2025 HybriD3 Materials Theory Training Workshop

THE UNIVERSITY
of NORTH CAROLINA
at CHAPEL HILL

Dynamics from DFT

Molecular Dynamics,

Electron Dynamics,

and Linear Response (if time permits)

Yosuke Kanai

UNC Chapel Hill

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

Molecular Dynamics (MD) simulation in which classical atomic nuclei move according to forces that are obtained from DFT (or another electronic structure theory) calculation.

- **Born Oppenheimer Molecular Dynamics (BOMD)**
- **Car Parrinello (extended Lagrangian) Molecular Dynamics (CPMD)**

Recall Classical Mechanics formulations

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

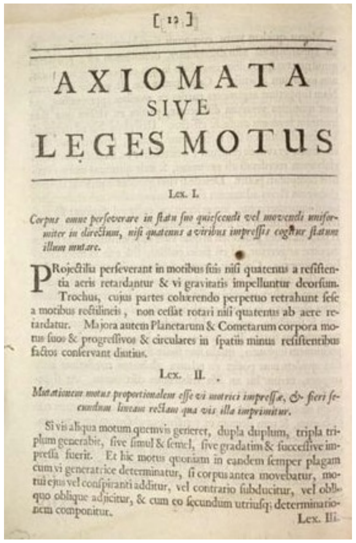
Newton (1643-1727):

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

Atom positions

Equation of Motion

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



[12]

AXIOMATA
SIVE
LEGES MOTUS

Lex. I.

Corpus omne perſeverare in ſtatu ſuo quieſcendi vel movendi uniformiter in directum, niſi quatenus a viribus impreſſis cogitur ſtatum illum mutare.

Projectilia perſeverant in motibus ſuis niſi quatenus a reſiſtentia aeris retardantur & vi gravitatis impelluntur deorſum. Trochus, cujus partes cohærendo perpetuo retrahunt ſeſe a motibus rectilineis, non ceſſat rotari niſi quatenus ab aere retardatur. Majora autem Planetarum & Cometarum corpora motus ſuos & progreſſivos & circulares in ſpatiis minus reſiſtentibus factos conſervant diutius.

Lex. II.

Mutationem motus proportionalem eſſe vi motrici impreſſæ, & fieri ſecundum lineam rectam qua vis illa imprimitur.

Si vis aliqua motum quemvis generet, dupla duplum, tripla triplum generabit, ſive ſimul & ſemel, ſive gradatim & ſucceſſive impreſſa fuerit. Et hic motus quoniam in eandem ſemper plagam cum vi generatrice determinatur, ſi corpus antea movebatur, motui ejus vel conſpiranti additur, vel contrario ſubducitur, vel oblique adjicitur, & cum eo ſecundum utriuſq; determinationem componitur.

Lex. III.

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):

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

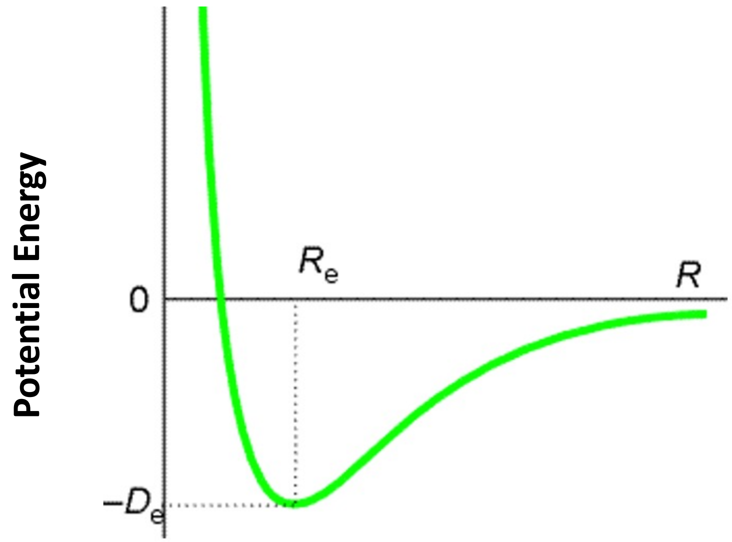
$$M_I\ddot{\boldsymbol{R}}_I=\boldsymbol{F}_I=-\nabla_{\boldsymbol{R}_I}U(\boldsymbol{R})$$

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

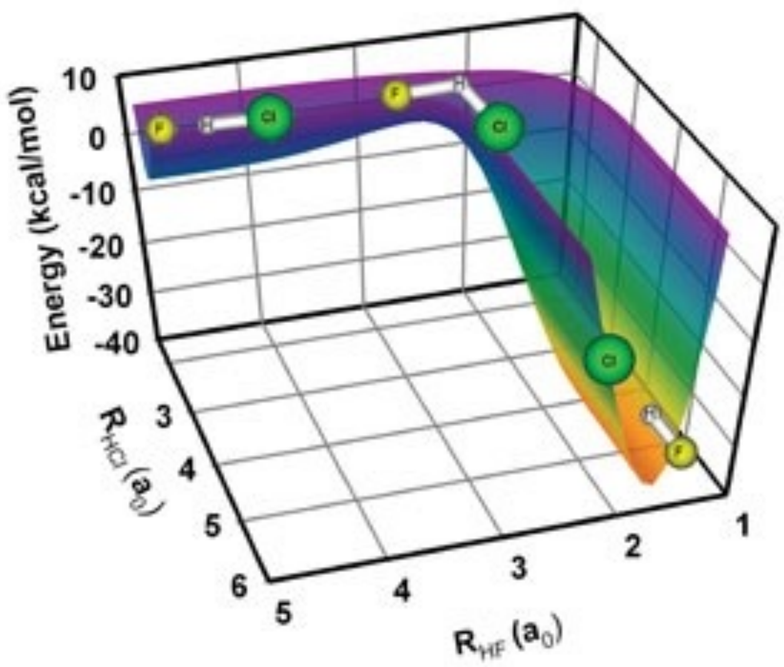
"Classical" MD - a set of analytical functions with empirical parameters are used to model U(R) approximately.

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



<u>Molecular Dynamics simulation</u> $M_I \ddot{\boldsymbol{R}}_I = \boldsymbol{F}_I = -\nabla_{\boldsymbol{R}_I} U(\boldsymbol{R})$

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

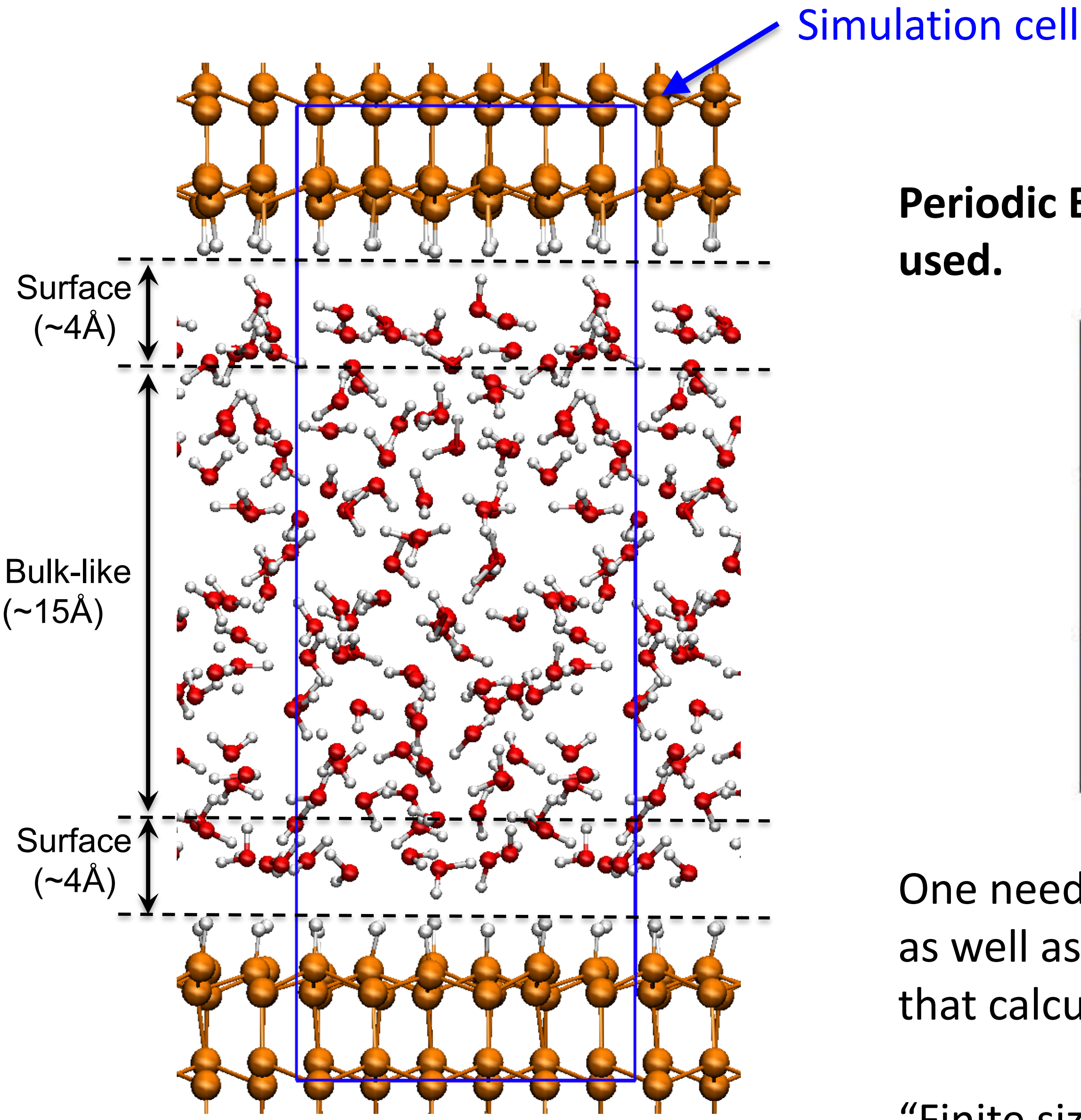
Einstein's relation for Diffusion Coefficient

$$\langle \mathbf{R}^2 \rangle (t) = 2nDt$$

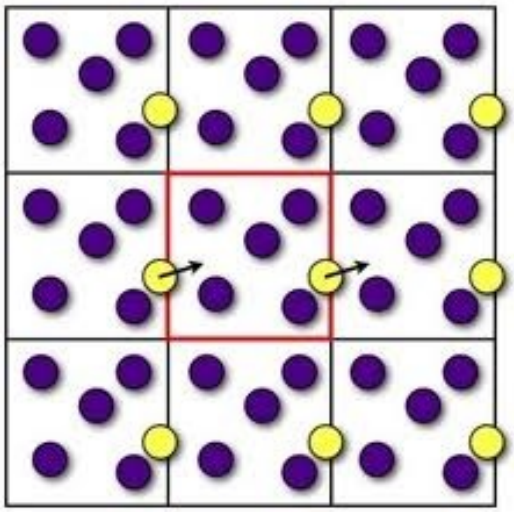
By Donghwa Lee

Dependence of Water Dynamics on Molecular Adsorbates near Hydrophobic Surfaces: First-Principles Molecular Dynamics Study
D. Lee, E. Schwegler, Y. Kanai. J. Phys. Chem. C, 118, 8508 (2014)

How is the interface modeled?



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 {$\mathbf{R}_I(t)$}, calculate U({R}) or equivalently the force on atoms ($\mathbf{F}=-\nabla_R U$).

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

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

e.g. $\mathbf{R}_I(t+\Delta t)=\mathbf{2R}_I(t)-\mathbf{R}_I(t-\Delta t)+\Delta t^2\mathbf{F}_I(t)/M_I$

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

e.g. Velocity scaling thermostat

Update atomic positions: $\mathbf{R}_i(t)=\mathbf{R}_i(t+\Delta t)$

Molecular Dynamics details omitted in the lecture

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

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

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

NVE – microcanonical ensemble vs. NVT – canonical ensemble

Thermostats

Velocity scaling approaches
e.g. Berendesen

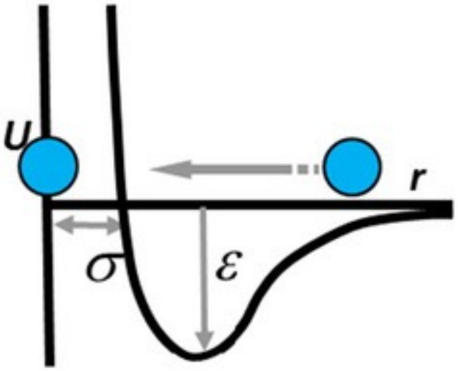
$$M_I\ddot{\boldsymbol{R}}_I = \boldsymbol{F}(\boldsymbol{R})\text{-}(M_I/\tau)(T^*/T-1)\,\dot{\boldsymbol{R}}_I$$

Extended Lagrangian approaches
e.g. Nose

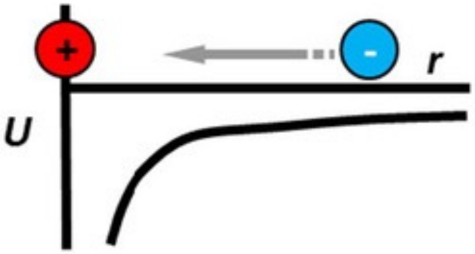
$$L_{Nose} = \sum_I \frac{M_I}{2}s^2\dot{\boldsymbol{R}}_I^{\,2} - U(\boldsymbol{R}) + \frac{Q}{2}\dot{s}^2 - gk_BT^*\ln s$$

A typical mathematical expression for Potential Energy, U, in classical MD

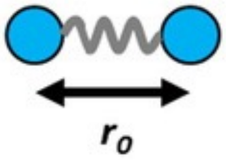
$$U(\{R_i\}) = \sum_{i<j}\sum 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



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

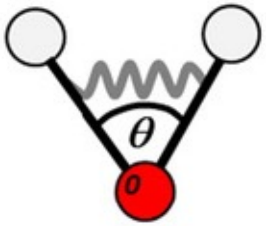


$$+ \sum_{bonds}\frac{1}{2}k_b(r-r_0)^2$$

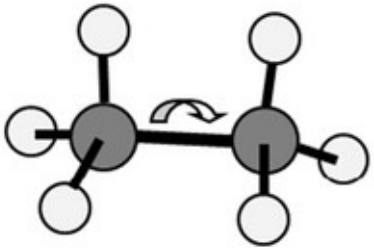


Empirical parameters are determined by fitting to experiments and electronic structure calculations.

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



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



First Principles (Born Oppenheimer) Molecular Dynamics

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

$$\downarrow$$

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

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

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

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

Note : Atom → Nucleus (R_I) + *Electrons* (r_i)

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

$$\uparrow$$

Classical nuclear-nuclear repulsion

Where does DFT come in?

Hellmann-Feynman Theorem

Force on nucleus that is indexed with I

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

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

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

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

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

Recall the expression for the Hamiltonian

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

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

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

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

Electron density

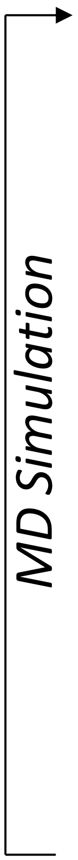
$$\rho(\mathbf{r}; \mathbf{R}) \equiv N \int \Psi_0^*(\mathbf{r}, \mathbf{r}_{2 \ldots} \mathbf{r}_{\mathrm{n}}; \mathbf{R})\, \Psi_0(\mathbf{r}, \mathbf{r}_{2 \ldots} \mathbf{r}_{\mathrm{n}}; \mathbf{R})\, d\mathbf{r}_{2 \ldots} d\mathbf{r}_{\mathrm{n}}$$

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

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

First-Principles Molecular Dynamics based on DFT

$$\boxed{\begin{array}{l} m_e = 1 \\ \hbar = 1 \end{array}}$$



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

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

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

2. Calculate force on each nucleus/ion:

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

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

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

Remark about Different Implementations in Practice

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

Codes : FHI-aims

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

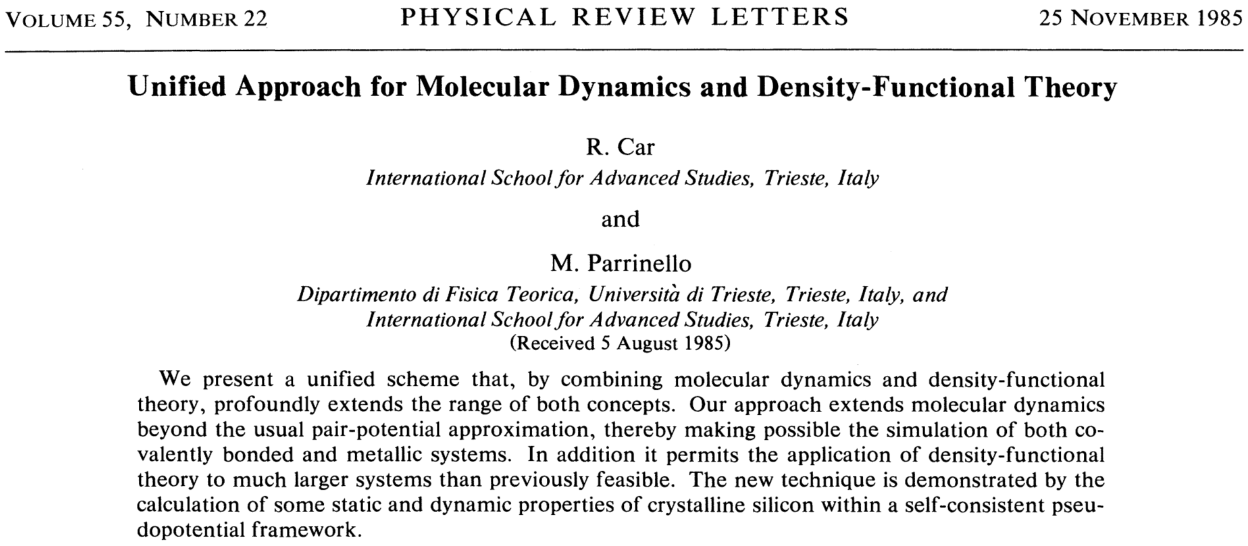
Planewaves - Pseudopotential (PW-PP) :

Planewaves are used as basis set functions with "pseudo"-potentials to replace core electrons.

Codes: Quantum-Espresso, VASP, Qbox/Qb@ll

Popular for FPMD - the forces are easy to implement.

Car Parrinello (extended Lagrangian) Molecular Dynamics: “CPMD”



VOLUME 55, NUMBER 22 PHYSICAL REVIEW LETTERS 25 NOVEMBER 1985

Unified Approach for Molecular Dynamics and Density-Functional Theory

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

and

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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 beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

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 (QE), Qbox, Qb@ll, etc.

*CP2K does not have CPMD!

Car Parrinello extended Lagrangian

Lagrange multiplier for
enforcing orthonormality

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

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 set 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

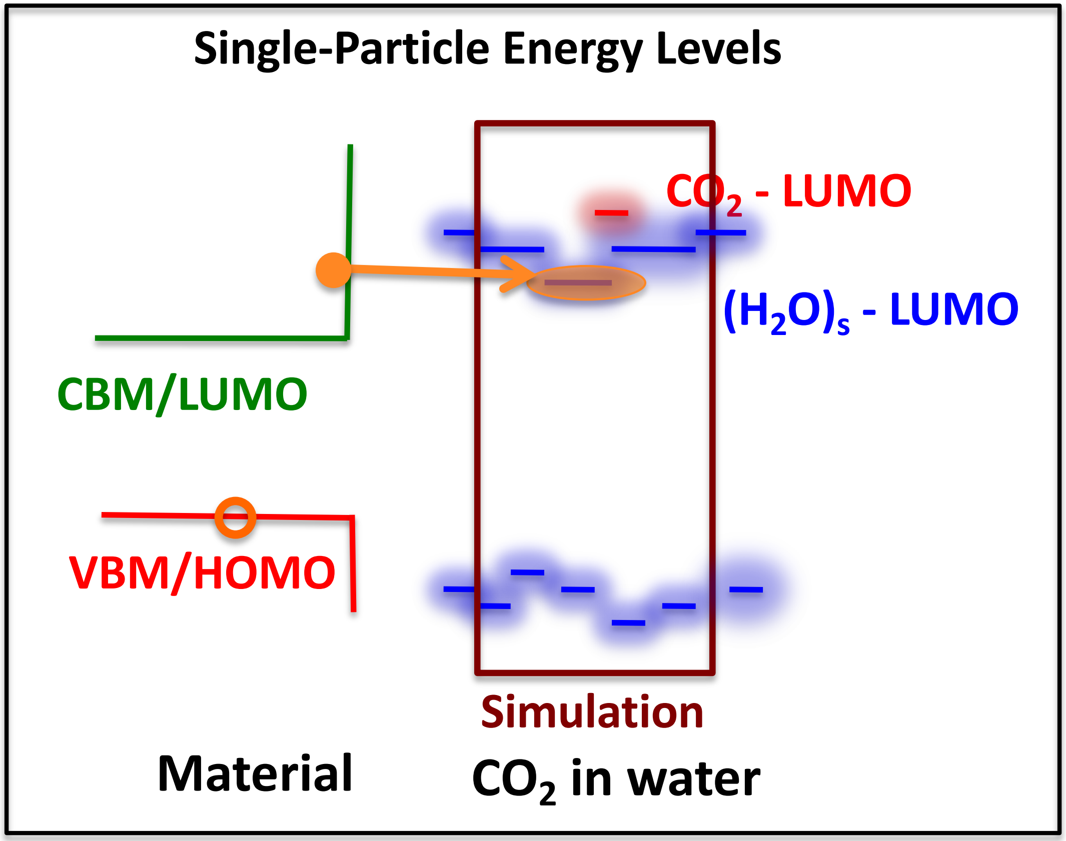
“The heart of the matter is the ‘‘on the fly’’ calculation of the potential energy surface for nuclear motion, without performing a self-consistent diagonalization of the Kohn–Sham Hamiltonian at each time step…

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

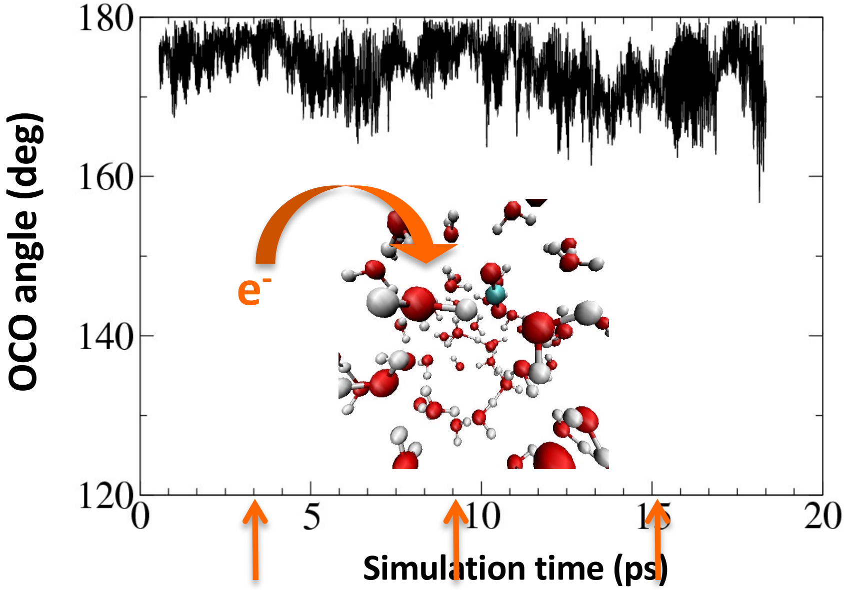
Roberto Car in “AB INITIO Molecular Dynamics: Dynamics and Thermodynamic Properties” (2006)

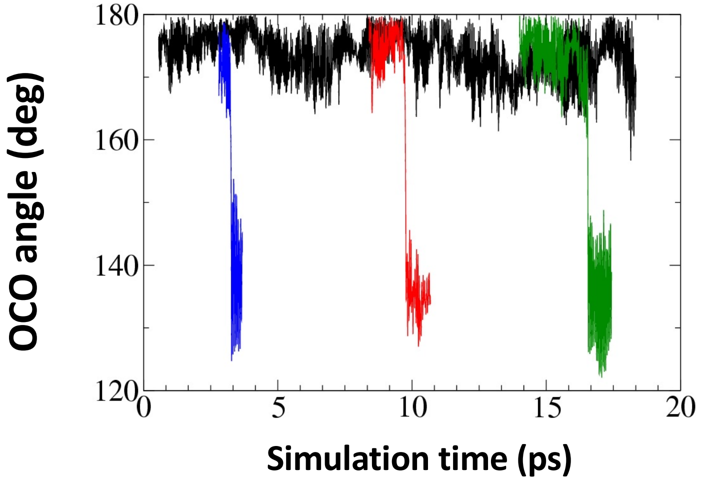
Applications

Electron localization on CO_2 in Water



Injection of an extra electron:

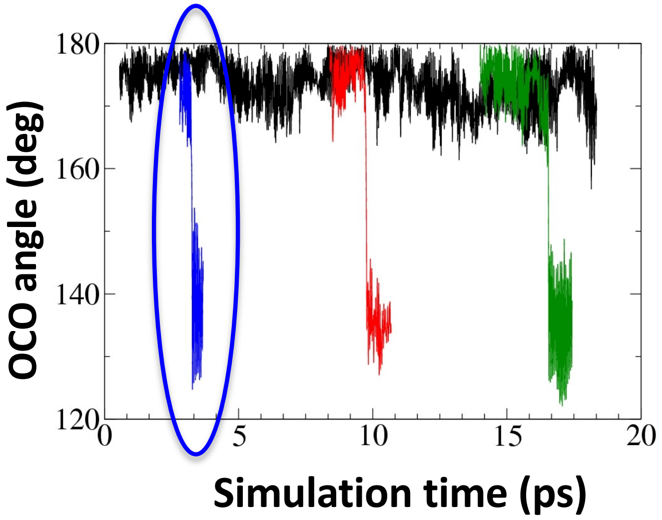


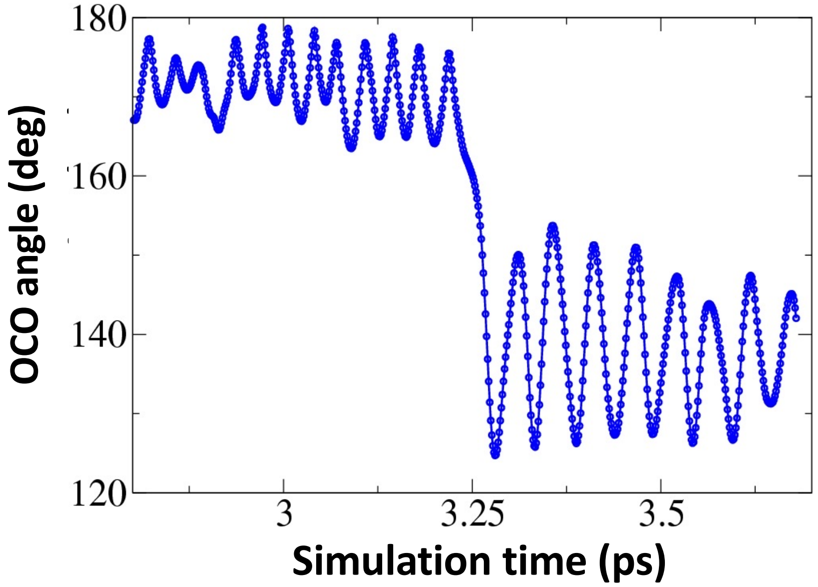


Experiment

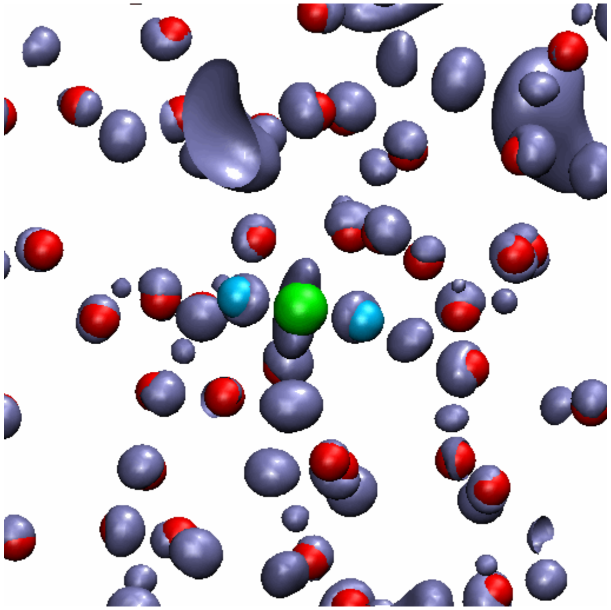
Zhang, LH. Et al. Angwdt. Chemie, 53, 9746 (2014)

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.

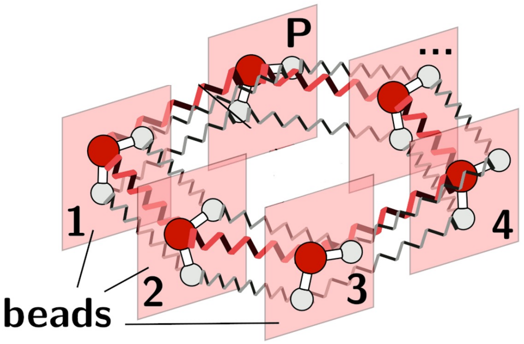
Large stochastic fluctuations prompt the electron to localize further, and it reciprocally causes the angle to become smaller as CO_2 anion.

A few selections of Challenges and Advanced Topics for FPMD

You have exciting opportunities to contribute and advance the field!

Challenge and Advanced Topic: Nuclear Quantum Effects (NQE)

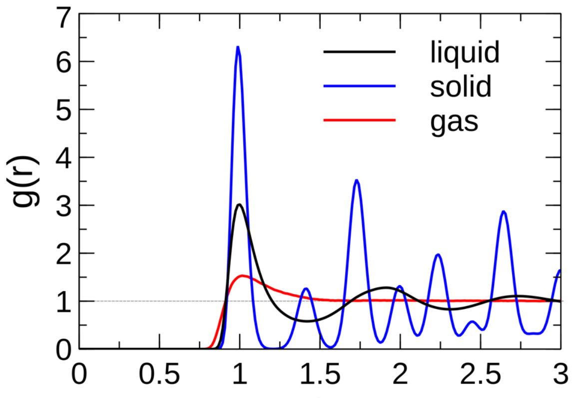
Path integral (PI) method allows us to model atomic nuclei as QM particles.

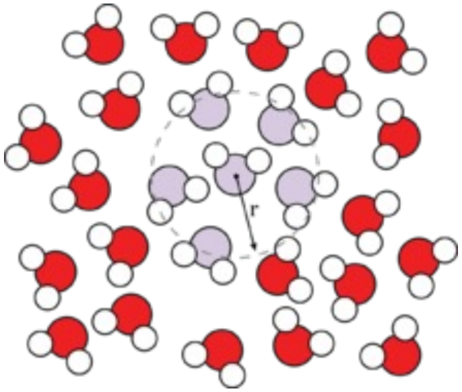


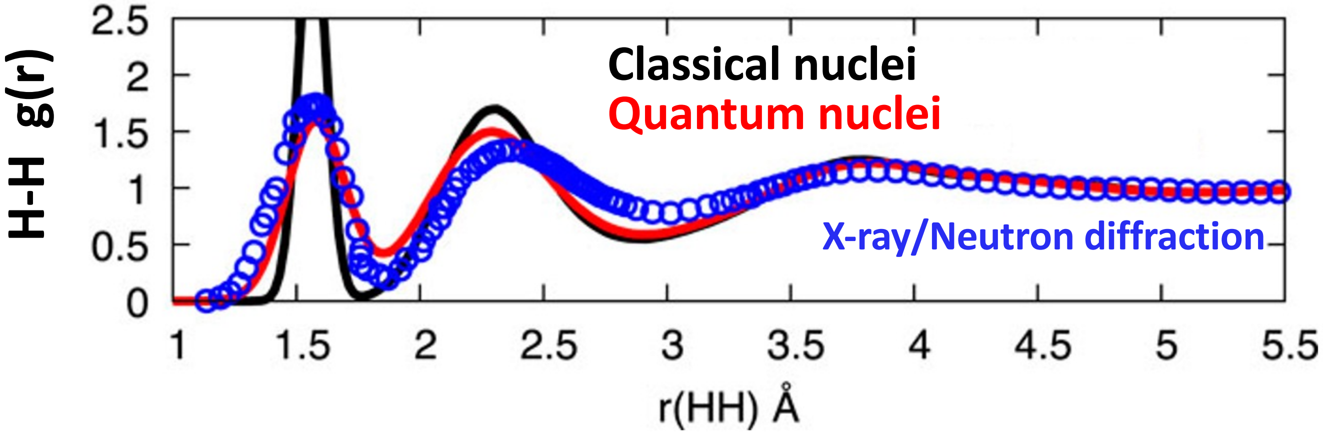
An artificial neural network (ANN) was used to “machine-learn” FPMD simulation w/ meta-GGA (SCAN).

Yao and Kanai, J. Chem. Phys. 153, 044114 (2020)

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



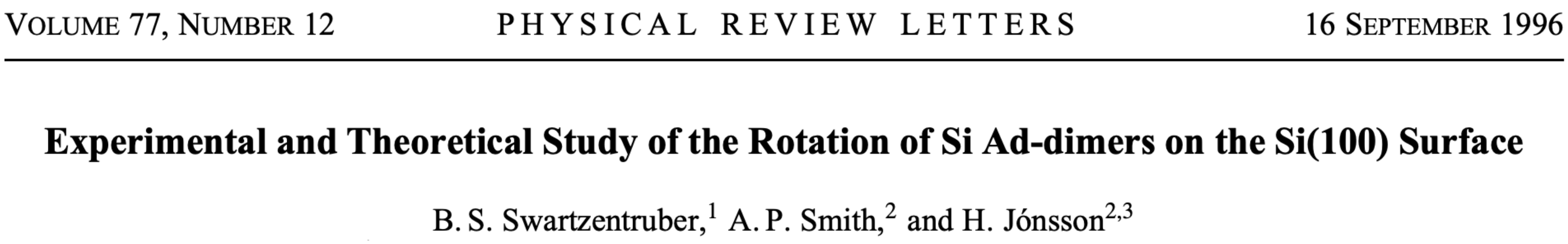




Soper and Benmore, Phys. Rev. Lett. , 101, 065502 (2008)

Challenge and Advanced Topic: “Rare Event” Problem

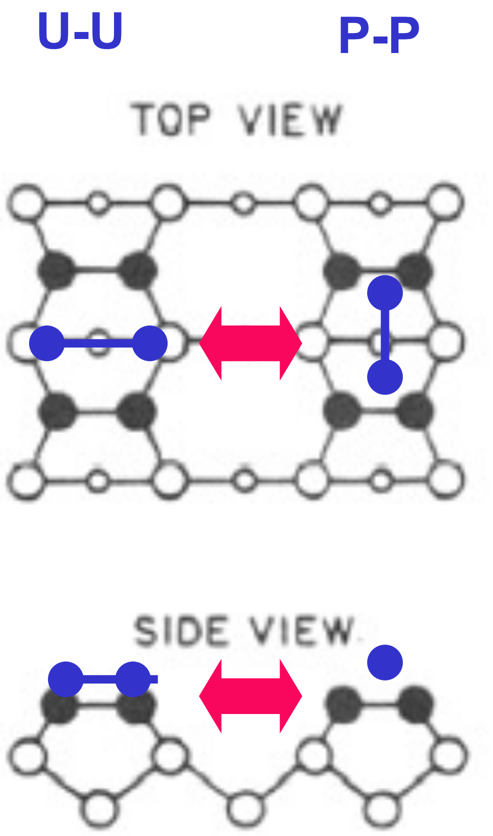
Si-Si ad-dimer rotation on Si(001) surface



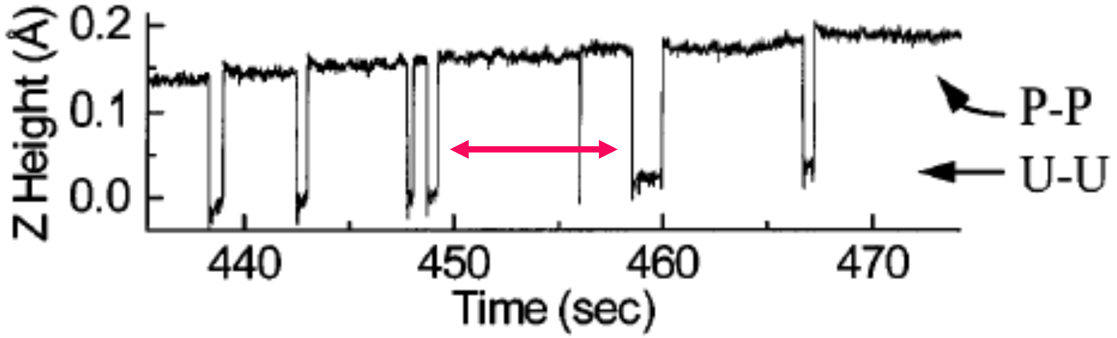
VOLUME 77, NUMBER 12 PHYSICAL REVIEW LETTERS 16 SEPTEMBER 1996

Experimental and Theoretical Study of the Rotation of Si Ad-dimers on the Si(100) Surface

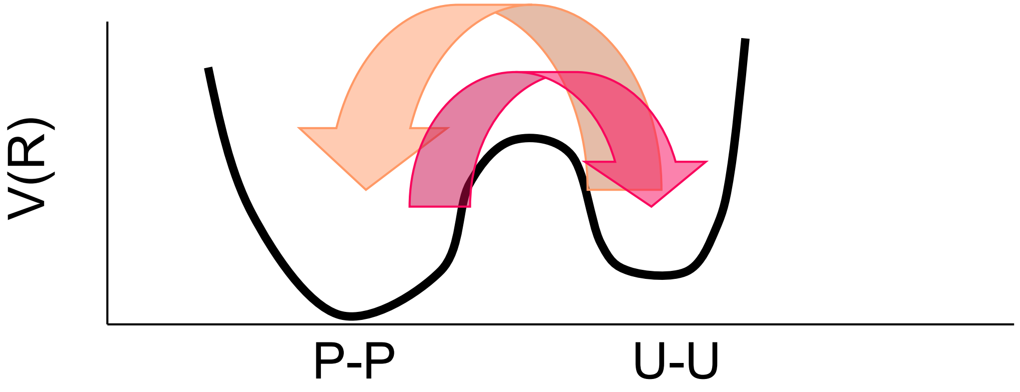
B. S. Swartzentruber,[1] A. P. Smith,[2] and H. Jónsson[2,3]



Time-resolved STM



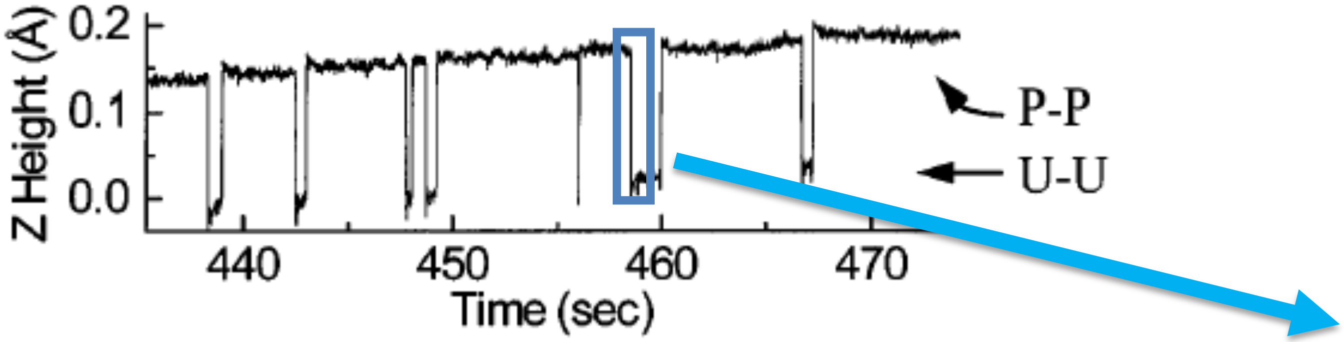
Time between subsequent transitions 1 ~10 sec

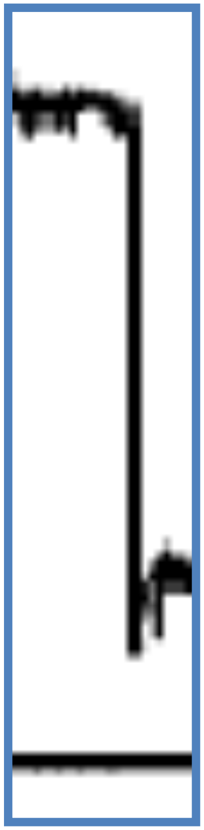


Challenge and Advanced Topic: “Rare Event” Problem

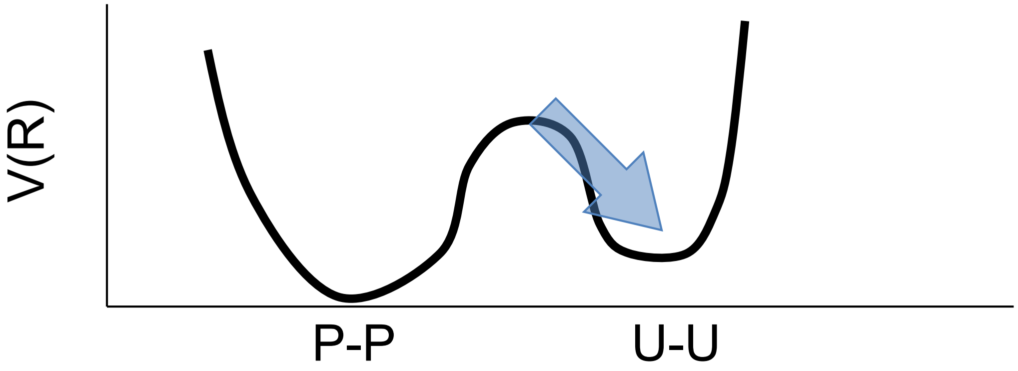
How many MD steps do we need before observing a *“single”* transition event on average in an MD simulation?

With a MD time step of Δt = 1 femto-sec, 10^{16} steps are needed !!!!





But, the transition itself takes place extremely fast.



Challenge and Advanced Topic: "Rare Event" Problem

Why not increase the MD time step ?

1. A very fast process (< 1 ps) when it happens. Needs a very good time resolution.
2. Numerical integrator (e.g. Verlet) restricts the largest possible time step.

Rare-event problem

Unlikely to observe such a transition if the energy barrier is high.

Advanced methods such as

Nudged Elastic Band
String Method
Meta Dynamics, etc

are needed to find "Minimum energy path" and/or Transition States.

Time-Dependent Density Functional Theory

Many-body dynamics is governed by time-dependent density!

$$O(t) = \left\langle \Psi(t) \middle| \hat{O} \middle| \Psi(t) \right\rangle = O[\rho(t); \Psi(t_0)]$$

Hohenberg-Kohn Theorem (1965): *Phys. Rev. 136, B684 (1964)*

One-to-one correspondence between the external potential and the ground-state (equilibrium) density $\rho_0(\mathbf{r})$.

$$\begin{tikzcd}
\Psi_0^A(\{\mathbf{r}_\mathrm{i}\}) \arrow[dr] & & \\
& \rho_0(\mathbf{r}) & \text{cannot happen.} \\
\Psi_0^B(\{\mathbf{r}_\mathrm{i}\}) \arrow[ur] & &
\end{tikzcd}$$

A fun read “A half century of density functional theory” A. Zangwill, Physics Today 68, 34 (2015)

Runge-Gross Theorem (1984): *Phys. Rev. Lett. 52, 997 (1984)*

One-to-one correspondence between time-dependent density and time-dependent potential, given the same initial many-body state at t_0.

$$\begin{tikzcd}
\Psi^A(t)[\Psi(t_0)] \arrow[dr] & & \\
& \rho\,(\mathbf{r}, t) & \text{cannot happen.} \\
\Psi^B(t)[\Psi(t_0)] \arrow[ur] & &
\end{tikzcd}$$

Kohn-Sham Ansatz

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) = -\nabla\cdot\mathbf{j}(\mathbf{r},t)$$

$$\mathbf{j}(\mathbf{r},t) = -\tfrac{i}{2}N\int d\mathbf{r}_2\int d\mathbf{r}_3 \ldots \int d\mathbf{r}_N\{\Psi^*(\mathbf{r},\mathbf{r}_2,\ldots\mathbf{r}_N,t)\nabla\Psi(\mathbf{r},\mathbf{r}_2,\ldots\mathbf{r}_N,t) - \nabla\Psi^*(\mathbf{r},\mathbf{r}_2,\ldots\mathbf{r}_N,t)\Psi(\mathbf{r},\mathbf{r}_2,\ldots\mathbf{r}_N,t)\}$$

A set of single-particle orbitals that yield the true <u>density</u> (Kohn-Sham system)

$$\rho(\mathbf{r},t) = \tfrac{1}{\Omega}\int_{BZ} d\mathbf{k}\sum_{i}^{N} f_{i,\mathbf{k}}\left|\phi_{i,\mathbf{k}}(\mathbf{r},t)\right|^2$$

$$|\phi_{i,\mathbf{k}}(t)\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}|u_{i,\mathbf{k}}(t)\rangle$$

$$i\frac{\partial}{\partial t}\phi_{i,\mathbf{k}}(\mathbf{r},t) = \underbrace{\left\{\frac{1}{2}\left(-i\nabla+\mathbf{A}_{ext}(\mathbf{r},t)\right)^2 + v_{ext}(\mathbf{r},t) + \int d\mathbf{r}'\,\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{XC}(\mathbf{r},t)\right\}}_{\widehat{H}_{KS}}\phi_{i,\mathbf{k}}(\mathbf{r},t)$$

$$\mathbf{j}(\mathbf{r},t) = \tfrac{1}{2\Omega}\int_{BZ} d\mathbf{k}\sum_{i}^{N}\phi_{i,\mathbf{k}}^*(\mathbf{r},t)\left(-i\nabla+\mathbf{A}_{ext}(\mathbf{r},t)\right)\phi_{i,\mathbf{k}}(\mathbf{r},t) + c.c.$$

Quantum Dynamics via Time-Dependent Kohn-Sham Eq.

Energy functional as Constant-of-Motion

$$E[\rho(t)] = \frac{1}{2\Omega}\int_{BZ} d\mathbf{k} \sum_i f_i \left\langle \phi_{i,\mathbf{k}}(t) \middle| \left(-i\nabla + \mathbf{A}_{ext}(\mathbf{r},t)\right)^2 \middle| \phi_{i,\mathbf{k}}(t) \right\rangle$$
$$+ \iint d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r},t)\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + \int \rho(\mathbf{r},t)v_{ext}(\mathbf{r},t)d\mathbf{r} + E_{XC}[\rho(t)]$$

Adiabatic approximation $v_{XC}[\rho](\mathbf{r},t) \to v_{XC}[\rho(t)](\mathbf{r},t)$

$$\frac{d}{dt}E(t) = \frac{1}{2\Omega}\int_{BZ} d\mathbf{k} \sum_i f_{i,\mathbf{k}} \left\langle \phi_{i,\mathbf{k}}(t) \middle| \hat{H}_{KS}[\rho(t)] \middle| \frac{d}{dt}\phi_{i,\mathbf{k}}(t) \right\rangle + c.c.$$

$= 0$ when $\mathbf{A}_{ext}/\ v_{ext}$ is time-independent

Schleife, et al. J. Chem. Phys. 137, 22A546 (2012)

Interaction w/ Electromagnetic Field

Gauge invariance for applied EM field

$$\hat{H}_{KS}(t) = \frac{1}{2}\left(-i\nabla + \mathbf{A}(\mathbf{r},t)\right)^2 + \phi(\mathbf{r},t) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + v_{XC}(\mathbf{r},t) - \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I(t)|}$$

EM-field effect can be described either via $\mathbf{A}$ or ϕ.

$$\boldsymbol{E} = -\nabla\phi - \frac{\partial \mathbf{A}}{\partial t} \qquad \boldsymbol{B} = \nabla\times \mathbf{A}$$

"Delta kick" - E-field is applied suddenly at t=0 (all frequencies).

Macroscopic current

$$\boldsymbol{J}(t) = \int d\mathbf{r}\, \mathbf{j}(\mathbf{r};t)$$

Conductivity

$$\sigma_{\mu\nu}(\omega) = \frac{1}{E_\nu(\omega)}\int^T dt e^{i\omega t} J_\mu(t)$$

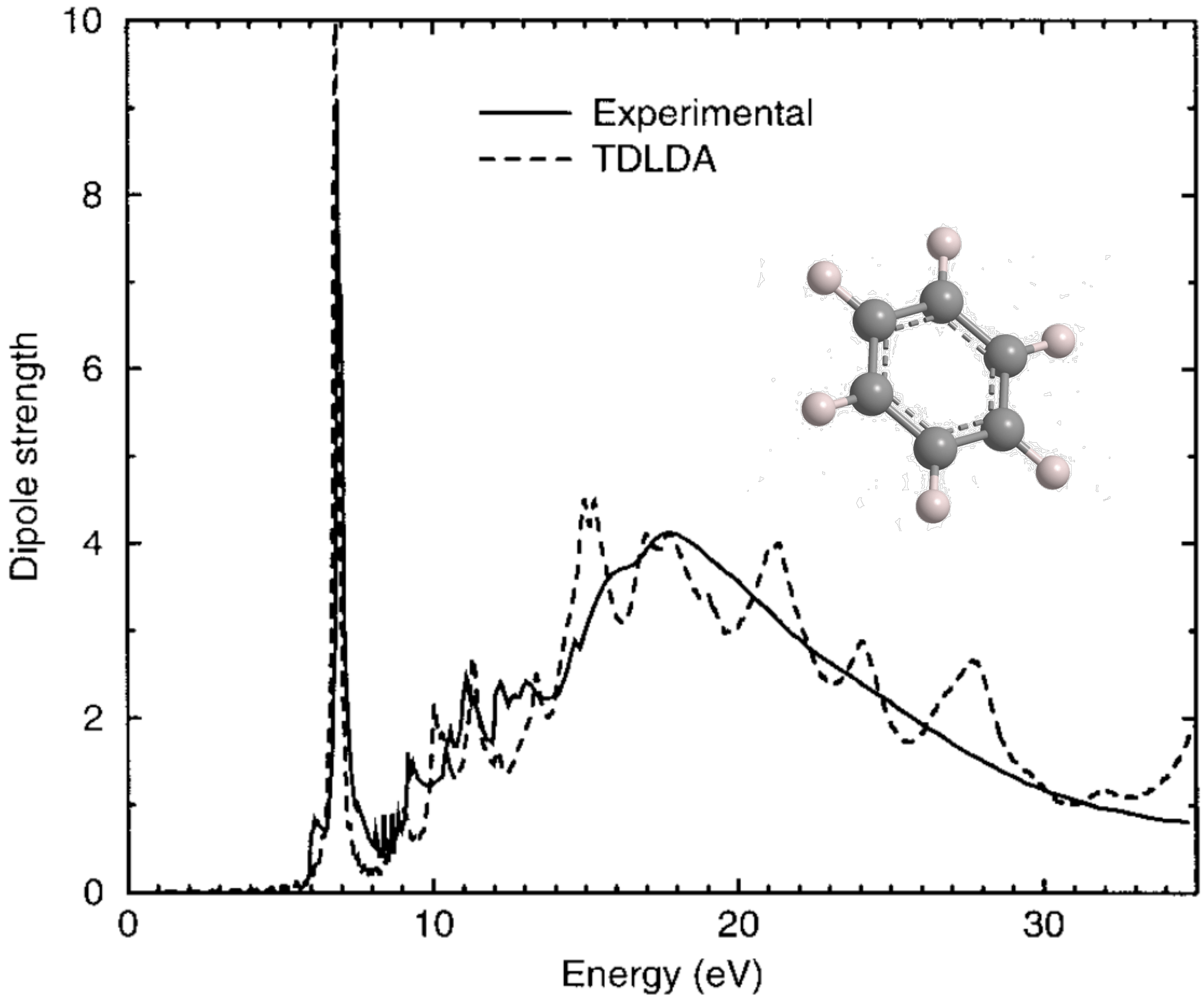
Dipole strength function (molecules)

$$S(\omega) = \frac{4\pi\omega}{3c} Tr\left[Im\ \sigma_{\mu\nu}(\omega)\right]$$

Dielectric function (extended systems)

$$\varepsilon(\omega) = 1 + \frac{4\pi i}{3\omega} Tr\left[\sigma_{\mu\nu}(\omega)\right]$$

Great Success! : Optical absorption spectrum of Benzene



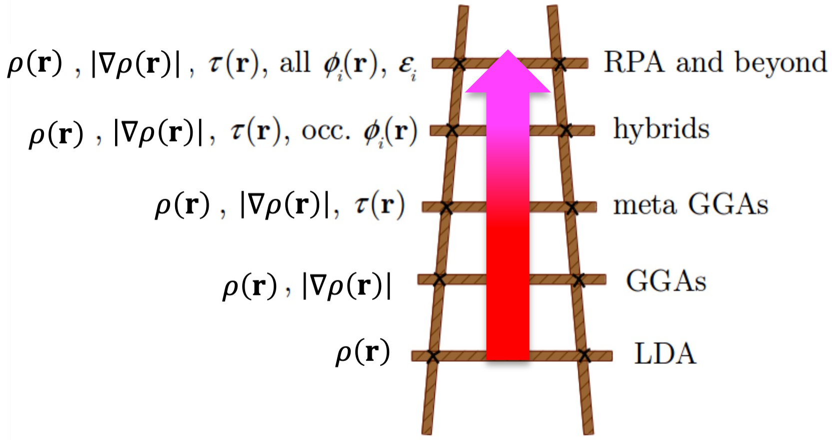
“Time-dependent local-density approximation in real time: Application to conjugated molecules”

Yabana and Bertsch, Int’l J. Quantum Chem. 75, 55 (1999)

The devil is the details: Exchange and Correlation (XC) Functional

v_{XC}!

Heaven of Chemical Accuracy



$\rho(\mathbf{r})$, $|\nabla\rho(\mathbf{r})|$, $\tau(\mathbf{r})$, all $\phi_i(\mathbf{r})$, ε_i — RPA and beyond

$\rho(\mathbf{r})$, $|\nabla\rho(\mathbf{r})|$, $\tau(\mathbf{r})$, occ. $\phi_i(\mathbf{r})$ — hybrids

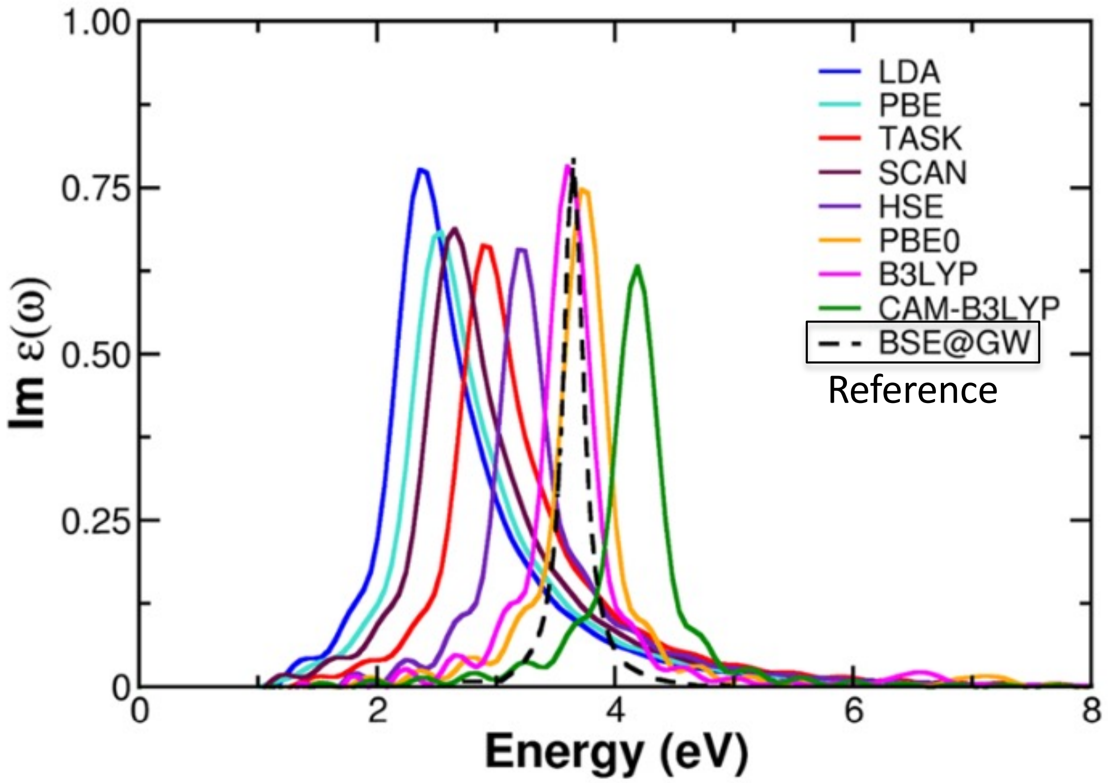
$\rho(\mathbf{r})$, $|\nabla\rho(\mathbf{r})|$, $\tau(\mathbf{r})$ — meta GGAs

$\rho(\mathbf{r})$, $|\nabla\rho(\mathbf{r})|$ — GGAs

$\rho(\mathbf{r})$ — LDA

Hartree's Earth

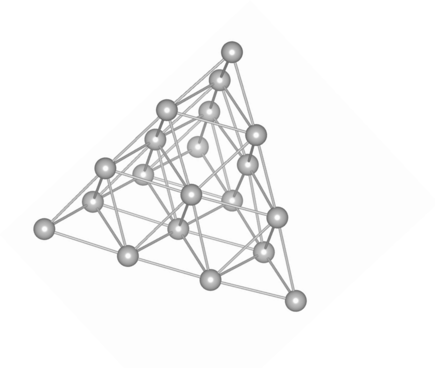
Hydrogen Chain



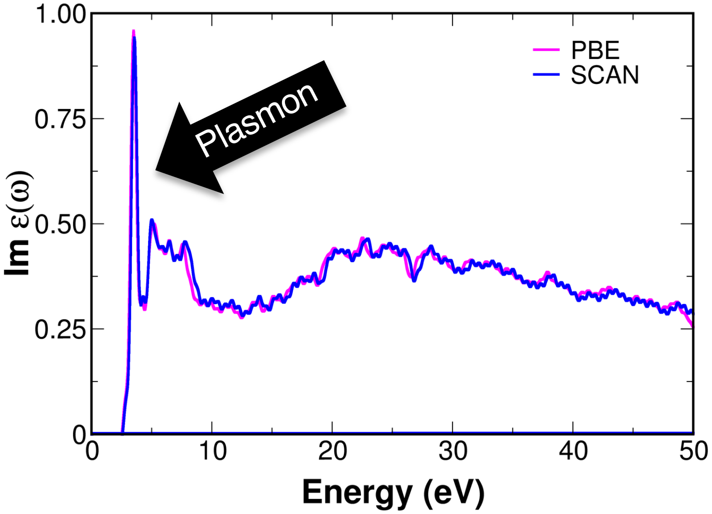
Reference

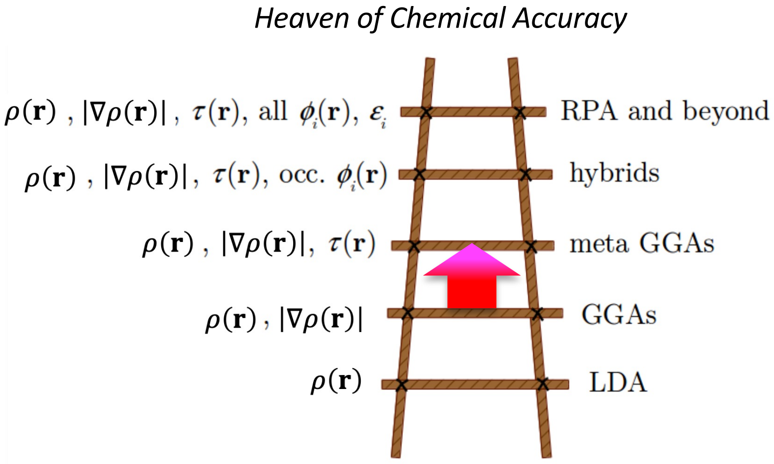
Real-Time TDDFT for Simulating Nonequilibrium Electron Dynamics (Perspective)
J. Xu, T. E. Carney, R. Zhou, C. Shepard, Y. Kanai
J. Am. Chem. Soc. 146, 5011 (2024)

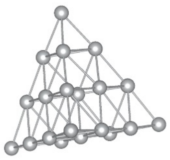
Application : Ag_{20} cluster at H-Si(111) surface

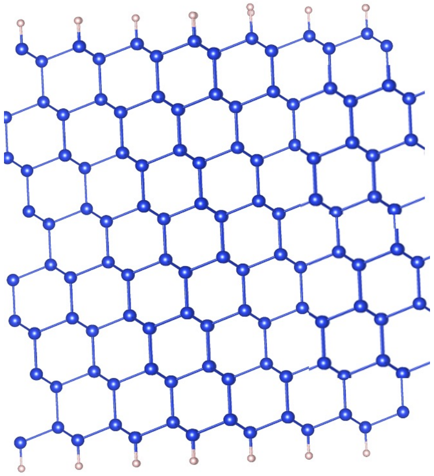


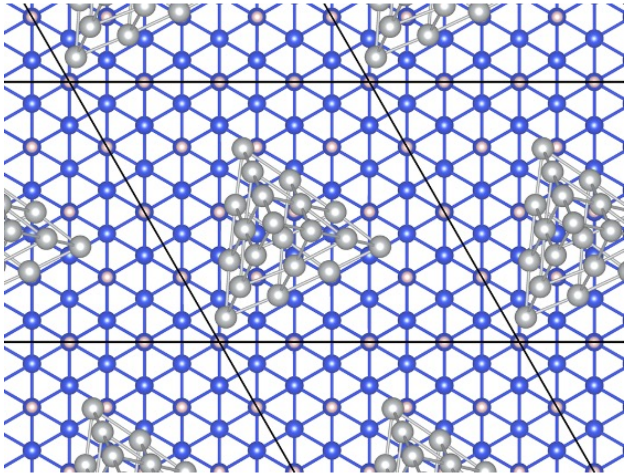
Ag_{20} Cluster



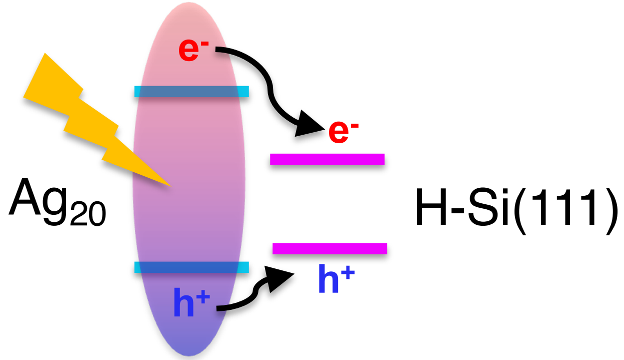








Type-I level alignment



J. Bost, C. Shepard and Y. Kanai

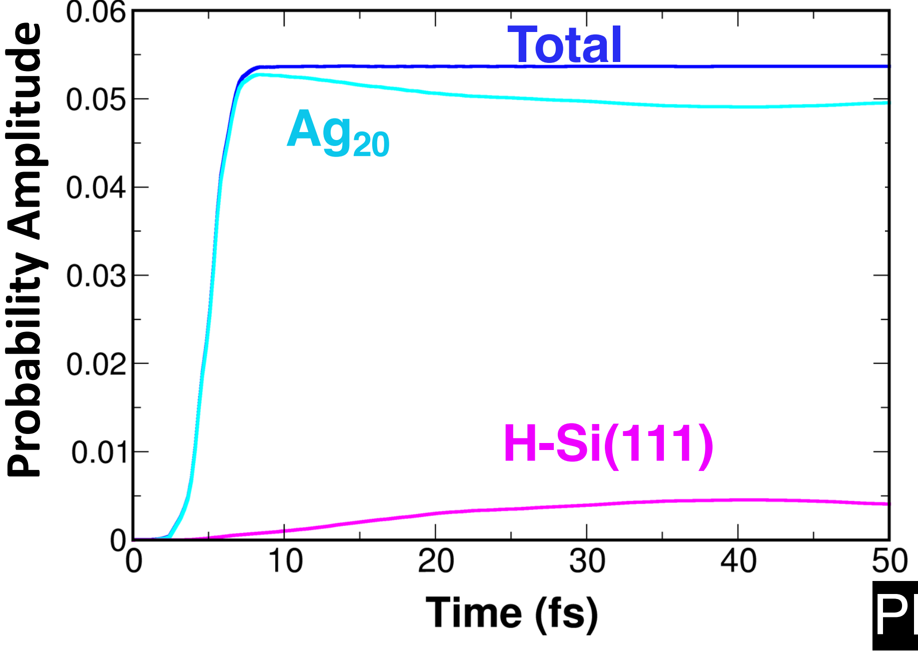
Journal of Physics: Condensed Matter, 37, 045502 (2024)

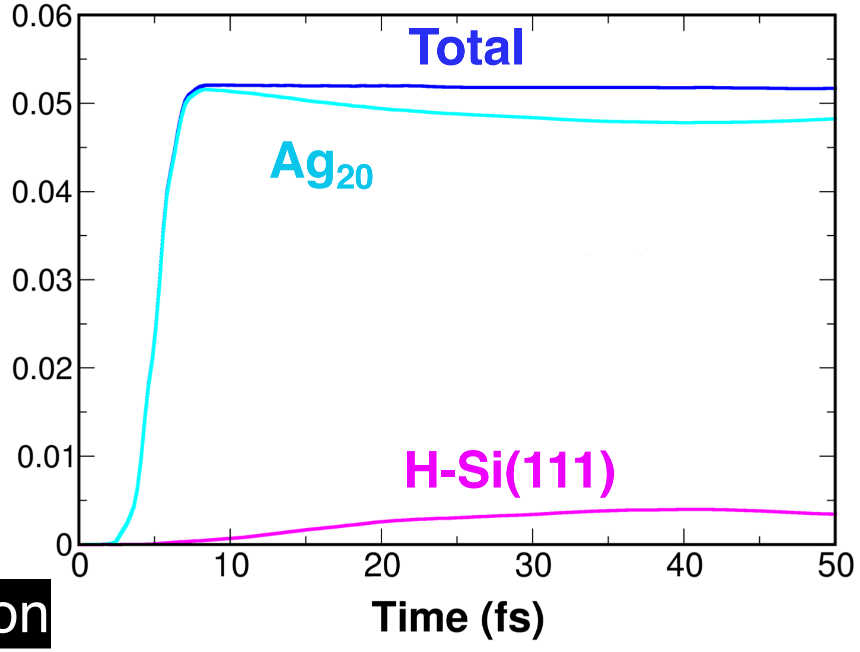
Excitation of Ag_{20} cluster at H-Si(111) surface

Hole

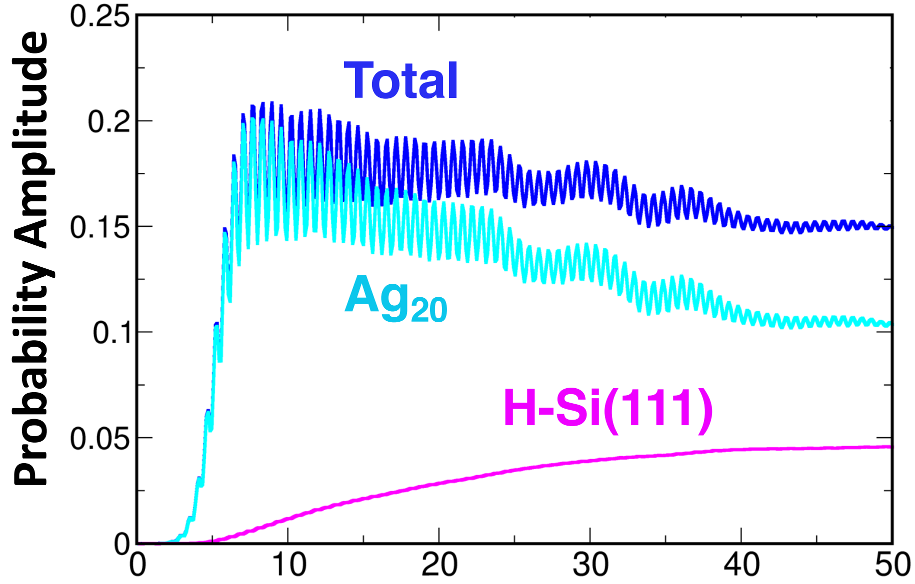
Normal Excitation

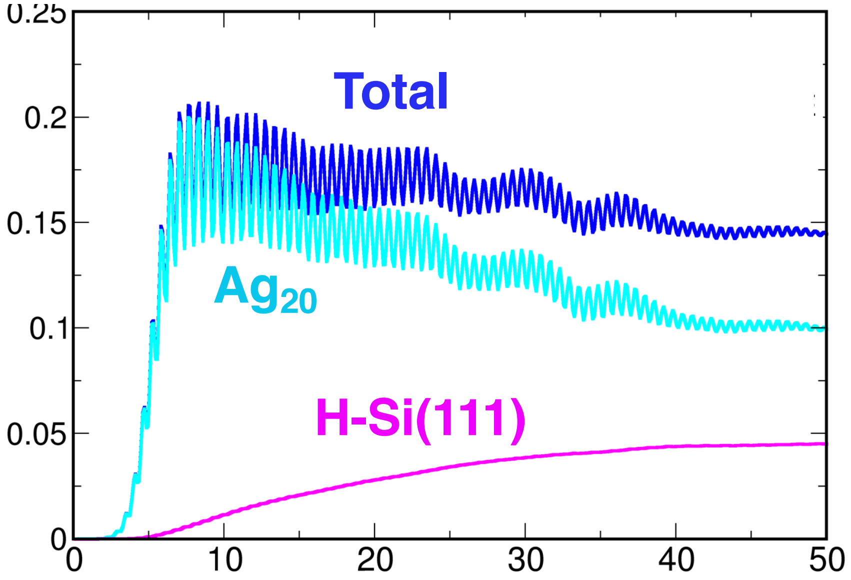
Excited Electron





Plasmon





Accounting for Electron Dynamics in Molecular 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

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

Ehrenfest Dynamics, with Real-time Time-Dependent DFT

$$M_I \ddot{\boldsymbol{R}}_I = -\nabla_{\boldsymbol{R}_\mathrm{I}} E^{DFT}[\rho(t); \boldsymbol{R}]$$

$$\rho(\mathbf{r}, t) = \frac{1}{\Omega} \int_{BZ} d\mathbf{k} \sum_i^N f_{i,\mathbf{k}} \left|\phi_{i,\mathbf{k}}(\mathbf{r}, t)\right|^2$$

$$i \frac{\partial}{\partial t} \phi_{i,\mathbf{k}}(\mathbf{r}, t) = \left\{\frac{1}{2}\left(-i\nabla + \mathbf{A}_{ext}(\mathbf{r}, t)\right)^2 + v_{ext}(\mathbf{r}, t) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{XC}(\mathbf{r}, t)\right\} \phi_{i,\mathbf{k}}(\mathbf{r}, t)$$

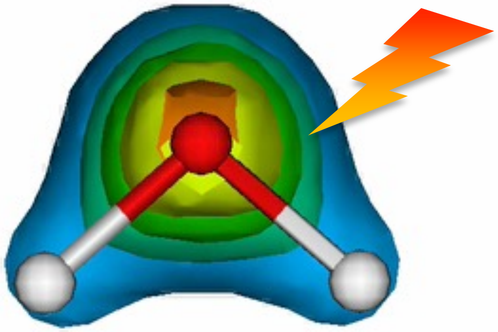
Ehrenfest Dynamics with RT-TDDFT

RT-TDDFT with MD for atomic nuclei (i.e. Ehrenfest Dynamics)

Coupled dynamics of quantum electrons and classical atomic nuclei

$$M_I \frac{d^2}{dt^2}\mathbf{R}_I(t) = -\nabla_I\left(E^{DFT}[\rho(t)]\right)$$

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \hat{H}_{KS}(t)\phi_i(\mathbf{r},t)$$



Electrons are "excited" with 8.75 eV photons.

Electron dynamics (i.e. excitation) induces the movement of classical atomic nuclei.