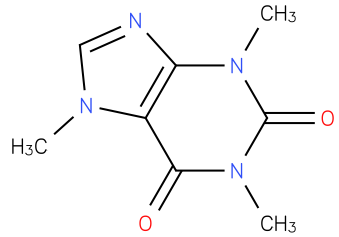


Born-Oppenheimer Approximation





$$\longrightarrow \hat{H}(\mathbf{r}_i, \mathbf{R}_I) \longrightarrow \Psi(\mathbf{r}_i, \mathbf{R}_I)$$

Coordinates of N nuclei
Coordinates of n electrons

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) = \hat{T}_n(\mathbf{R}_I) + \hat{T}_e(\mathbf{r}_i) + \hat{V}_{ee}(\mathbf{r}_i) + \hat{V}_{en}(\mathbf{r}_i, \mathbf{R}_I) + \hat{V}_{nn}(\mathbf{R}_I) + \hat{V}_{\text{ext}}$$

Full
Hamiltonian

Kinetic energy
of nuclei

Kinetic energy
of electrons

Electronic
repulsion

Electron-nuclei
attraction

Nuclear
repulsion

External
potential

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) = \hat{T}_n(\mathbf{R}_I) + \hat{T}_e(\mathbf{r}_i) + \hat{V}_{ee}(\mathbf{r}_i) + \hat{V}_{en}(\mathbf{r}_i, \mathbf{R}_I) + \hat{V}_{nn}(\mathbf{R}_I) + \hat{V}_{\text{ext}}$$

What if Hamiltonian would be separable into electronic and nuclear parts?

Equipartition theorem (thermodynamics):

The time-averaged kinetic energy in a degree of freedom only depends on the temperature.

$$\begin{aligned} E_{\text{kin},n} &\approx E_{\text{kin},e} \\ \Rightarrow m_n v_n^2 &\approx m_e v_e^2 \\ \Rightarrow \frac{v_e}{v_n} &\approx \sqrt{\frac{m_n}{m_e}} & \frac{m_n}{m_e} &\approx 1800 \end{aligned}$$

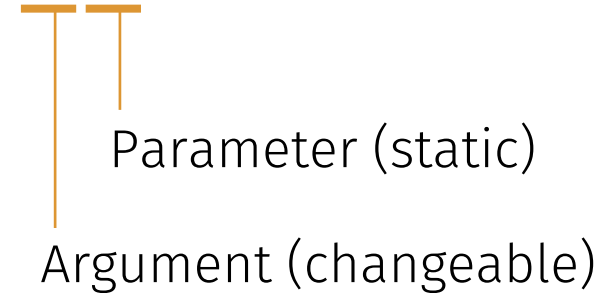
Separation: slow nuclei and fast electrons live on different time scales.

Approximation: Hamiltonians and wave functions of the two are separable by time scales.

$$\hat{H}(\mathbf{r}_i, \mathbf{R}_I) \equiv \hat{H}_e(\mathbf{r}_i | \mathbf{R}_I) + \hat{H}_n(\mathbf{R}_I)$$

$$\Psi(\mathbf{r}_i, \mathbf{R}_I) \equiv \Psi_e(\mathbf{r}_i | \mathbf{R}_I) \Psi_n(\mathbf{R}_I)$$

$$f(x|b) = f_b(x) \equiv \log_b x$$



1. Consider nuclei fixed (and potentially classically).
2. Solve Schrödinger equation for electrons only.

$$\hat{H}_e(\mathbf{r}_i | \mathbf{R}_I) \Psi(\mathbf{r}_i | \mathbf{R}_I) = E \Psi(\mathbf{r}_i | \mathbf{R}_I)$$

System defines molecular Hamiltonian \hat{H}

$$\hat{H} = \hat{T} + \hat{V} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{ext}$$

$$= - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2$$

Kinetic energy of the electrons

$$- \sum_{i,j} \frac{Z_i e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{r}_j|}$$

Coulomb interaction electrons-nuclei

$$+ \sum_{i,j>i} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

Coulomb interaction electrons-electrons

$$+ \sum_{i,j>i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|}$$

Coulomb interaction nuclei-nuclei

Wave function

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$$

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$$

Impractical:

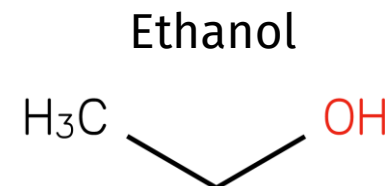
- $3n$ dimensions for n electrons
- Almost always no closed form expression
- Numerical solution: discretisation in basis functions

Costly: $[s] \simeq \exp(2n)/10^4$ $[\text{MB}] \simeq \exp(n)/2$

Methane
 CH_4



N_2
 $\text{N} \equiv \text{N}$



1. In principle, properties could be done arbitrarily accurately, but that is too expensive.
2. Two core approximations:
 - Electrons feel static nuclei and nuclei feel averaged electrons. (“Born-Oppenheimer”)
 - Finite accuracy of wave function / numerics. (“Discretisation”)
3. Mental picture: static atoms and electron density.