First Principles Molecular Dynamics with DFT

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First Principles (ab Initio) Molecular Dynamics (some books call it "Quantum MD")

Molecular Dynamics (MD) simulation in which nuclei (i.e. atoms-electrons) move according to forces that are obtained from DFT calculation.

- **Born Oppenheimer Molecular Dynamics (BOMD)**

- **Car Parrinello (extended Lagrangian) Molecular Dynamics (CPMD)**

Recall Classical Mechanics formulations

$$\dot{A} \equiv \frac{dA}{dt} \qquad \ddot{A} \equiv \frac{d^2 A}{dt^2}$$

Newton (1643-1727):

$$U = U(\boldsymbol{R}^N)$$

Atom positions

Equation of Motion

$$\boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} U = M_I \ddot{\boldsymbol{R}}_I$$

AXIOMATA
SIVE
LEGES MOTUS

Lagrange (1736-1813):

$$L(\boldsymbol{R}, \dot{\boldsymbol{R}}) = \sum_{I=1}^{N} \frac{M_I \dot{\boldsymbol{R}}_I^2}{2} - U$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\boldsymbol{R}}_I} = \frac{\partial L}{\partial \boldsymbol{R}_I}$$

Hamilton (1805-1865):

$$H(\boldsymbol{P}, \boldsymbol{R}) = \sum_{I=1}^{N} \boldsymbol{P}_I \cdot \dot{\boldsymbol{R}}_I - L$$

$$= \sum_{I=1}^{N} \frac{\boldsymbol{P}_I^2}{2M_I} + U$$

$$\dot{\boldsymbol{R}}_I = \frac{\partial H}{\partial \boldsymbol{P}_I} = \frac{\boldsymbol{P}_I}{M_I} \qquad \dot{\boldsymbol{P}}_I = \frac{\partial H}{\partial \boldsymbol{R}_I} = \boldsymbol{F}_I$$

Principle of Least Action is omitted here.

Modern Molecular Dynamics formulation

Lagrange (1736-1813):

$$L(\boldsymbol{R}, \dot{\boldsymbol{R}}) = \sum_{I=1}^{N} \frac{M_I \dot{\boldsymbol{R}}_I^2}{2} - U \qquad\qquad \frac{d}{dt} \frac{\partial L}{\partial \dot{\boldsymbol{R}}_I} = \frac{\partial L}{\partial \boldsymbol{R}_I}$$

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I = -\nabla_{R_I} U(\boldsymbol{R})$$

$U(\boldsymbol{R})$ **: Potential Energy - a mathematical function of 3 N_{atom} variables.**

**"Classical" MD -   a set of analytical functions with empirical parameters are
used to model U(R) approximately.**

**First-Principles MD - U(R) is obtained by approximately solving electronic Schrödinger Eq.
for a particular R from first principles (e.g. using DFT).**

Potential Energy Curve for O-O
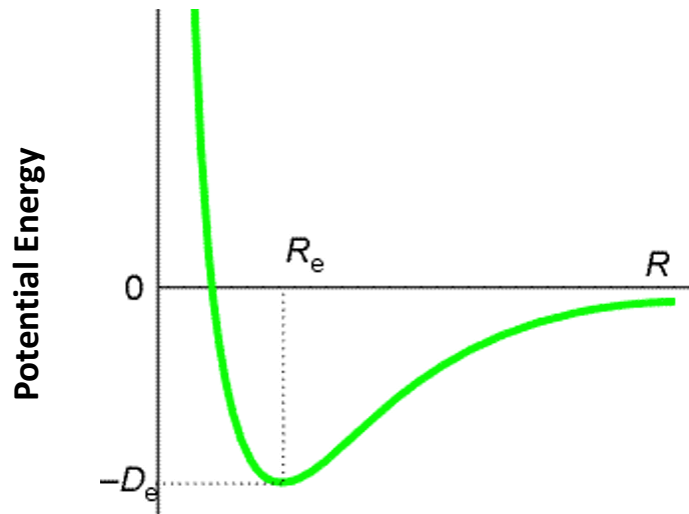
Potential Energy Surface for F-H-Cl
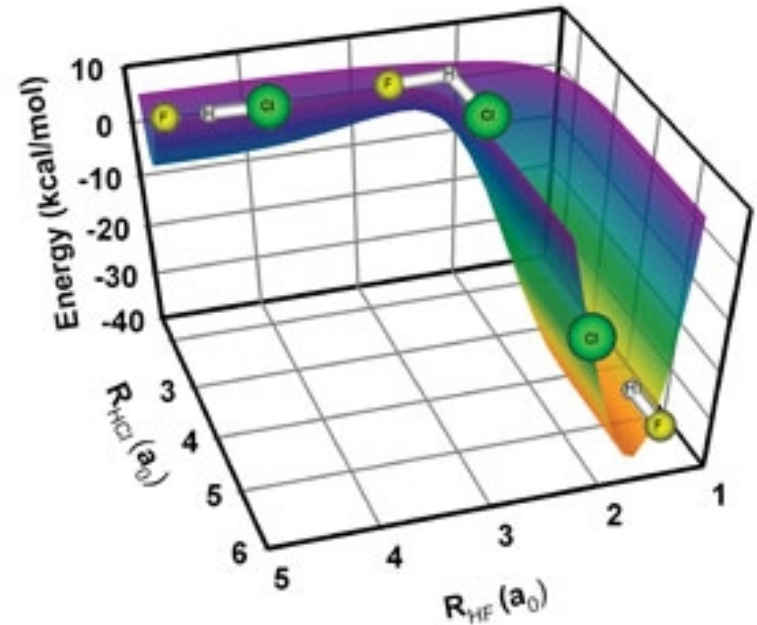
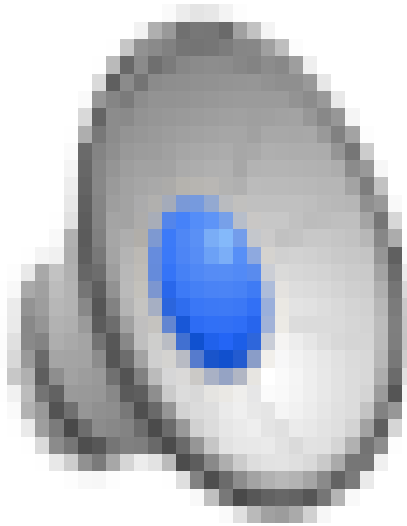**Molecular Dynamics simulation** $M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} U(\boldsymbol{R})$

Various properties can be obtained as a function of Volume, Pressure, and Temperature.

$$T = \frac{1}{3Nk_B}\left\langle \sum_{I=1}^{N} \boldsymbol{M}_I \dot{\boldsymbol{R}}_I \cdot \dot{\boldsymbol{R}}_I \right\rangle$$

Classical ensemble average

$$P = \frac{1}{3V}\left\langle \sum_{I=1}^{N} \boldsymbol{M}_I \dot{\boldsymbol{R}}_I \cdot \dot{\boldsymbol{R}}_I - \boldsymbol{R}_I \cdot \nabla_{\boldsymbol{R}_I} U(\boldsymbol{R})) \right\rangle$$

Example. Simulation of Liquid Water at Silicon Surface

By Donghwa Lee

How is the interface modeled?

Simulation cell

Surface (~4Å)

Bulk-like (~15Å)

Surface (~4Å)
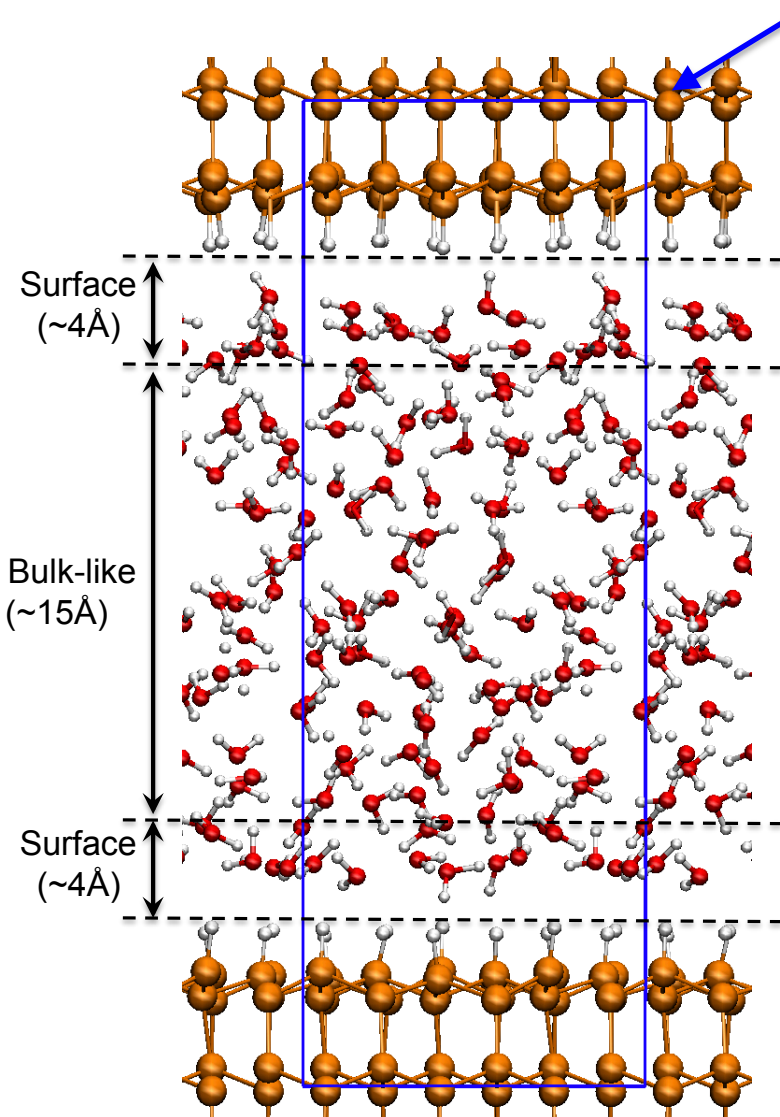
Periodic Boundary Conditions (PBC) is used.
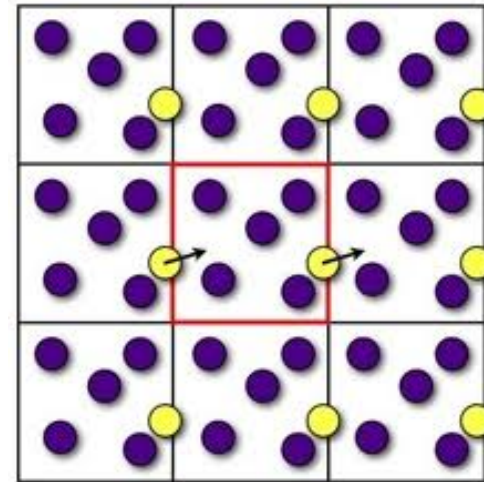
One needs to make sure the water region as well as silicon part is large enough such that calculated properties are converged.

"Finite size error" needs to be minimized.

Molecular Dynamics Simulation Step

For a given {$R_I(t)$}, calculate U({R}) or equivalently the force on atoms (F=-∇_RU).

Move the atoms using a <u>numerical integrator</u> (e.g. Verlet algorithm)

* Approximately solve $M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I = -\nabla_{R_I} U(\boldsymbol{R})$ on a computer with a finite Δt.

e.g. **$R_I(t+\Delta t)=2R_I(t)-R_I(t-\Delta t)+\Delta t^2 F_I(t)/M_I$**

* T and P can be controlled by using so-called "thermostats".

e.g. Velocity scaling thermostat

Update atomic positions: $R_i(t)=R_i(t+\Delta t)$

Molecular Dynamics details omitted

Numerical Integrator for Computational Simulation

Many numerical approaches exist. Velocity Verlet is probably the most widely used integrator.

Calculating Ensemble-averaged quantities from Time-averages: Ergodicity

$$\langle O \rangle = \iint O(\boldsymbol{R}, \dot{\boldsymbol{R}}) P(\boldsymbol{R}, \dot{\boldsymbol{R}}) \, d\boldsymbol{R} d\dot{\boldsymbol{R}} = \lim_{t \to \infty} \frac{1}{t} \int_{t_0}^{t_0+t} O(\boldsymbol{R}(t'), \dot{\boldsymbol{R}}(t')) dt'$$

$$P(\boldsymbol{R}, \dot{\boldsymbol{R}}) = Q^{-1} e^{-H(\boldsymbol{R}, \dot{\boldsymbol{R}})/k_B T} \qquad Q = \iint e^{-H(\boldsymbol{R}, \dot{\boldsymbol{R}})/k_B T} \, d\boldsymbol{R} d\dot{\boldsymbol{R}}$$

NVE – microcanonical ensemble   vs.   NVT – canonical ensemble

Thermostats
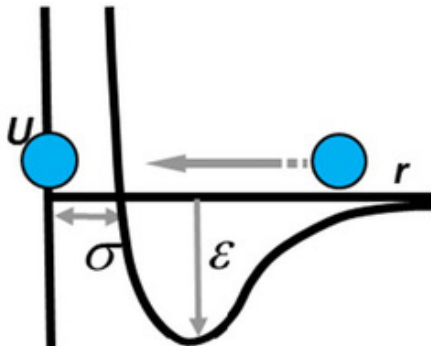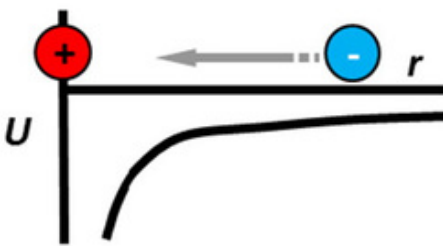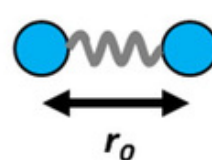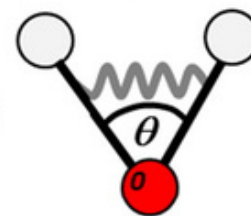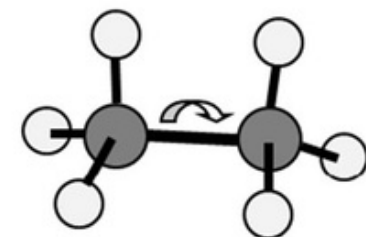
Velocity scaling approaches
e.g. Berendesen

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}(\boldsymbol{R}) \text{-} (M_I/\tau)(T^*/T - 1)\, \dot{\boldsymbol{R}}_I$$

Extended Lagrangian approaches
e.g. Nose

$$L_{Nose} = \sum_I \frac{M_I}{2} s^2 \dot{\boldsymbol{R}}_I{}^2 - U(\boldsymbol{R}) + \frac{Q}{2} \dot{s}^2 - g k_B T^* \ln s$$

A typical mathematical expression for Pottential Energgy, U, in classical MD

$$U(\{R_i\}) = \sum_{i<j} \sum 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

$$+ \sum_{i<j} \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

$$+ \sum_{bonds} \frac{1}{2}k_b(r-r_0)^2$$

$$+ \sum_{angles} \frac{1}{2}k_a(\theta-\theta_0)^2$$

$$+ \sum_{torsions} k_\phi\left[1+\cos(n\phi-\delta)\right]$$

Empirical parameters are determined by fitting to experiments and electronic structure calculations.

First Principles (Born Oppenheimer) Molecular Dynamics

$$M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} U(\boldsymbol{R})$$

$$U(\boldsymbol{R}) = E\left(\left|\Psi_0(\boldsymbol{R})\right\rangle, \boldsymbol{R}\right)$$

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} E\left(\left|\Psi_0(\boldsymbol{R})\right\rangle, \boldsymbol{R}\right) = -\nabla_{\boldsymbol{R}_I} \min_{\Psi} \left\langle \Psi(\boldsymbol{R}) \left| \hat{H} \right| \Psi(\boldsymbol{R}) \right\rangle$$

Note : Atom $\rightarrow$ Nucleus (R_I) + Electrons (r_i)

$$\hat{H} = \sum_i -\frac{\hbar}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{i \neq i'} \frac{e^2}{|\mathbf{r_i} - \mathbf{r_{i'}}|} - \sum_{iI} \frac{Z_I e^2}{|\mathbf{r_i} - \mathbf{R_I}|} + \frac{1}{2}\sum_{I \neq I'} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

Classical nuclear-nuclear repulsion

Where does DFT come in?

Hellmann-Feynman Theorem

$$\Psi(\mathbf{r}^n; \boldsymbol{R})$$

Parametric dependence on nuclear positions (i.e. not explicit function of nuclear positions)

Force on nucleus that is indexed with _I_

$$\boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} \min_{\Psi} \left\langle \Psi(\boldsymbol{R}) \middle| \hat{H} \middle| \Psi(\boldsymbol{R}) \right\rangle = -\nabla_{\boldsymbol{R}_I} \left\langle \Psi_0(\boldsymbol{R}) \middle| \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle$$

$$= -\left\langle \Psi_0(\boldsymbol{R}) \middle| \nabla_{\boldsymbol{R}_I} \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle - \left\langle \nabla_{\boldsymbol{R}_I} \Psi_0(\boldsymbol{R}) \middle| \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle - \left\langle \Psi_0(\boldsymbol{R}) \middle| \hat{H} \middle| \nabla_{\boldsymbol{R}_I} \Psi_0(\boldsymbol{R}) \right\rangle$$

$$= -\left\langle \Psi_0(\boldsymbol{R}) \middle| \nabla_{\boldsymbol{R}_I} \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle - E_0 \left\langle \nabla_{\boldsymbol{R}_I} \Psi_0(\boldsymbol{R}) \middle| \Psi_0(\boldsymbol{R}) \right\rangle - E_0 \left\langle \Psi_0(\boldsymbol{R}) \middle| \nabla_{\boldsymbol{R}_I} \Psi_0(\boldsymbol{R}) \right\rangle$$

$$= -\left\langle \Psi_0(\boldsymbol{R}) \middle| \nabla_{\boldsymbol{R}_I} \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle - E_0 \nabla_{\boldsymbol{R}_I} \left\langle \Psi_0(\boldsymbol{R}) \middle| \Psi_0(\boldsymbol{R}) \right\rangle$$

$$= -\left\langle \Psi_0(\boldsymbol{R}) \middle| \nabla_{\boldsymbol{R}_I} \hat{H} \middle| \Psi_0(\boldsymbol{R}) \right\rangle$$

Recall the expression for the Hamiltonian

$$\hat{H} = \sum_i -\frac{\hbar}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{i \neq i'}\frac{e^2}{|\mathbf{r_i} - \mathbf{r_{i'}}|} - \sum_{iI}\frac{Z_I e^2}{|\mathbf{r_i} - \mathbf{R}_I|} + \frac{1}{2}\sum_{I \neq I'}\frac{Z_I Z_{I'} e^2}{|\mathbf{R}_I - \mathbf{R}_{I'}|}$$

Classical nuclei repulsion

Its derivative with respect to $\mathbf{R_I}$ is

$$\nabla_{R_I}\hat{H} = -\sum_i \nabla_{R_I}\frac{Z_I e^2}{|\mathbf{r_i} - \mathbf{R_I}|} + \sum_{I'}\nabla_{R_I}\frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

Force on a nucleus, **I**, is then given by

$$F_I = -\left\langle \Psi_0(\boldsymbol{R}) \left| \nabla_{R_I} \hat{H} \right| \Psi_0(\boldsymbol{R}) \right\rangle$$

$$= -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \sum_i \int \Psi_0^*(\mathbf{r}_1 \dots \mathbf{r_n}; \mathbf{R}) \nabla_{R_I} \frac{Z_I e^2}{|\mathbf{r_i} - \mathbf{R_I}|} \Psi_0(\mathbf{r}_1 \dots \mathbf{r_n}; \mathbf{R}) d\mathbf{r}_1 \dots d\mathbf{r_n}$$

Electron density

$$\rho(\mathbf{r}; \mathbf{R}) \equiv N \int \Psi_0^*(\mathbf{r}, \mathbf{r}_{2 \dots} \mathbf{r_n}; \mathbf{R}) \, \Psi_0(\mathbf{r}, \mathbf{r}_{2 \dots} \mathbf{r_n}; \mathbf{R}) \, d\mathbf{r}_{2 \dots} d\mathbf{r_n}$$

$$= -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \int \rho(\mathbf{r}; \mathbf{R}) \nabla_{R_I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} d\mathbf{r}$$

* DFT naturally gives the essential ingredient for performing MD simulations.

First-Principles Molecular Dynamics based on DFT

$$m_e = 1$$
$$\hbar = 1$$

MD Simulation

1. For positions of nuclei, $\{R_1 \ldots R_N\}$, and <u>solve DFT-KS equations self-consistently</u>

$$[-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} + \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'} + v_{XC}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{occ} 2|\psi_i(\mathbf{r})|^2$$

2. Calculate force on each nucleus/ion:

$$F_I = -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \int \rho(\mathbf{r};\mathbf{R})\nabla_{R_I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} d\mathbf{r}$$

3. Integrate equation of motion for the nuclei: perform a time step (Δt) and find new positions for the nuclei

$$M_I \ddot{\boldsymbol{R}}_I(t) = \boldsymbol{F}_I(\boldsymbol{R}(t))$$

What about Hellmann-Feynman (HF) force in practice ?

$$F_I = -\nabla_{R_I} \min_{\Psi} \langle \Psi(R) | \hat{H} | \Psi(R) \rangle = -\nabla_{R_I} \langle \Psi_0(R) | \hat{H} | \Psi_0(R) \rangle$$

$$= -\langle \Psi_0(R) | \nabla_{R_I} \hat{H} | \Psi_0(R) \rangle - \langle \nabla_{R_I} \Psi_0(R) | \hat{H} | \Psi_0(R) \rangle - \langle \Psi_0(R) | \hat{H} | \nabla_{R_I} \Psi_0(R) \rangle$$

$$= -\langle \Psi_0(R) | \nabla_{R_I} \hat{H} | \Psi_0(R) \rangle - E_0 \langle \nabla_{R_I} \Psi_0(R) | \Psi_0(R) \rangle - E_0 \langle \Psi_0(R) | \nabla_{R_I} \Psi_0(R) \rangle$$

$$= -\langle \Psi_0(R) | \nabla_{R_I} \hat{H} | \Psi_0(R) \rangle - E_0 \nabla_{R_I} \langle \Psi_0(R) | \Psi_0(R) \rangle \quad = -\langle \Psi_0(R) | \nabla_{R_I} \hat{H} | \Psi_0(R) \rangle$$

Only if the wave function is the exact G.S. solution of the Schrodinger equation.

*Basis set completeness

<u>In the DFT language (in terms of electron density)</u>

$$F_I = -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} - \nabla_{R_I} E^{DFT}[\rho; \mathbf{R}]$$

$$= -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \int \rho(\mathbf{r}; \mathbf{R}) \nabla_{R_I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} d\mathbf{r} - \int \frac{\delta E^{DFT}}{\delta \rho(\mathbf{r}; \mathbf{R})} \nabla_{R_I} \rho(\mathbf{r}; \mathbf{R}) d\mathbf{r}$$

Nuclei repulsion   HF force $\tilde{F}_I$

$$F_I = -\sum_{I'} \nabla_{R_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \int \rho(\mathbf{r};\mathbf{R}) \nabla_{R_I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} d\mathbf{r} + \tilde{F}_I$$

Forces in Kohn-Sham DFT: $E^{KS-DFT}\left[\{\psi_i\}, \mathbf{R}\right]$

$$\tilde{F}_I = \sum_i \int \left(\nabla_{R_I} \psi_i^*(\mathbf{r};\mathbf{R}) \frac{\delta E}{\delta \psi_i^*(\mathbf{r};\mathbf{R})} + \nabla_{R_I} \psi_i(\mathbf{r};\mathbf{R}) \frac{\delta E}{\delta \psi_i(\mathbf{r};\mathbf{R})} \right) d\mathbf{r}$$

$$= \sum_i \int \left(\nabla_{R_I} \psi_k^*(\mathbf{r};\mathbf{R})(\hat{H}_{KS} - \varepsilon_i)\psi_i(\mathbf{r};\mathbf{R}) + \nabla_{R_I} \psi_i(\mathbf{r};\mathbf{R})(\hat{H}_{KS} - \varepsilon_i)\psi_i^*(\mathbf{r};\mathbf{R}) \right) d\mathbf{r}$$

Vanishes only for <u>exact</u> KS eigenfunctions.

Forces in Kohn-Sham DFT <u>numerical calculations</u>:

$$\psi_i(\mathbf{r};\mathbf{R}) = \sum_m c_m^{(i)} \chi_m(\mathbf{r};\mathbf{R})$$

$$H_{mg} = \left\langle \chi_m \left| \hat{H}_{KS} \right| \chi_g \right\rangle$$

*Basis set completeness

$$\tilde{F}_I = \sum_i \sum_{g,m} \nabla_{R_I} c_m^{(i)} (H_{mg} - \varepsilon_i) c_g^{(i)} + \sum_{g,m} c_m^{(i)} c_g^{(i)} \int \nabla_{R_I} \chi_m^*(\mathbf{r};\mathbf{R})(\hat{H}_{KS} - \varepsilon_i)\chi_g(\mathbf{r};\mathbf{R}) d\mathbf{r} + c.c.$$

Vanishes for exact KS eigenfunc.   Vanishes if basis set is R-independent.

$$\sum_g (H_{mg} - \varepsilon_i) c_g^{(i)} = 0$$

Remark about Basis Set

Numerical Atom-Centered Orbitals (NAO):   discussed by V. Blum

Codes : FHI-aims, etc

Gaussians Type Orbitals (GTO) :   Gaussian functions centered on atomic nuclei are used as basis set functions. Many integrals can be calculated analytically.

Codes : GAUSSIAN, Q-Chem

Planewaves (PW) : Planewaves are used as basis set functions, convenient when the periodic boundary conditions is used. It is often used with pseudopotentials to replace core electrons.

Codes: Quantum-Espresso, Qbox/Qb@ll

Popular for FPMD because the basis set does not depend on the nuclear positions (no Pulay force to implement in codes).

Car Parrinello (extended Lagrangian) Molecular Dynamics: "CPMD"

Unified Approach for Molecular Dynamics and Density-Functional Theory

R. Car
International School for Advanced Studies, Trieste, Italy

and

M. Parrinello
*Dipartimento di Fisica Teorica, Università di Trieste, Trieste, Italy, and
International School for Advanced Studies, Trieste, Italy*
(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics

1985 Trieste

By Thomas D. Kühne

Review : Car-Parrinello Molecular Dynamics
Jurg Hutter, Wires – Computational
Molecular Science, 2, 513 (2012)

Popular codes for performing CPMD
CPMD, CP code (Q-Espresso), Qbox, Qb@ll,
etc.

*CP2K does not have CPMD!

Car Parrinello extended Lagrangian

$$L^{CP}(\boldsymbol{R}, \dot{\boldsymbol{R}}; \{\psi_i\}) = \sum_{i=1}^{n} \frac{\mu}{2} \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_{I=1}^{N} \frac{M_I \dot{\boldsymbol{R}}_I^2}{2} - E[\{\psi_i\}; \boldsymbol{R}] + \sum_{i,j} \Lambda_{i,j} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right)$$

Fictitious mass parameter for electronic degrees of freedom.

$\psi_i(\mathbf{r}, t)$ are treated as if they are **classical fields.**

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\boldsymbol{R}}_I} = \frac{\partial L}{\partial \boldsymbol{R}_I}$$

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} E + \sum_{i,j} \Lambda_{i,j} \nabla_{\boldsymbol{R}_I} \langle \psi_i | \psi_j \rangle$$

$$= -\sum_{I'} \nabla_{\boldsymbol{R}_I} \frac{Z_I Z_{I'} e^2}{|\mathbf{R_I} - \mathbf{R_{I'}}|} + \int \rho(\mathbf{r}; \mathbf{R}) \nabla_{\boldsymbol{R}_I} \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R_I}|} d\mathbf{r} + \sum_{i,j} \Lambda_{i,j} \nabla_{\boldsymbol{R}_I} \langle \psi_i | \psi_j \rangle$$

$$\frac{d}{dt} \frac{\partial L}{\partial \langle \dot{\psi}_i |} = \frac{\partial L}{\partial \langle \psi_i |}$$

$$\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E}{\delta \langle \psi_i |} + \sum_j \Lambda_{i,j} | \psi_j \rangle$$

$$= -\hat{H}_{KS} | \psi_i \rangle + \sum_j \Lambda_{i,j} | \psi_j \rangle$$

Why/when can CPMD work?

There needs to be "adiabatic" separation (no energy exchange) between artificial electronic motion and real ionic/nuclear motion.

To achieve such, How do you find an appropriate fictitious electron parameter μ ?

Characteristic frequency of the slowest "electronic motion" is related to HOMO-LUMO energy gap, and it must be higher than fastest nuclear/ionic motion.

$$\omega_e^{\min} \approx \left(\frac{E_{gap}}{\mu} \right)^{1/2} > \omega_{Ion}^{\max}$$

Example: System with H atom: μ~ 500 a.u.
Δt ~ 5-10 a.u. = 0.1-0.2 femto-seconds

Car Parrinello Molecular Dynamics in a nutshell

"The heart of the matter is the ''on the fly'' calculation of the potential energy surface for nuclear motion, without performing a self-consistent diagonalization of the Kohn–Sham Hamiltonian at each time step…

The Car–Parrinello approach has remarkable time stability, which derives from energy conservation in the extended parameter space of electrons and nuclei…

Considerably larger drifts occur in Born–Oppenheimer simulations due to accumulation of the systematic errors in the electron minimization."

Roberto Car in "AB INITIO Molecular Dynamics: Dynamics and Thermodynamic Properties" (2006)

Applications

Electron localization on CO_2 in Water

Single-Particle Energy Levels

Injection of an extra electron:

CO_2 - LUMO

$(H_2O)_s$ - LUMO

CBM/LUMO

VBM/HOMO

Simulation

Material

CO_2 in water

e⁻
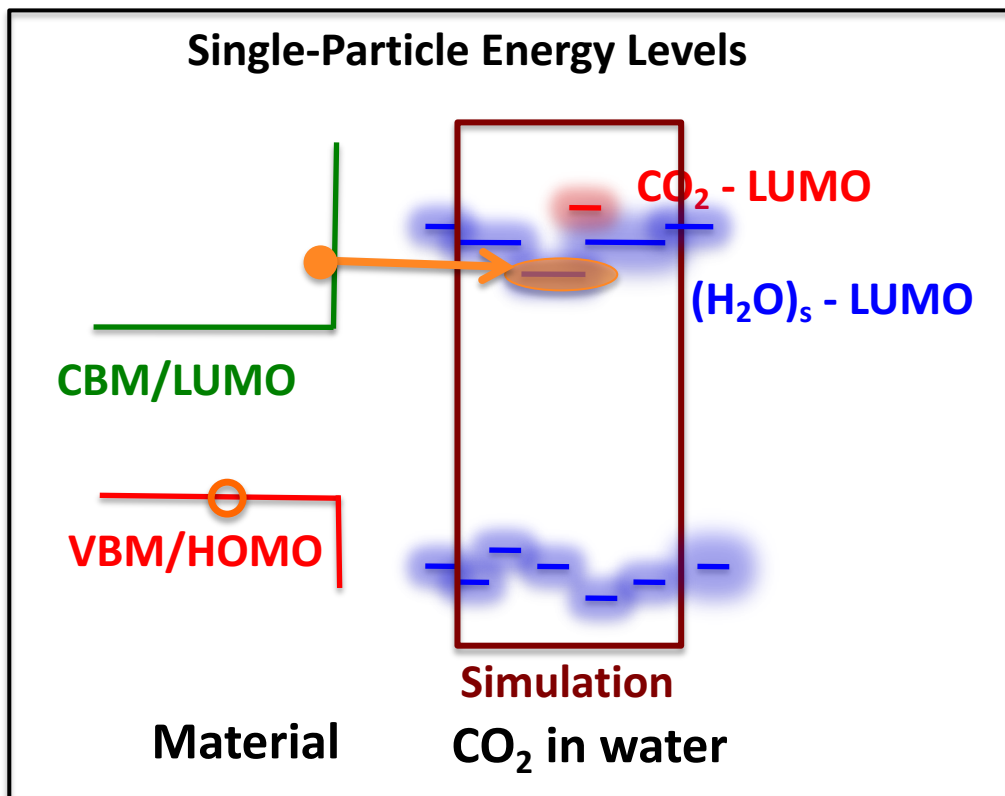
Experiment
Zhang, LH. Et al. Angwdt. Chemie, 53, 9746 (2014)
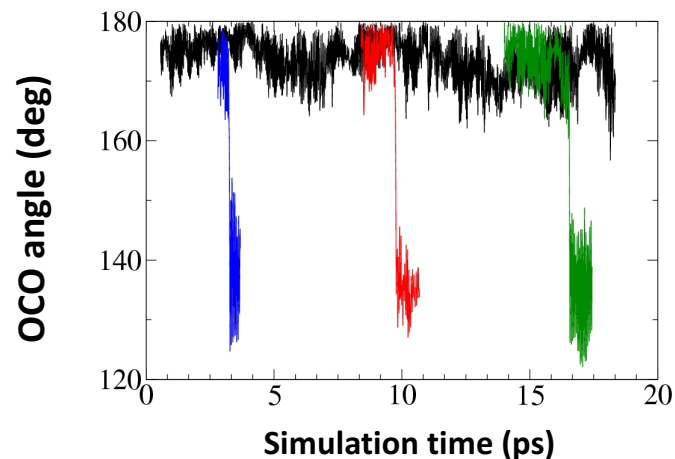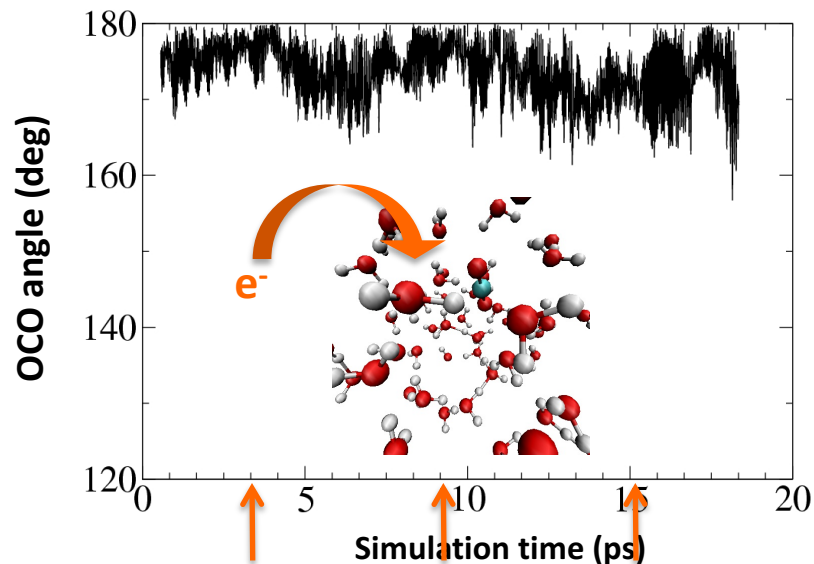
Electron Localization on CO_2 in water
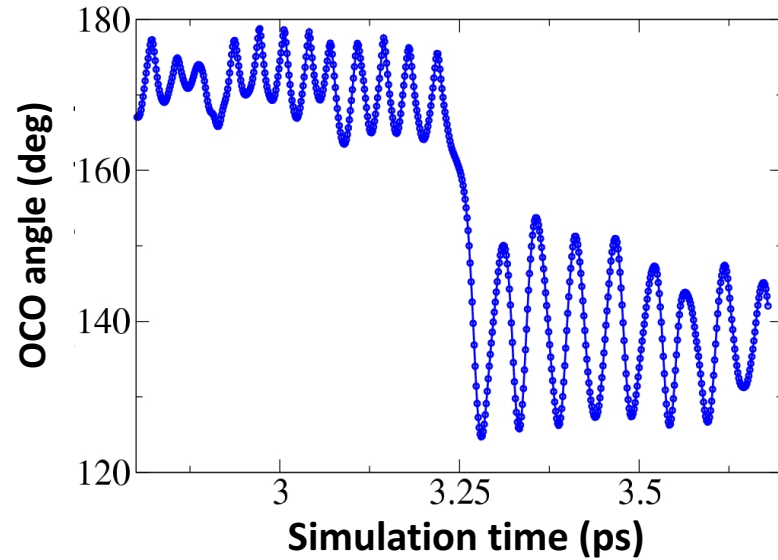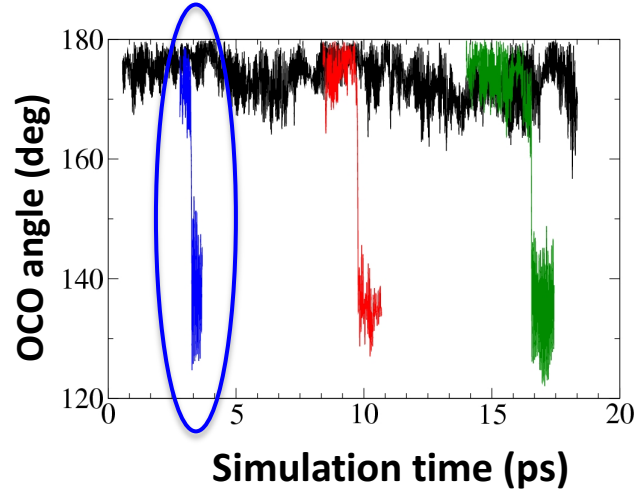
Density associate w/ the extra electron (spin density)
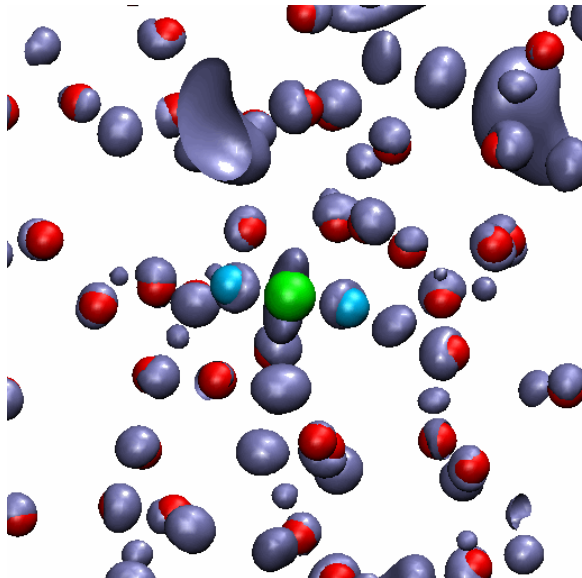
Key observations

The electron dynamically localizes somewhat around CO_2 as the bending angle fluctuates.

Large stochastic fluctuations prompt the electron to localize further, and it reciprocally causes the angle to become smaller as CO_2 anion.
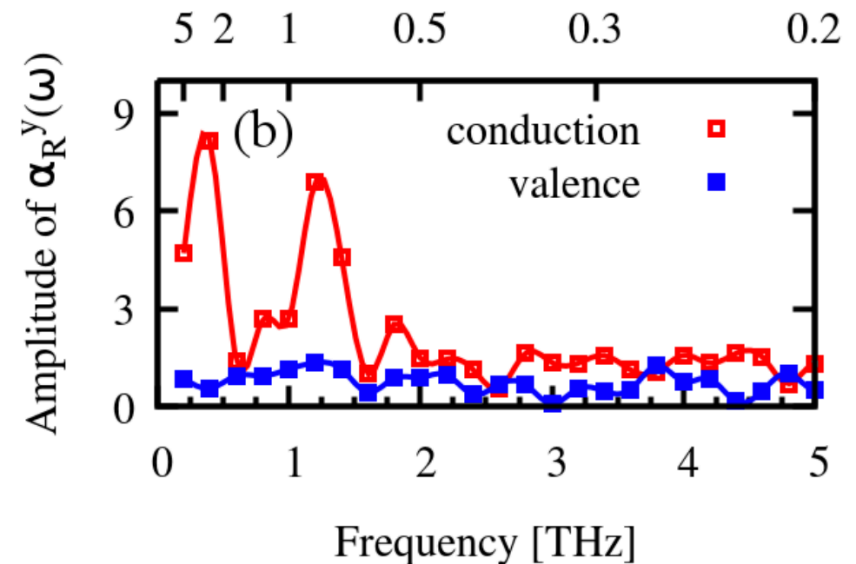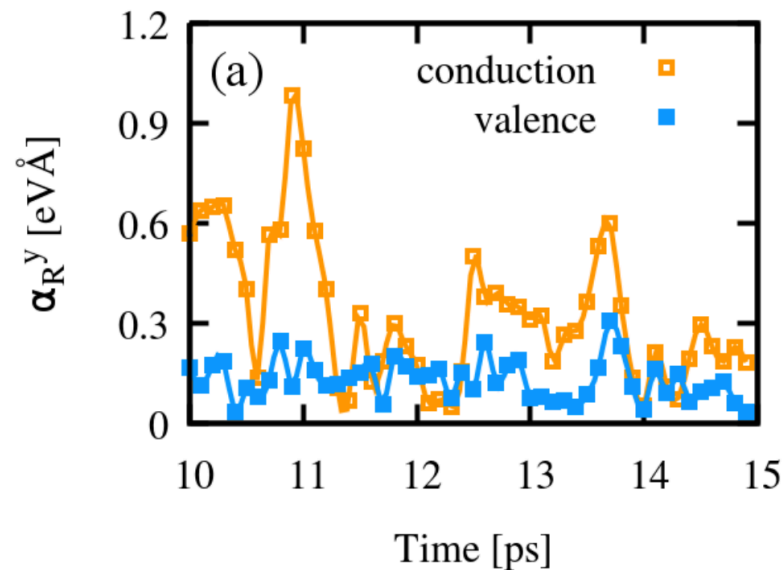
Band splitting due to Spin Orbit Coupling (SOC)

$$E^{\pm}\left(\vec{k}\right) = \frac{\hbar^2 \vec{k}^2}{2m^*}$$

$$E^{\pm}\left(\vec{k}\right) = \frac{\hbar^2 \vec{k}^2}{2m^*} \pm \alpha_R \left|\vec{k}\right|$$

CsPbI$_3$
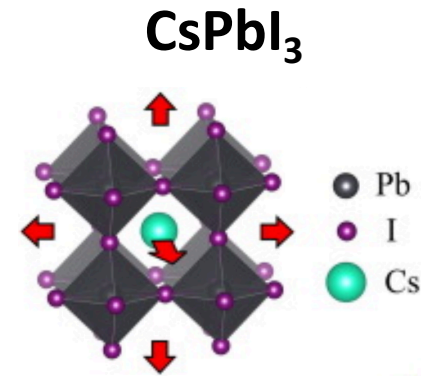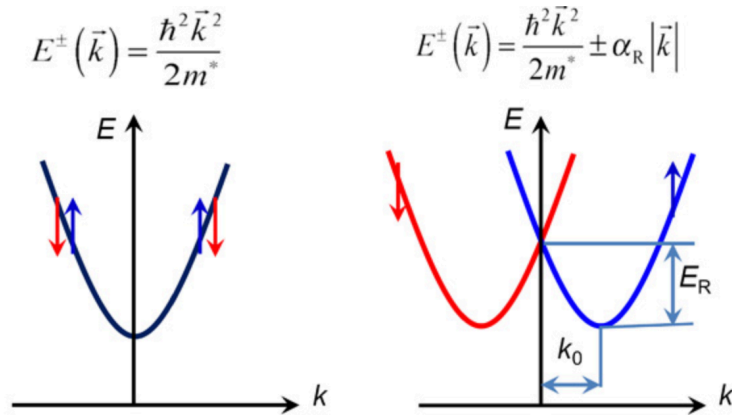
Influence of Disorder and Anharmonic Fluctuations on the Dynamical Rashba Effect in Purely Inorganic Lead-Halide Perovskites

Arthur Marronnier, Guido Roma*, Marcelo A. Carignano, Yvan Bonnassieux, Claudine Katan, Jacky Even, Edoardo Mosconi, and Filippo De Angelis
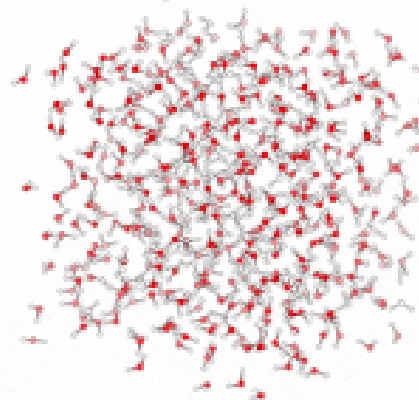
Challenges in FPMD

You have exciting opportunities to contribute and advance the field!

Challenges : Exchange-Correlation (XC) Functional
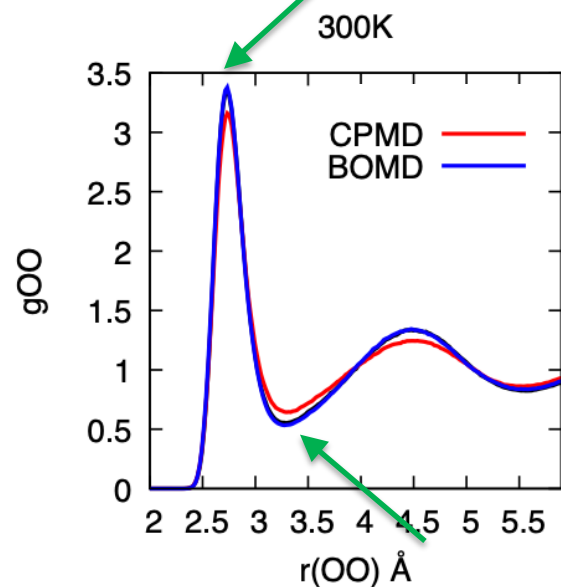

Pair Correlation Function, g(r)
Probability of finding another particle (e.g. O atom) at a given distance from a particle.

|	T(K)	Length(ps)	$r_{max.1}$	$g_{max.1}$	$r_{min.1}$	$g_{min.1}$	$r_{max.2}$	$g_{max.2}$
PBE	300	150	2.72	3.72	3.25	0.31	4.41	1.56
BLYP	300	~20	2.75	3.23	3.35	0.40	4.50	1.50
SCAN+rVV10	300	~20	2.7	3.1	3.3	0.6	4.6	1.2
BLYP-D3	300	64	2.77	3.08	3.36	0.79	4.48	1.15
revPBE-D3	300	~100	2.77	2.77	3.29	0.66	4.35	1.28
revPBE0-D3	300	~300	2.80	2.56	3.50	0.90	4.45	1.09
B97M-rV	300	200	2.83	2.68	3.56	0.93	4.54	1.03
Exp	298		2.75-2.80	2.53-2.73	3.45	0.80-0.85	4.40-4.50	1.12
Exp	296		2.75	2.62	3.45	0.84	4.43	1.13

Challenges : Nuclear Quantum Effect (NQE)

Nuclei can be treated as quantum-mechanical particles using Feynman's path integral (PI) formulation.   TRPMD is a recent PI method by Ceriotti, et al.
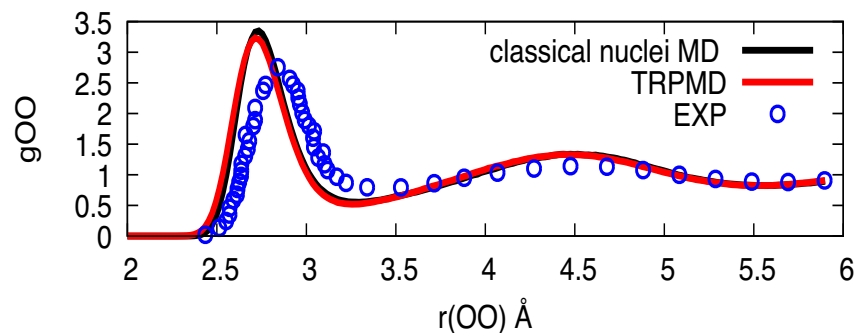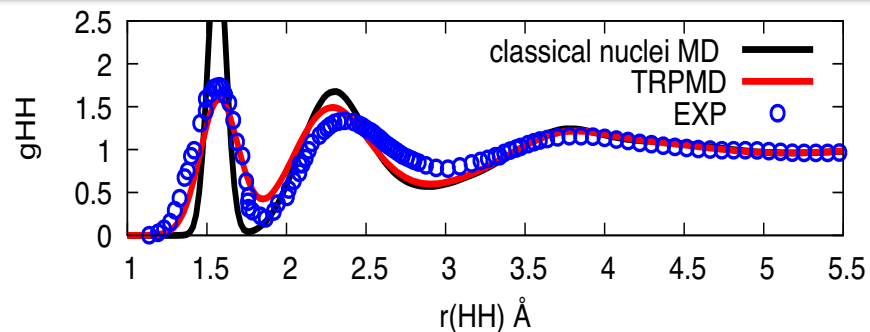

Artificial neural network technique was used to "learn" FPMD simulation.

Yao and Kanai, J. Chem. Phys. 153, 044114 (2020)
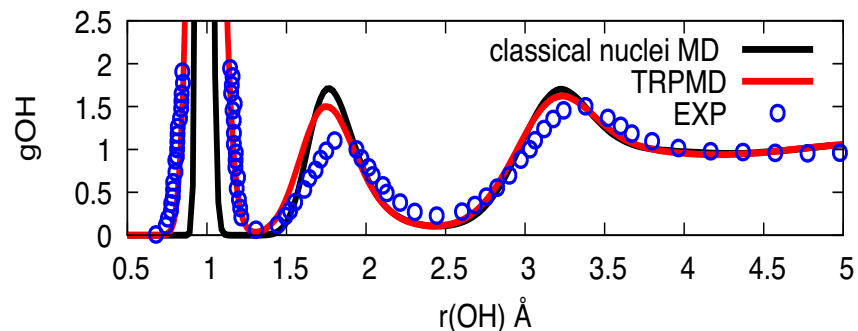
Agreement to experiment improves when NQE is accounted for properties like gOH and gHH.

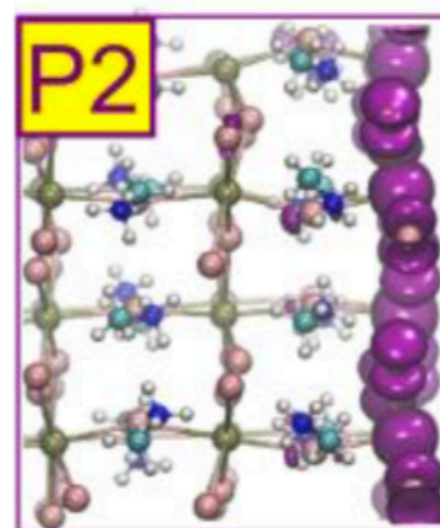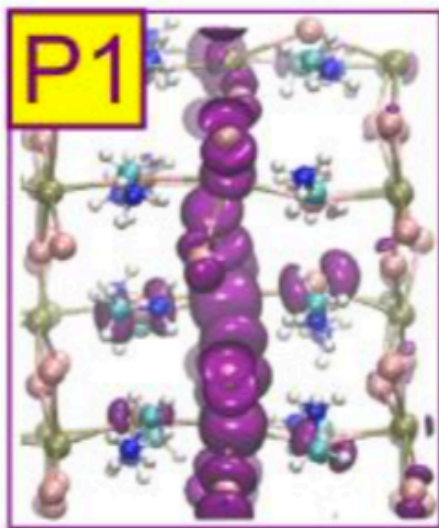The disagreement for gOO remains, likely due to XC error.

Challenges : "Rare" event problem

Charge Localization, Stabilization, and Hopping in Lead Halide Perovskites: Competition between Polaron Stabilization and Cation Disorder
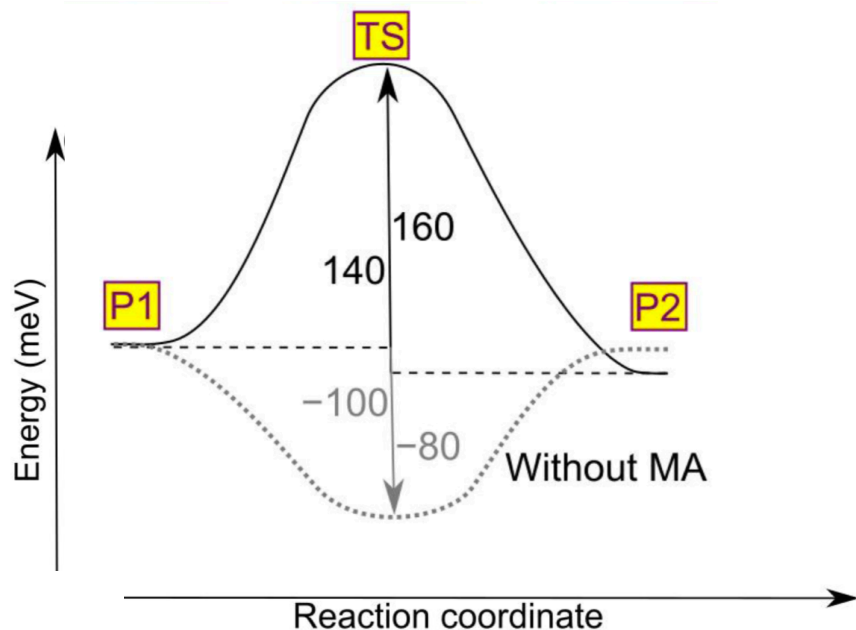F. Ambrosio, D. Meggiolaro, E. Mosconi, and F. De Angelis

ACS Energy Lett. 4, 2013 (2019)
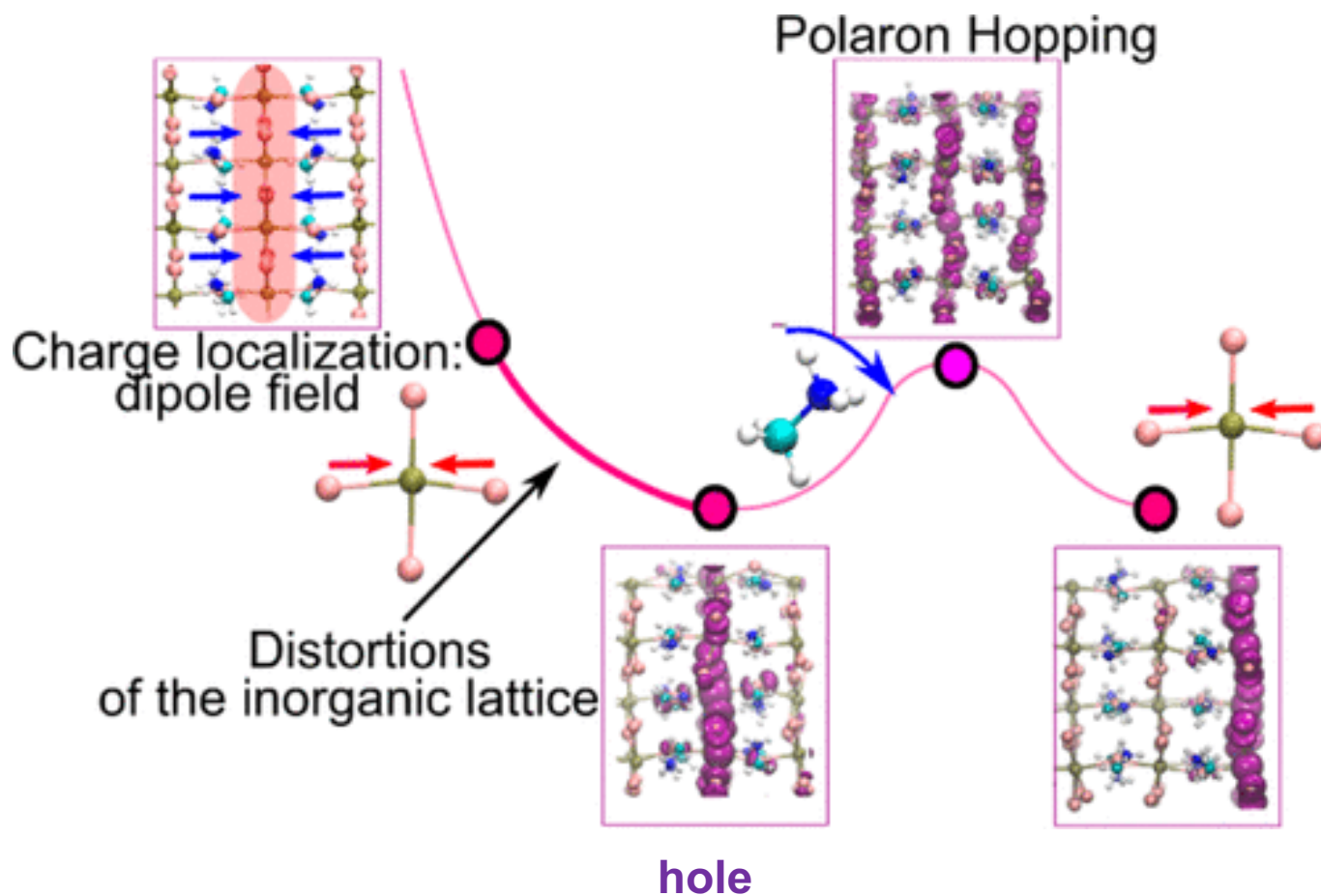
hole

Rare-event problem

You may not observe such a transition if energy barrier is high (unless FPMD is very very long).

Advanced approaches (Nudged Elastic Band, String, Meta-Dynamics) are needed but they are not without inconveniences.

Energy (meV)

TS

P1   P2

160

140

−100

−80   Without MA

Reaction coordinate

Challenges : Accounting for Electron Dynamics

In FPMD (both BOMD and CPMD*), electrons remain in the ground state of given nucler positions; no quantum dynamics of electrons are included.

Electron dynamics in CPMD is fictitious, not real quantum dynamics

Born Oppenheimer Molecular Dynamics

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} E^{DFT}[\rho_0; \boldsymbol{R}]$$

Ehrenfest Dynamics (with Time-Dependent DFT)

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_I} E^{DFT}[\rho(t); \mathbf{R}] \qquad \rho(\mathbf{r},t) = \sum_i^{occ} 2|\phi_i(\mathbf{r},t)|^2$$
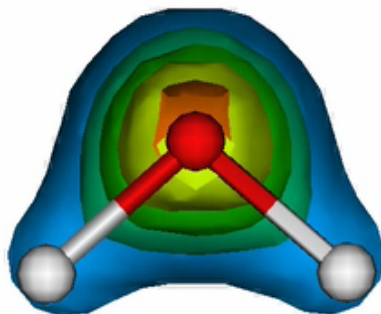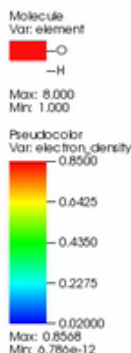
$$i\hbar \frac{d}{dt}|\phi_i(t)\rangle = \hat{H}_{KS}[\rho(\mathbf{r},t)]|\phi_i(t)\rangle$$

$$= \left\{ \hat{T} + \hat{V}_{ext}(t) + \hat{V}_{Hatree}[\rho(t)] + \hat{V}_{XC}[\rho(t)] \right\}|\phi_i(t)\rangle$$

Challenges : Accounting for Electron Dynamics

Ehrenfest Dynamics example : Nuclei can move in response to the quantum dynamics of electrons caused by optical excitation.

A single water molecule at rest is electronically excited with electric field (in Z direction) that corresponds to 8.75 eV photon absorption.

Molecule
Var: element
—O
—H
Max: 8.000
Min: 1.000

Pseudocolor
Var: electron_density
— 0.8500
— 0.6425
— 0.4350
— 0.2275
— 0.02000
Max: 0.8568
Min: 6.786e-12

By Chris Shepard

Electric field pulse applied at this point

END