The Molecular Hamiltonian, Atomic Units, and the Born–Oppenheimer Approximation

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Feedback

Midterm: Tuesday, March 4, 10:00am-11:15am

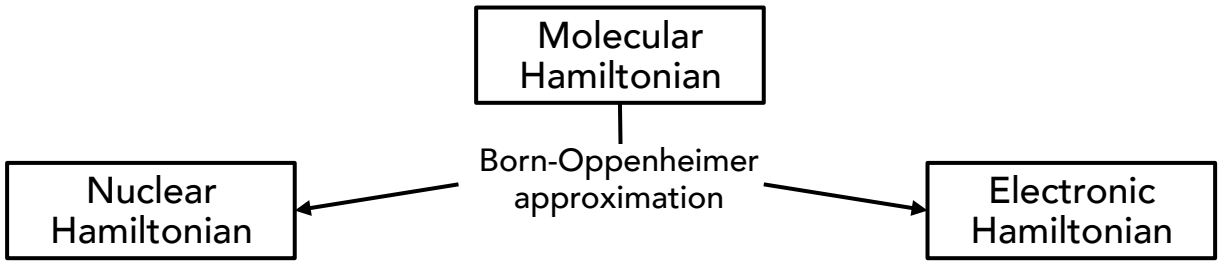
Final: Friday, May 2, 8:00am-10:30am

Timeline of the project

- **Pick a project**
- **Running computations in ORCA**
- **Final presentations**

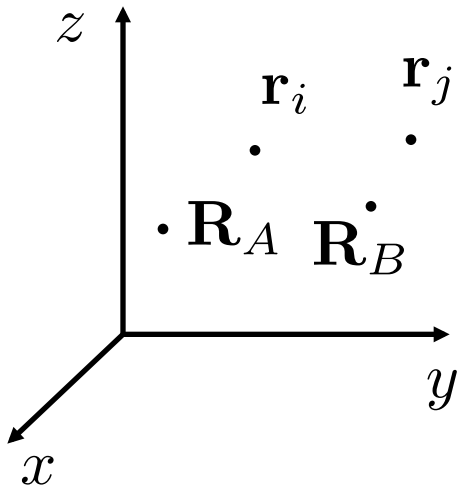
Python

$$\langle \phi_i | \phi_j \rangle = S_{ij} \qquad |\phi_i\rangle \langle \phi_j| = ?$$


Molecular Hamiltonian
Born-Oppenheimer approximation
Nuclear Hamiltonian
Electronic Hamiltonian

Molecular Hamiltonian

	Number	Indices	Position	Mass	Charge
Electrons	N	i, j	$\mathbf{r}_i$	m_e	$-\mathrm{e}$
Nuclei	M	A, B	$\mathbf{R}_A$	M_A	$+ eZ_A$



$$\hat{H} = \hat{T}_\mathrm{e} + \hat{T}_\mathrm{N} + \hat{V}_\mathrm{ee} + \hat{V}_\mathrm{NN} + \hat{V}_\mathrm{eN}$$

$$\hat{T}_\mathrm{e} = -\sum_i^N \frac{\hbar^2}{2m_\mathrm{e}} \nabla_i^2$$

$$\hat{T}_\mathrm{N} = -\sum_A^M \frac{\hbar^2}{2M_A} \nabla_A^2$$

$$\hat{V}_\mathrm{ee} = \sum_{i<j}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{V}_\mathrm{NN} = \sum_{A<B}^M \frac{e^2 Z_A Z_B}{4\pi\epsilon_0 |\mathbf{R}_A - \mathbf{R}_B|}$$

$$\hat{V}_\mathrm{eN} = -\sum_i^N \sum_A^M \frac{e^2 Z_A}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_A|}$$

Atomic Units

To simplify computation we adopt *atomic units*, which are defined by

- Unit of length: the bohr (a_0 = 0.52917721 Å)
- Unit of mass: the mass of the electron (m_e)
- Unit of charge: the magnitude of the charge of the electron
- Unit of energy is the Hartree (E_h):
  - = 27.21138 eV
  - = 627.5095 kcal mol^{-1}
  - = 219474.6 cm^{-1}
  - = 3.157 x 10^5 K

With these definitions, the unit of action is ħ and $4\pi\varepsilon_0 = 1$.

$$\hat{H} = -\frac{1}{2m_\mathrm{e}}\sum_i^N \nabla_i^2 - \sum_A^M \frac{1}{2M_A}\nabla_A^2 + \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{A<B}^M \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_i^N \sum_A^M \frac{1}{|\mathbf{r}_i - \mathbf{R}_A|}$$

Born-Oppenheimer approximation

The electronic Hamiltonian

$$\hat{H}_{\mathrm{e}}(\mathbf{R}) = \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{NN}} + \hat{V}_{\mathrm{eN}},$$

$$\hat{H}_{\mathrm{e}}\Psi_n(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\Psi_n(\mathbf{r};\mathbf{R})$$

The exact wave function

$$\Phi(\mathbf{r},\mathbf{R}) = \sum_n \Psi_n(\mathbf{r};\mathbf{R})\chi_n(\mathbf{R})$$

$$\hat{H}\Phi(\mathbf{r},\mathbf{R}) = \mathcal{E}\Phi(\mathbf{r},\mathbf{R})$$

Born-Oppenheimer approximation

Insert into the Schrödinger equation and project on the left with Ψ_n.
After integrating over the electronic degrees of freedom:

$$\left[\hat{T}_{\mathrm{N}} + E_n(\mathbf{R})\right] \chi_n(\mathbf{R})$$
$$- \sum_m \sum_A^M \frac{1}{M_A} \langle \Psi_n | \nabla_A | \Psi_m \rangle \cdot \nabla_A \chi_m(\mathbf{R})$$
$$- \sum_m \sum_A^M \frac{1}{2M_A} \langle \Psi_n | \nabla_A^2 | \Psi_m \rangle \chi_m(\mathbf{R})$$
$$= \mathcal{E} \chi_n(\mathbf{R})$$

Nonadiabatic couplings (vibronic couplings)

$$\mathbf{d}_{nm}^A(\mathbf{R}) = -\frac{1}{M_A} \langle \Psi_n | \nabla_A | \Psi_m \rangle \qquad D_{nm}^A(\mathbf{R}) = -\frac{1}{M_A} \langle \Psi_n | \nabla_A^2 | \Psi_m \rangle$$