Ab Initio Molecular Dynamics: A Virtual Laboratory

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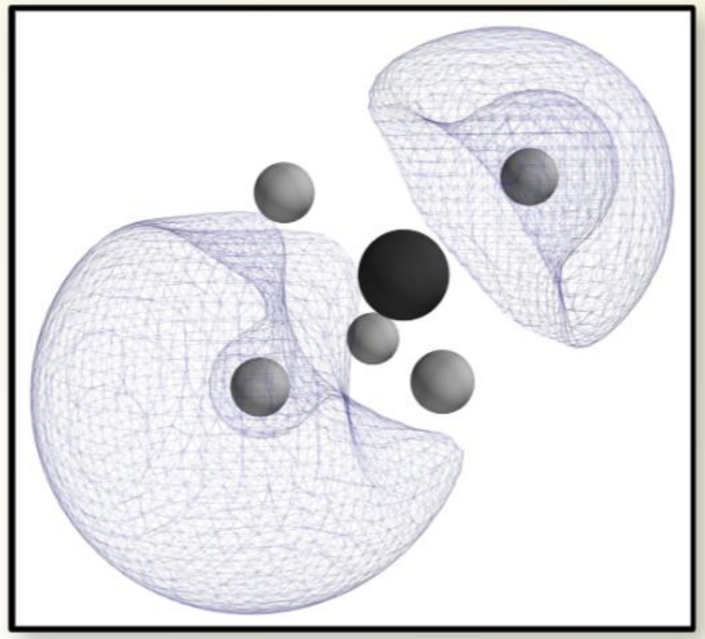
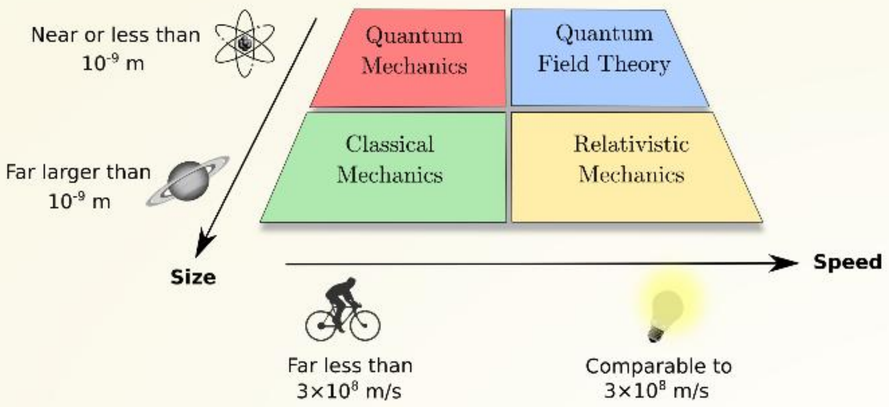




Classical Mechanics

Newton's equation:

$$\mathbf{F} = m\mathbf{a}$$

N-body problem:

$$X_i(t), \quad i = 1, 2, \ldots, N$$

Quantum Mechanics

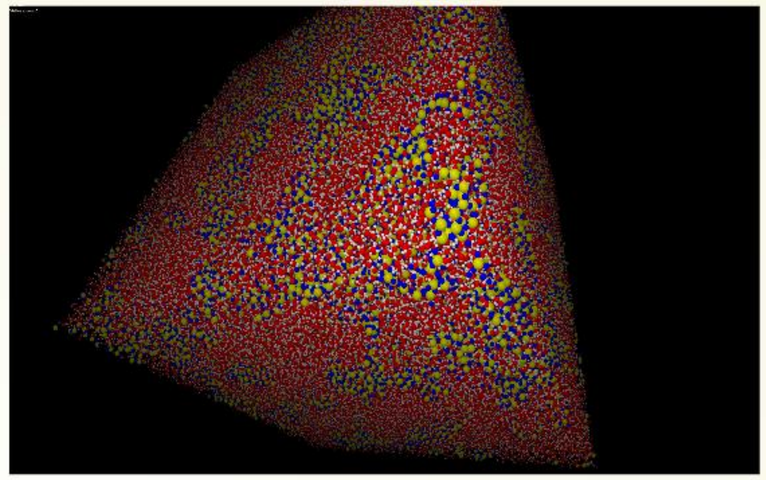
Schrödinger equation:

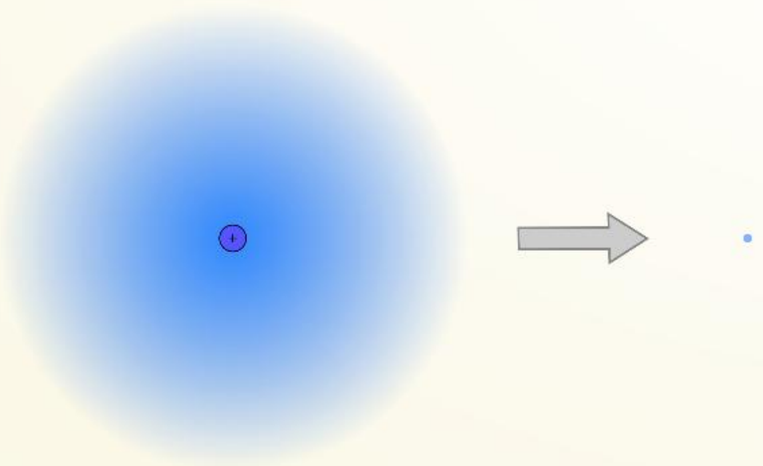
$$i\hbar\frac{\partial}{\partial t}\Psi = \mathcal{H}\Psi$$

N-body problem:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N, t)$$

Molecular Dynamics





$$\mathbf{F}_i = m\mathbf{a}_i$$

Molecular Dynamics:

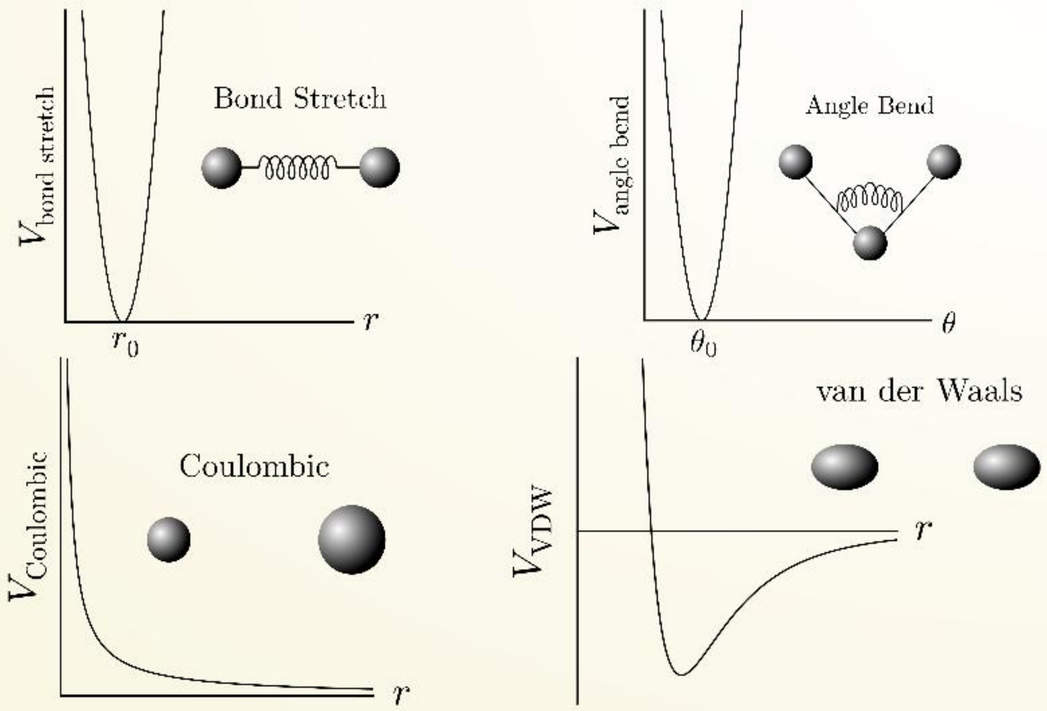
Laws of Interaction

Potential:

$$V = \sum_{k}^{N} V_1(\mathbf{R}_k) + \sum_{k<l}^{N} V_2(\mathbf{R}_k, \mathbf{R}_l) + \sum_{k<l<m}^{N} V_3(\mathbf{R}_k, \mathbf{R}_l, \mathbf{R}_m) + \dots$$

Force:

$$\mathbf{F} = -\nabla V$$



Molecular Dynamics:

Limitations:

Quantum effects
Challenging task

Schrödinger Equation

$$i\hbar\frac{\partial}{\partial t}\Psi = \mathcal{H}\Psi$$

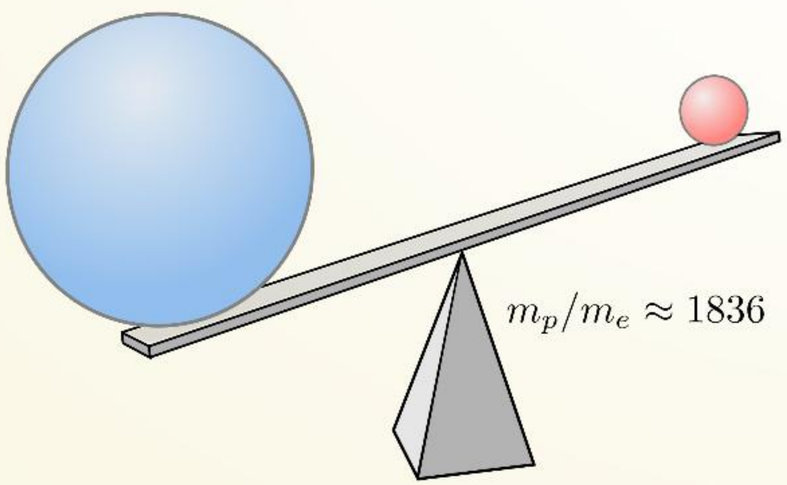
Hamiltonian

$$\mathcal{H} = -\sum_{i}^{N_c}\frac{\nabla_i^2}{2} - \sum_{n}^{N_n}\frac{\nabla_n^2}{2M_n} - \sum_{n}^{N_n}\sum_{i}^{N_c}\frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + \sum_{i<j}^{N_c}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n<m}^{N_n}\frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|}$$

Wave Function

$$\Psi\left(\{\mathbf{R}_n\}, \{\mathbf{r}_i\}, t\right)$$

Born-Oppenheimer Approximation



Separable wave function:

$$\Psi(\{\mathbf{R}_n\},\{\mathbf{r}_i\},t) \quad \Rightarrow \quad \begin{matrix}\chi(\{\mathbf{R}_n\},t)\\ \Psi_{\mathrm{el}}(\{\mathbf{r}_i\};\{\mathbf{R}_n\})\end{matrix}$$

Electronic Schrödinger equation:

$$\left(-\sum_i^{N_e}\frac{\nabla_i^2}{2}+V_{\mathrm{Ne}}(\mathbf{r},\mathbf{R})\right)\Psi_{\mathrm{el}}=E_{\mathrm{Ne}}(\mathbf{R})\Psi_{\mathrm{el}}$$

Nuclear Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\chi=\left(-\sum_n^{N_n}\frac{\nabla_n^2}{2M_n}+E_{\mathrm{Ne}}(\mathbf{R})\right)\chi$$

Born-Oppenheimer Molecular Dynamics

Electrons as quantum particles:

$$\underbrace{\left(-\sum_{i}^{N_e}\frac{\nabla_i^2}{2}+V_{\mathrm{Ne}}(\mathbf{r},\mathbf{R})\right)}_{\mathcal{H}_{\mathrm{Ne}}}\Psi_{\mathrm{el}}=E_{\mathrm{Ne}}(\mathbf{R})\Psi_{\mathrm{el}}$$

Nuclei as classical point particles:

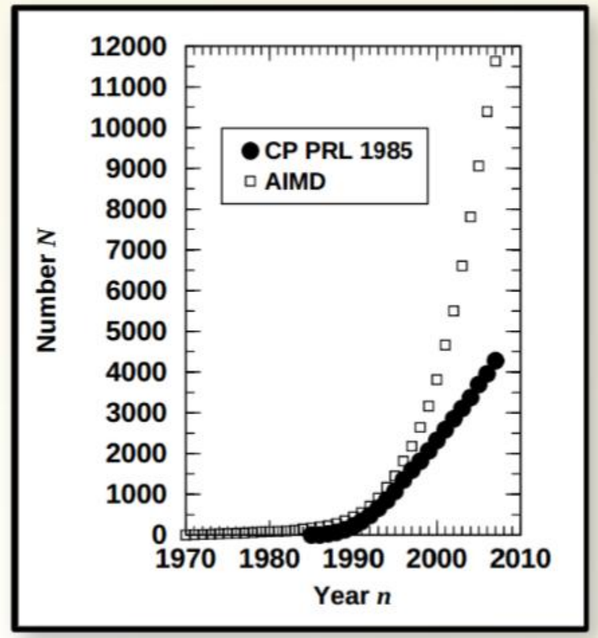
$$M_n\ddot{\mathbf{R}}_n=-\nabla_n\min_{\Psi_{\mathrm{el},0}}\left\{\langle\Psi_{\mathrm{el},0}|\mathcal{H}_{\mathrm{Ne}}|\Psi_{\mathrm{el},0}\rangle\right\}$$

$$V_{\mathrm{CM}}=\sum_{k}^{N}V_1(\mathbf{R}_k)+\sum_{k<l}^{N}V_2(\mathbf{R}_k,\mathbf{R}_l)+\sum_{k<l<m}^{N}V_3(\mathbf{R}_k,\mathbf{R}_l,\mathbf{R}_m)+\ldots$$

$$\Downarrow$$

$$V_{\mathrm{BOMD}}=-\nabla_n\min_{\Psi_{\mathrm{el},0}}\left\{\langle\Psi_{\mathrm{el},0}|\mathcal{H}_{\mathrm{Ne}}|\Psi_{\mathrm{el},0}\rangle\right\}$$

Ab Initio Molecular Dynamics



Born-Oppenheimer Molecular Dynamics

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$$V_{\mathrm{CM}}=\sum_k^N V_1(\mathbf{R}_k)+\sum_{k<l}^N V_2(\mathbf{R}_k,\mathbf{R}_l)+\sum_{k<l<m}^N V_3(\mathbf{R}_k,\mathbf{R}_l,\mathbf{R}_m)+\ldots$$

$$\Downarrow$$

$$V_{\mathrm{BOMD}}=-\nabla_n\min_{\Psi_{\mathrm{el},0}}\left\{\langle\Psi_{\mathrm{el},0}|\mathcal{H}_{\mathrm{Ne}}|\Psi_{\mathrm{el},0}\rangle\right\}$$

Electronic Schrödinger Equation:

$$\left(-\sum_{i}^{N_e}\frac{\nabla_i^2}{2}+V(\mathbf{r},\mathbf{R})\right)\Psi=E\Psi$$

Variational Principle:

$$E=\langle\Psi|\mathcal{H}|\Psi\rangle\geq\langle\Psi_0|\mathcal{H}|\Psi_0\rangle=E_0$$

Hartree-Fock

Slater Determinant

$$\Psi_0 \approx \Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{q}_1) & \psi_2(\mathbf{q}_1) & \cdots & \psi_{N_e}(\mathbf{q}_1) \\ \psi_1(\mathbf{q}_2) & \psi_2(\mathbf{q}_2) & \cdots & \psi_{N_e}(\mathbf{q}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{q}_{N_e}) & \psi_2(\mathbf{q}_{N_e}) & \cdots & \psi_{N_e}(\mathbf{q}_{N_e}) \end{vmatrix}$$

Pauli exclusion principle ✓
Electronic correlations ✗

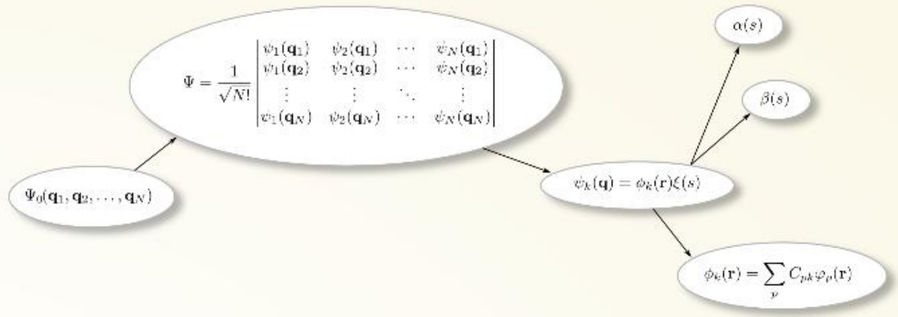
Hartree-Fock

Fock Operator

$$\mathcal{F} = -\frac{1}{2}\nabla^2 - \sum_{n=1}^{N_n} \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} + V^{\mathrm{HF}},$$

$$V^{\mathrm{HF}}\psi_k(\mathbf{q}) = \sum_l \left[\int \frac{\psi_l^*(\mathbf{q}')\psi_l(\mathbf{q}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{q}' \; \psi_k(\mathbf{q}) - \int \frac{\psi_l^*(\mathbf{q}')\psi_k(\mathbf{q}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{q}' \; \psi_l(\mathbf{q}) \right]$$

Spin Orbitals



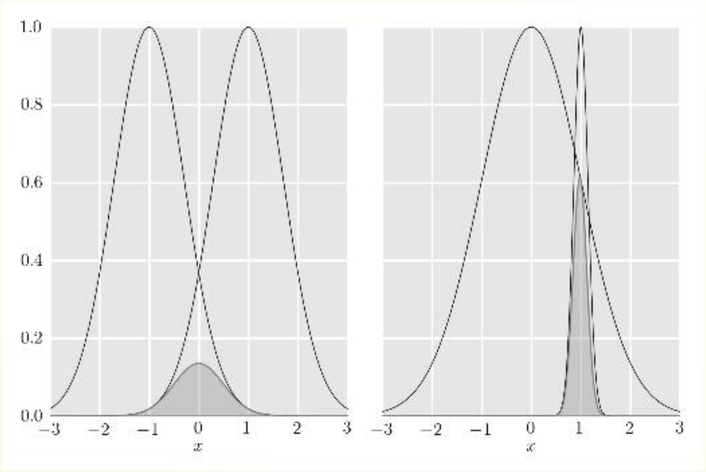
Which basis set to use?

$$\int \varphi_p^*(\mathbf{r}) O(\mathbf{r}) \varphi_q(\mathbf{r}) \, \mathrm{d}\mathbf{r}$$

$$\int \varphi_p^*(\mathbf{r}) \varphi_r^*(\mathbf{r}') \, \frac{1}{|\mathbf{r} - \mathbf{r}'|} \, \varphi_q(\mathbf{r}) \varphi_s(\mathbf{r}') \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$

Gaussian Type Orbitals

$$\varphi_{ijk}^{\mathrm{GTO}}(\mathbf{r}) = x^i y^j z^k \exp(-\alpha r^2)$$
$$= \varphi_i^{\mathrm{GTO}}(x)\varphi_j^{\mathrm{GTO}}(y)\varphi_k^{\mathrm{GTO}}(z),$$
$$\varphi_i^{\mathrm{GTO}}(x) = x^i \exp(-\alpha x^2)$$



McMurchie-Davidson Scheme

Recap

Ab Initio Molecular Dynamics

Electrons as quantum particles:

$$\underbrace{\left(-\sum_i^{N_e}\frac{\nabla_i^2}{2}+V(\mathbf{r},\mathbf{R})\right)}_{\mathcal{H}}\Psi=E\Psi$$

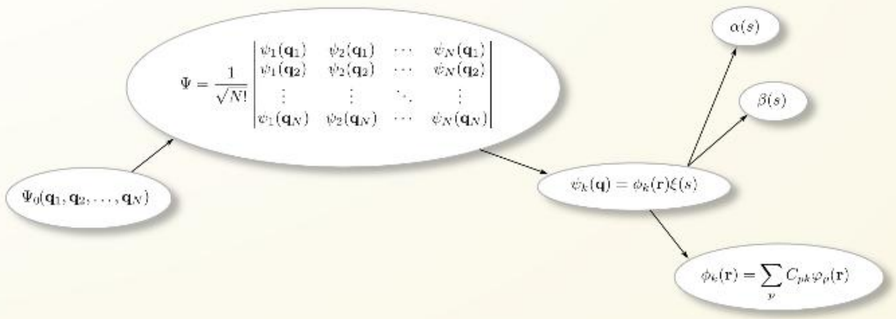
Nuclei as classical point particles:

$$M_n\ddot{\mathbf{R}}_n=-\nabla_n\min_{\Psi_0}\left\{\langle\Psi_0|\mathcal{H}|\Psi_0\rangle\right\}$$

Hartree-Fock

$$\Psi_0\approx\Psi=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(\mathbf{q}_1) & \psi_2(\mathbf{q}_1) & \cdots & \psi_{N_e}(\mathbf{q}_1)\\ \psi_1(\mathbf{q}_2) & \psi_2(\mathbf{q}_2) & \cdots & \psi_{N_e}(\mathbf{q}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \psi_1(\mathbf{q}_{N_e}) & \psi_2(\mathbf{q}_{N_e}) & \cdots & \psi_{N_e}(\mathbf{q}_{N_e})\end{vmatrix}$$

$$\mathcal{F}=-\frac{1}{2}\nabla^2-\sum_{n=1}^{N_n}\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}+V^{\mathrm{HF}}$$



Implementations

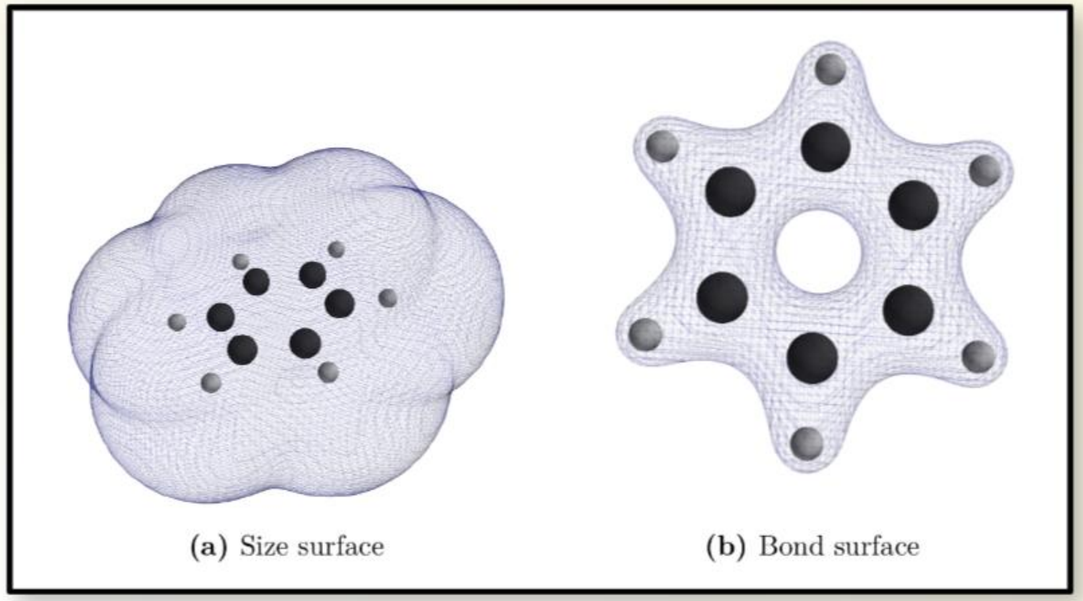
Hartree-Fock code based on McMurchie-Davidson scheme

Born-Oppenheimer molecular dynamics code based on Hartree-Fock calculations

Numerous verification tests:

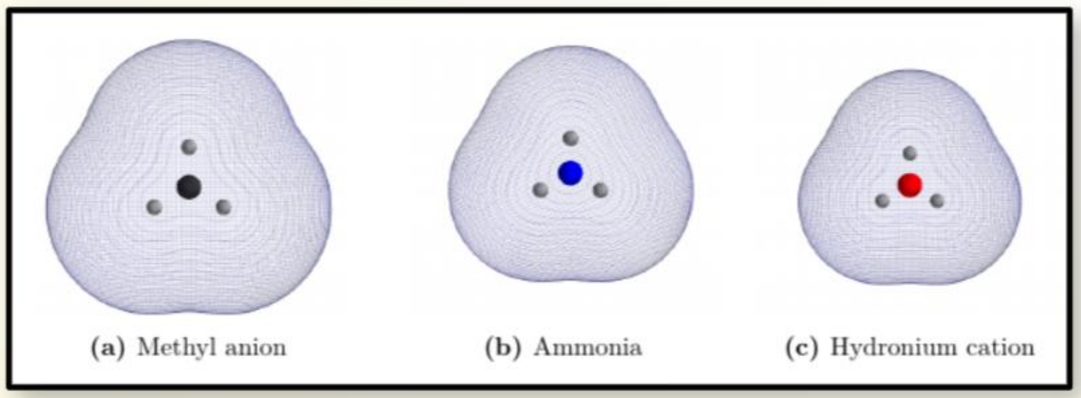
Unit tests, benchmarking

Graphical Models



(a) Size surface

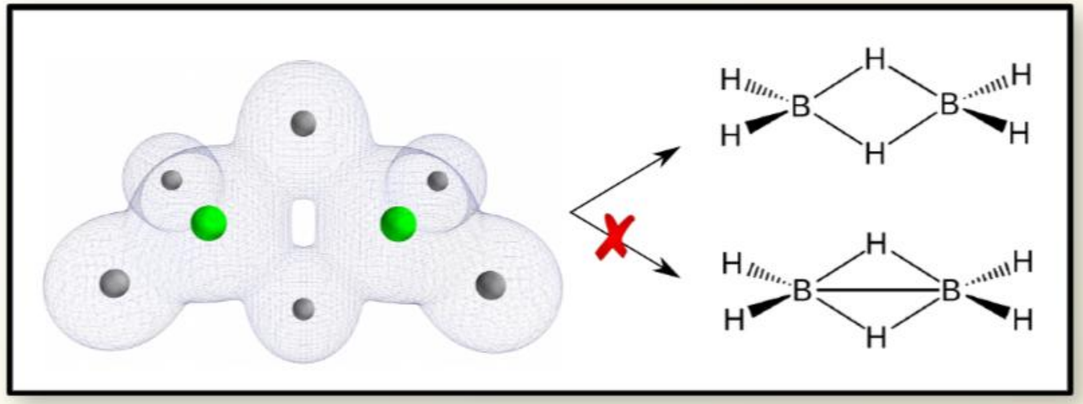
(b) Bond surface



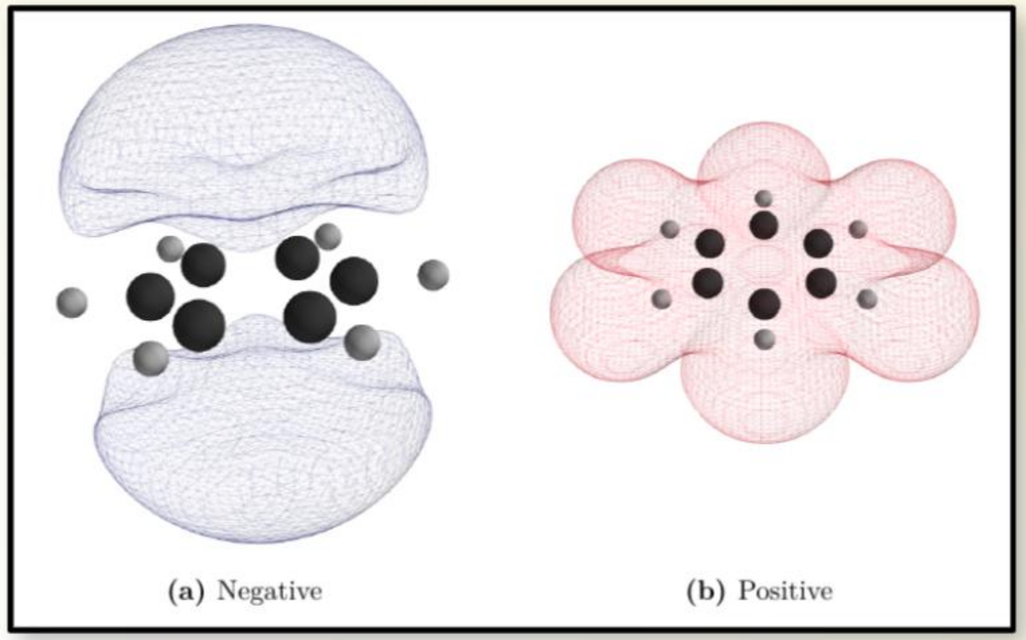
(a) Methyl anion

(b) Ammonia

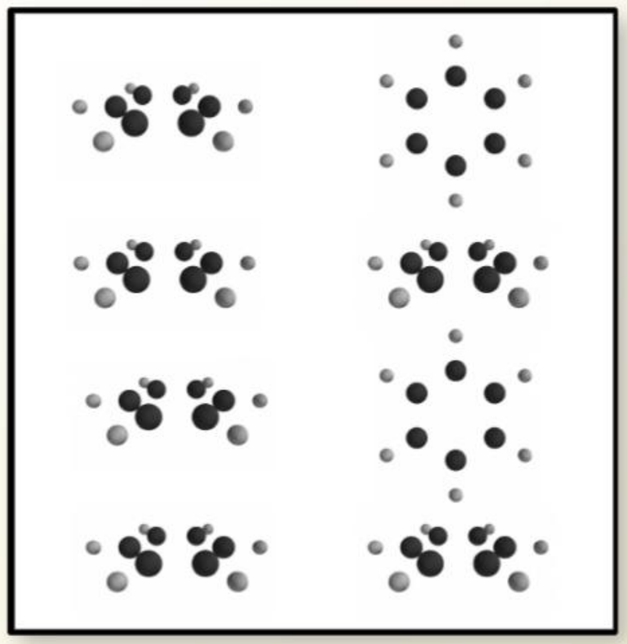
(c) Hydronium cation



Electrostatic Potential

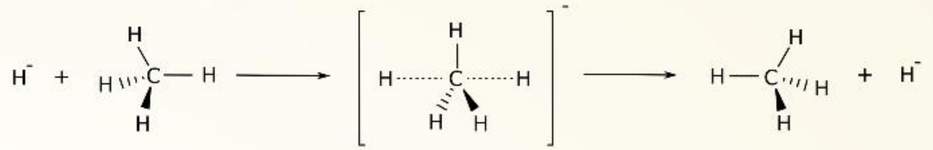


(a) Negative (b) Positive

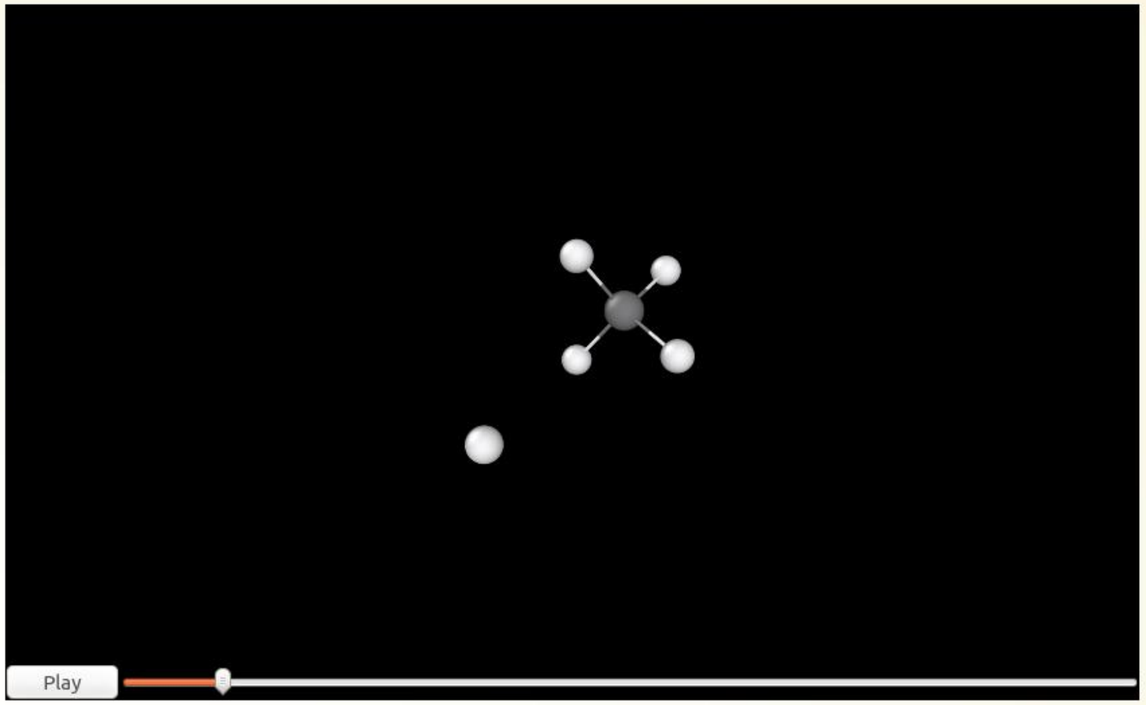


An application of Born-Oppenheimer molecular dynamics

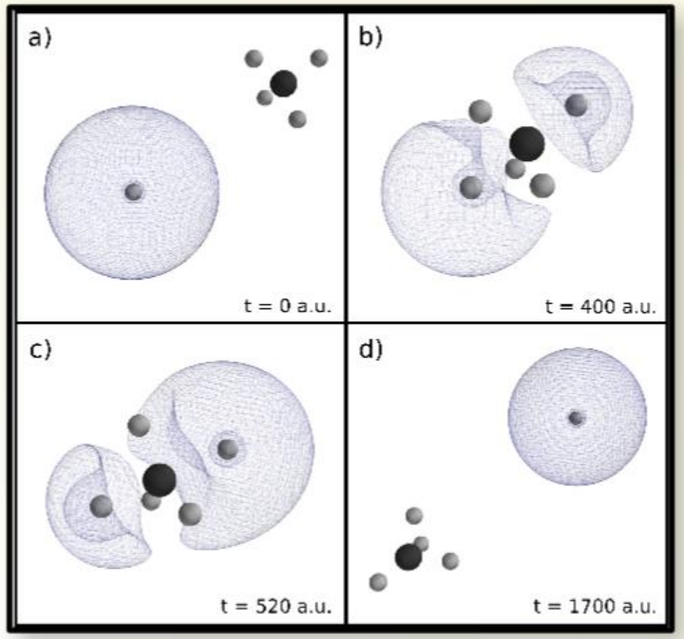
Nucleophilic Substitution Reaction



Nucleophilic Substitution Reaction



Negative Electrostatic Potential



Future Prospects

McMurchie-Davidson scheme
+
Car-Parrinello

McMurchie-Davidson scheme
+
Density functional theory

Hartree-Fock + Quantum Monte Carlo

Potential parameterizations