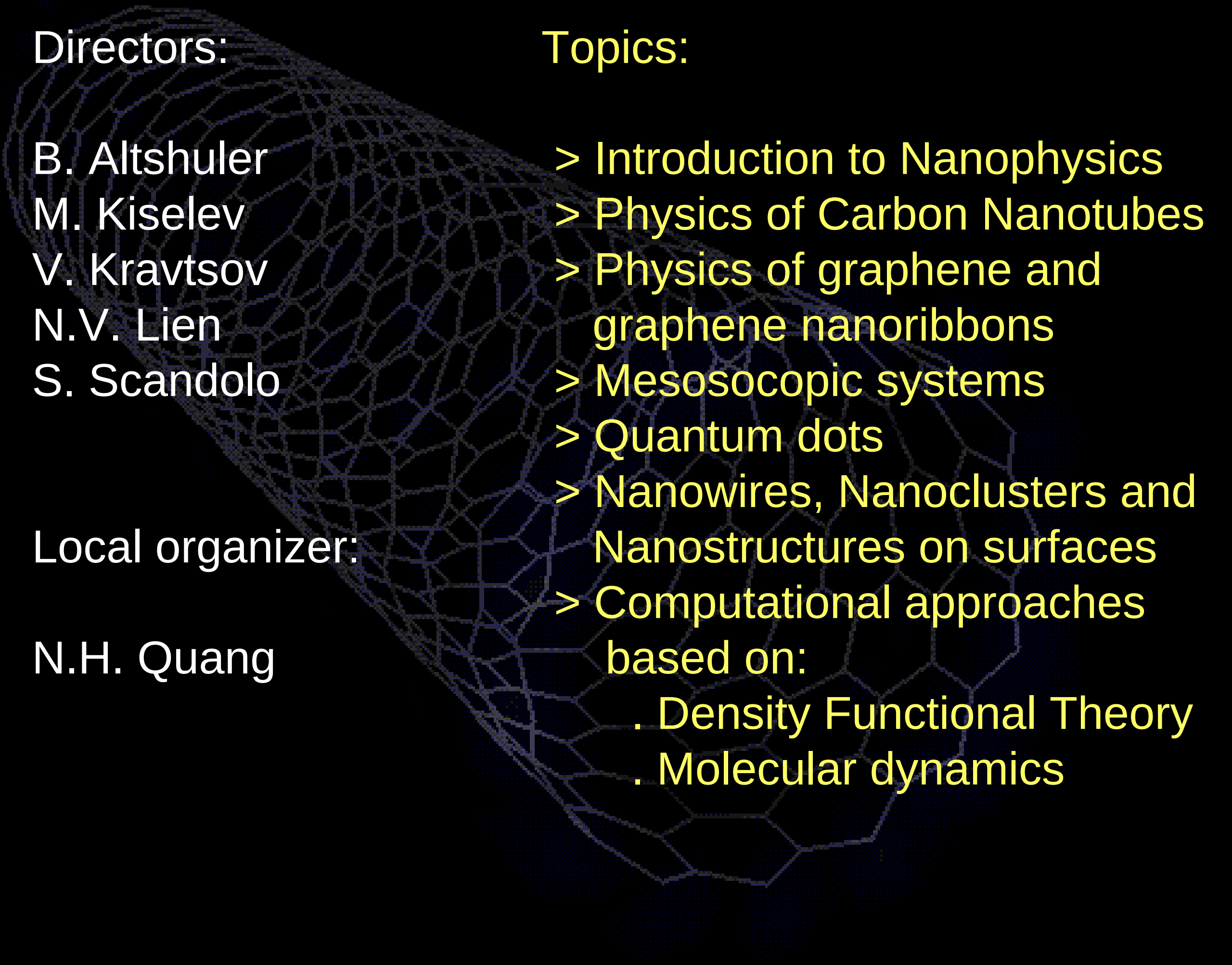
Regional School on Physics at the Nanoscale: Theoretical and computational aspects

14-25 December 2009, Hanoi, Vietnam



Directors:

B. Altshuler
M. Kiselev
V. Kravtsov
N.V. Lien
S. Scandolo

Local organizer:

N.H. Quang

Topics:

- > Introduction to Nanophysics
- > Physics of Carbon Nanotubes
- > Physics of graphene and graphene nanoribbons
- > Mesosocopic systems
- > Quantum dots
- > Nanowires, Nanoclusters and Nanostructures on surfaces
- > Computational approaches based on:
  - . Density Functional Theory
  - . Molecular dynamics

The Abdus Salam International Centre for Theoretical Physics (under UNESCO / IAEA), Trieste, Italy

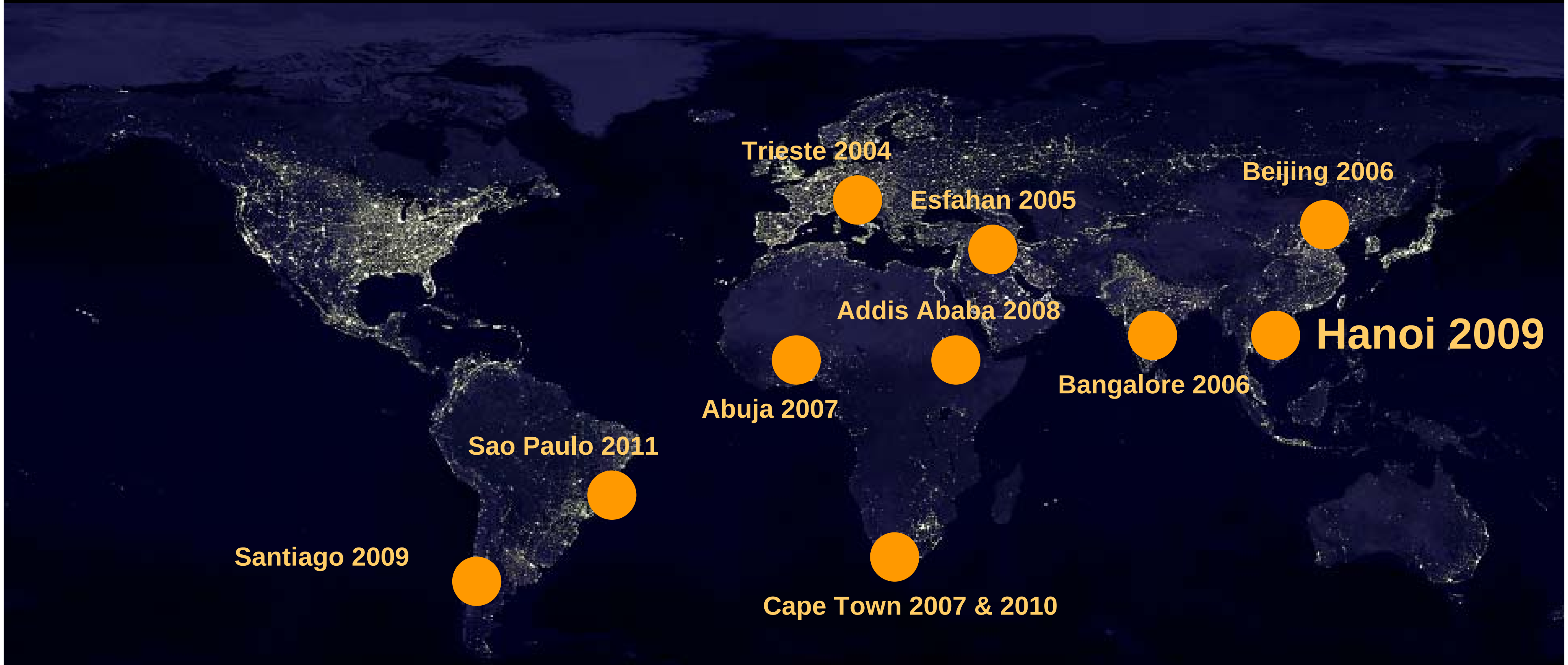
ICTP’s mission:

To foster the growth of advanced studies and research in physics and mathematics, *especially among researchers from developing countries*

Programs:

- Conferences / Schools throughout the year
- Associates (our faculty “in the field”)
- Visitors (junior, STEP, TRIL, etc)
- Diploma Course

Recent ICTP Schools on theoretical nano / materials science



65 participants:

Bangladesh

India

Indonesia

Lao People's Democratic Republic

Malaysia

Nepal

New Zealand

Pakistan

People's Republic of China

Philippines

Sri Lanka

Thailand

Vietnam

Republic of Korea

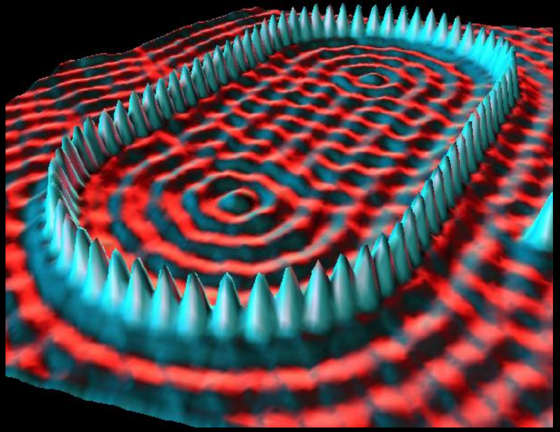
Small is different

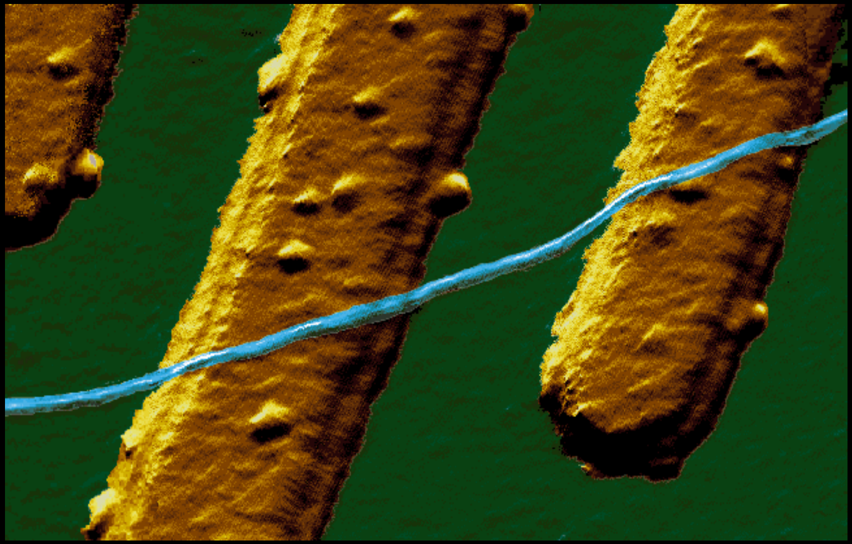
New science

Example:
CdS nanoparticles
of different size have
different colors

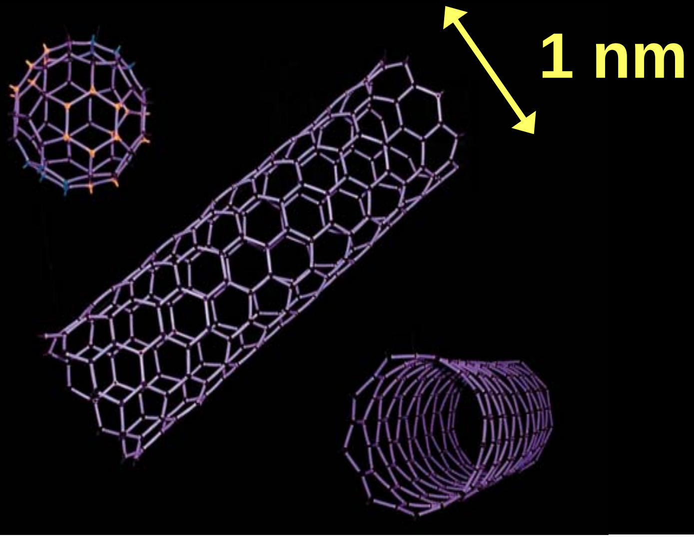
New technologies

Example:
Ability to deposit objects
on surfaces with nanoscale
precision

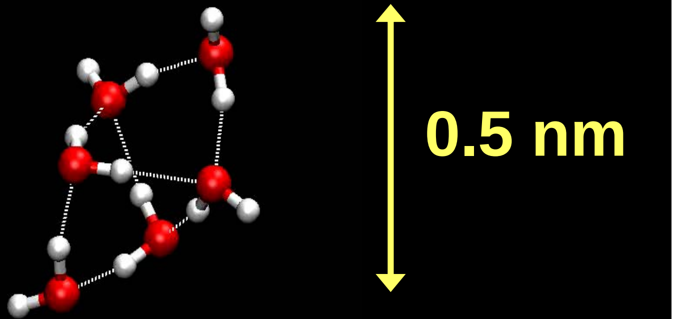




Is Ohm’s law still valid in carbon nanotubes?



Does a water nanodrop behave like liquid water?




The 6th School on Simulation and Modeling Ph
Hanoi, 26 - 29 November 2007
29 11 2007


АЭРОФЛОТ

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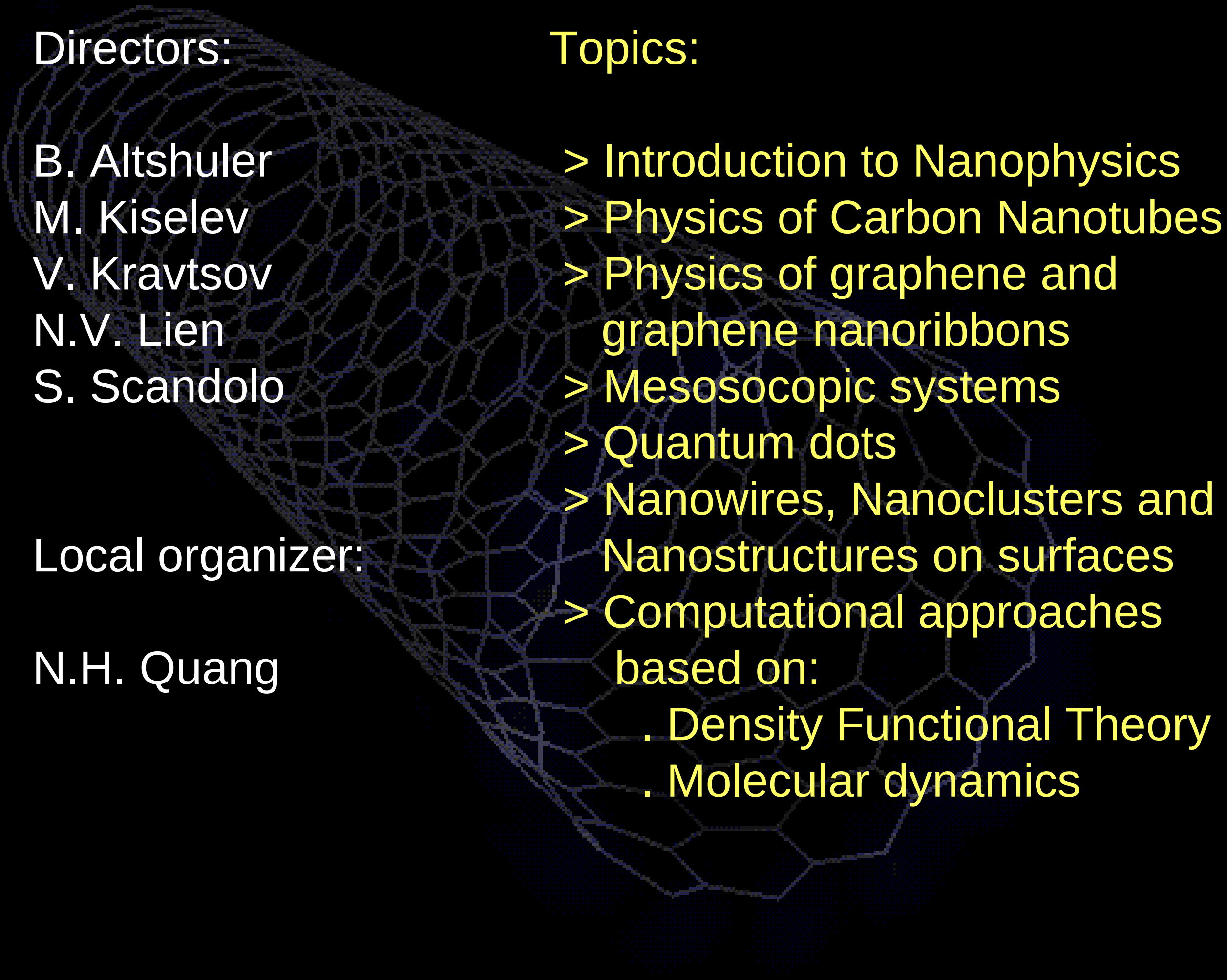

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> Computational approaches based on:
  . Density Functional Theory
  . Molecular dynamics

Ab-initio simulations in the nanosciences: (1) Methods

Sandro Scandolo

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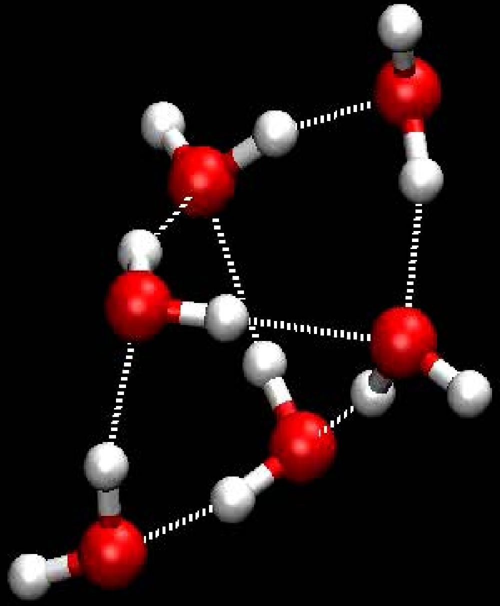
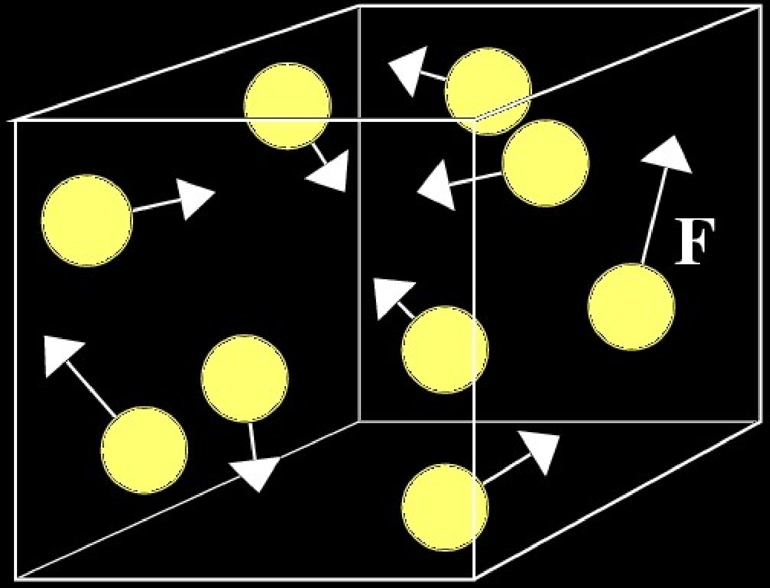


Regional School on Science at the Nanoscale, Hanoi December 2009

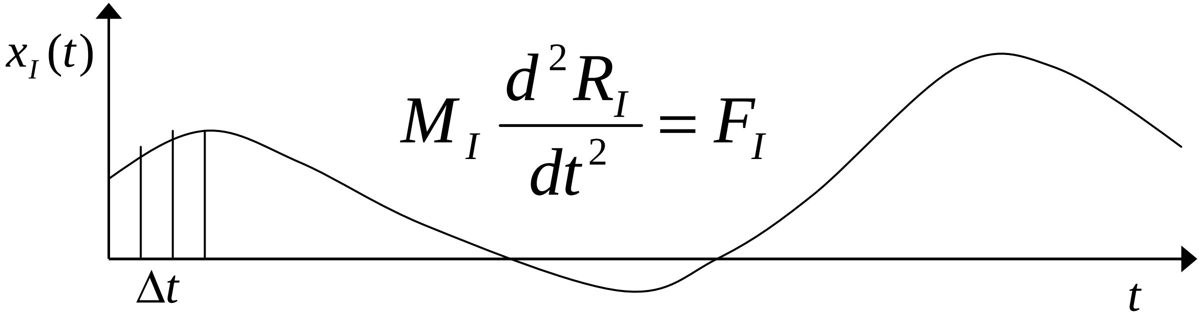
Molecular Dynamics

$$M \ddot{R} = F = -\frac{dV}{dR}$$



(with periodic boundary conditions)

How to integrate Newton’s equations



$$M_I \frac{d^2 R_I}{dt^2} = F_I$$

$$(1) \quad R_I(t+\Delta t) = R_I(t) + v_I(t)\Delta t + \frac{1}{2}\frac{F_I}{M_I}\Delta t^2 + O(\Delta t^3)$$

$$(2) \quad R_I(t-\Delta t) = R_I(t) - v_I(t)\Delta t + \frac{1}{2}\frac{F_I}{M_I}\Delta t^2 - O(\Delta t^3)$$

$$(1)+(2) \quad R_I(t+\Delta t) + R_I(t-\Delta t) = 2R_I(t) + \frac{F_I}{M_I}\Delta t^2 + O(\Delta t^4)$$

Verlet’s algorithm

$$\boxed{R_I(t+\Delta t) = 2R_I(t) - R_I(t-\Delta t) + \frac{F_I}{M_I}\Delta t^2 + O(\Delta t^4)}$$

A typical molecular dynamics protocol

Initialize: select starting atomic positions and velocities as close as possible to thermal equilibrium

Integrate: compute all forces and determine new positions using Verlet's algorithm

Equilibrate: let the system loose memory of the initial configurations, i.e. let it reach thermal equilibrium

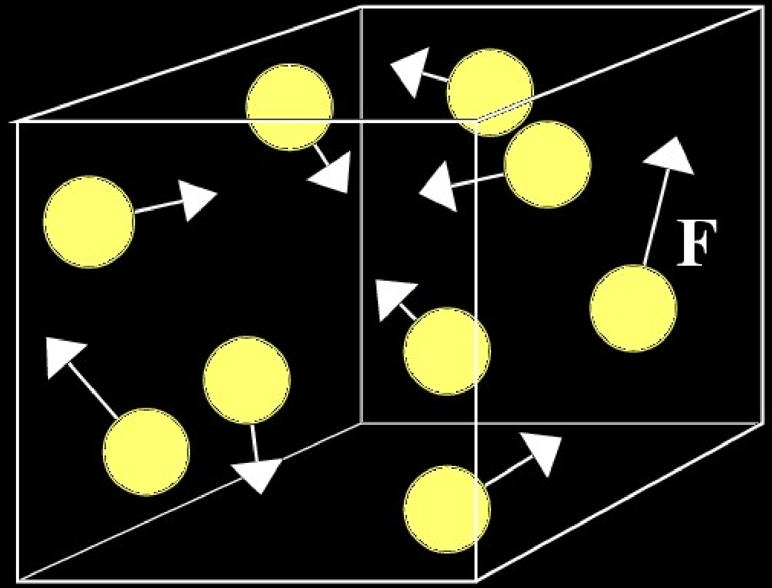
Average: accumulate averages of observables of interest (A)

$$\langle A \rangle = \frac{1}{T}\int_0^T A(\vec{R}(t),\vec{P}(t))\,dt \qquad \langle A \rangle = \frac{\int A(\vec{R},\vec{P})\exp(-\beta E)\,d\vec{R}d\vec{P}}{\int \exp(-\beta E)d\vec{R}d\vec{P}}$$

Average in Molecular Dynamics = Average in Statistical Mechanics

Molecular Dynamics

$$M\ddot{R} = F = -\frac{dV}{dR}$$



(with periodic boundary conditions)

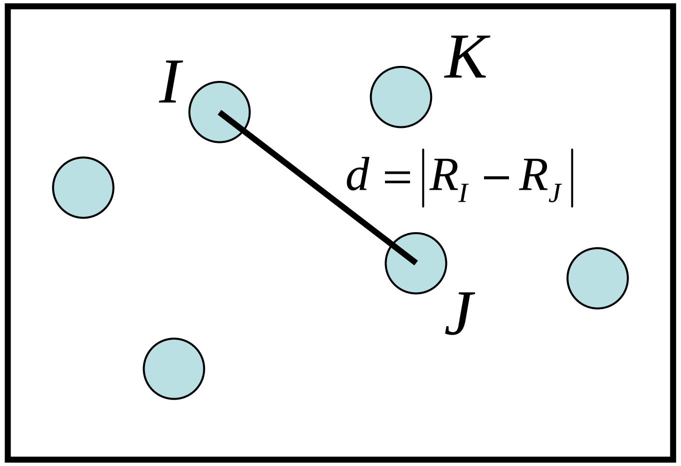
Sum of pair interactions?

How to treat chemical complexity?

Where are the electrons?

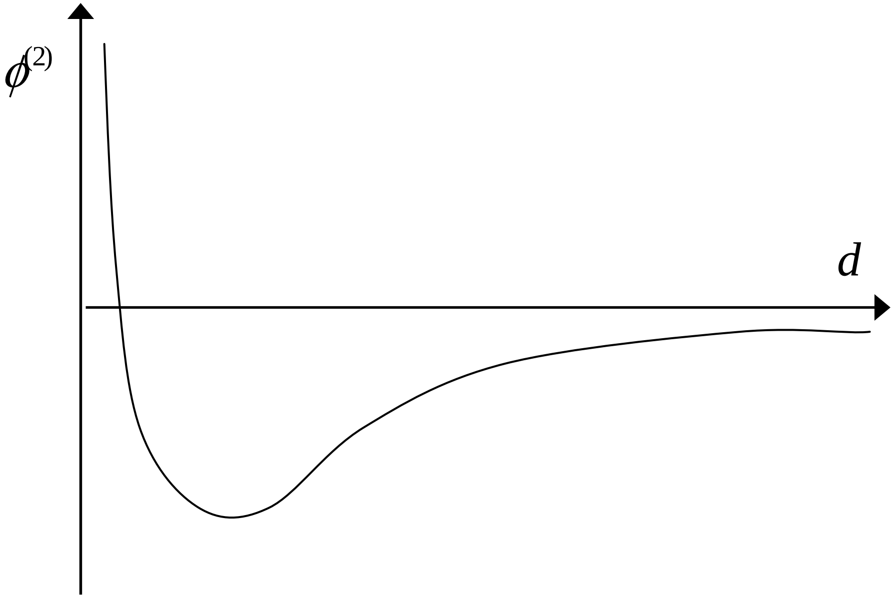
Interatomic potentials

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$



A very simple choice:

$$E(\{R\}) = \frac{1}{2}\sum_{I,J}\phi^{(2)}(|R_I - R_J|)$$



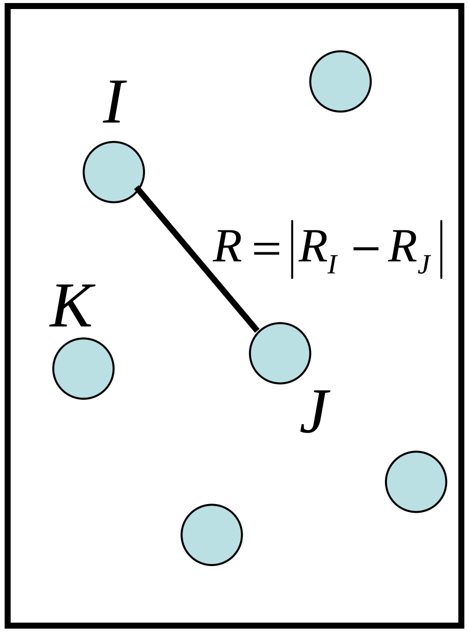
But the interaction between two atoms is partially mediated by the presence of a third atom…

$$E(\{R\}) = \frac{1}{2}\sum_{I,J}\phi^{(2)}(I,J) + \frac{1}{6}\sum_{I,J,K}\phi^{(3)}(I,J,K) + \ldots$$

“Empirical” potentials

Starting point: Pair potentials (Lennard-Jones, Born-Mayer, Coulomb, etc)

$$4\varepsilon\left[\left(\frac{R_0}{R}\right)^{12}-\left(\frac{R_0}{R}\right)^{6}\right], \quad -\frac{Ze^2}{R}+\varepsilon e^{-\alpha R}, \; etc\ldots$$



\+ three-body corrections

$$\phi^{(3)}(I,J,K)=V_0\left[\cos\alpha+1/3\right] \qquad \alpha=I\hat{J}K$$

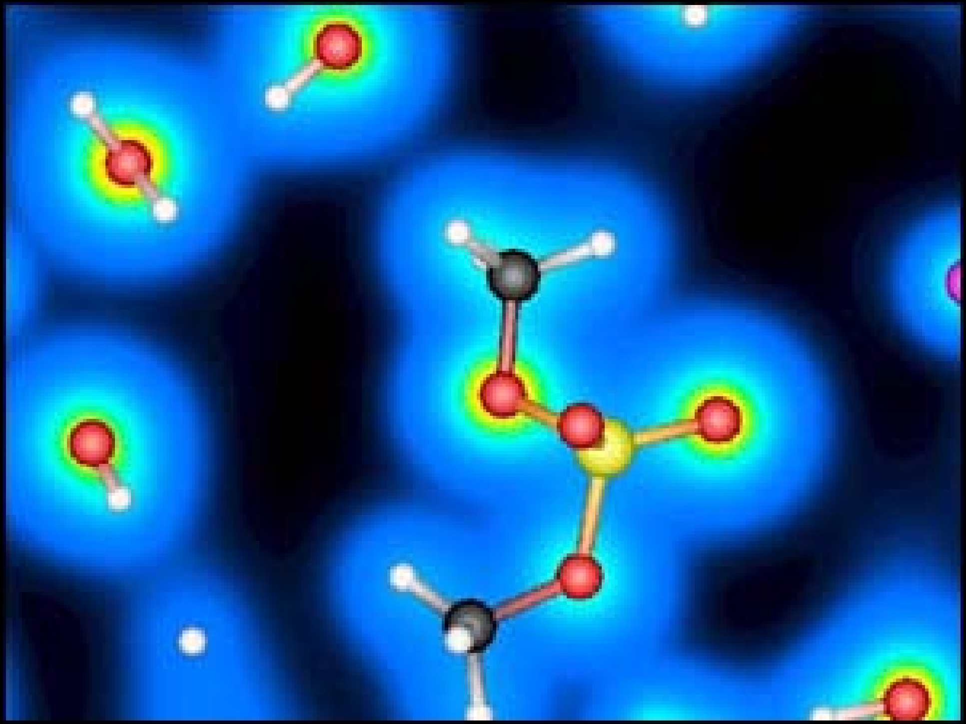
\+ density dependent terms (embedded atom models)

\+ atomic distorsion terms (includes polarization)

\+ charge transfer terms

Parameters are determined from “empirical” data, such as experimental EOS, vibrations, phase diagrams, dynamical properties, etc.

Quantum simulations: The "standard model"



"Molecular dynamics" for atoms

$Ma = F = -dE/dR$

Schroedinger equation for electrons

$H\psi = E\psi$

e^--e^- interactions:
Density Functional Theory
e^--nuclei interactions:
Pseudopotentials

"Ab-initio" molecular dynamics = Classical molecular dynamics in potential energy surface generated by th electrons in their quantum ground state

Where are the electrons? The adiabatic approximati

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$

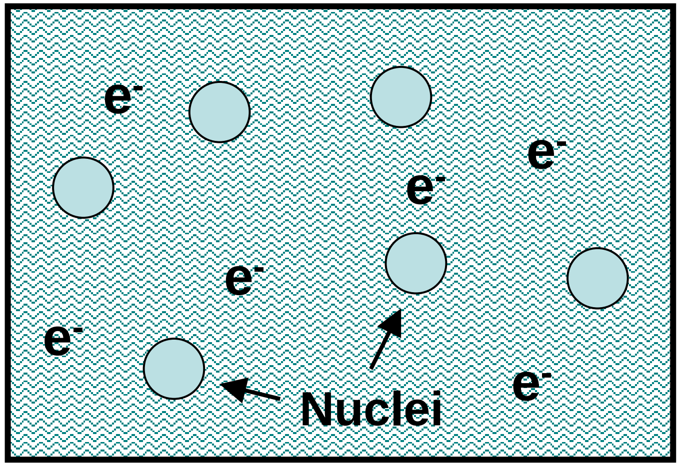
Electrons respond much faster than nuclei to external forces, because of their lighter mass, therefore:

Electrons are always in their instantaneous quantum mechanical ground state, for each given {R}.

$$E(\{R\}) = \langle \psi_e | H_e(\{R\}) | \psi_e \rangle$$

Consequence:

Every MD step requires the calculation of the QM ground state of the electrons



The electronic Hamiltonian H_e depends parametrically on the nuclear positions {R}

$$H_e = -\sum_{i=1,N_e} \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i=1,N_e}^{j=1,i-1} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i=1,N_e}^{I=1,N} \frac{Z_I e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} + \sum_{I=1,N}^{J=1,I-1} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|}$$

Density functional theory

$$H_e = -\sum_{i=1,N_e} \frac{\hbar^2}{2m_e}\nabla_i^2 + \boxed{\sum_{i=1,N_e}^{j=1,i-1} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}} - \sum_{i=1,N_e}^{I=1,N} \frac{Z_I e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_I|} + \sum_{I=1,N}^{J=1,I-1} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|}$$

Electron-electron (many-body) interaction

Density-functional theory [W. Kohn et al. 1964-1965] states that the e-e interaction can be written as a one-electron “effective” term:

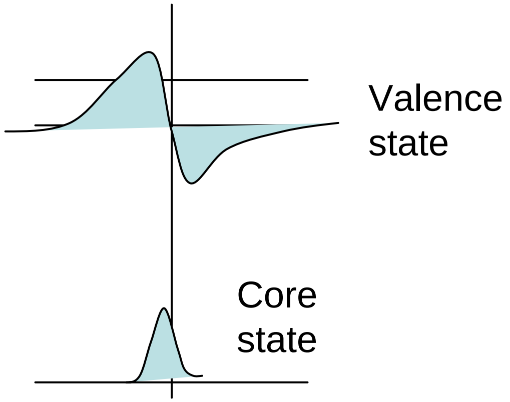
$$\sum_j \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \equiv \int \frac{\rho_e(\vec{r}\,')}{|\vec{r}_i - \vec{r}\,'|} d\vec{r}\,' + V_{xc}(\rho_e(\vec{r}_i))$$

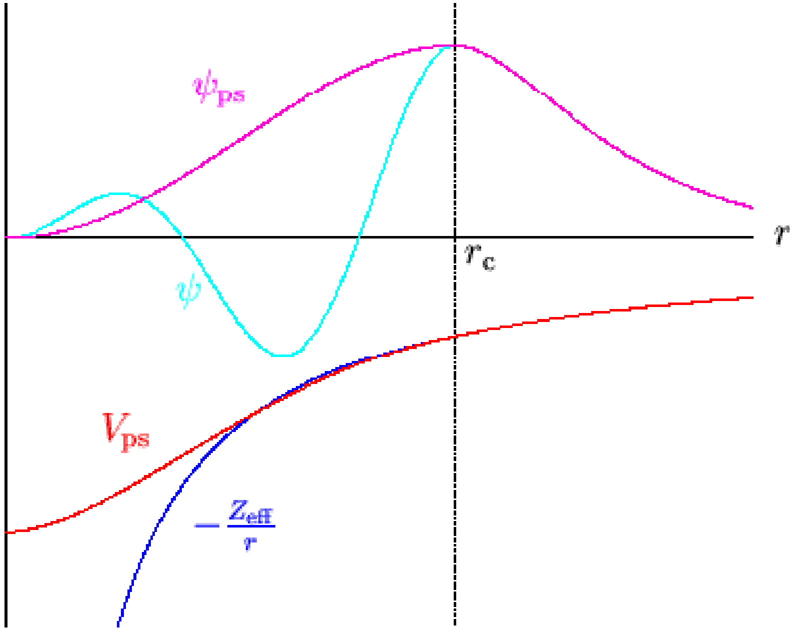
However, the exact functional form of V_{xc} is not (yet) known. Current approximations to the exact V_{xc} go under different names (LDA, BLYP, BP, GGA, “hybrid”, et al). While GGA and hybrid functionals provide slightly better results than other approximations, the choice of the V_{xc} is often made in such a way to improve agreement with exps (“ab fine”??).

The pseudopotential approximation

Electron-ion interaction

$$H_e = -\sum_{i=1,N_e} \frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{i=1,N_e}^{j=1,i-1} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \boxed{-\sum_{i=1,N_e}^{I=1,N} \frac{Z_I e^2}{|\boldsymbol{r}_i - \boldsymbol{R}_I|}} + \sum_{I=1,N}^{J=1,I-1} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|}$$





\+ Core states are irrelevant

\+ Valence states have nodes as a consequence of orthogonality with core states

The *1/r* Coulomb potential can be replaced by a suitably constructed effective potential, or pseudopotential

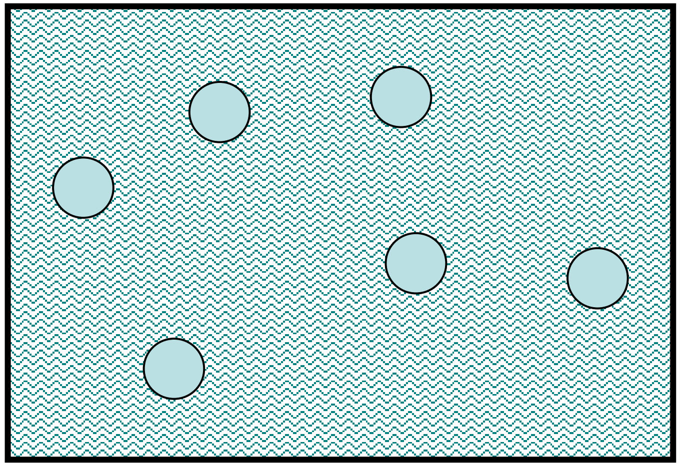
“Ab-initio” forces: the Hellmann-Feynman theorem

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I} = -\frac{d\left\langle \psi_0 \middle| H_e(\{R\}) \middle| \psi_0 \right\rangle}{dR_I}$$

How to keep electron in the ground state

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$

$$E(\{R\}) = \langle \psi_0 | H_e(\{R\}) | \psi_0 \rangle$$



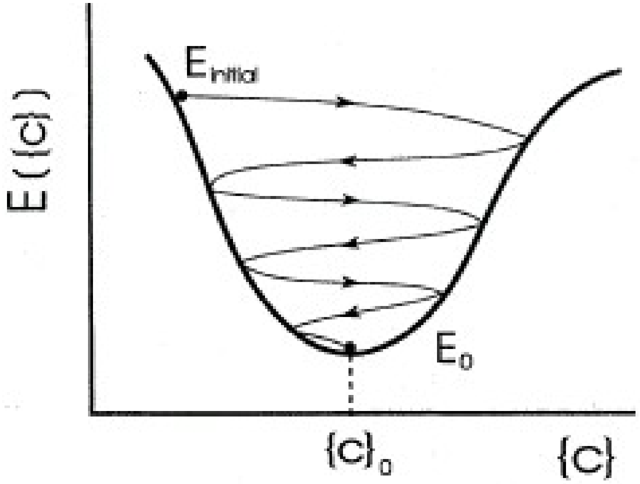
If we expand wavefunctions in a basis set

$$\psi = \sum_i c_i \varphi_i$$

$$\langle \psi | H_e | \psi \rangle = \sum_{i,j} c_i c_j^* \langle \varphi_i | H_e | \varphi_j \rangle$$

finding the ground state is equivalent to minimizing a quadratic form in the {c}'s (variational principle). So, standard minimization schemes can be used, e.g. steepest descent:

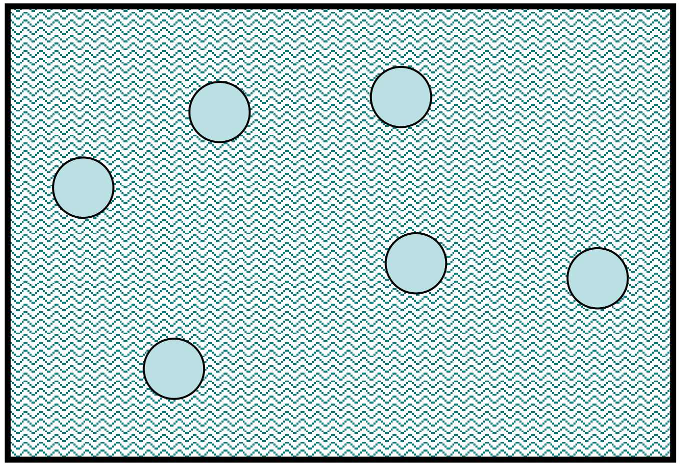
$$\dot{\psi} = -\frac{\delta}{\delta \psi} \langle \psi | H_e | \psi \rangle = -H_e \psi$$

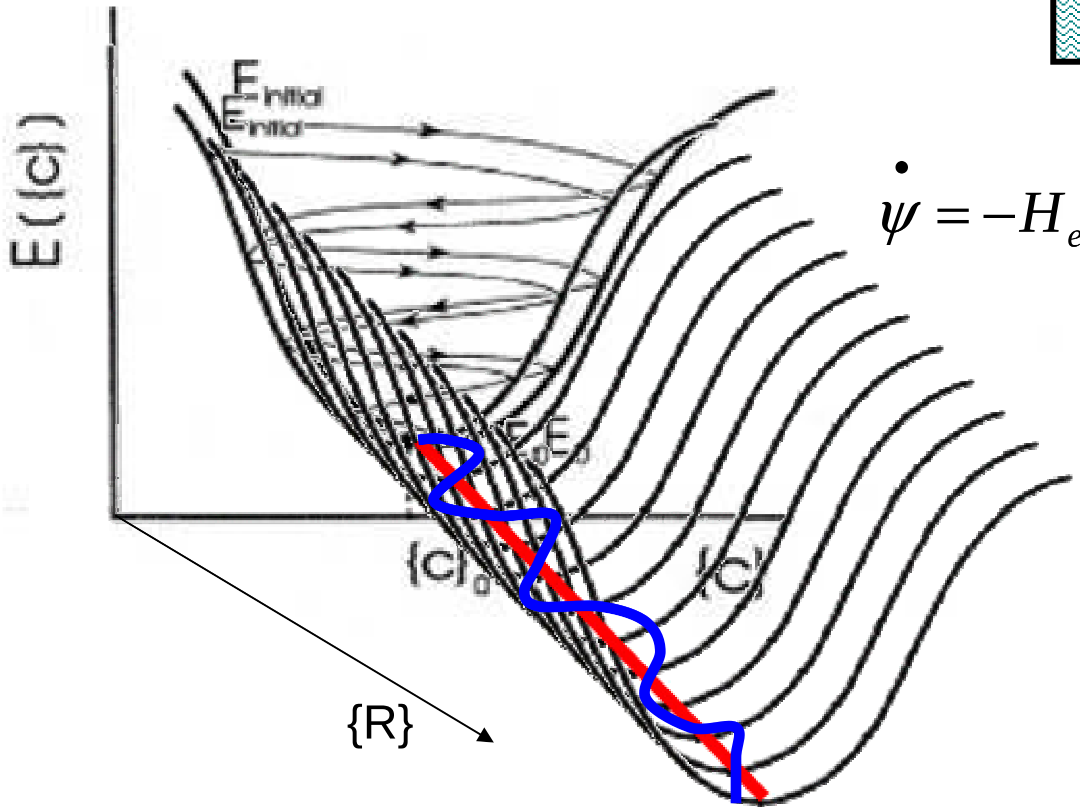


How to keep electron in the ground state

$$M_I \frac{d^2 R_I}{dt^2} = F_I = -\frac{dE(\{R\})}{dR_I}$$

$$E(\{R\}) = \langle \psi_0 | H_e(\{R\}) | \psi_0 \rangle$$





$$\dot{\psi} = -H_e(\{R\})\psi$$

down to the minimum for each {R}

$$\ddot{\psi} = -H_e(\{R\})\psi \quad \textbf{???}$$

$$M_I \ddot{R}_I = -\frac{dE(\{R\})}{dR_I}$$

The Car-Parrinello algorithm

Born-Oppenheimer -versus- Car-Parrinello AIMD

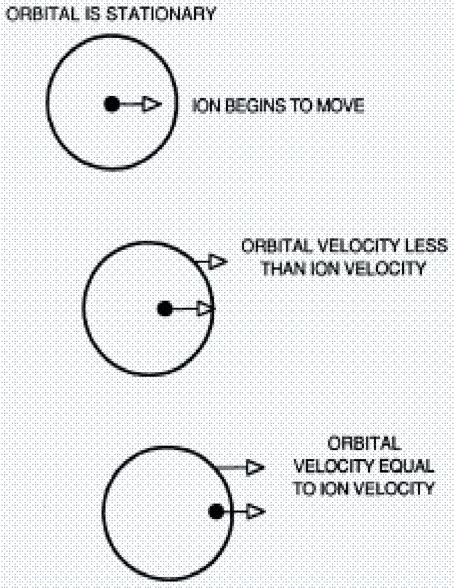


FIG. 24. Schematic illustration of how an orbital will eventually lag behind a moving ion during a simulation with $\mu\dot{\psi}=-[H-\lambda]\psi$, as discussed in the text. Convention the same as in Fig. 23.

Born-Oppenheimer

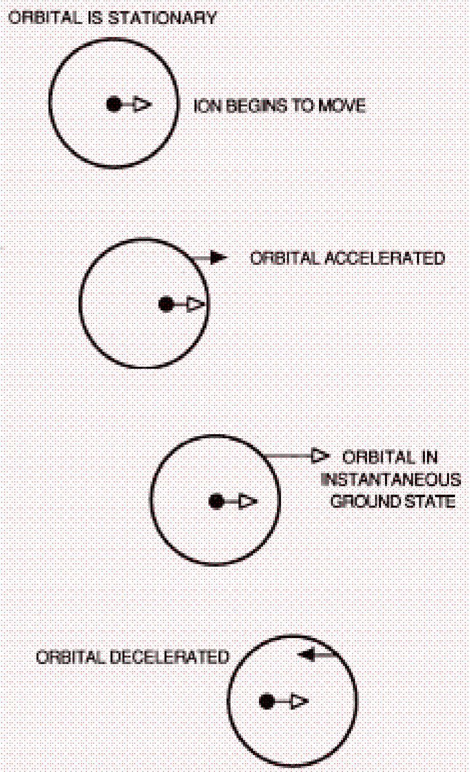


FIG. 23. Schematic illustration of how an orbital will oscillate around a moving ion during a simulation with $\mu\ddot{\psi}=-[H-\lambda]\psi$, as discussed in the text. Velocities and accelerations are designed as open and filled arrows, respectively.

Car-Parrinello

Born-Oppenheimer -versus- Car-Parrinello forces

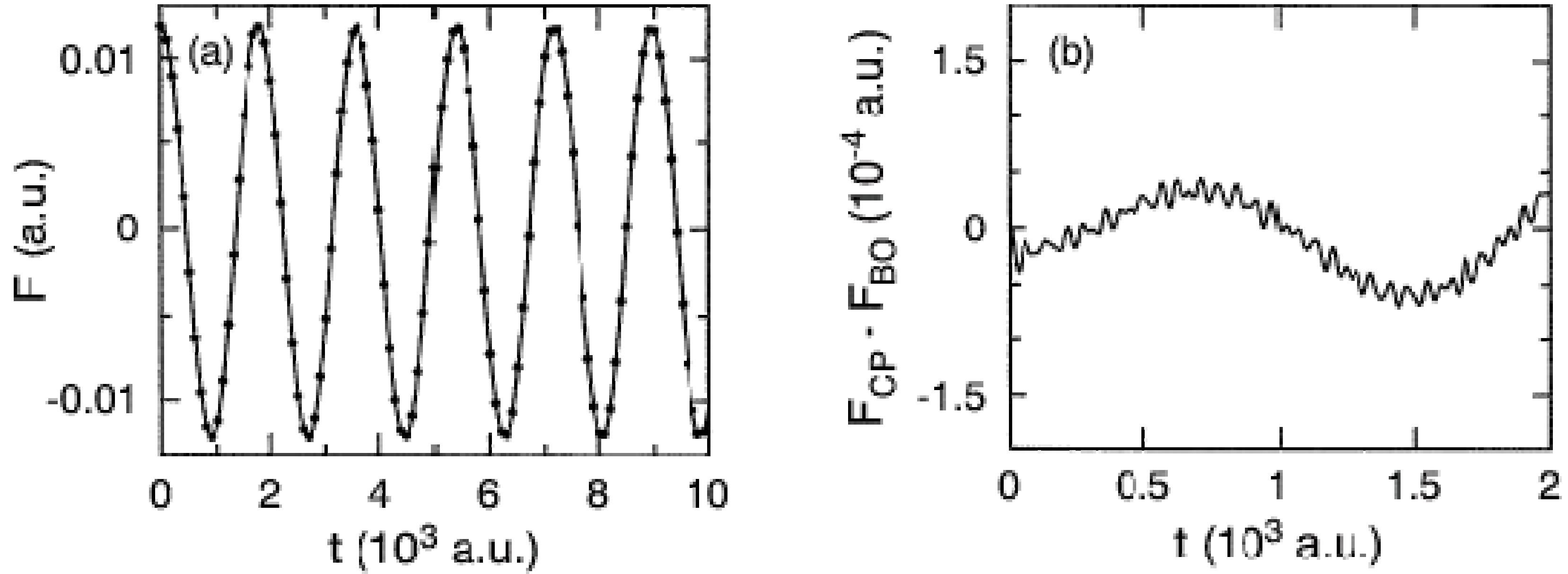
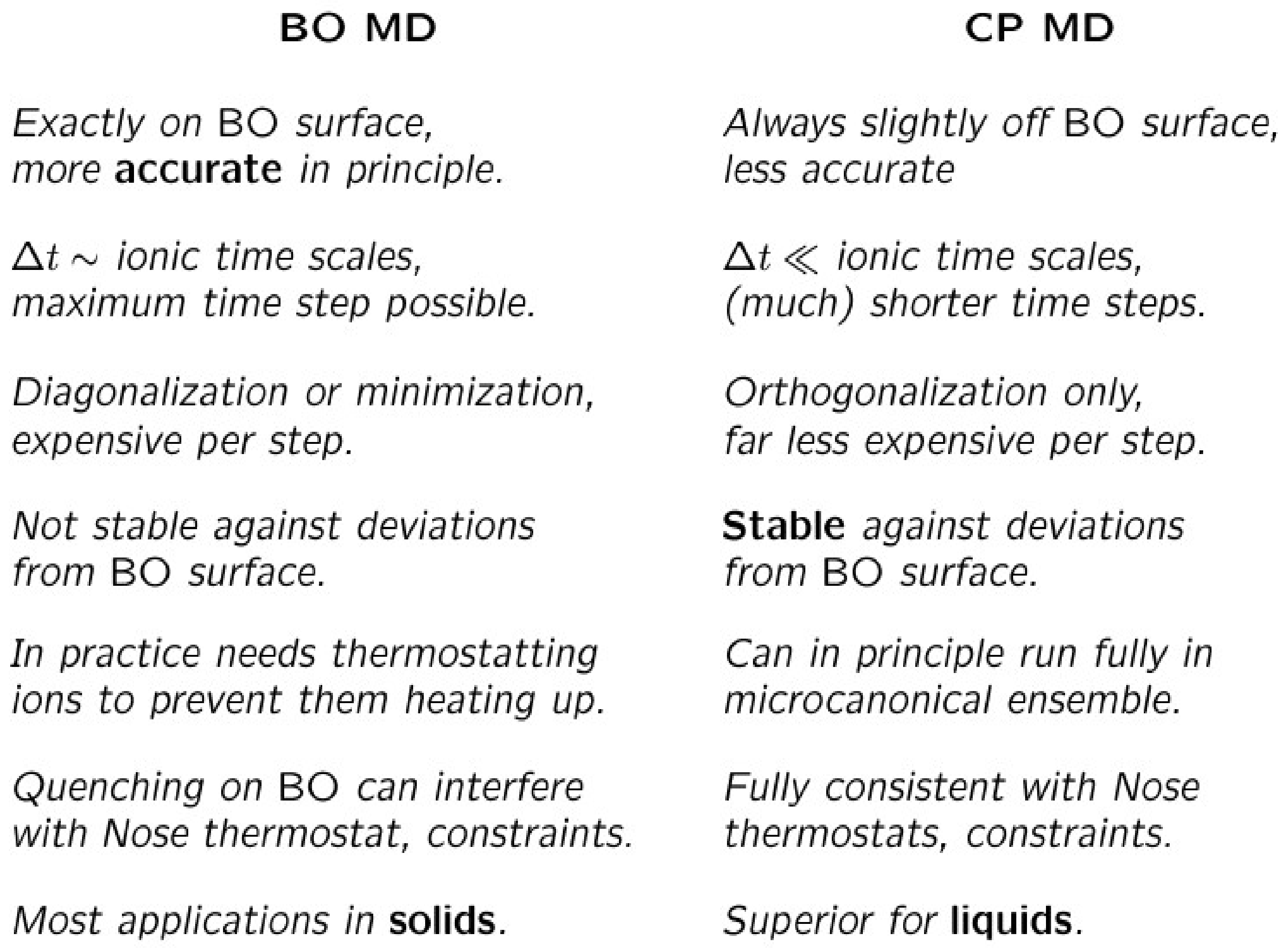


Figure 4. (a) Comparison of the x–component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well–converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. [467].

Born-Oppenheimer -versus- Car-Parrinello: summary



BO MD	CP MD
Exactly on BO surface, more **accurate** *in principle.*	*Always slightly off BO surface, less accurate*
$\Delta t \sim$ *ionic time scales, maximum time step possible.*	$\Delta t \ll$ *ionic time scales, (much) shorter time steps.*
Diagonalization or minimization, expensive per step.	*Orthogonalization only, far less expensive per step.*
Not stable against deviations from BO surface.	**Stable** *against deviations from BO surface.*
In practice needs thermostatting ions to prevent them heating up.	*Can in principle run fully in microcanonical ensemble.*
Quenching on BO can interfere with Nose thermostat, constraints.	*Fully consistent with Nose thermostats, constraints.*
Most applications in **solids**.	*Superior for* **liquids**.

from M Sprik

Ab-initio Molecular Dynamics: bibliography

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- M. Payne, M. Teter, D. Allan, T. Arias, J. Joannopoulos, *Rev. Mod. Phys.* 64, 1045 (1992).
- D. Marx, J. Hutter, "Ab Initio Molecular Dynamics: Theory and Implementation", in "*Modern Methods and Algorithms of Quantum Chemistry*" (p. 301-449), Editor: J. Grotendorst, (NIC, FZ Jülich 2000)
- http://www.theochem.ruhr-uni-bochum.de/research/marx/cprev.en.html
- R. Rousseau and S. Scandolo, “Car-Parrinello Molecular Dynamics”, in “*Encyclopedia of Condensed Matter Physics*”, edited by G. Bassani, G. Liedl, and P. Wyder, Elsevier, Amsterdam (2005)

Asian-Pacific School, Beijing, July 2004

QUANTUM ESPRESSO

Quantum ESPRESSO is an open-source suite of computer codes for electronic-structure calculations and materials modeling. It is based on density-functional theory, plane waves, and pseudopotentials.

Features include:

- structural optimizations,
- phonons
- elastic constants
- ab-initio molecular dynamics
- dielectric and Raman tensors
- infrared spectra
- NMR spectra
- etc…

“First-principles codes for computational crystallography in the Quantum-ESPRESSO package”
S. Scandolo et al., Z. Kristallogr. 220, 574 (2005)

www.quantum-espresso.org