First-principles Molecular Dynamics Simulations

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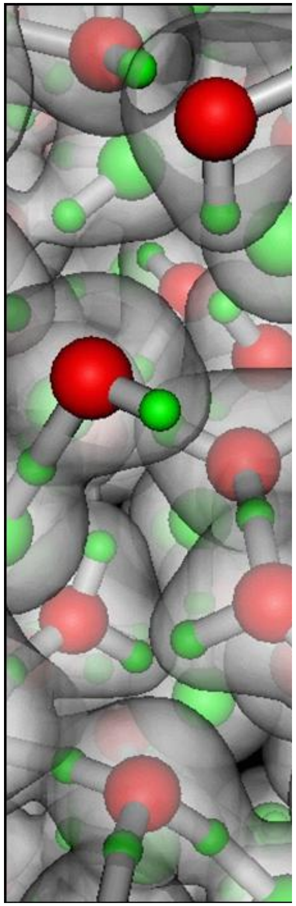
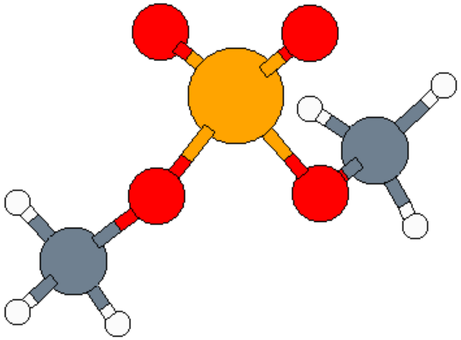
MICCoM Computational School, Jul 17-19, 2017

Outline

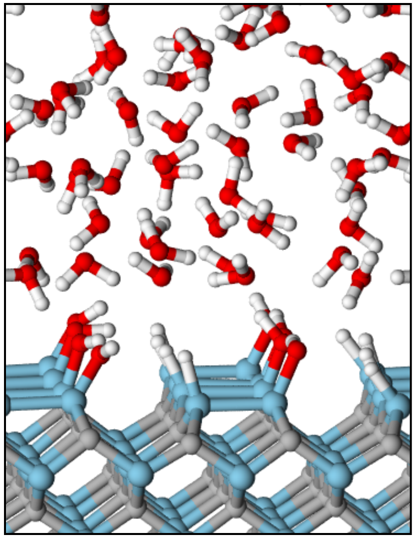
- Molecular dynamics simulations
- Electronic structure calculations
- First-Principles Molecular Dynamics (FPMD)
- Applications





Molecular Dynamics

- An atomic-scale simulation method
  - Compute the trajectories of all atoms
  - extract statistical information from the trajectories



Atoms move according to Newton's law:

$$\boxed{m_i \ddot{\mathbf{R}}_i = \mathbf{F}_i}$$

Molecular dynamics: general principles

- Integrate Newton's equations of motion for N atoms

$$m_i \ddot{\mathbf{R}}_i(t) = \mathbf{F}_i(\mathbf{R}_1,\ldots,\mathbf{R}_N) \quad i = 1,\ldots,N$$

$$\mathbf{F}_i(\mathbf{R}_1,\ldots,\mathbf{R}_N) = -\nabla_i E(\mathbf{R}_1,\ldots,\mathbf{R}_N)$$

- Compute statistical averages from time averages (ergodicity hypothesis)

$$\langle A \rangle = \int_\Omega dr^{3N}\, dp^{3N} A(\mathbf{r},\mathbf{p}) e^{-\beta H(\mathbf{r},\mathbf{p})} \cong \frac{1}{T}\int_0^T A(t)\,dt$$

- Examples of $A(t)$: potential energy, pressure, …

Simple energy model

- Model of the hydrogen molecule (H_2): harmonic oscillator

$$E(\mathbf{R}_1,\mathbf{R}_2) = E(|\mathbf{R}_1 - \mathbf{R}_2|)$$

$$= \alpha(|\mathbf{R}_1 - \mathbf{R}_2| - d_0)^2$$

- This model does not describe intermolecular interactions

Simple energy model

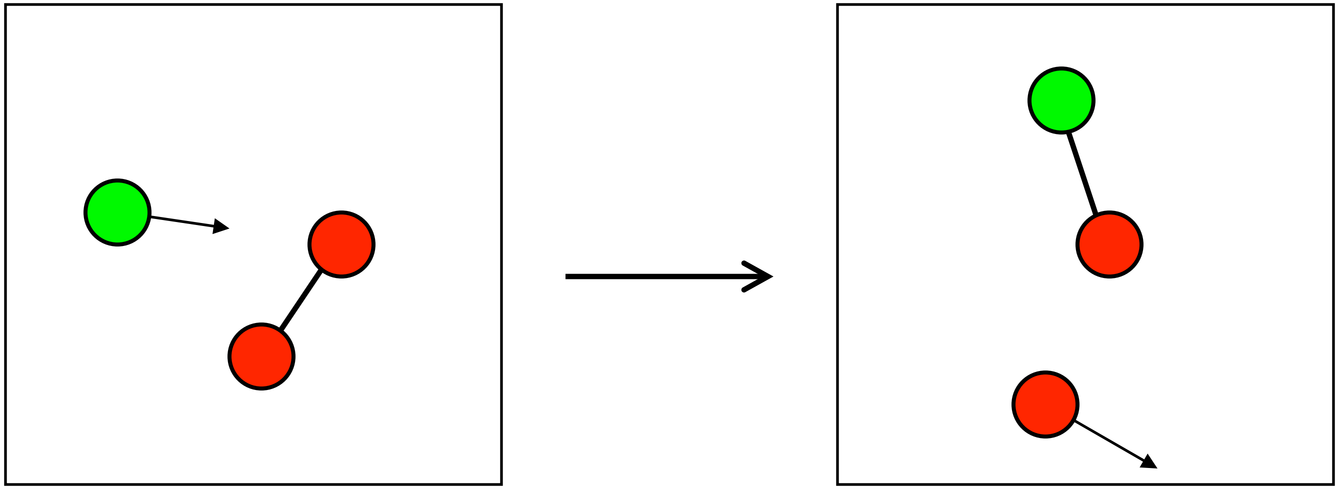
- Model of the hydrogen molecule including both intra- and intermolecular interactions:

$$E(\mathbf{R}_1,\ldots,\mathbf{R}_N) = \sum_{\{i,j\}\in M} E_{\text{intra}}(|\mathbf{R}_i - \mathbf{R}_j|) + \sum_{\substack{i\in M \\ j\in M'}} E_{\text{inter}}(|\mathbf{R}_i - \mathbf{R}_j|)$$

- This model does not describe adequately changes in chemical bonding

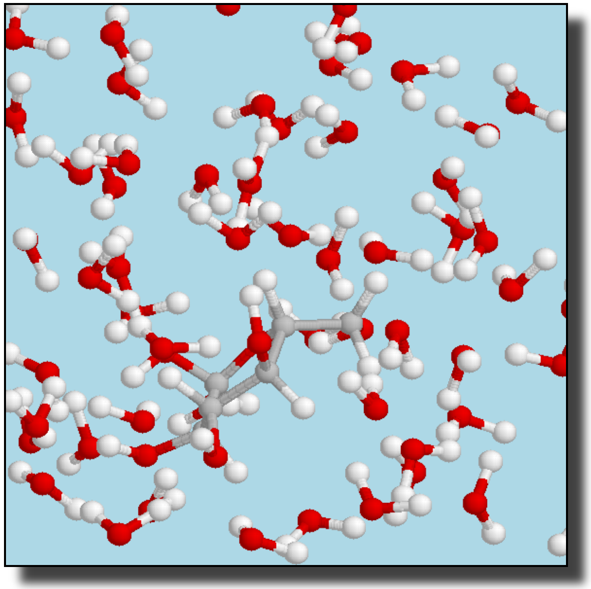
Simple energy model

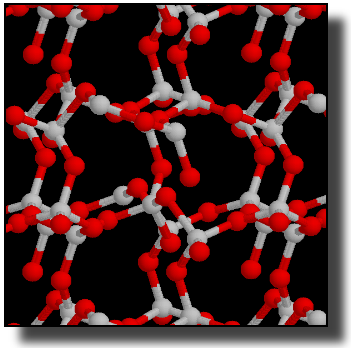
- Description of the reaction $H_2 + H \rightarrow H + H_2$

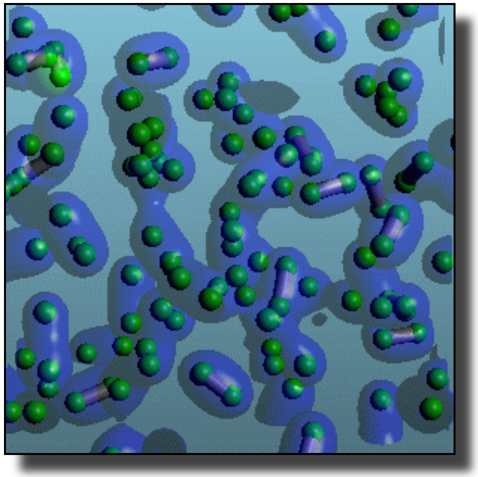


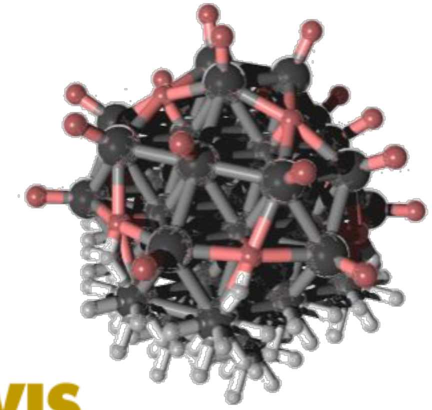
- The model fails!

What is a good energy model?









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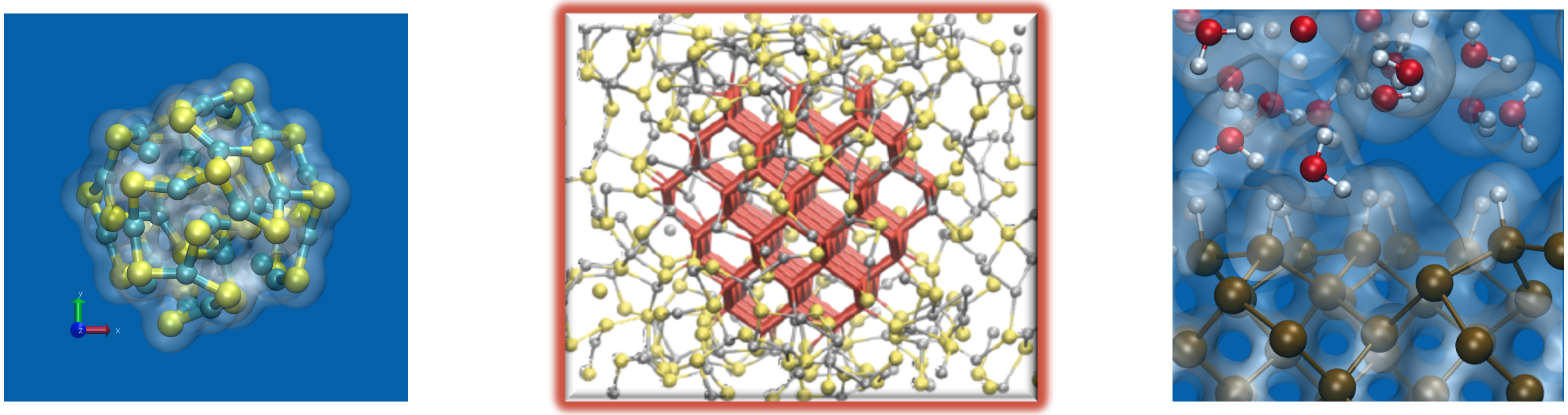
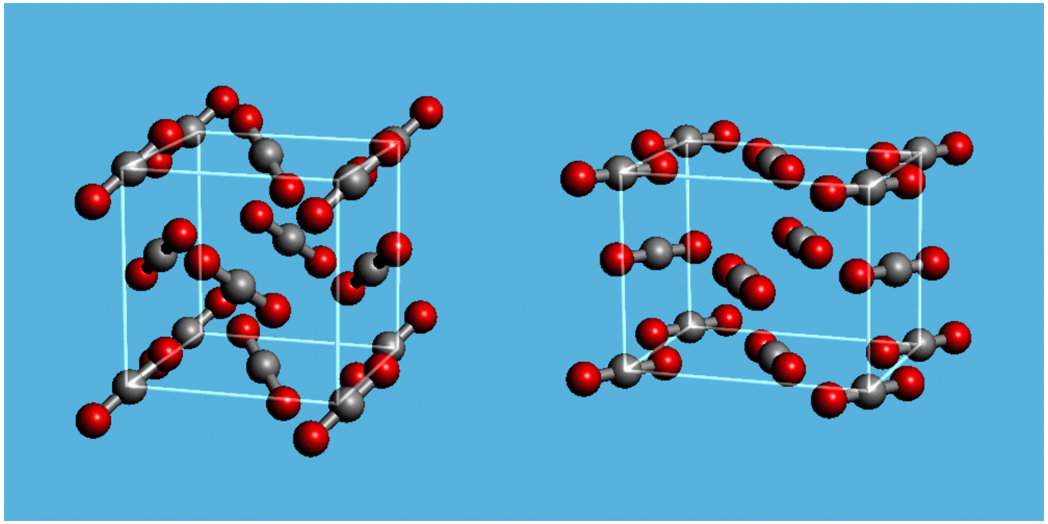
Atomistic simulation of complex structures

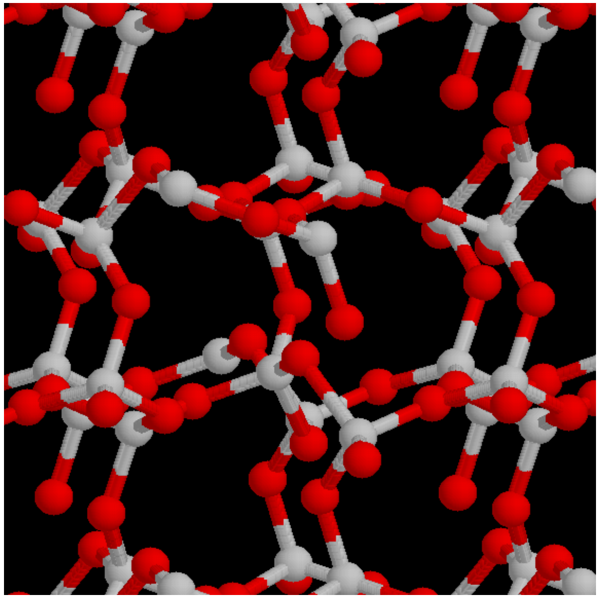
- Complex structures
  - Nanoparticles
  - Assemblies of nanoparticles
  - Embedded nanoparticles
  - Liquid/solid interfaces



A difficult case: Structural phase transitions in CO_2



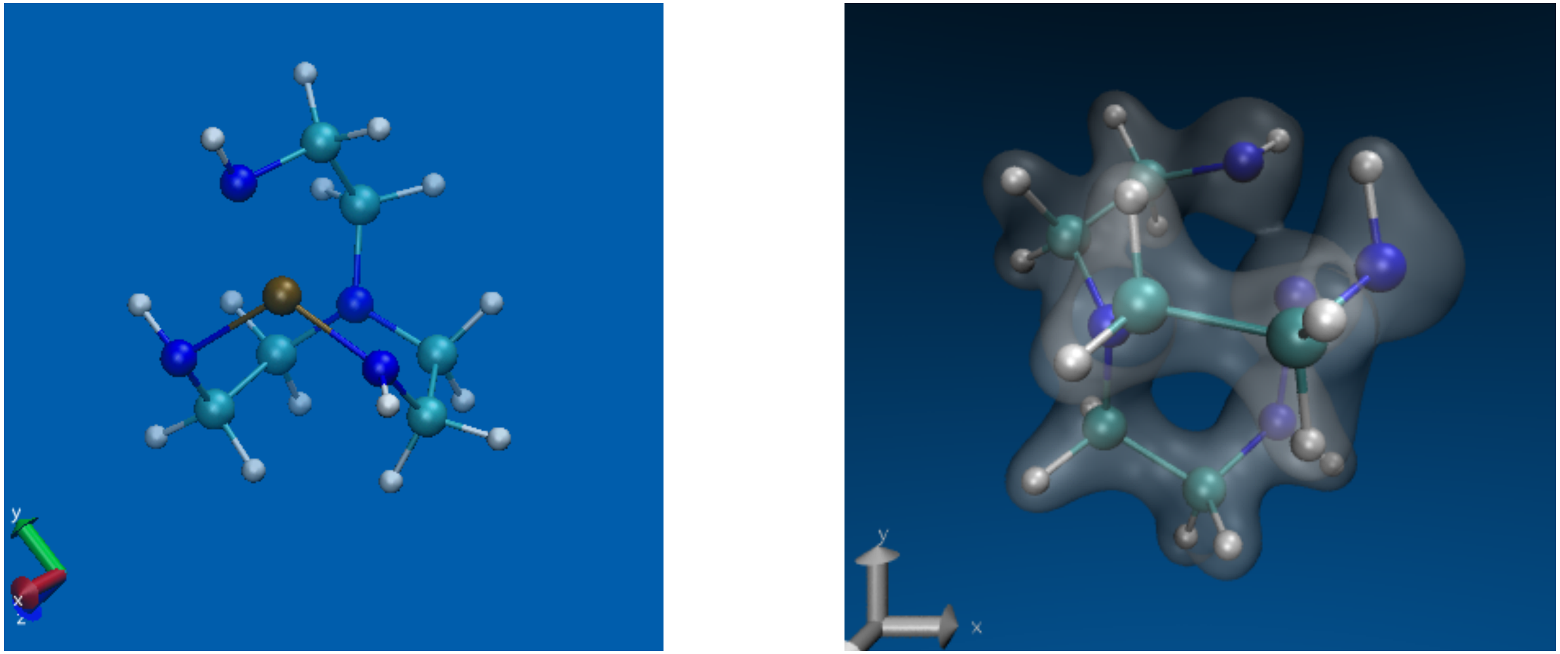
Molecular phases



polymeric phase

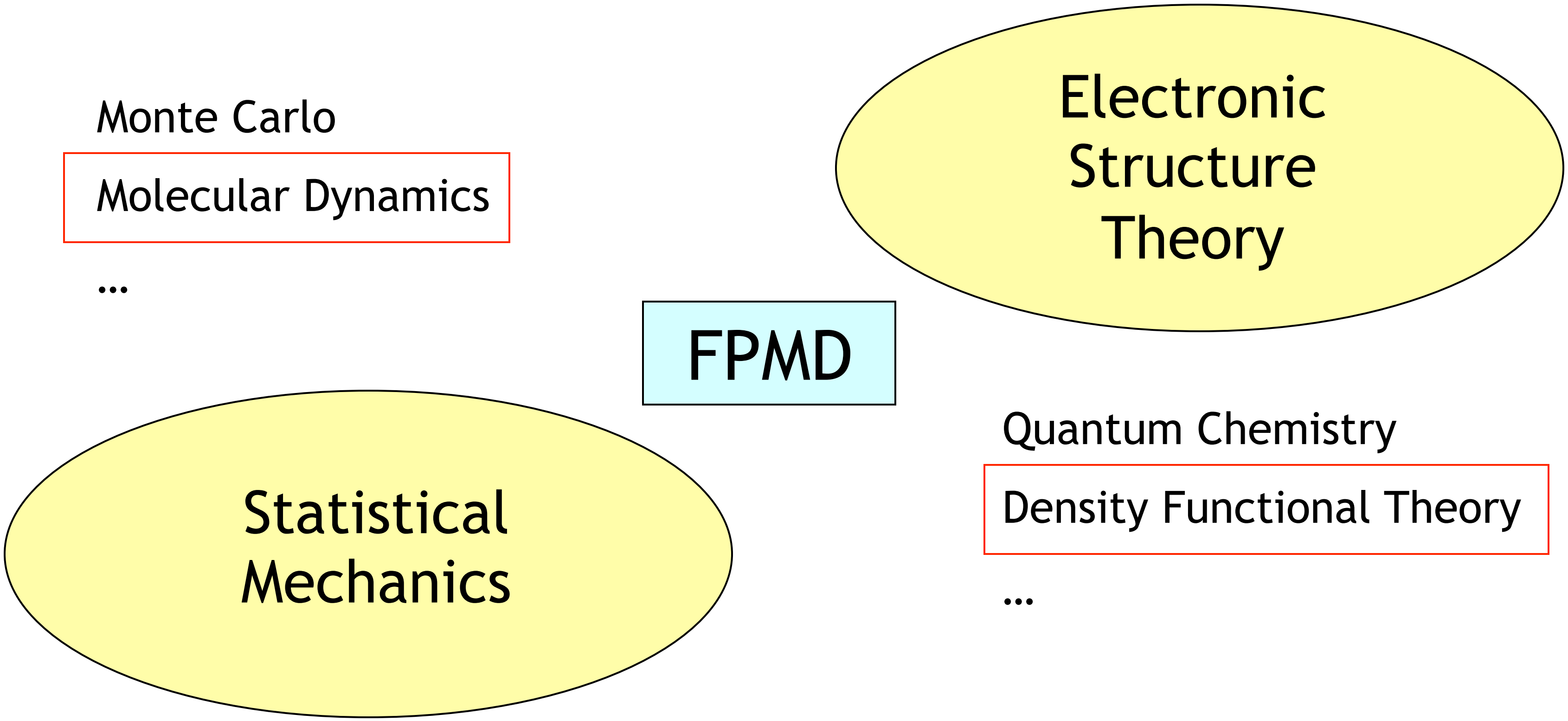
The energy is determined by quantum mechanical properties

- First-Principles Molecular Dynamics: Derive interatomic forces from quantum mechanics



Ni-tris(2-aminoethylamine)

First-Principles Molecular Dynamics



Monte Carlo

Molecular Dynamics

…

Electronic Structure Theory

FPMD

Statistical Mechanics

Quantum Chemistry

Density Functional Theory

…

R. Car and M. Parrinello (1985)

Electronic structure calculations

- Problem: determine the electronic properties of an assembly of atoms using the laws of quantum mechanics.
- Solution: solve the Schroedinger equation!

The Schroedinger equation for *N* electrons

- A partial differential equation for the wave function ψ:

$$\mathbf{r}_i \in R^3, \qquad \psi \in L^2(R^{3N})$$

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) = H(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)\,\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$$

- H is the Hamiltonian operator:

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^{\ 2} + V(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$$

The time-independent Schroedinger equation

- If the Hamiltonian is time-independent, we have

$$\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) = \psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\, e^{iEt/\hbar}$$

- where $\psi(\mathrm{r})$ is the solution of the *time-independent* Schroedinger equation:

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N)\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \underset{\uparrow}{E}\,\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

energy

Solving the Schroedinger equation

- The time-independent Schroedinger equation can have many solutions:

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N)\psi_n(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E_n\,\psi_n(\mathbf{r}_1,\ldots,\mathbf{r}_N) \quad n = 0,1,2\ldots$$

- The *ground state* wave function ψ_0 describes the state of lowest energy E_0
- *Excited states* are described by $\psi_1,\ \psi_2,..$ and have energies $E_1, E_2,.. > E_0$

Hamiltonian operator for *N* electrons and *M* nuclei

- Approximation: treat nuclei as classical particles
- Nuclei are located at positions R_i , electrons at r_i

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M)=$$

$$-\frac{\hbar^2}{2m_\mathrm{e}}\sum_{i=1}^{N}\nabla_i^2-\sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_j e^2}{\left|\mathbf{r}_i-\mathbf{R}_j\right|}+\sum_{i<j}^{N}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

$$+\sum_{i<j}^{M}\frac{Z_i Z_j e^2}{\left|\mathbf{R}_i-\mathbf{R}_j\right|}+\frac{1}{2}\sum_{i=1}^{M}M_i\dot{\mathbf{R}}_i^2$$

The adiabatic approximation

- The Hamiltonian describing an assembly of atoms is time-dependent because atoms move:

$$H(\mathbf{r},t) = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + V(\mathbf{r},t)$$

$$V(\mathbf{r},t) = \sum_j V_{\text{ion}}(r - R_j(t)) + V_{\text{e-e}}(\mathbf{r})$$

time-dependence

through ionic positions

The adiabatic approximation

- If ions move sufficiently slowly, we can assume that electrons remain in the electronic ground state at all times

$$\psi(\mathbf{r},t) = \psi_0(\mathbf{r})$$

$$H(\mathbf{r},\{R_i(t)\})\psi_0(\mathbf{r}) = E_0\psi_0(\mathbf{r})$$

Ground state energy

Ground state wave function

Mean-field approximation

- The problem of solving the *N*-electron Schroedinger equation is formidable (*N!* complexity).

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N)\psi_n(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E_n\psi_n(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

  - Wave functions must be antisymmetric (Pauli principle)

$$\psi(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_N) = -\psi(\mathbf{r}_1,\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_N)$$

exchanged

- Assuming that electrons are independent (i.e. feel the same potential) reduces this complexity dramatically.
  - The potential is approximated by an *average effective* potential

Independent particles, solutions are Slater determinants

- A *Slater determinant* is a simple form of antisymmetric wave function :

$$\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \det\{\varphi_i(\mathbf{r}_j)\}$$

- The one-particle wave functions φ_i satisfy the one-particle Schroedinger equation:

$$h(\mathbf{r})\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$$

$$h(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + \underset{\uparrow}{V_{\mathrm{eff}}}(\mathbf{r})$$

Note: *effective* potential

Electron-electron interaction

$$H(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_M) =$$

$$-\frac{\hbar^2}{2m_\mathrm{e}}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{j=1}^{M}\frac{Z_j e^2}{\left|\mathbf{r}_i-\mathbf{R}_j\right|} + \boxed{\sum_{i<j}^{N}\frac{e^2}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}}$$

$$+\sum_{i<j}^{M}\frac{Z_i Z_j e^2}{\left|\mathbf{R}_i-\mathbf{R}_j\right|} + \frac{1}{2}\sum_{i=1}^{M} M_i\dot{\mathbf{R}}_i^2$$

Density Functional Theory

- Introduced by Hohenberg & Kohn (1964)
- Chemistry Nobel prize to W.Kohn (1999)
- The electronic density is the fundamental quantity from which all electronic properties can be derived $E = E[\rho]$

$$E[\rho] = T[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho]$$

- Problem: the functional $E[\rho]$ is unknown!

The Local Density Approximation

- Kohn & Sham (1965)

$$E[\rho] = T[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{\mathrm{xc}}[\rho]$$

- Approximations:
  - The kinetic energy is that of a non-interacting electron gas of same density
  - The exchange-correlation energy density depends locally on the electronic density

$$E_{\mathrm{xc}} = E_{\mathrm{xc}}[\rho(\mathbf{r})] = \int \varepsilon_{\mathrm{xc}}(\rho(\mathbf{r}))\rho(\mathbf{r})d\mathbf{r}$$

The Local Density Approximation

$$V_{\text{e-e}} = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}))$$

- The mean-field approximation is sometimes not accurate, in particular for
  - strongly correlated electrons
  - excited state properties

The Kohn-Sham equations

- Coupled, non-linear, integro-differential equations:

$$\begin{cases} -\Delta\phi_i + V(\rho,\mathbf{r})\phi_i = \varepsilon_i\phi_i \quad i = 1\ldots N_{\text{el}} \\ V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\ \rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{el}}} |\phi_i(\mathbf{r})|^2 \\ \int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij} \end{cases}$$

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Numerical methods

- Basis sets: solutions are expanded on a basis of *N* orthogonal functions

$$\phi_i(\mathbf{r}) = \sum_{j=1}^{N} c_{ij}\varphi_j(\mathbf{r})$$

$$\int_{\Omega} \varphi_j^*(\mathbf{r})\varphi_k(\mathbf{r}) = \delta_{jk} \qquad \Omega \subset R^3$$

- The solution of the Schroedinger equation reduces to a linear algebra problem

Numerical methods: choice of basis

- Gaussian basis (non-orthogonal)

$$\varphi_i(\mathbf{r}) = e^{-\alpha_i|\mathbf{r}-\mathbf{R}|^2}$$

- Plane wave basis (orthogonal)

$$\varphi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{R}}$$

- Other representations of solutions:
  - values on a grid
  - finite element basis

Numerical methods: choice of basis

- Hamiltonian matrix:

$$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle = \int_{\Omega} \varphi_i^*(\mathbf{r})\, H \varphi_j(\mathbf{r})\, d^3\mathbf{r}$$

- Schroedinger equation: an algebraic eigenvalue problem

$$\mathbf{Hc}_n = \varepsilon_n \mathbf{c}_n \qquad \mathbf{c}_n \in C^N$$

Numerical methods: choice of basis

- Non-orthogonal basis sets lead to generalized eigenvalue problems

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \int_{\Omega} \phi_i^*(\mathbf{r})\, \phi_j(\mathbf{r})\, d^3\mathbf{r} \neq \delta_{ij}$$

$$\mathbf{Hc}_n = \varepsilon_n \mathbf{Sc}_n \qquad \mathbf{c}_n \in C^N$$

Solving large eigenvalue problems

- The size of the matrix H often exceeds 10^3-10^4
- Direct diagonalization methods cannot be used
- Iterative methods:
  - Lanczos type methods
  - subspace iteration methods
- Many algorithms focus on one (or a few) eigenpairs
- Electronic structure calculations involve many eigenpairs (~ # of electrons)
- robust methods are necessary

Solving the Kohn-Sham equations: fixed-point iterations

- The Hamiltonian depends on the electronic density

$$
\begin{cases}
-\Delta\phi_i + V(\rho,\mathbf{r})\phi_i = \varepsilon_i\phi_i \quad i = 1\ldots N_{\text{el}} \\
V(\rho,\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \dfrac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + V_{\text{XC}}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r})) \\
\rho(\mathbf{r}) = \sum\limits_{i=1}^{N_{\text{el}}} |\phi_i(\mathbf{r})|^2 \\
\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\,d\mathbf{r} = \delta_{ij}
\end{cases}
$$

Self-consistent iterations

- For k=1,2,…
  - Compute the density ρ_k
  - Solve the Kohn-Sham equations

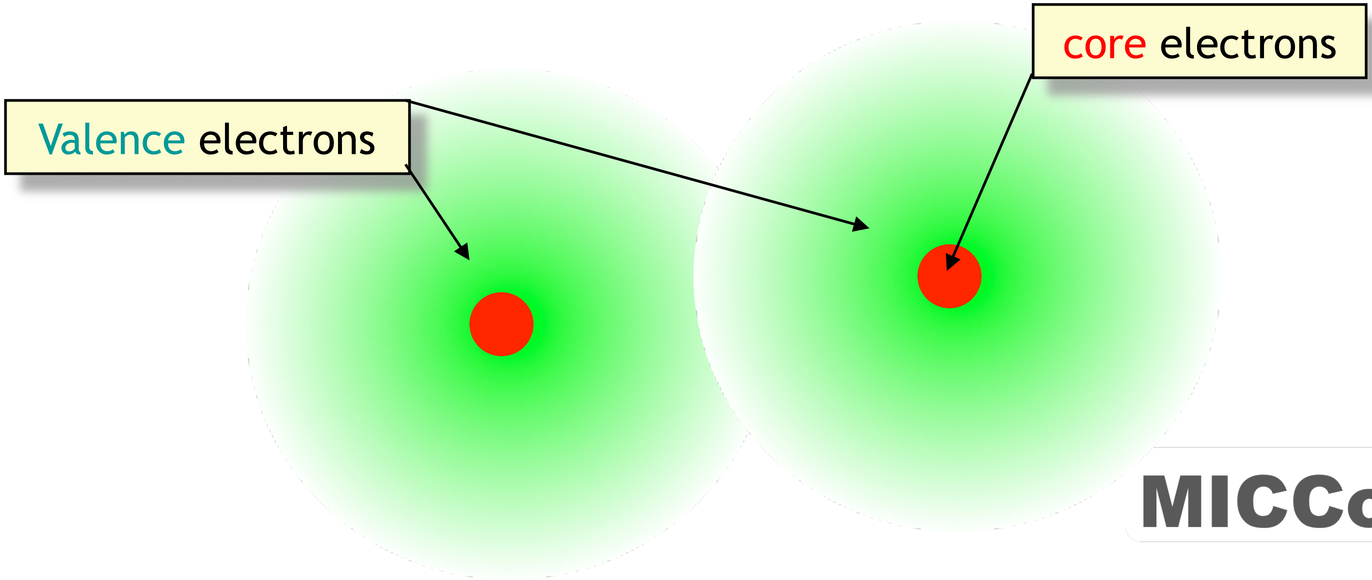
- The iteration *may* converge to a fixed point

Simplifying the electron-ion interactions: Pseudopotentials

- The electron-ion interaction is singular

$$V_{\text{e-ion}}(\mathbf{r}) = -\frac{Ze^2}{|\mathbf{r}-\mathbf{R}|}$$

- Only valence electrons play an important role in chemical bonding



Simplifying the electron-ion interactions: Pseudopotentials

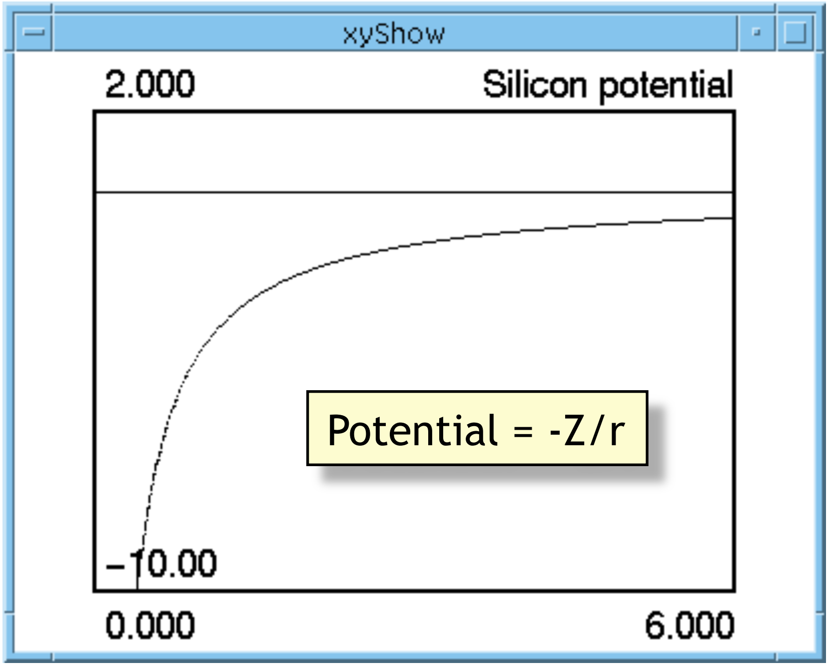
- The electron-ion potential can be replaced by a smooth function near the atomic core

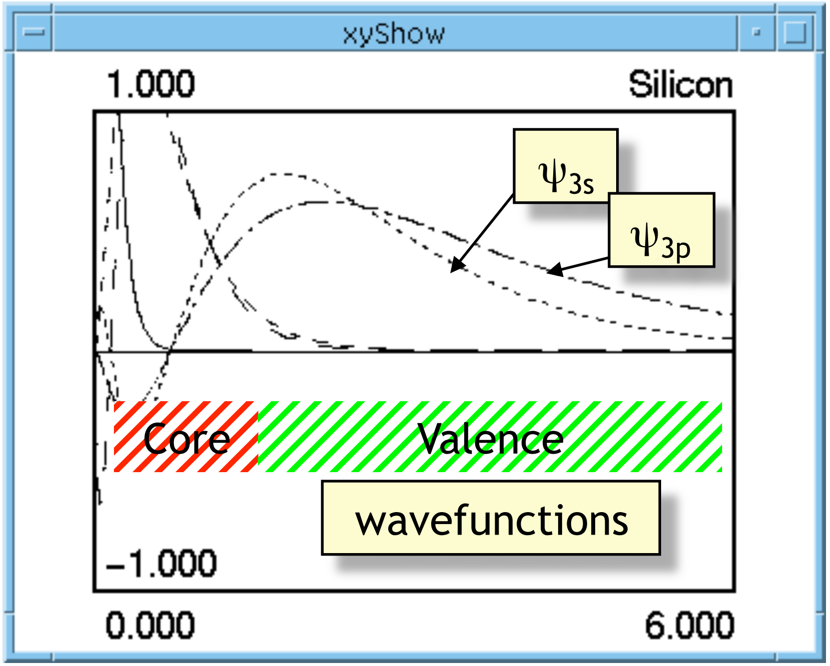
$$V_{\text{e-ion}}(\mathbf{r}) = \begin{cases} -\dfrac{Ze^2}{|\mathbf{r}-\mathbf{R}|} & |\mathbf{r}-\mathbf{R}| > r_{\text{cut}} \\ f(|\mathbf{r}-\mathbf{R}|) & |\mathbf{r}-\mathbf{R}| < r_{\text{cut}} \end{cases}$$

- Core electrons are not included in the calculation (they are assumed to be "frozen")

Pseudopotentials: Silicon

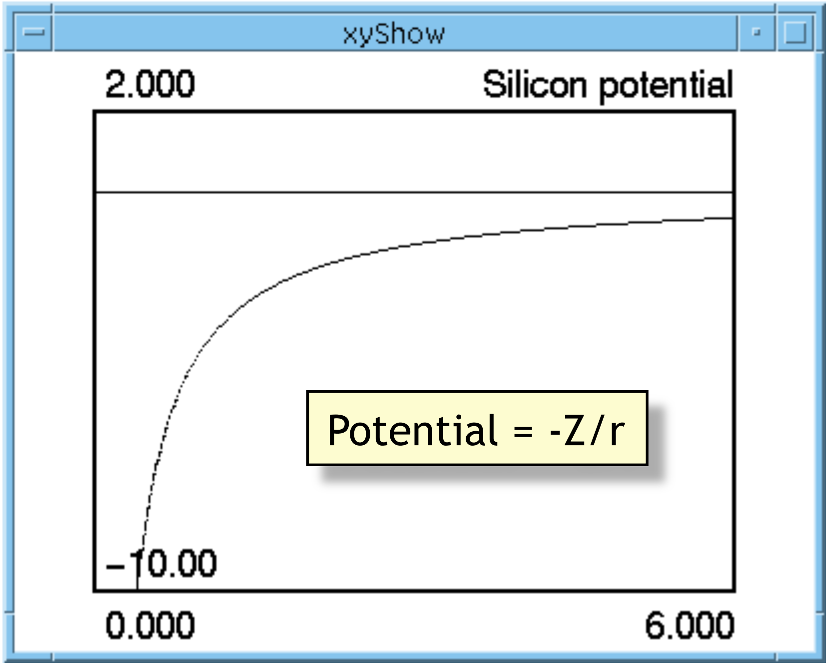
- Solutions of the Schroedinger equation for Si including all electrons (core+valence):

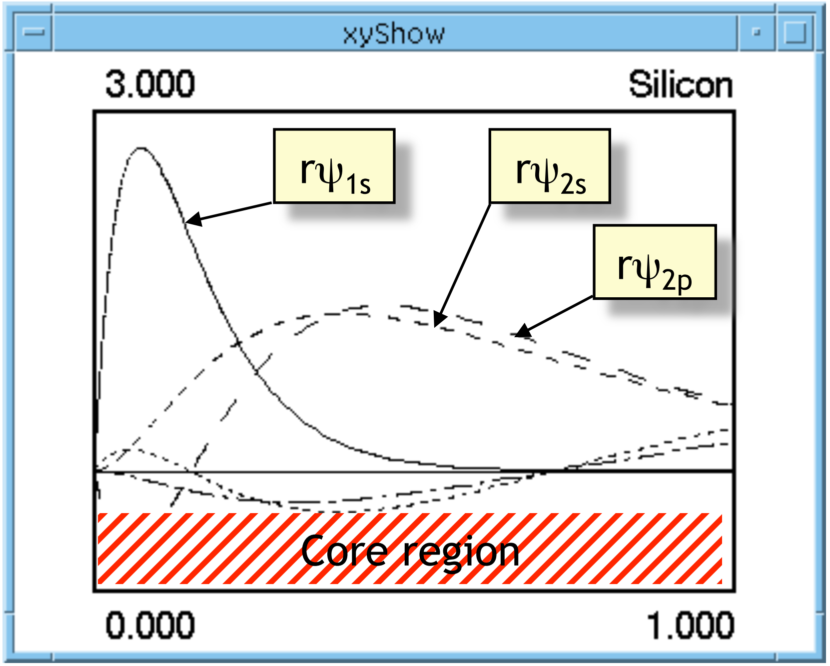




Pseudopotentials: Silicon

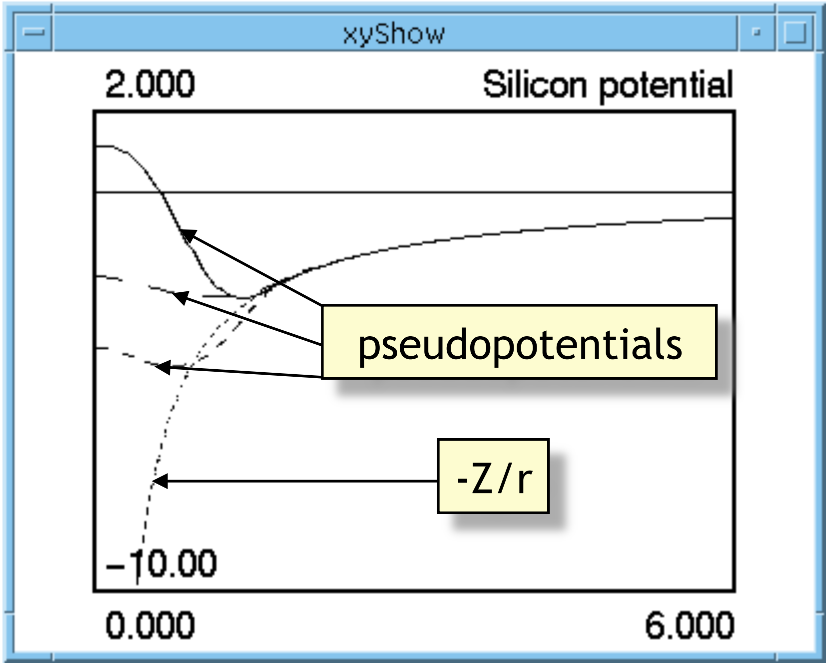
- Solutions of the Schroedinger equation for Si including all electrons (zoom on core region):





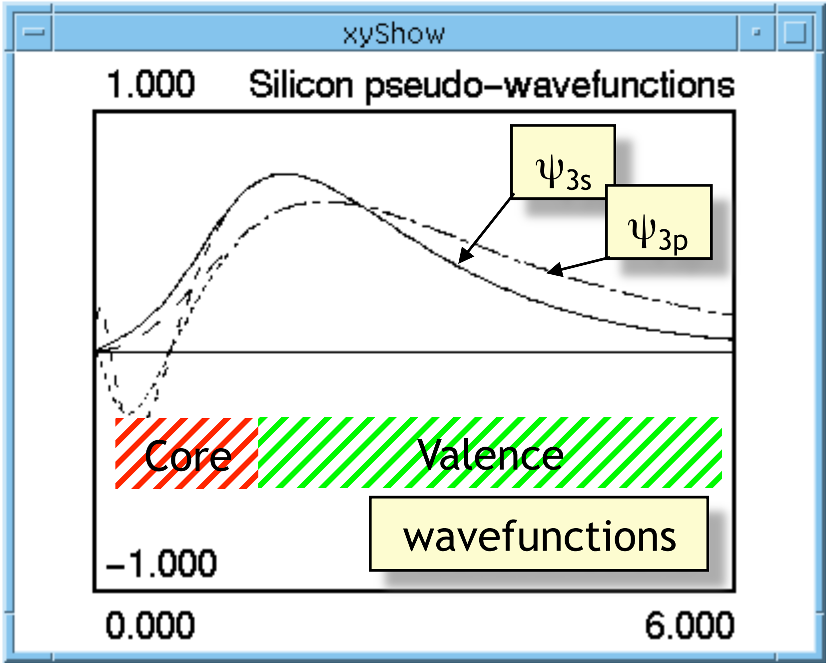
Pseudopotentials: Silicon

- The electron-ion potential can be replaced by a smooth function near the atomic core



pseudopotentials

-Z/r



ψ_{3s}

ψ_{3p}

Core

Valence

wavefunctions

Summary: First-principles electronic structure

- Time-independent Schroedinger equation
- Mean-field approximation
- Simplified electron-electron interaction:
  - Density Functional Theory, Local Density Approximation
- Simplified electron-ion interaction:
  - Pseudopotentials

Molecular dynamics: Computation of ionic forces

- Hamiltonian: $H(\lambda)$
- Hellman-Feynman theorem: if $\psi_0(\lambda)$ is the electronic ground state of $H(\lambda)$

$$\left.\frac{\partial E}{\partial \lambda}\right|_{\lambda_0} = \frac{\partial}{\partial \lambda}\left\langle \psi_0(\lambda)\middle| H(\lambda) \middle| \psi_0(\lambda)\right\rangle = \left\langle \psi_0(\lambda_0)\right| \left.\frac{\partial H(\lambda)}{\partial \lambda}\right|_{\lambda_0} \left|\psi_0(\lambda_0)\right\rangle$$

- For ionic forces: $\lambda = R_i$ (ionic positions)

$$F_i = -\frac{\partial E}{\partial R_i} = \left\langle \psi_0 \middle| \frac{\partial H}{\partial R_i} \middle| \psi_0 \right\rangle = \left\langle \psi_0 \middle| \frac{\partial}{\partial R_i} \sum_j V_{\text{e-ion}}(r - R_j) \middle| \psi_0 \right\rangle$$

Integrating the equations of motion: the Verlet algorithm

- The equations of motion are coupled, second order ordinary differential equations
- Any ODE integration method can be used
- Time-reversible integrators are preferred
- The *Verlet algorithm* (or *leapfrog method*) is time-reversible

$$x(t+\Delta t) = 2x(t) - x(t+\Delta t) + \frac{\Delta t^2}{m} F(x(t))$$

Integrating the equations of motion: the Verlet algorithm

- Derivation of the Verlet algorithm: Taylor expansion of *x(t)*

$$x(t+\Delta t) = x(t) + \Delta t \frac{dx}{dt} + \frac{\Delta t^2}{2}\frac{d^2x}{dt^2} + \frac{\Delta t^3}{6}\frac{d^3x}{dt^3} + O(\Delta t^4)$$

$$x(t-\Delta t) = x(t) - \Delta t \frac{dx}{dt} + \frac{\Delta t^2}{2}\frac{d^2x}{dt^2} - \frac{\Delta t^3}{6}\frac{d^3x}{dt^3} + O(\Delta t^4)$$

- Add the two Taylor expansions:

$$x(t+\Delta t) + x(t-\Delta t) = 2x(t) + \Delta t^2 \frac{d^2x}{dt^2} + O(\Delta t^4)$$

Integrating the equations of motion: the Verlet algorithm

- use Newton’s law

$$m\frac{d^2x}{dt^2} = f(x(t))$$

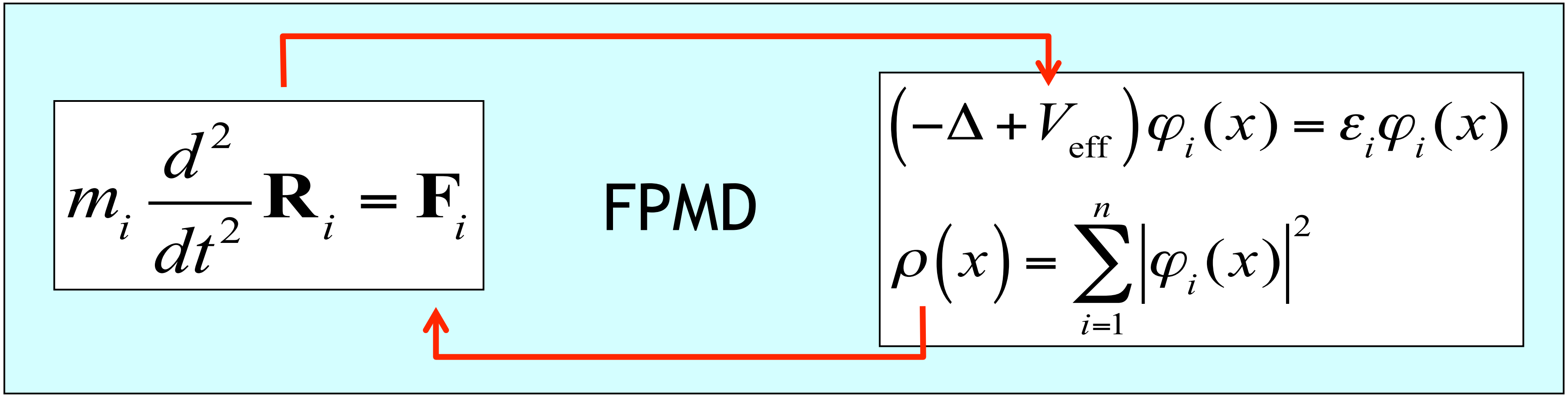
$$x(t+\Delta t) + x(t-\Delta t) = 2x(t) + \Delta t^2 \frac{d^2x}{dt^2} + O(\Delta t^4)$$

$$\boxed{x(t+\Delta t) = 2x(t) - x(t-\Delta t) + \frac{\Delta t^2}{m} F(x(t)) + O(\Delta t^4)}$$

First-Principles Molecular Dynamics

Molecular Dynamics

Density Functional Theory



$$m_i \frac{d^2}{dt^2}\mathbf{R}_i = \mathbf{F}_i$$

FPMD

$$\left(-\Delta + V_{\text{eff}}\right)\varphi_i(x) = \varepsilon_i \varphi_i(x)$$

$$\rho(x) = \sum_{i=1}^{n} \left|\varphi_i(x)\right|^2$$

Newton equations

Kohn-Sham equations

R. Car and M. Parrinello (1985)

FPMD: the Recipe

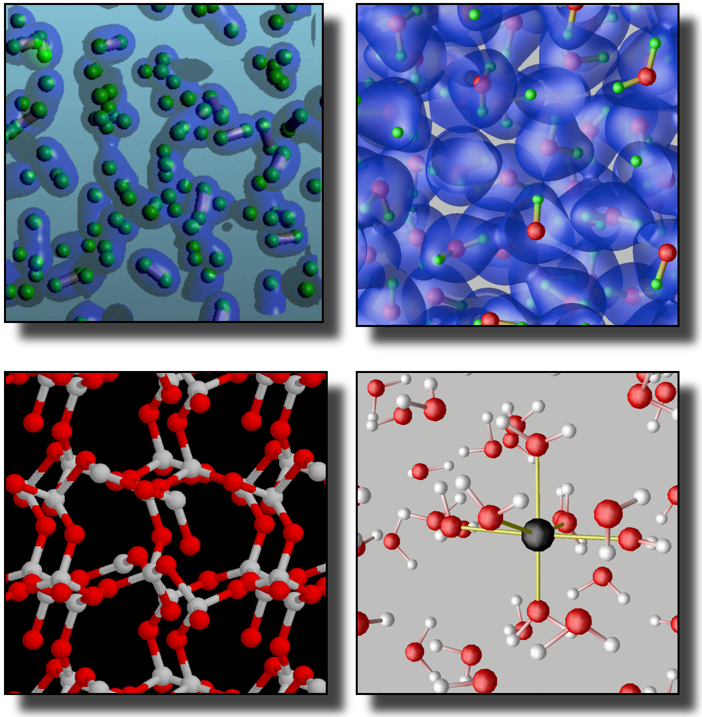
- Choose a starting geometry: atomic positions
- Choose an exchange-correlation functional
- Choose appropriate pseudopotentials
- Run!
- Publish!!

FPMD: the Recipe

- Choose a starting geometry: atomic positions
- Choose an exchange-correlation functional
- Choose appropriate pseudopotentials
- Run!
- ~~Publish!!~~
- Test!
  - Test sensitivity to starting geometry, finite size effects
  - Test sensitivity to duration of the simulation
  - Test accuracy of the basis set
  - Test choice of exchange-correlation functionals
  - Test accuracy of pseudopotentials

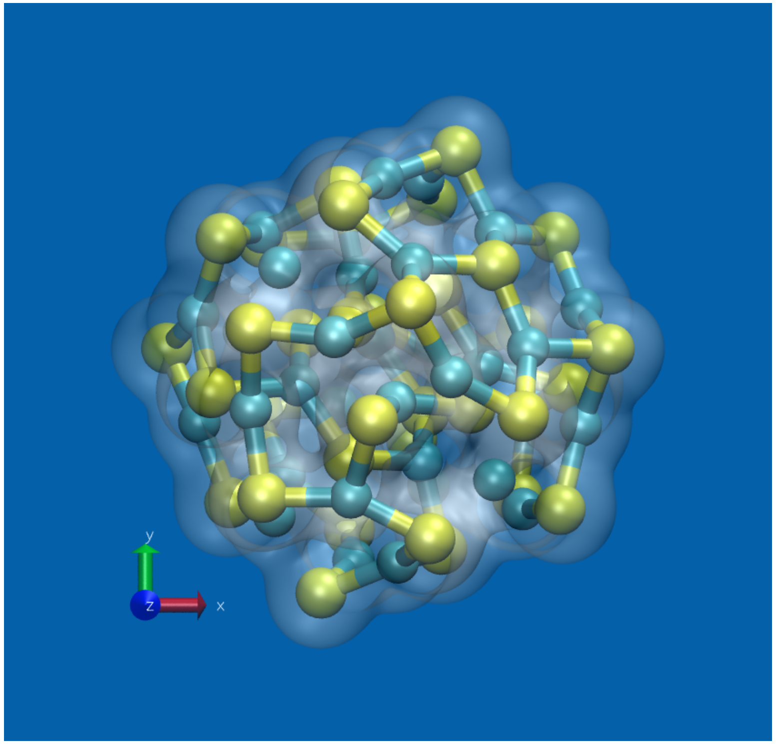
First-Principles Molecular Dynamics applications

- Solid state physics
- Surface physics
- Nanotechnology
- High pressure physics
- Chemical Physics
- Biochemistry
- Mechanisms of drug action
- Solvation processes



The absence of empirical parameters makes this approach widely applicable and *predictive*.

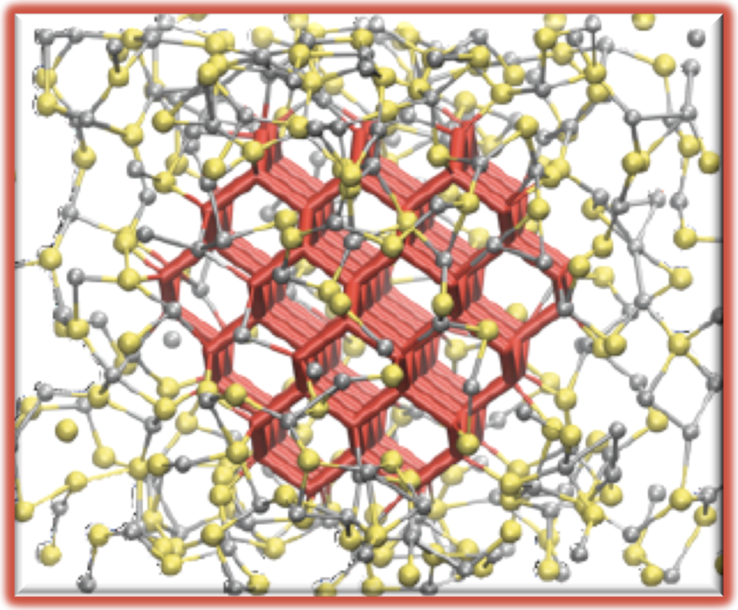
Nanoparticles



$Cd_{34}Se_{34}$

- Exploration of multiple locally stable structures
- Electronic properties at finite temperature

Embedded nanoparticles, assemblies of nanoparticles



Si/ZnS

- Annealing of structures at finite temperature
- Calculation of band gaps and band alignments

S. Wippermann, M. Vörös, A. Gali, F. Gygi, G. Zimanyi, G.Galli,

Phys. Rev. Lett. **112**, 106801 (2014) .

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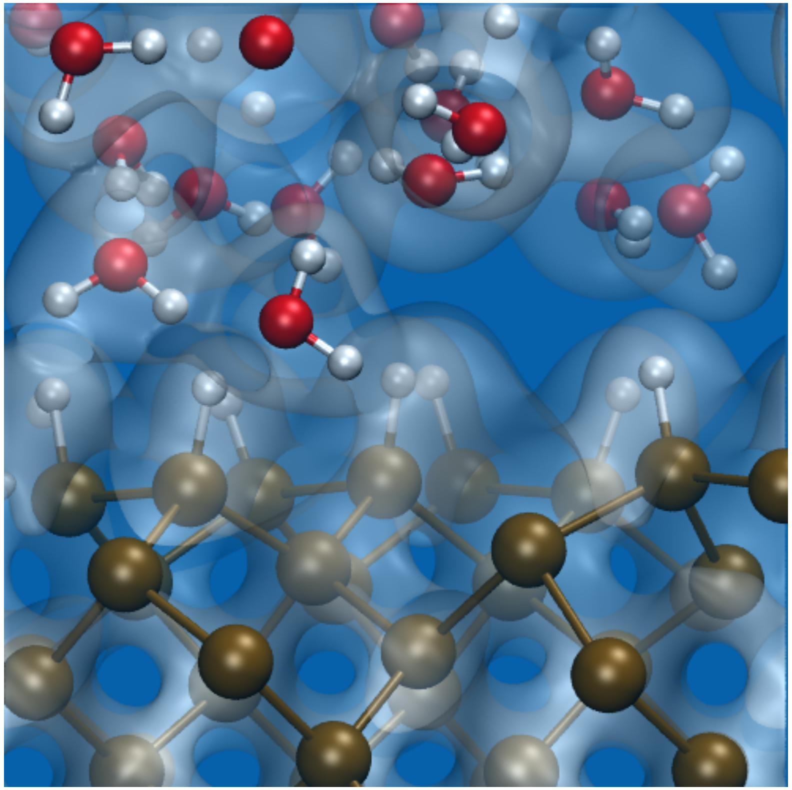
Liquids and Liquid-Solid Interfaces



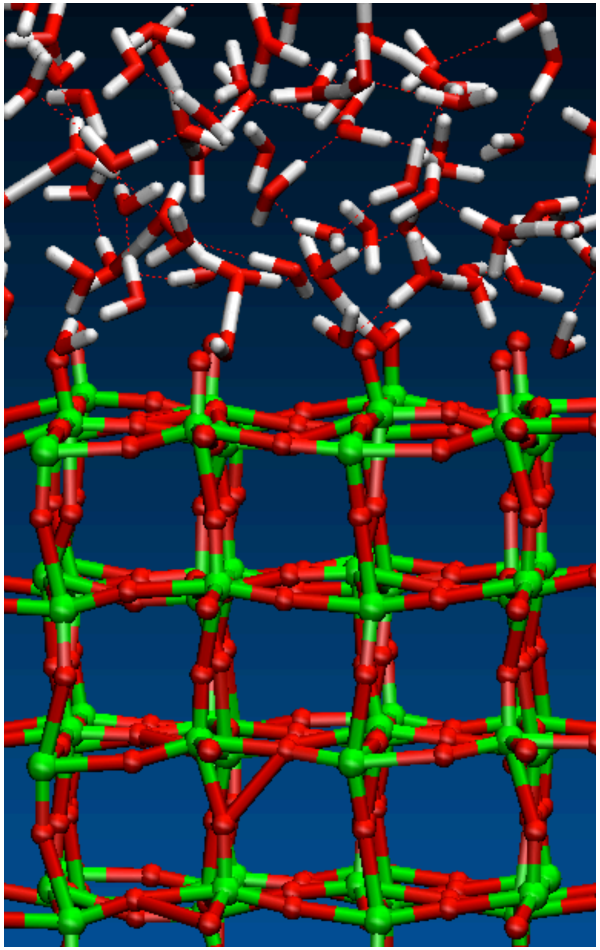
$H_2O/Si(100)H$

- Structure of water at the interface
- Electronic structure
  - band alignment of bulk solid and liquid
- Spectroscopy
  - IR and Raman spectra

Liquid-solid interfaces

- Water on oxide surfaces
- H_2O/WO_3

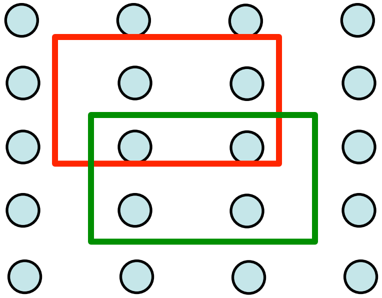
- Simulation of
  - surface relaxation and dynamics
  - structure of defects
  - electronic structure
  - spectroscopic signature of water at the interface



H_2O/WO_3

Electronic properties: Polarization

- The electronic polarization (per unit cell) of an infinite periodic system is ill-defined



$$P = \frac{1}{\Omega}\left[-e \sum_l Z_l R_l + \int r \rho(r)\, dr \right]$$

  - *P* depends on the choice of origin
- The *change* in polarization caused by a small perturbation is well defined
- The electric current caused by a perturbation (e.g. a deformation) can be computed

R. Resta, *Rev. Mod. Phys. 66, 899 (1994).*

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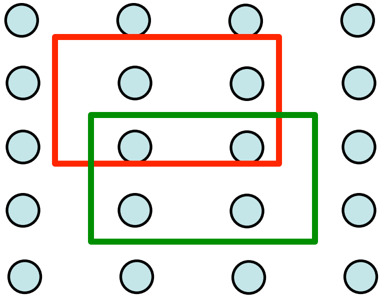

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Wannier functions

- A set of localized orbitals that span the same subspace as the Kohn-Sham eigenvectors
- minimize the spread $\sigma^2 = \langle \phi | \left(x - \langle \phi | x | \phi \rangle \right)^2 | \phi \rangle$
- Wannier centers: centers of charge of each Wannier function
- Polarization can be expressed in terms of the centers

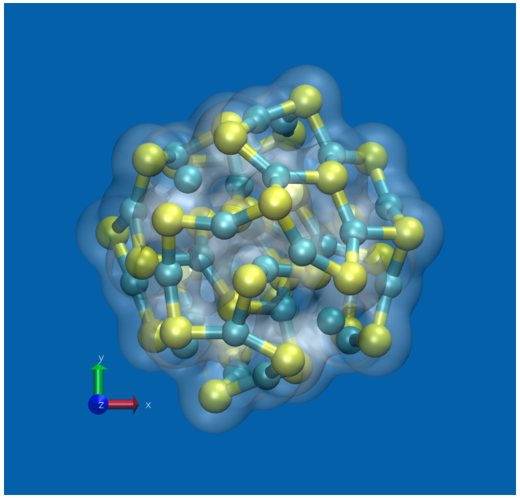
$$P = \frac{1}{\Omega}\left[-e \sum_l Z_l R_l + e \sum_n \int r\, w_n(r)\, dr \right]$$

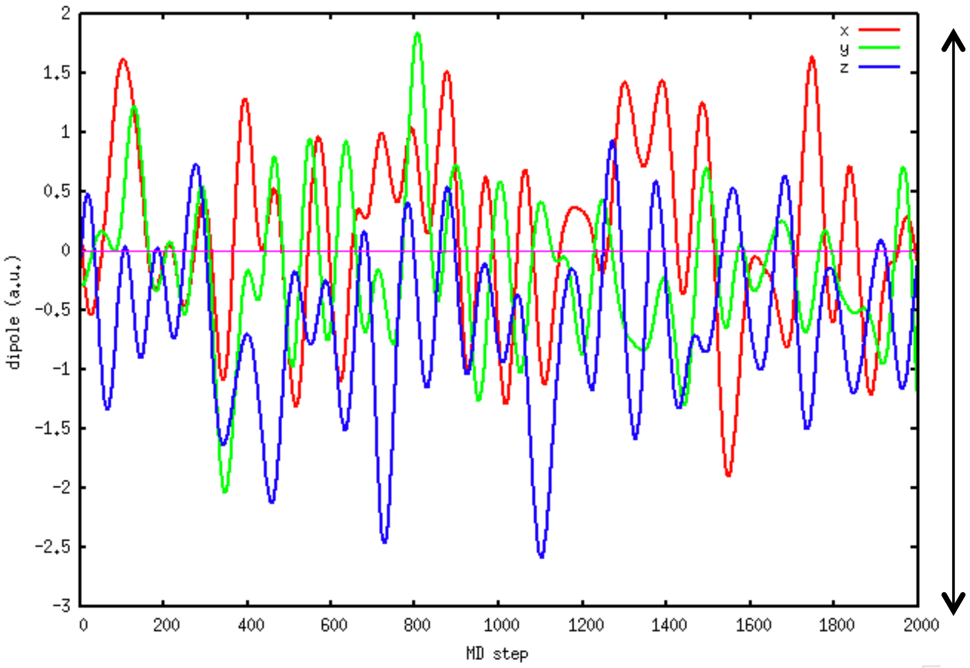
N. Marzari, A. Mostofi, J. Yates, I. Souza and D. Vanderbilt, *Rev. Mod. Phys*. 84, 1419 (2012).

Time-dependent polarization of nanoparticles

- PBE DFT MD 300K
- dt=1.9 fs

$Cd_{34}Se_{34}$





12 Debye

IR Spectroscopy

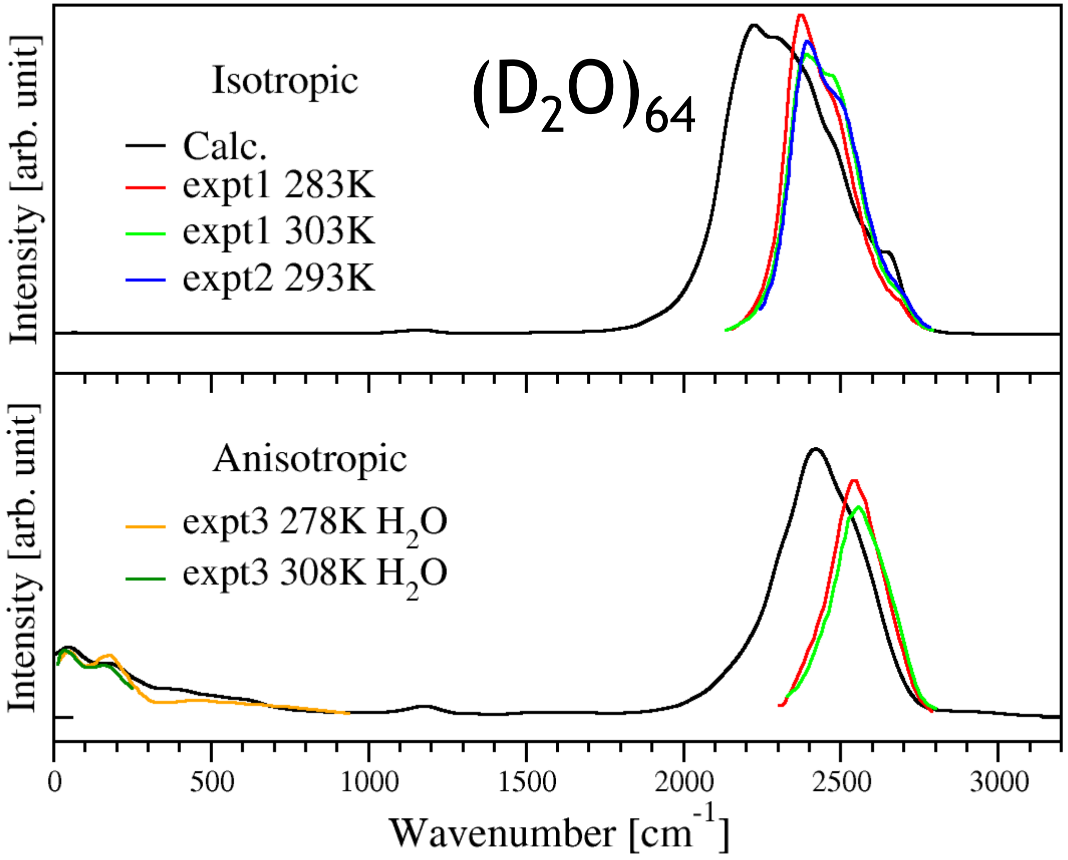
- IR spectra during MD simulations
- Autocorrelation function of P(t)

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3cVn(\omega)} \int_{-\infty}^{\infty} e^{-i\omega t} \left\langle \sum_{\mu\nu} P^{\mu}(0) \cdot P^{\nu}(t) \right\rangle dt$$

Raman Spectroscopy

- Compute the polarizability at each MD step
  - Use Density Functional Perturbation Theory (Baroni, Giannozzi, Testa, 1987)
  - Use a finite-difference formula with *P(t)* and finite field

On-the-fly Computation of Raman spectra



- Position of O-D stretching band: PBE functional yields a red shifted peak, compared to expt.
- Low frequency bands: satisfactory agreement with expt.
- Peak Intensities in good agreement with expt.

Q. Wan, L. Spanu, G. Galli, F. Gygi, JCTC **9**, 4124 (2013)

Solving the Kohn-Sham equations in a finite electric field

- In finite systems: add a linear potential

$$H_{KS} = \frac{p^2}{2m} + V(r) - eEx$$

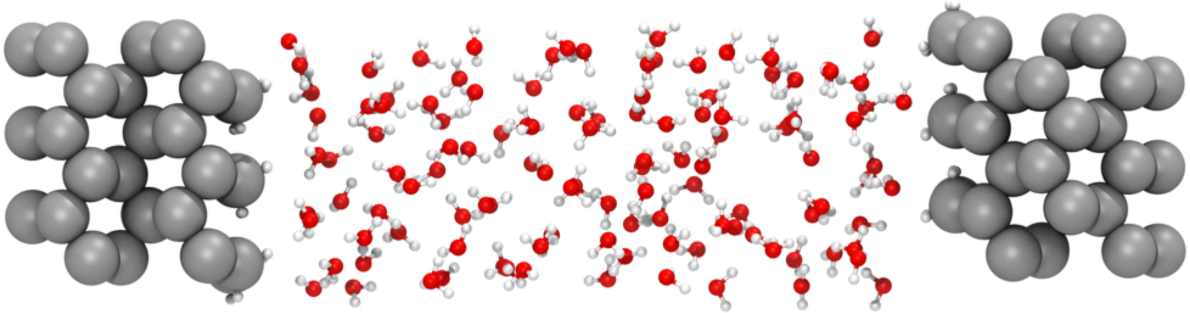
- The spectrum is not bounded below (no "ground state")
- In periodic systems: define the electric enthalpy:

$$F[\phi] = E_{KS}[\phi] - \Omega P[\phi] \cdot E$$

I. Souza, J. Iniguez, D. Vanderbilt, *Phys. Rev. Lett. 89, 117602 (2002).*

Si(100):H-H2O interface

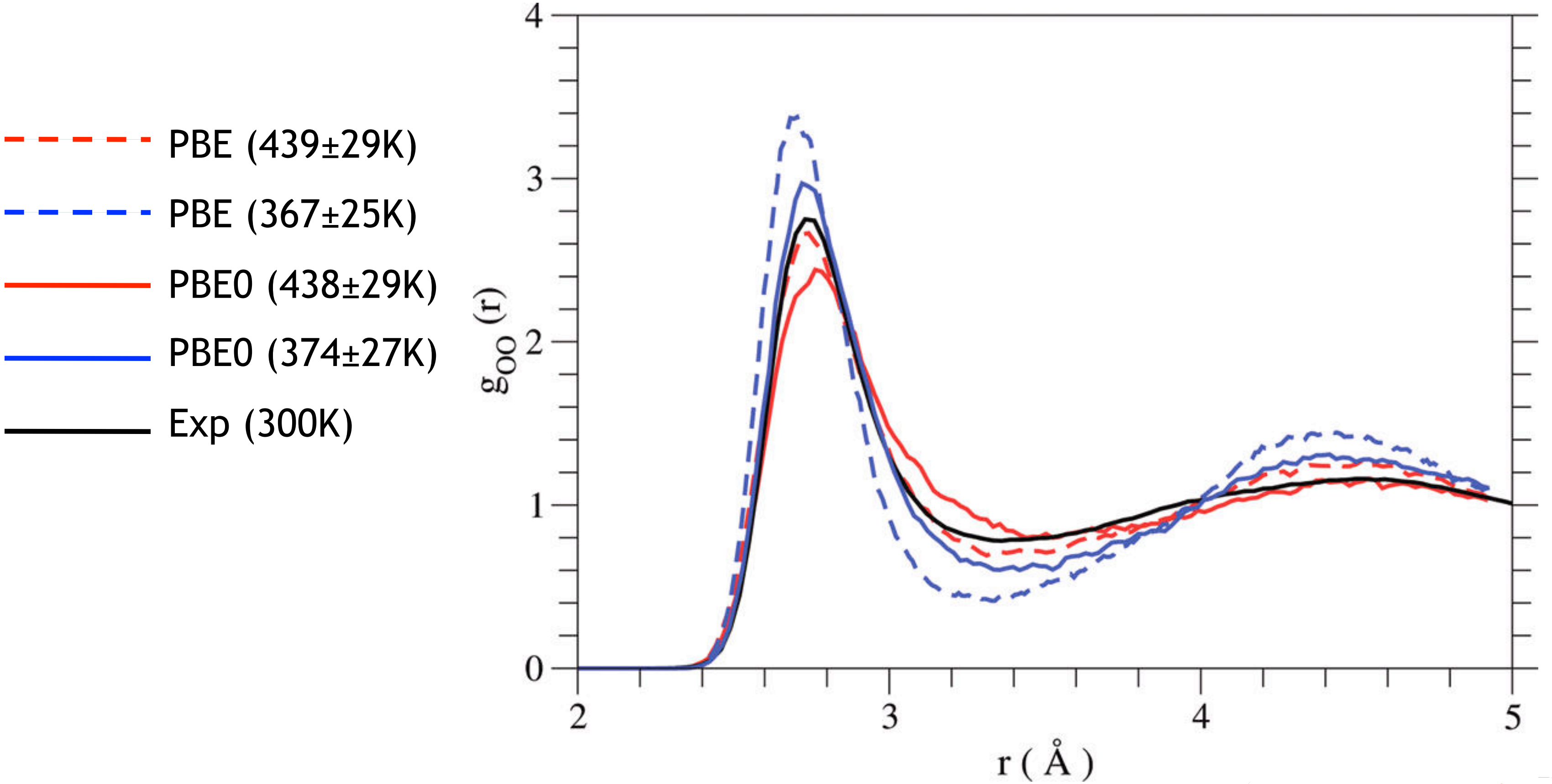
- DFT MD of the Si/H2O interface under finite field
- Si(100)-(3x3):H-H_2O, canted dihydride surface termination, 116 water molecules
- Analysis of time-dependent polarization
- Comparison with IR spectra



L. Yang, F. Niu, S. Tecklenburg, M. Pander, S. Nayak, A. Erbe,
S. Wippermann, F. Gygi, G. Galli

Validation of DFT: PBE vs PBE0 vs …

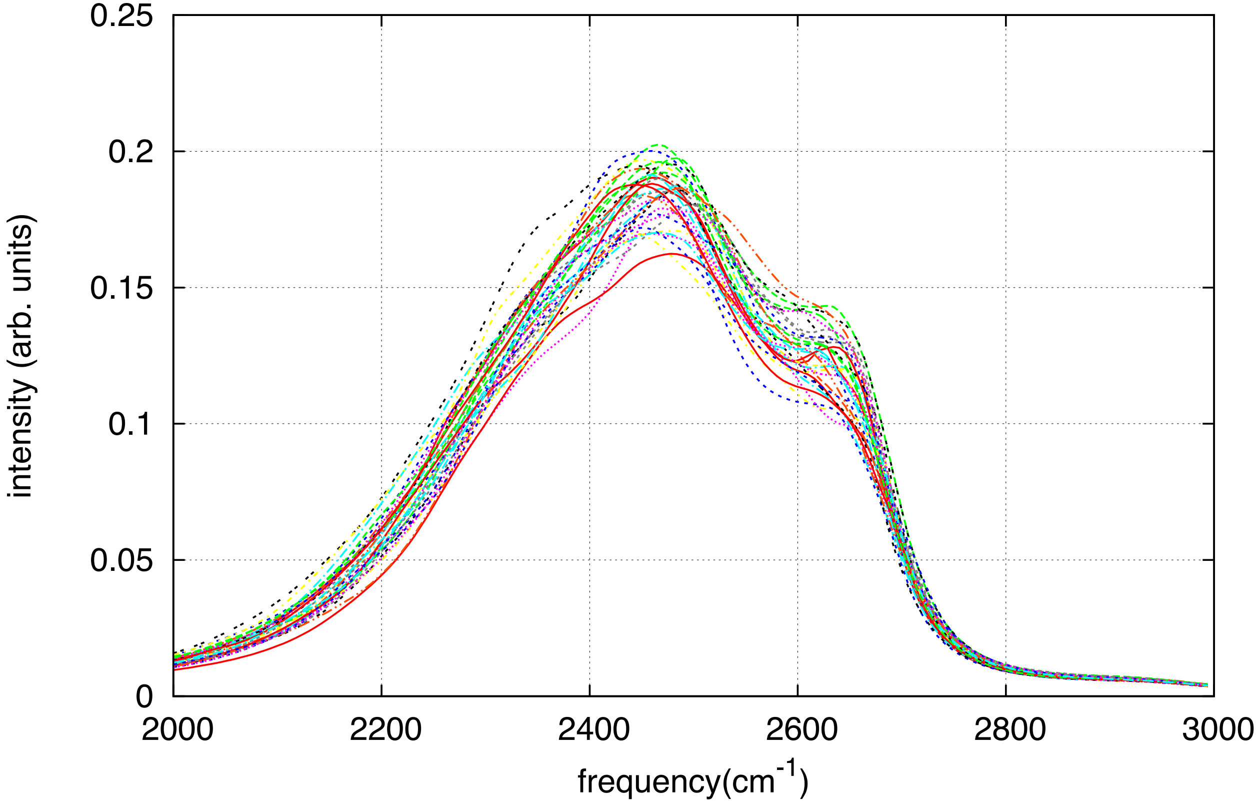
- Oxygen-oxygen pair correlation function in $(H_2O)_{32}$



C.Zhang, D.Donadio, F.Gygi, G.Galli, *JCTC* **7**, 1443 (2011)

Is my simulation reproducible?

- D_2O Power spectrum of ionic velocities (32 x 10 ps runs)

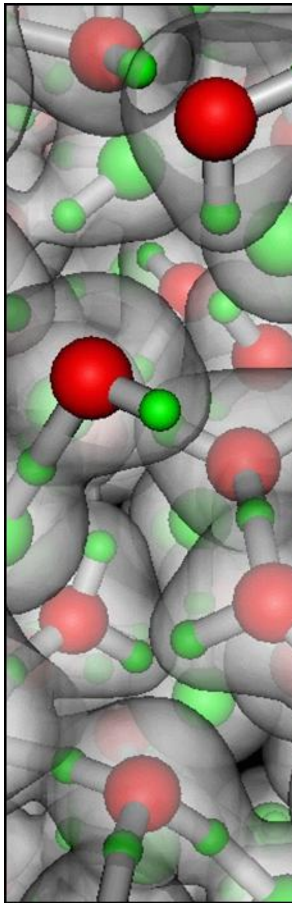


Validating/comparing levels of theory

- Need for (quantitative) statistical analysis
  - compute confidence intervals
- An accurate determination of structural and electronic properties requires multiple uncorrelated simulations
- Autocorrelation times may vary for different quantities
- Example: the PBE400 dataset
  - First-principles MD simulations of water
  - http://www.quantum-simulation.org/reference/h2o/pbe400

Summary

- Basic features of FPMD
- Approximations of electronic structure calculations
- Extensions: polarization, finite electric field
- Applications



Next FPMD steps:

- Today 1:45 pm: Qbox tutorial
- Tomorrow 1:30 pm: Qbox hands-on exercises