Car-Parrinello MD

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First Principles Molecular Dynamics

We call *Molecular Dynamics* (MD) a computer simulation technique in which the time evolution of a set of interacting atoms is followed by integrating their equations of motion.

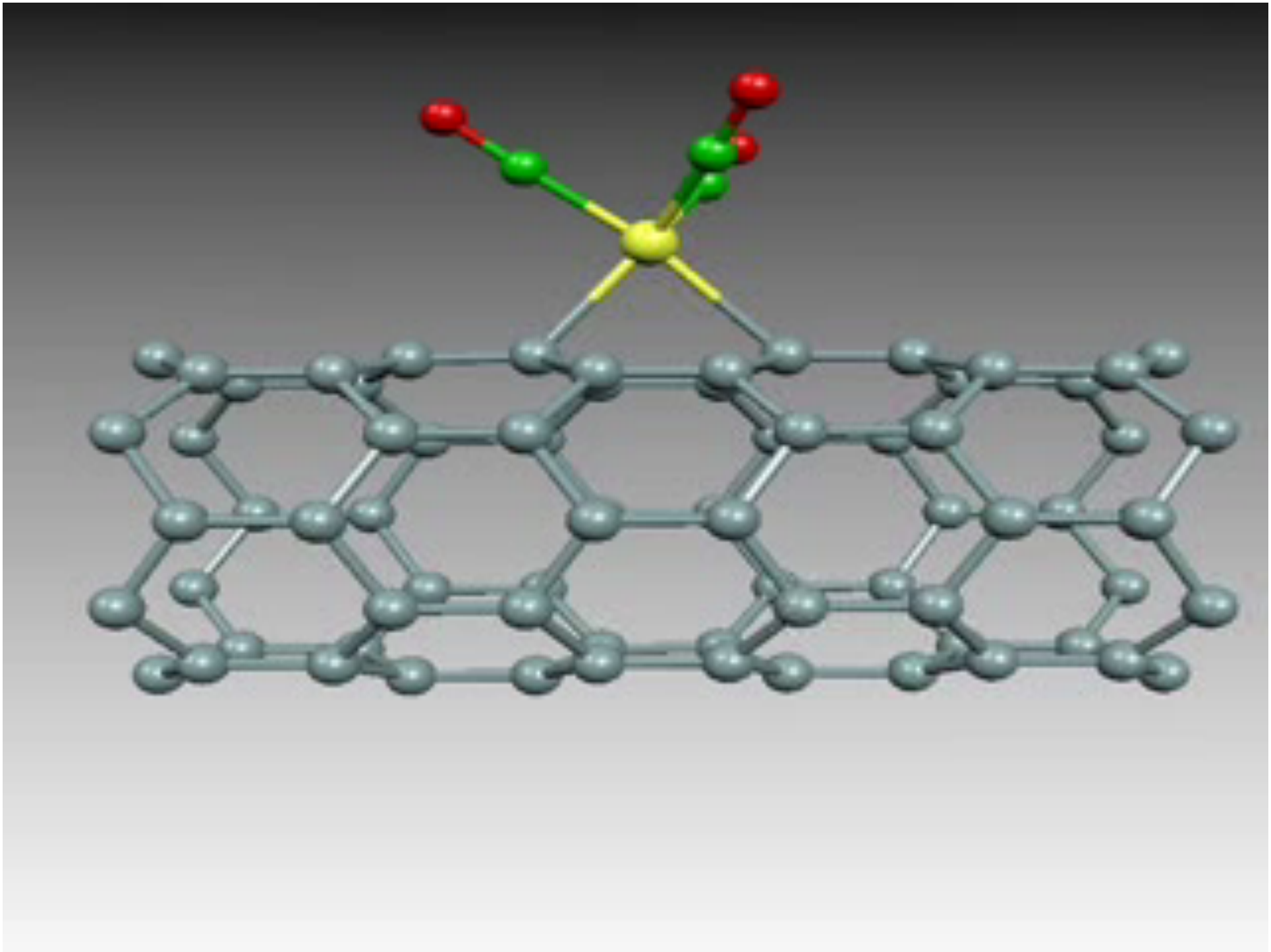
We limit our attention to a set of interacting atoms moving classically: the dynamics is described by Newton's law:

$$\mathbf{F}_i = m_i \mathbf{a}_i$$

$\mathbf{a}_i = d^2\mathbf{r}_i/dt^2$ $\mathbf{F}_i$ m_i

The interatomic potential:

$$\mathbf{F}_i = -\nabla_{\mathbf{r}_i} V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$



Evaluation of the energy and its derivatives:

•Quantum mechanics (ab initio)

•Multi-reference configuration interaction → N^{7-8} (MRCI)

•Coupled-cluster → N^{5-6} (CC)

•Density Functional Theory → N^{3-4} (DFT)

H_2O → 10 elettroni MRCI=30 min, CC=15 min, DFT=1 min

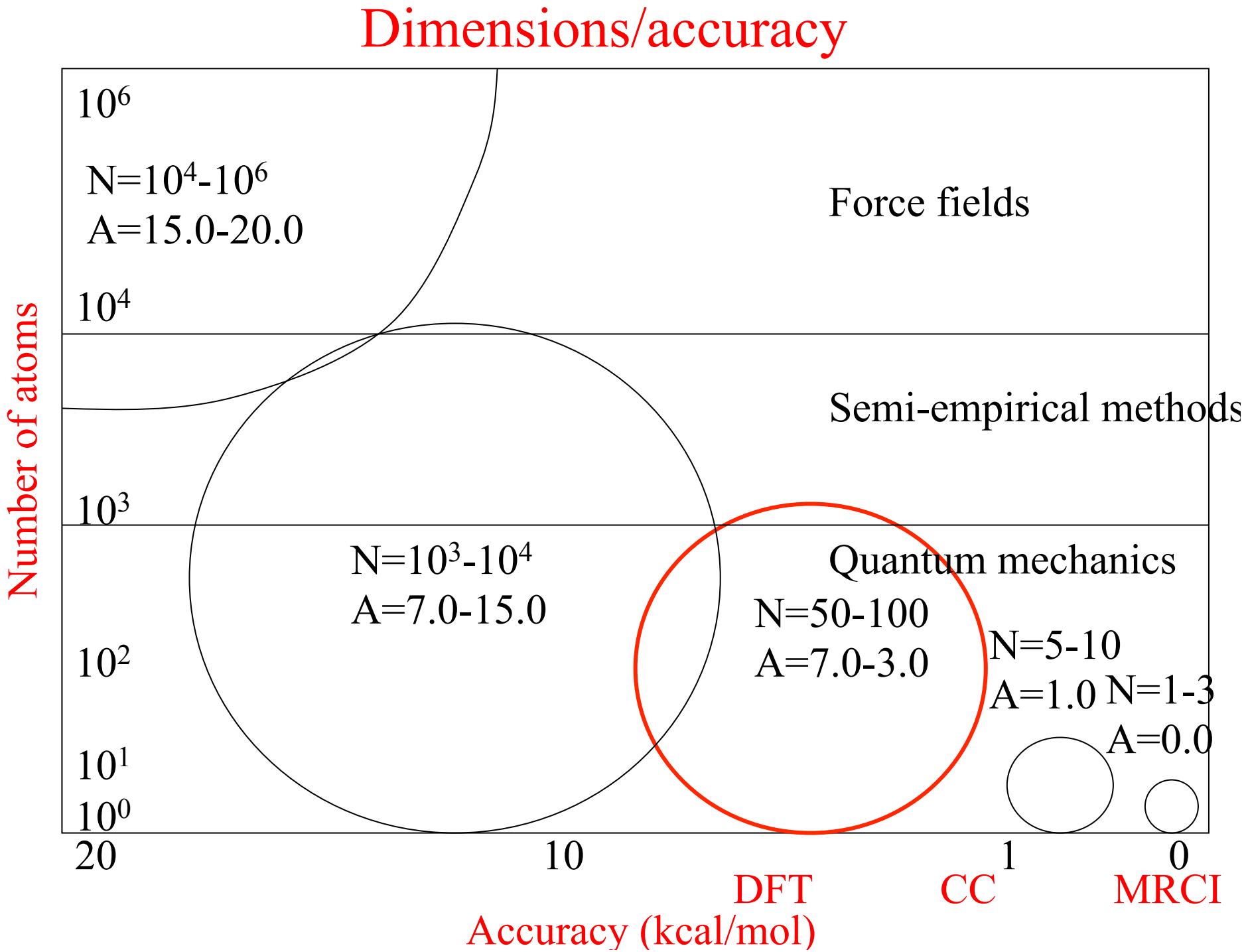
$2H_2O$ → 20 elettroni MRCI=7680(128 h) CC=960 (16h) DFT=8-16

•Semi-empirical methods

•INDO/MNDO/ZINDO → N^{2-3}

•Model potentials

•force fields → N^{2}

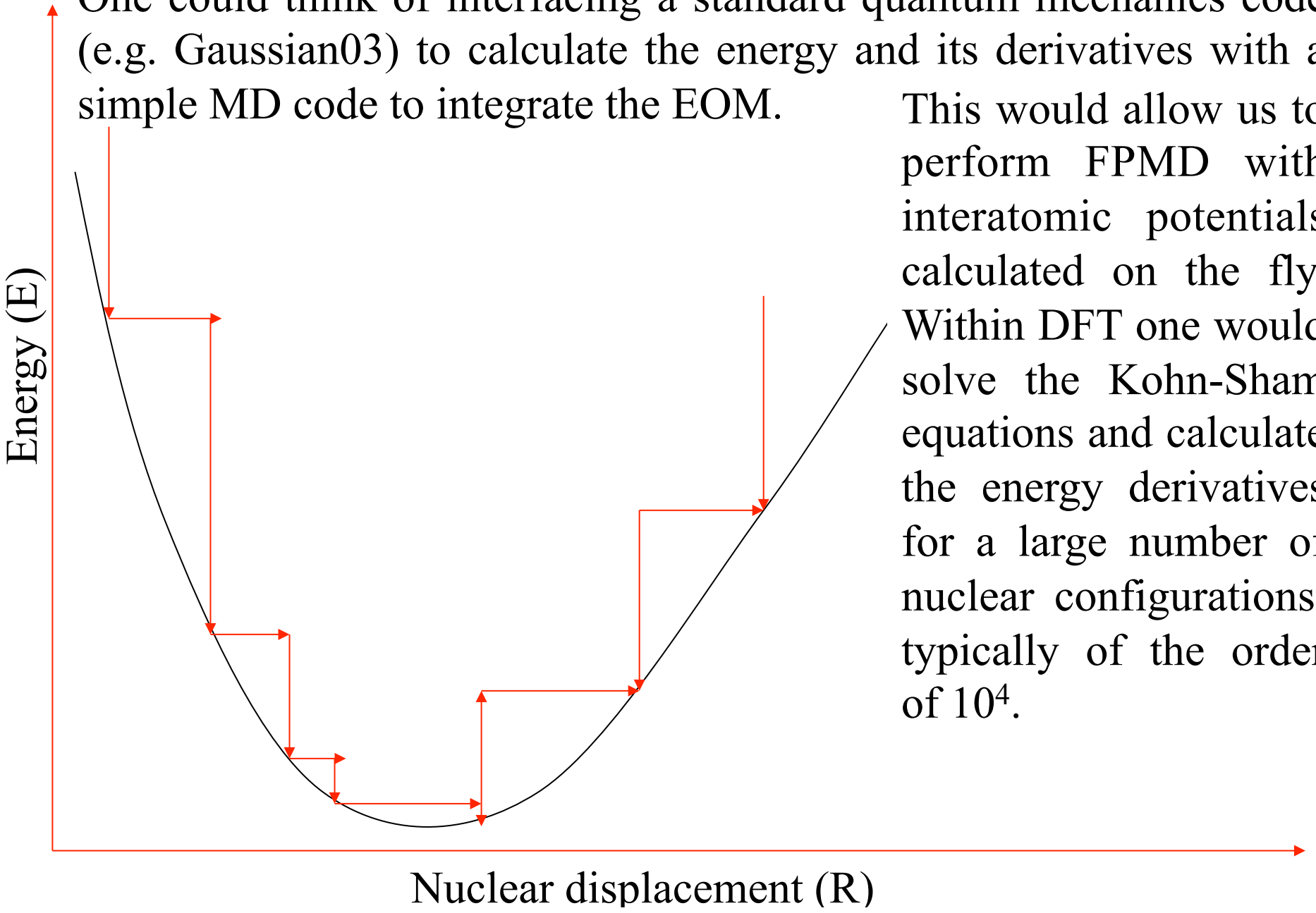

Dimensions/accuracy
Number of atoms
10^6
10^4
10^3
10^2
10^1
10^0
N=10^4-10^6
A=15.0-20.0
Force fields
Semi-empirical methods
N=10^3-10^4
A=7.0-15.0
Quantum mechanics
N=50-100
A=7.0-3.0
N=5-10
A=1.0
N=1-3
A=0.0
20
10
1
0
DFT
CC
MRCI
Accuracy (kcal/mol)

QM Computer codes:

• GAUSSIAN 09	- USA
• TURBOMOLE	- GERMANY
• MOLPRO	- GERMANY
• GAMESS	- UK / USA
• ADF	- NETHERLANDS
• QUANTUM ESPRESSO	- ITALY
• ABINIT	- BELGIUM
• CP2K	- SWITZERLAND

Born-Oppenheimer Molecular Dynamics (BOMD):

One could think of interfacing a standard quantum mechanics code (e.g. Gaussian03) to calculate the energy and its derivatives with a simple MD code to integrate the EOM.



This would allow us to perform FPMD with interatomic potentials calculated on the fly. Within DFT one would solve the Kohn-Sham equations and calculate the energy derivatives for a large number of nuclear configurations, typically of the order of 10^4.

Car-Parrinello Molecular Dynamics (CPMD)

Trieste 1985 → Trieste 2007→ Trieste 2012

Car-Parrinello Molecular Dynamics (CPMD)