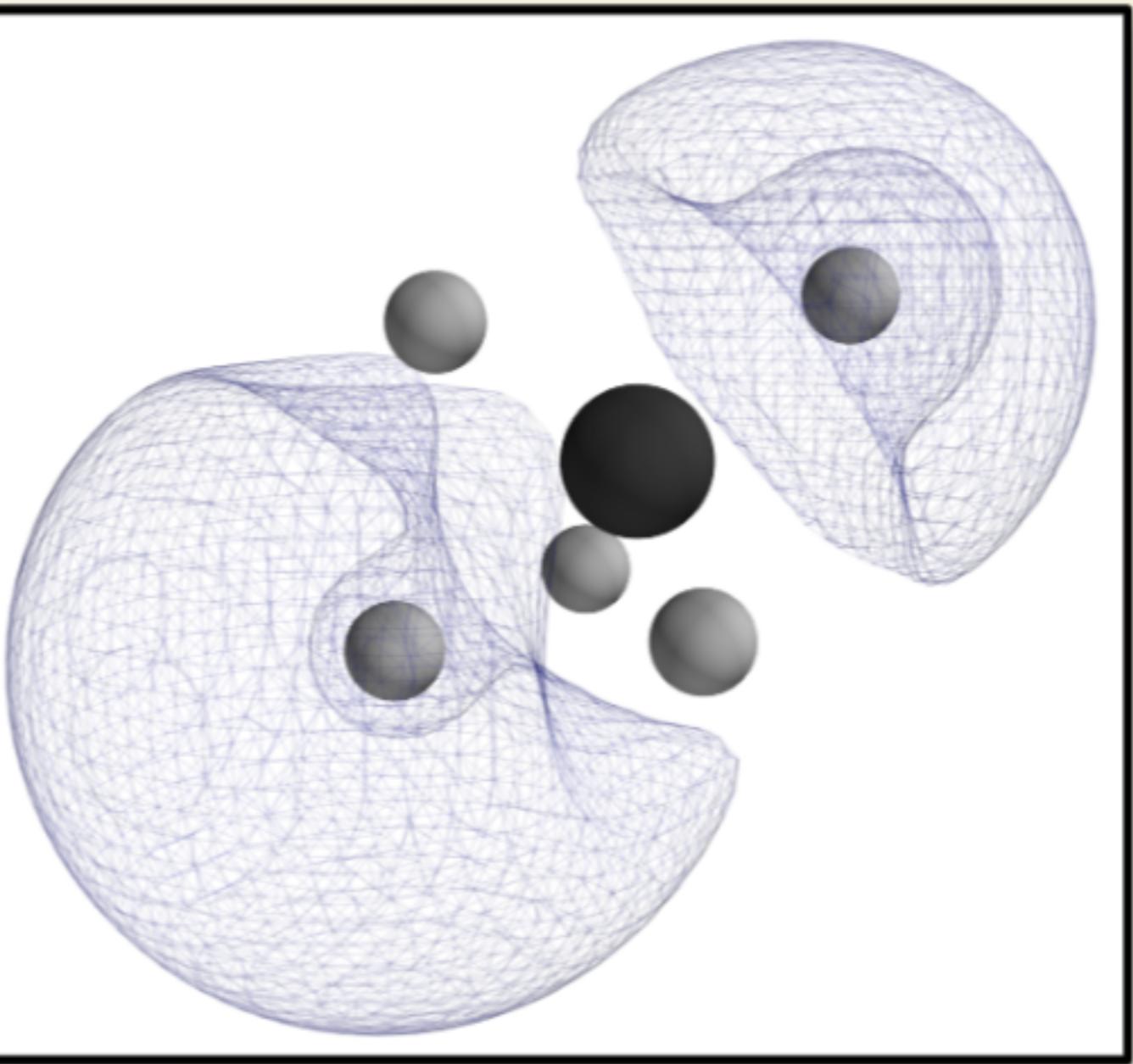
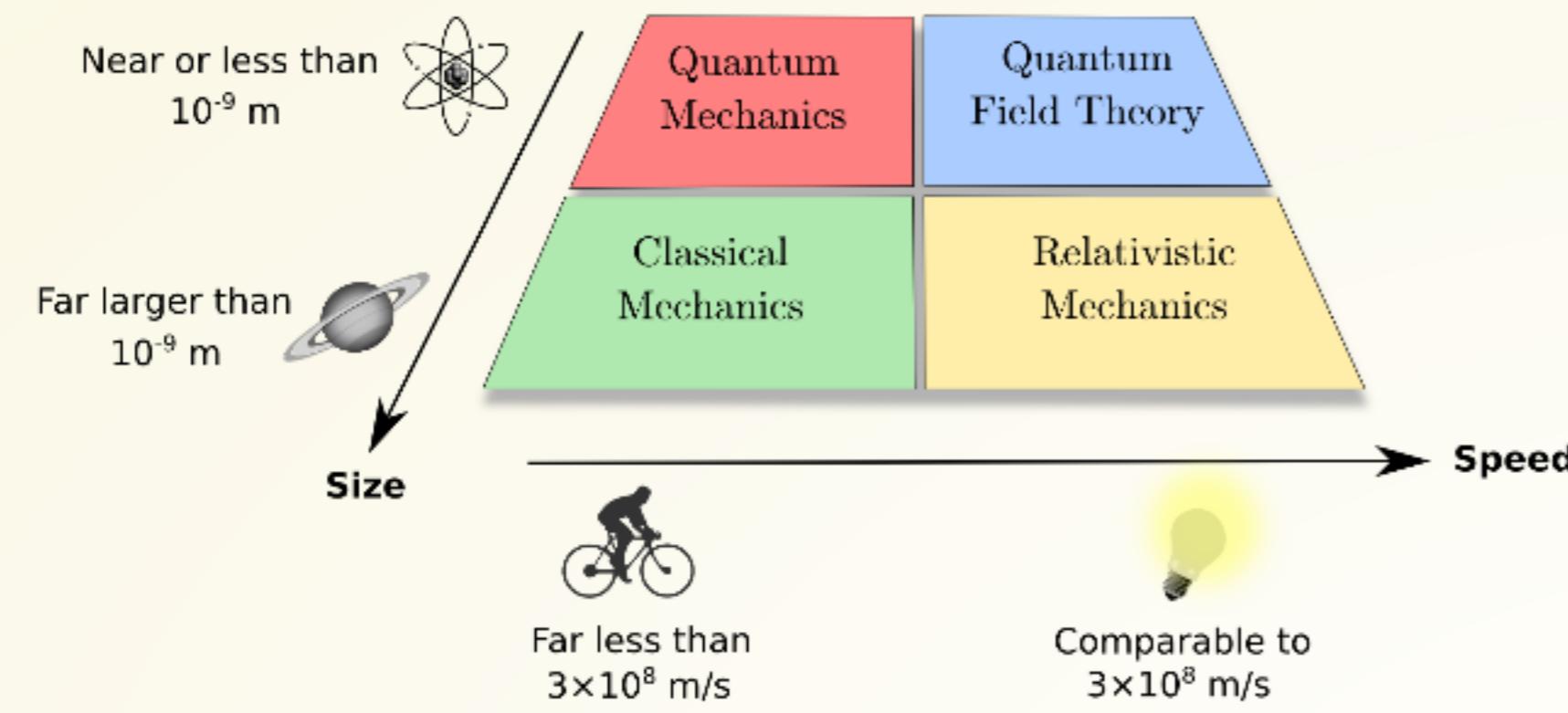


AB INITIO MOLECULAR DYNAMICS: A VIRTUAL LABORATORY

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June 2014





CLASSICAL MECHANICS

Newton's equation:

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

N-body problem:

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

QUANTUM MECHANICS

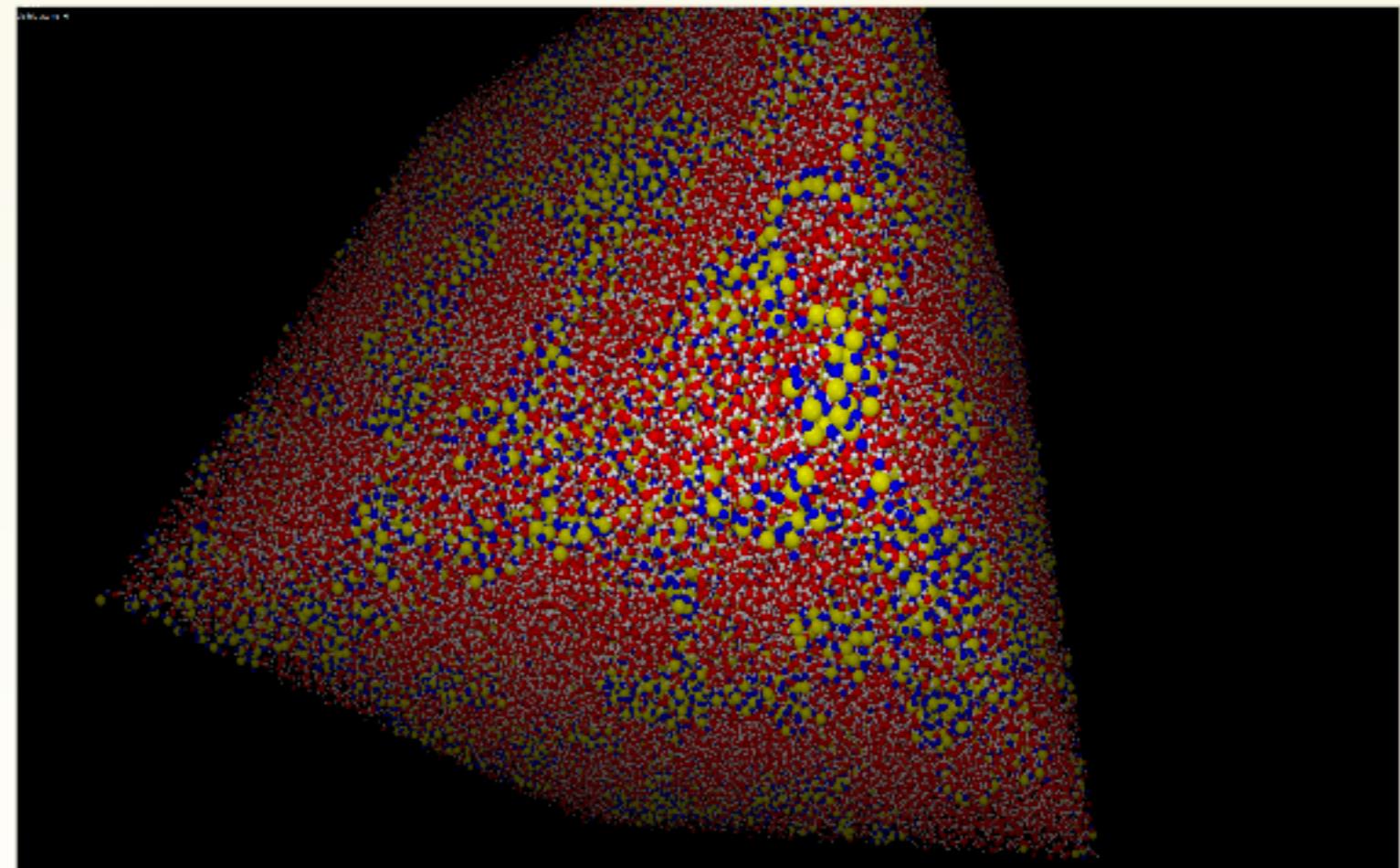
Schrödinger equation:

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

N-body problem:

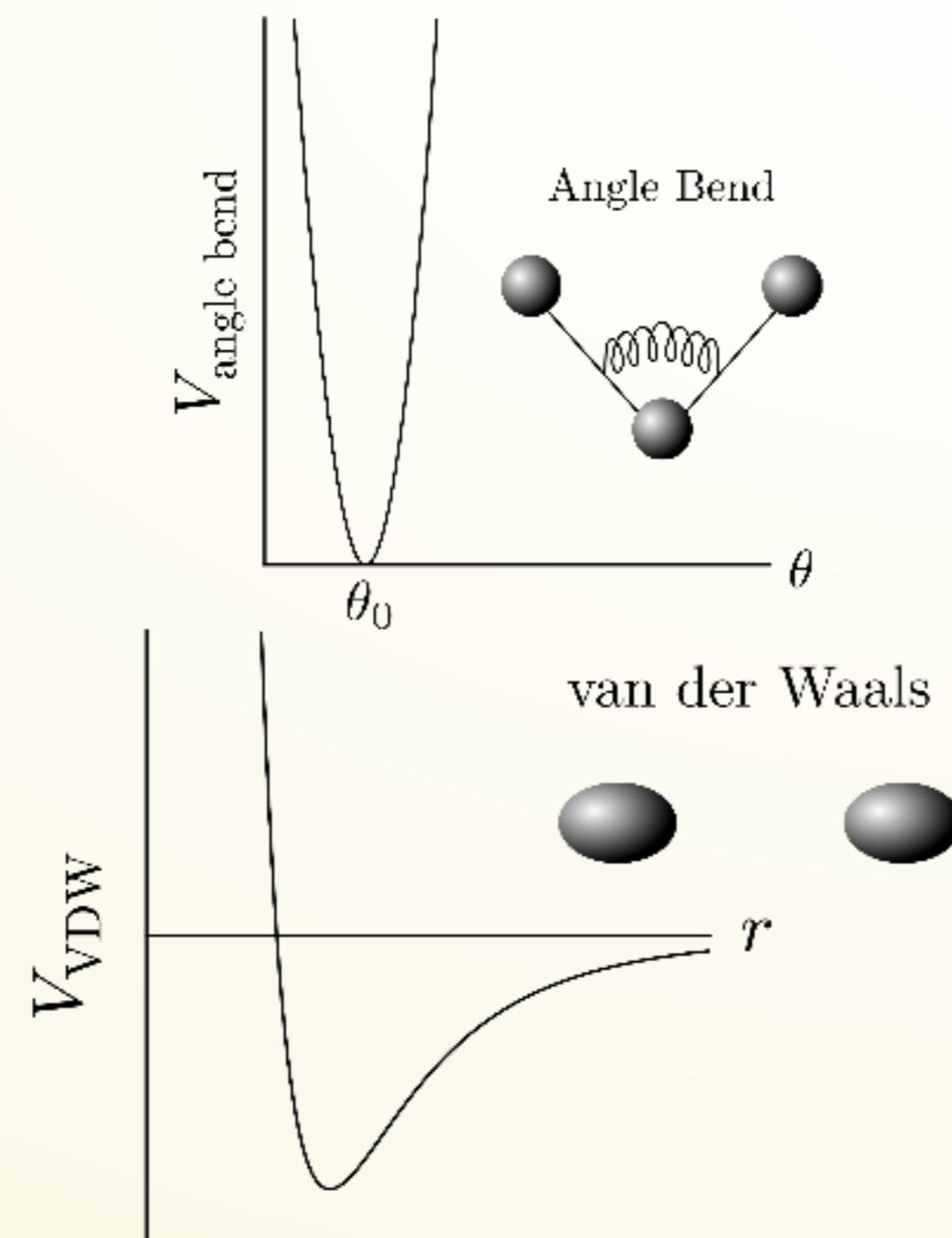
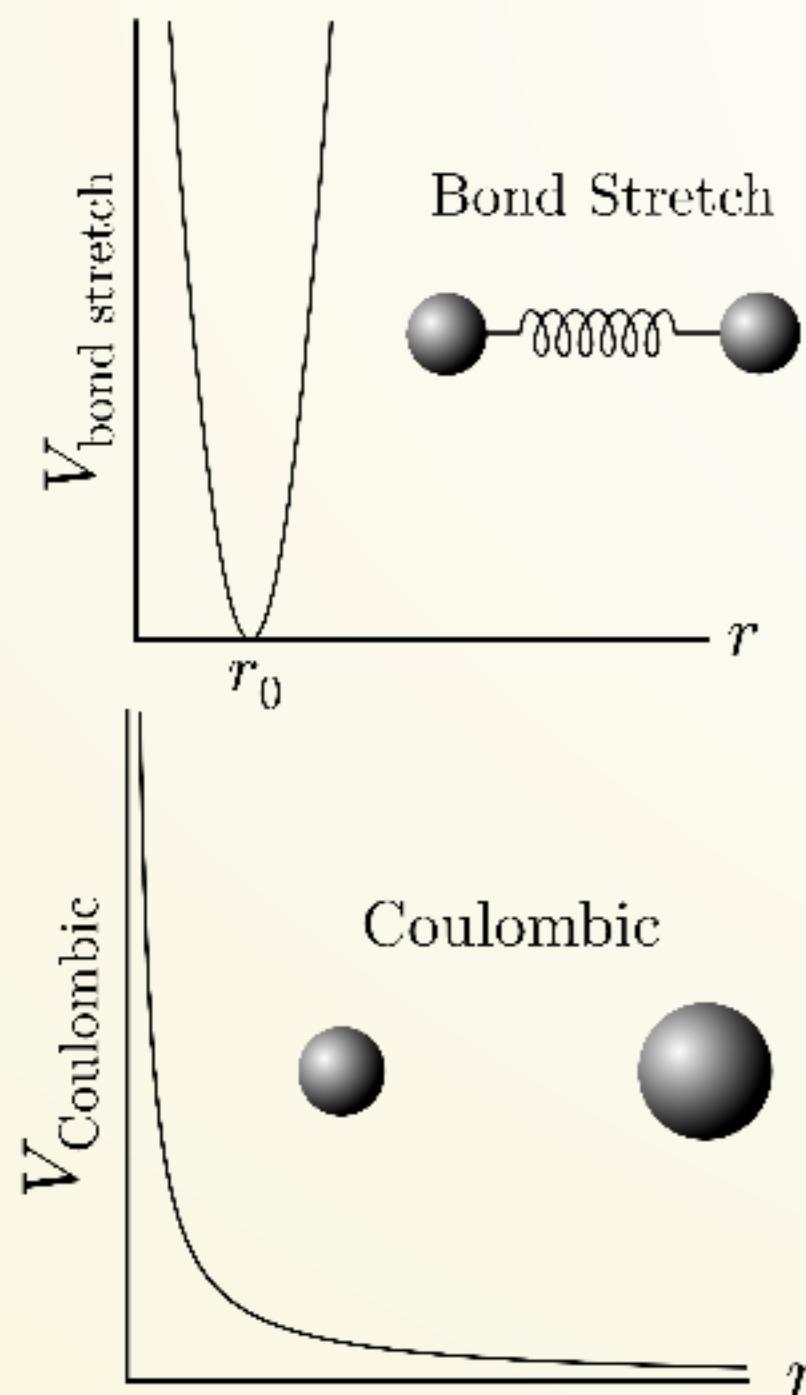
$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$$

MOLECULAR DYNAMICS



MOLECULAR DYNAMICS:

Laws of Interaction



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

FORCE:

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

MOLECULAR DYNAMICS:

Limitations:

Quantum effects
Challenging task

SCHRÖDINGER EQUATION

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

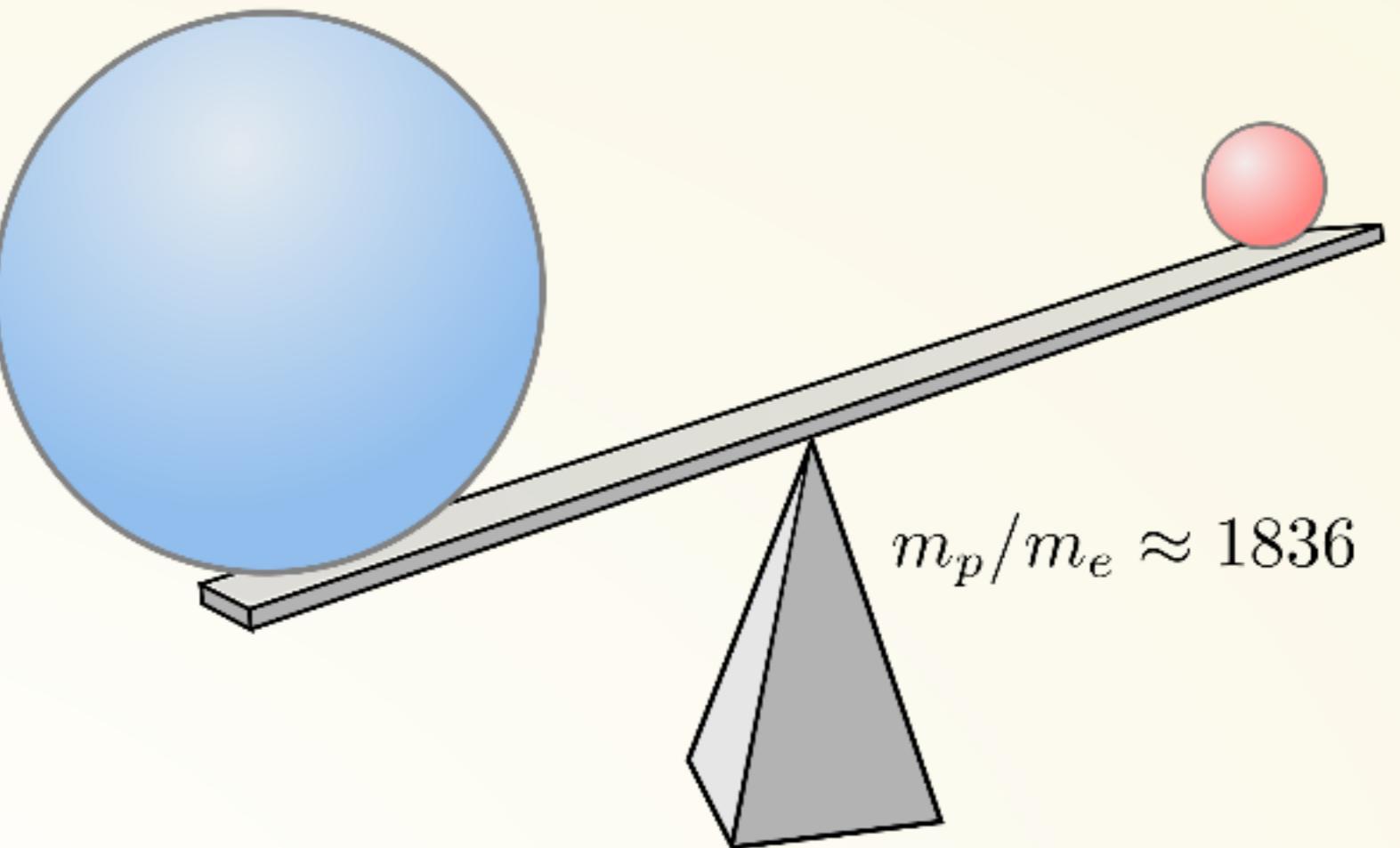
HAMILTONIAN

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

WAVE FUNCTION

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

BORN-OPPENHEIMER APPROXIMATION



SEPARABLE WAVE FUNCTION

BORN-OPPENHEIMER APPROXIMATION

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

ORIGINAL SCHRÖDINGER EQUATION

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

NUCLEAR & ELECTRONIC SCHRÖDINGER EQUATION

$$\begin{aligned} \left(-\sum_i^{N_e} \frac{\nabla_i^2}{2} + V_{\text{Ne}}(\mathbf{r}, \mathbf{R}) \right) \Psi_{\text{el}} &= E_{\text{Ne}}(\mathbf{R}) \Psi_{\text{el}} \\ \left(-\sum_n^{N_n} \frac{\nabla_n^2}{2M_n} + E_{\text{Ne}}(\mathbf{R}) \right) \chi &= i\hbar \frac{\partial}{\partial t} \chi \end{aligned}$$

BORN-OPPENHEIMER MOLECULAR DYNAMICS

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

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

↓

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

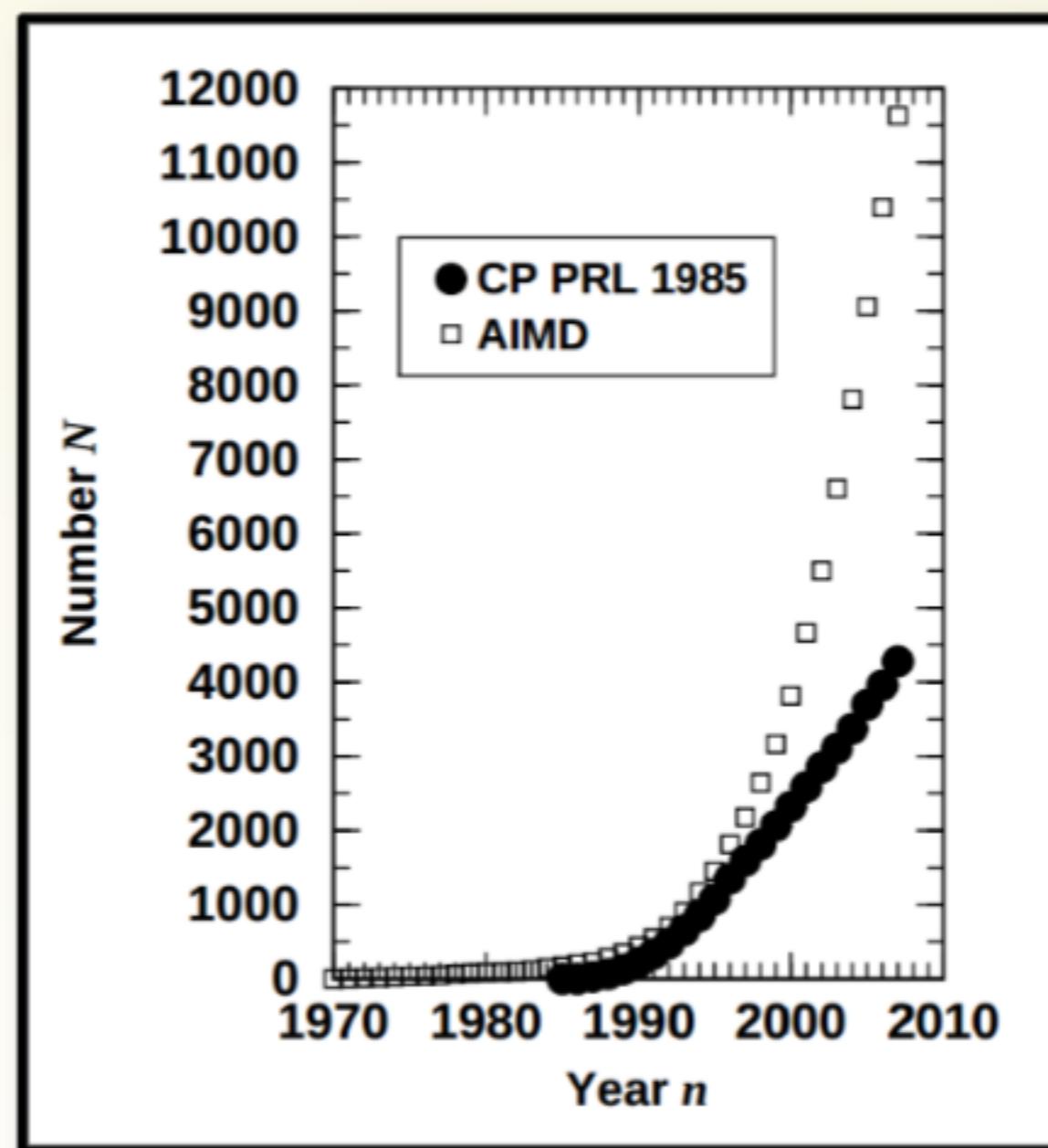
ELECTRONS AS QUANTUM
PARTICLES

NUCLEI AS CLASSICAL POINT
PARTICLES

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

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

AB INITIO MOLECULAR DYNAMICS



BORN-OPPENHEIMER MOLECULAR DYNAMICS

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

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ELECTRONS AS QUANTUM
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NUCLEI AS CLASSICAL POINT
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$$\underbrace{\left(-\sum_i^{N_e} \frac{\nabla_i^2}{2} + V_{\text{Ne}}(\mathbf{r}, \mathbf{R}) \right)}_{\mathcal{H}_{\text{Ne}}} \Psi_{\text{el}} = E_{\text{Ne}}(\mathbf{R}) \Psi_{\text{el}}$$

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

ELECTRONIC SCHRÖDINGER
EQUATION:

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

VARIATIONAL PRINCIPLE:

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

SLATER DETERMINANT

HARTREE-FOCK

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

Pauli exclusion principle ✓
Electronic correlations ✗

HARTREE-FOCK EQUATION

HARTREE-FOCK

$$\mathcal{F}\psi_k = \epsilon\psi_k$$

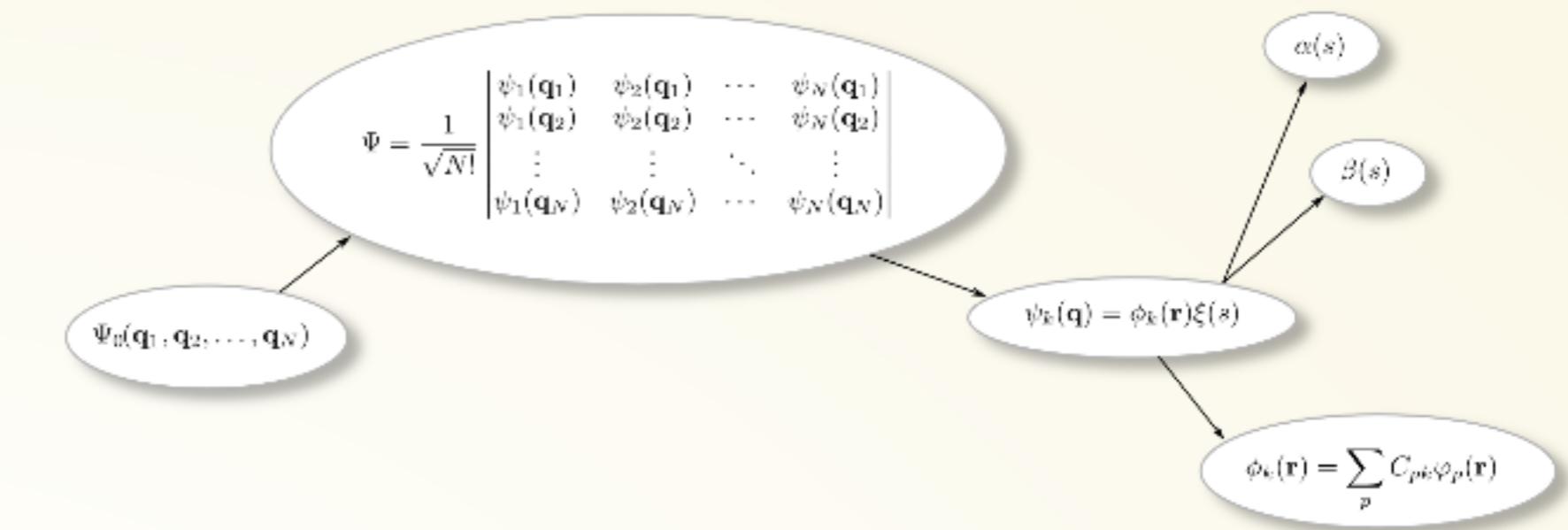
FOCK OPERATOR

HARTREE-FOCK POTENTIAL

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

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

SPIN ORBITALS



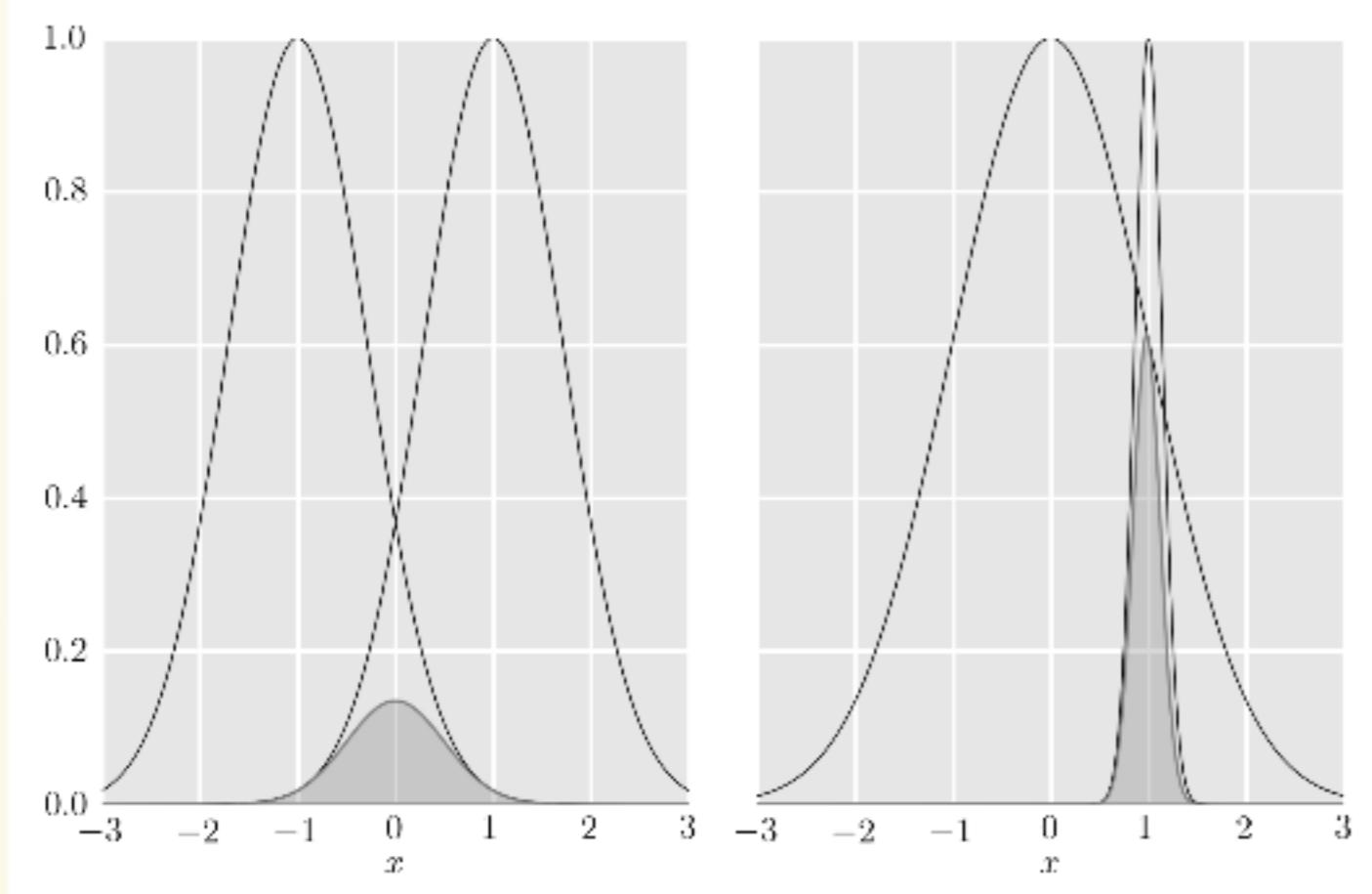
$$\int \varphi_p^*(\mathbf{r}) O(\mathbf{r}) \varphi_q(\mathbf{r}) \, d\mathbf{r}$$

Which basis set to use?

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

GAUSSIAN TYPE ORBITALS

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



McMURCHIE-DAVIDSON SCHEME

AB INITIO MOLECULAR DYNAMICS

Recap

Electrons as quantum particles:

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

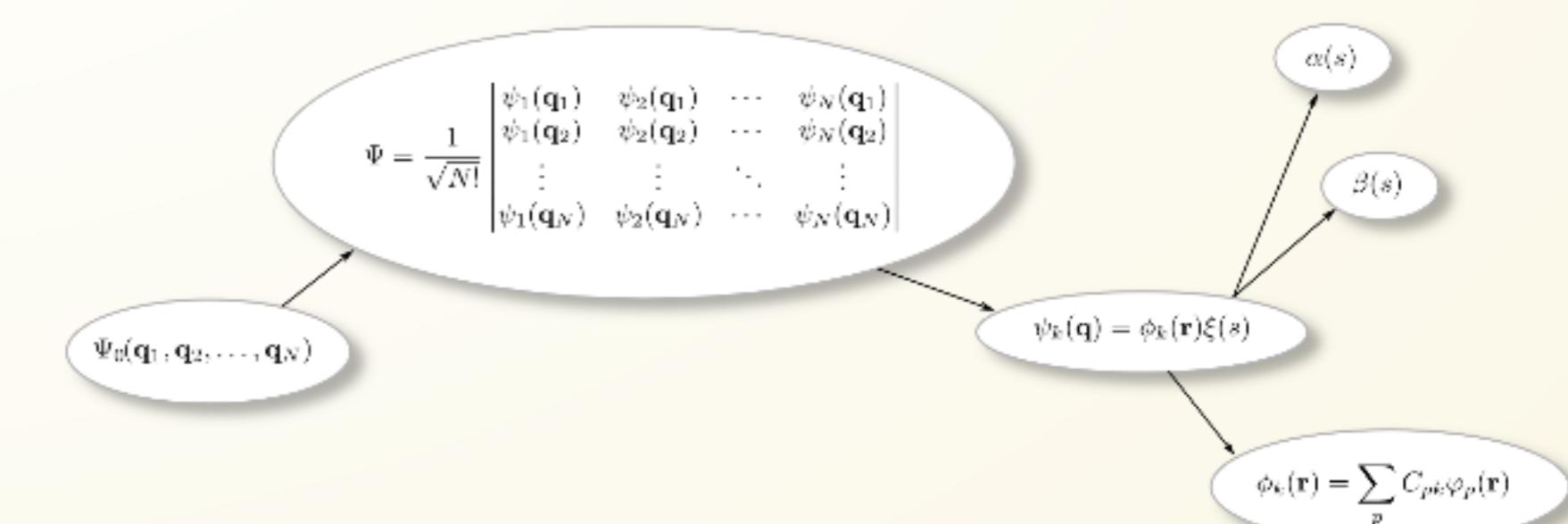
Nuclei as classical point particles:

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

HARTREE-FOCK

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

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



IMPLEMENTATIONS

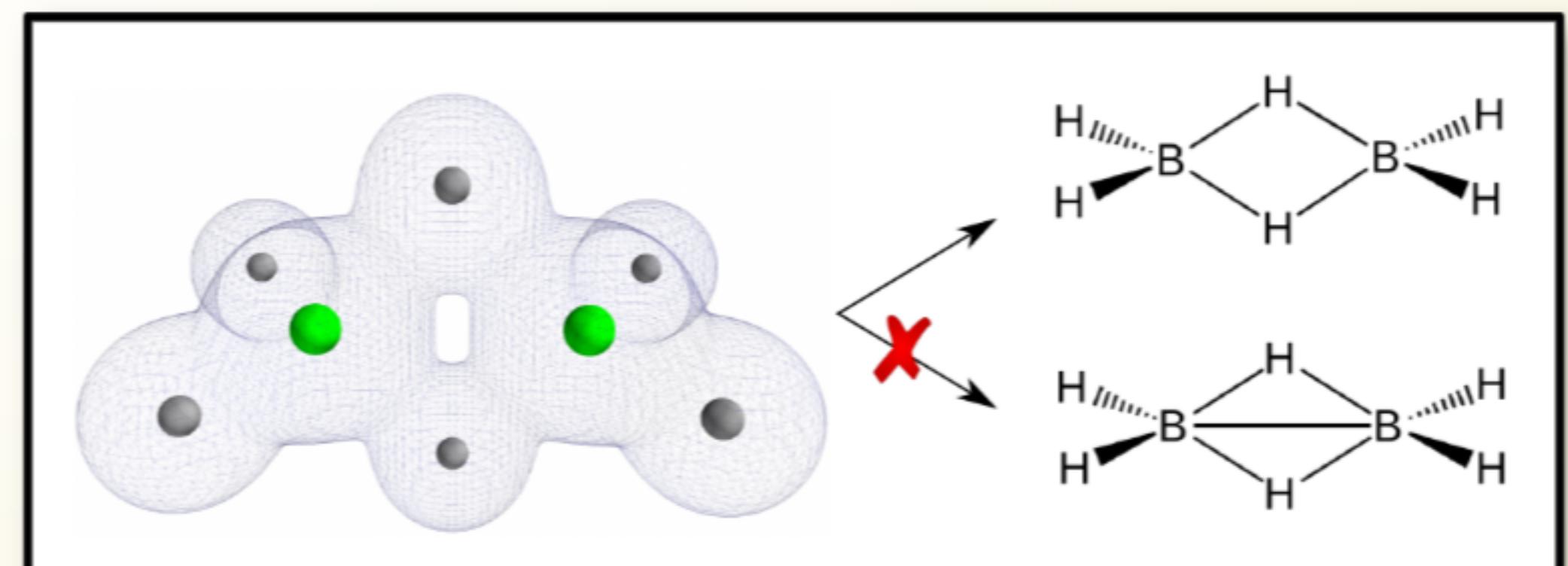
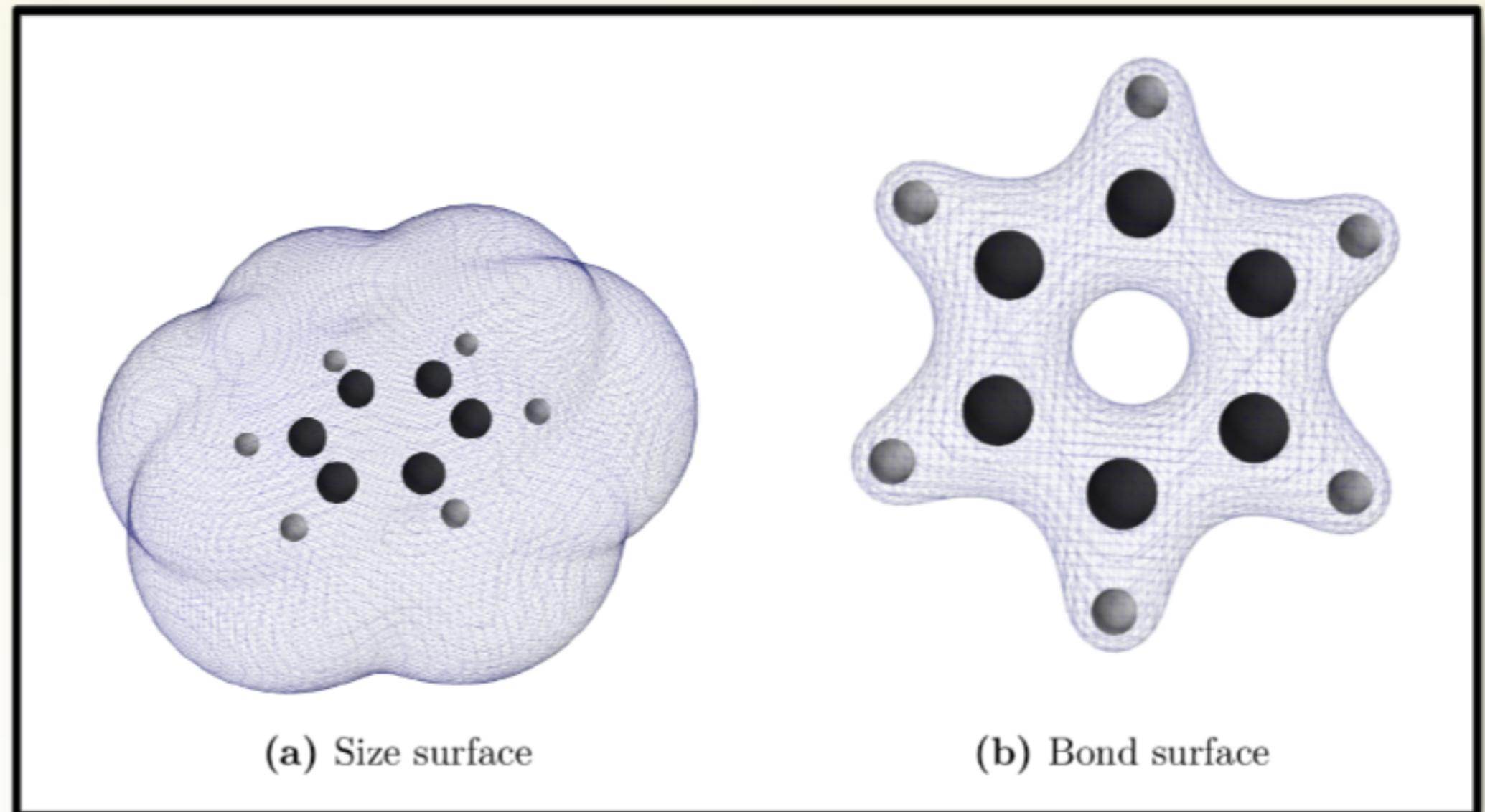
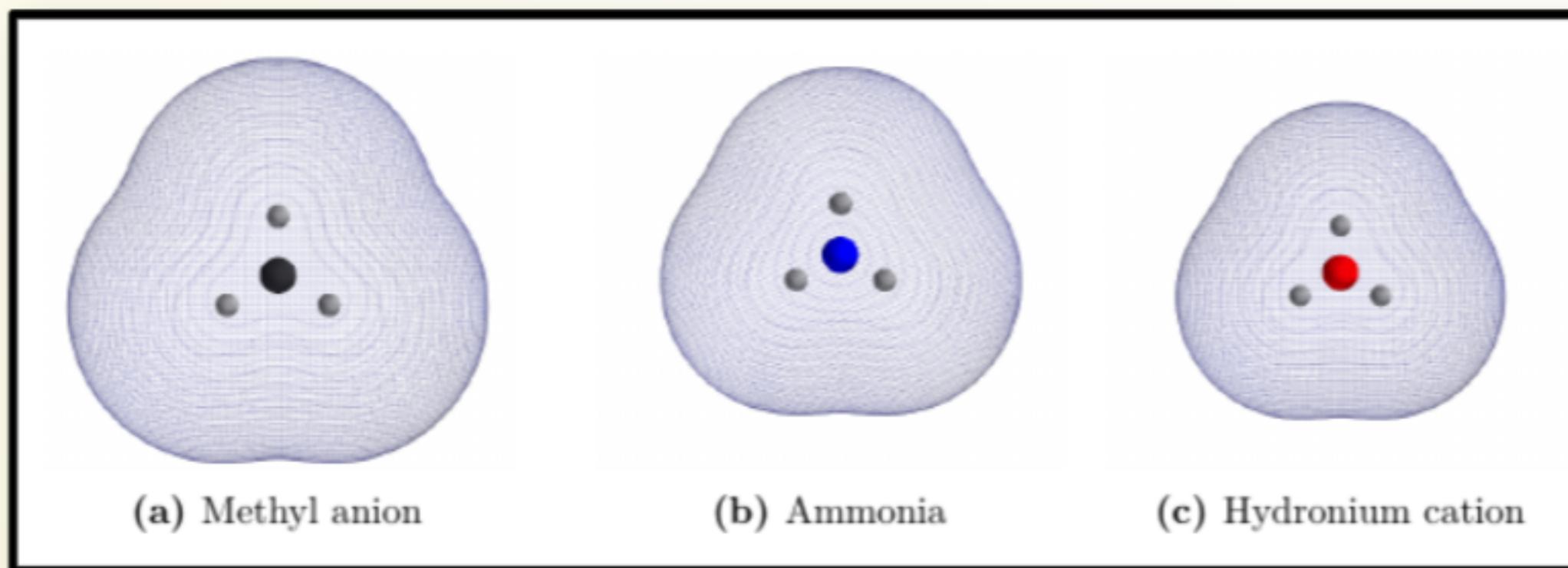
Hartree-Fock code based on
McMurchie-Davidson scheme

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

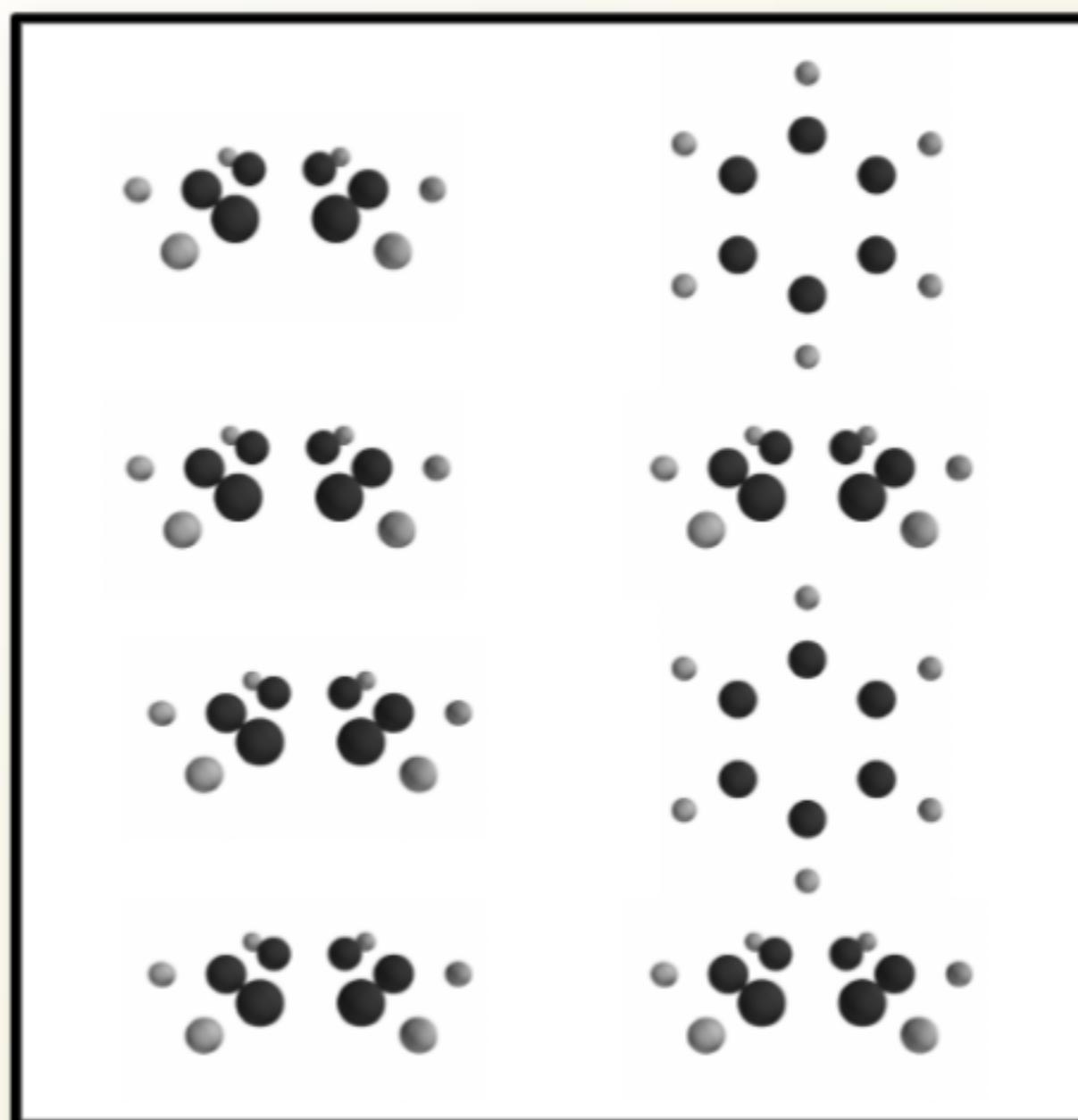
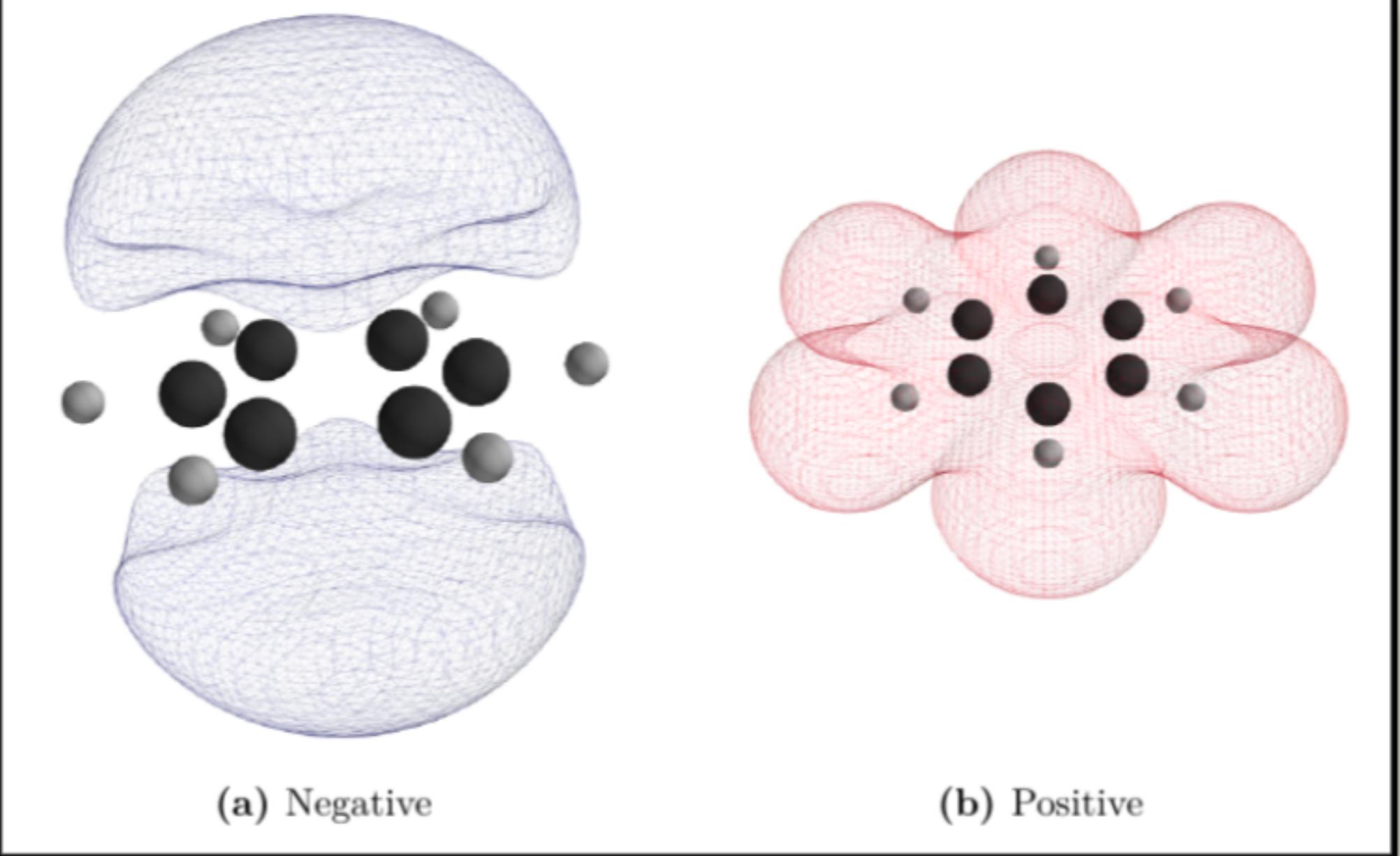
Numerous verification tests:

Unit tests, benchmarking

GRAPHICAL MODELS

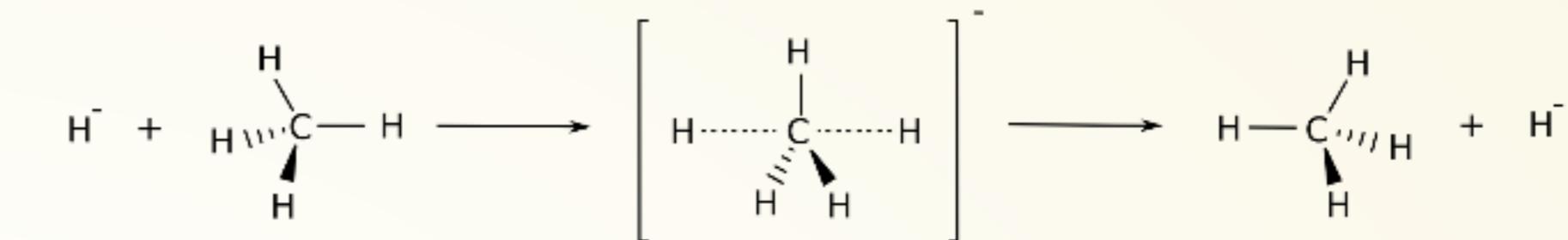


ELECTROSTATIC POTENTIAL

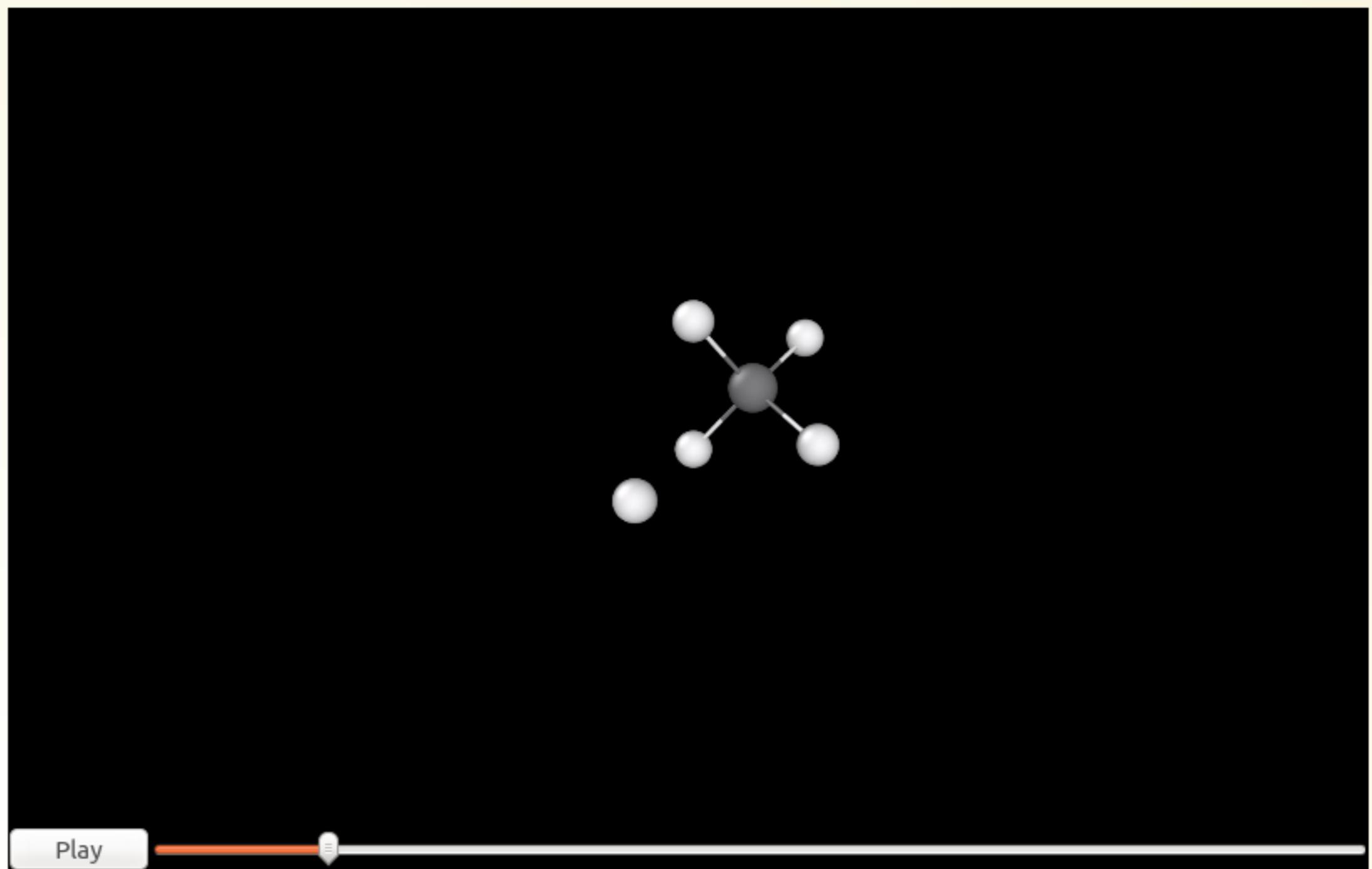


NUCLEOPHILIC SUBSTITUTION REACTION

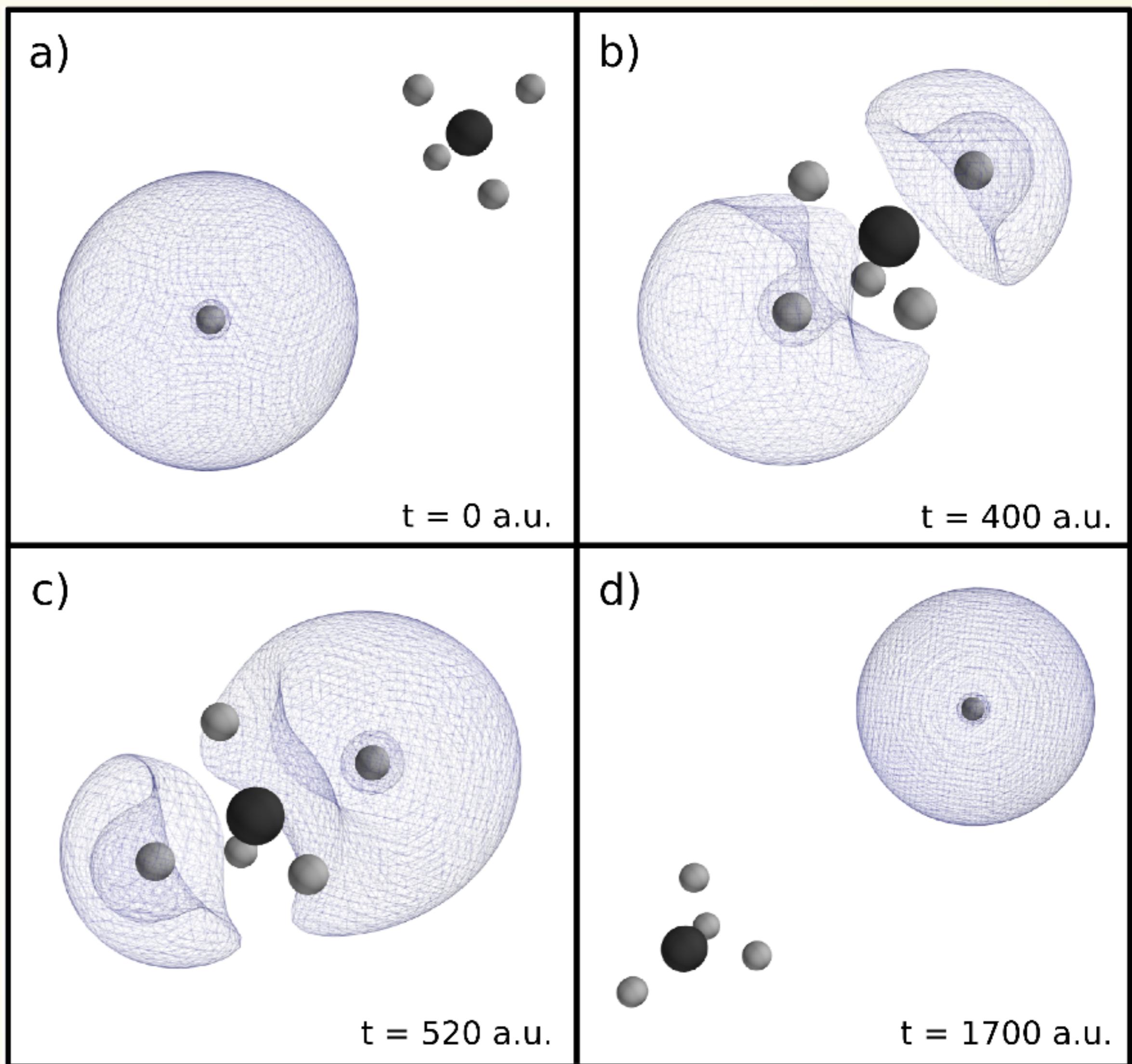
An application of
Born-Oppenheimer
molecular dynamics



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

Thank you for your attention!