

# *AB INITIO* MOLECULAR DYNAMICS

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# *Ab Initio* Molecular Dynamics

- Background
  - Review of Classical MD
- Essential Quantum Mechanics
  - Born-Oppenheimer Molecular Dynamics
- Basics of Density Functional Theory
  - Performance Implications



# Background

- Code Usage on ARCHER (2014-15) by CPU Time:

Rank	Code	Node hours	Method
1	VASP	5,443,924	DFT
3	CP2K	2,121,237	DFT
4	CASTEP	1,564,080	DFT
9	LAMMPS	887,031	Classical
10	ONETEP	805,014	DFT
12	NAMD	516,851	Classical
20	DL_POLY	245,322	Classical

- 52% of all CPU time used by Chemistry / Materials Science / Biomolecular Simulation



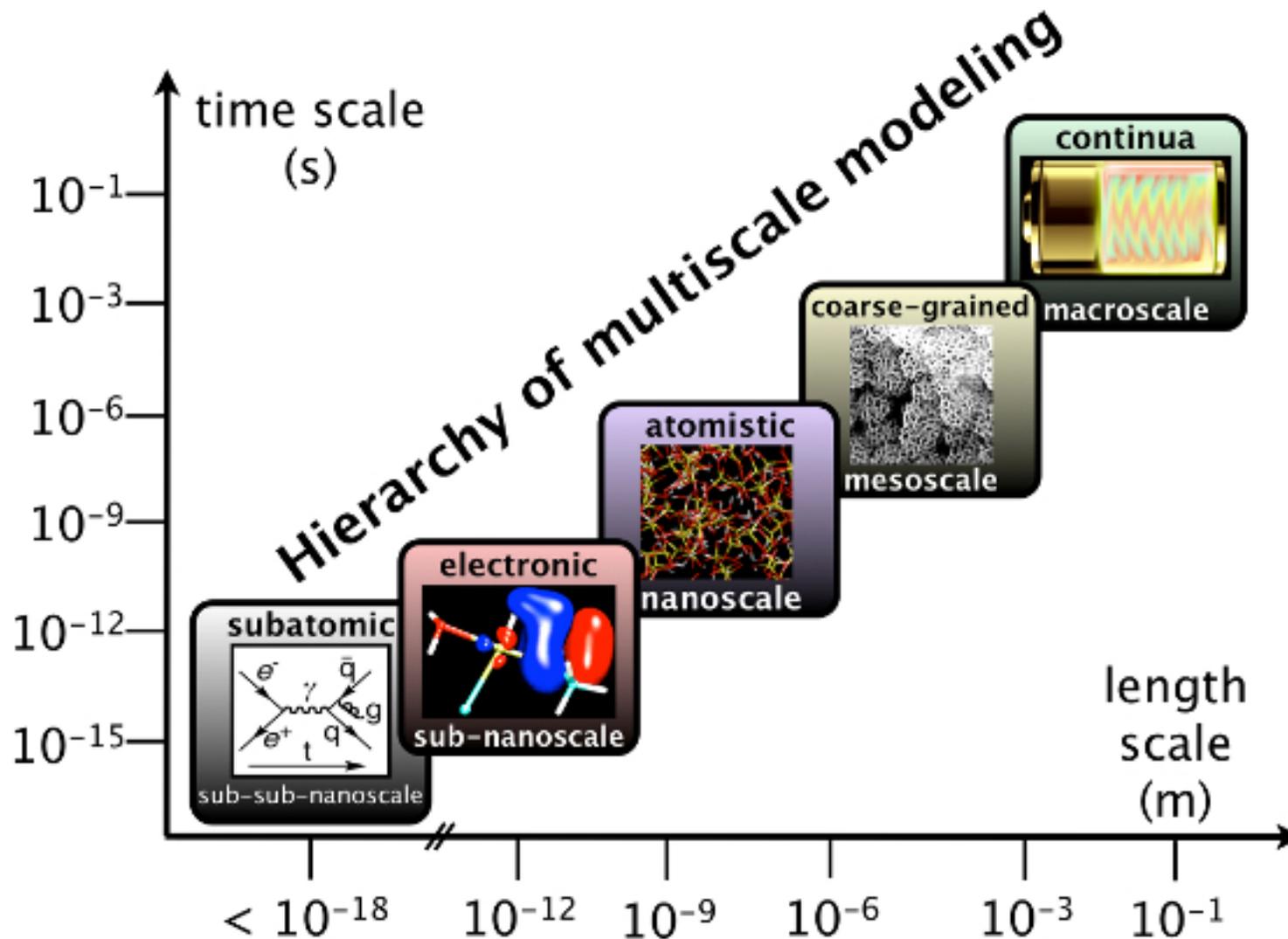


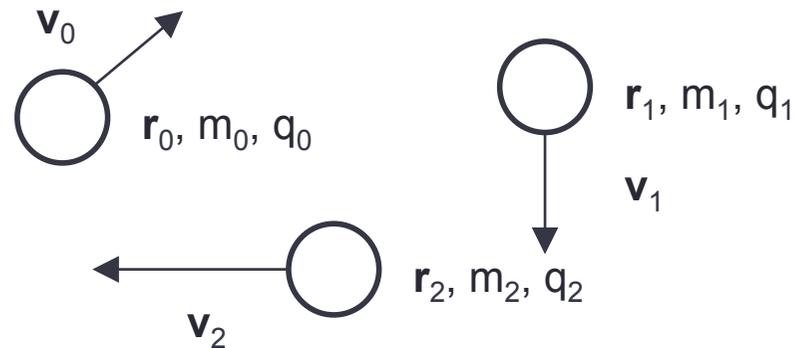
Image from Karlsruhe Institute of Technology (<http://www.hiu.kit.edu/english/104.php>)



# Classical Atomistic Simulation

- The main elements of the simulation model are:

- Particles



- Force field

- Pair potentials

- Three-body

- Four-body

- e.g. CHARMM, GROMOS, AMBER, AMOEBA, ReaxFF ...



# Classical Atomistic Simulation

- Molecular Dynamics

- Newton's 2<sup>nd</sup> Law

$$F = ma$$

- Integrate using e.g. Velocity Verlet algorithm

$$r(t), \dot{r}(t) \rightarrow r(t + \delta t), \dot{r}(t + \delta t)$$

- Structural/Geometry Optimisation
  - Minimise total energy w.r.t. atomic positions



# Classical Atomistic Simulation

- Successes:
  - Computationally cheap and parallelises well ( > 1,000,000,000 atoms on 10,000 cores)
  - Able to predict mechanical properties
    - Density, elasticity, compressability, heat capacity (of insulators)
  - Can predict structure
    - RDF of crystals, local ordering in liquids, protein folding ...
- Failures:
  - Anything involving electron transfer (i.e. all of Chemistry!)
    - Bonding, electrochemistry
    - Heat capacity of metals
    - Electronic structure/conductivity
    - Magnetic properties
    - etc.



# Essential Quantum Mechanics

- We need a model which can describe electrons...
- ... so turn to Quantum Mechanics – the Physics of the very small.
  - Thanks to Planck, Heisenberg, Einstein, Schrödinger *et al*, 1920s
- No longer think of point particles



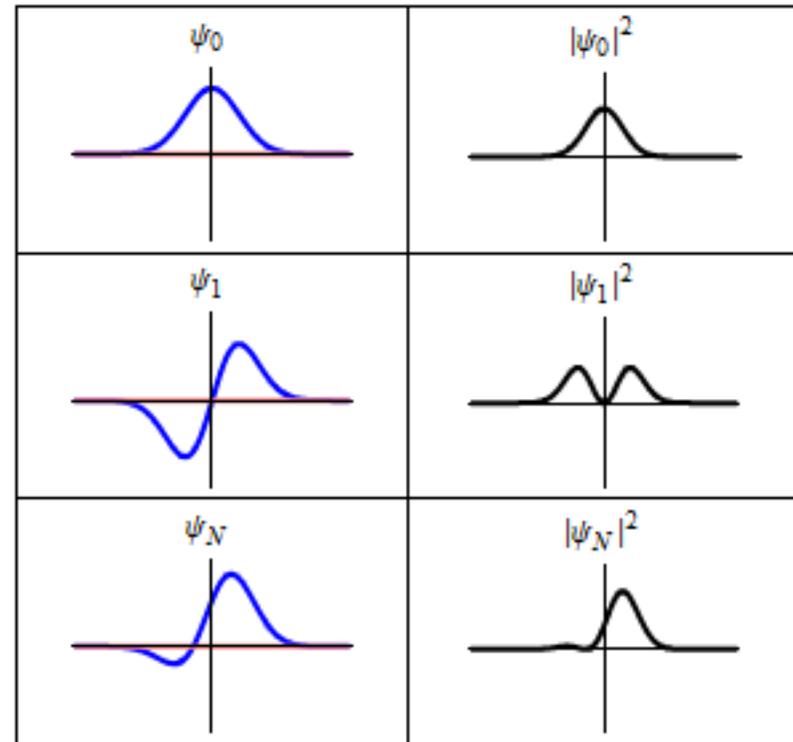
# Essential Quantum Mechanics

- Instead, particles are described by a wave-function:

$$\Psi(\vec{r}, t)$$

- No longer have defined positions but instead a probability distribution function:

$$|\Psi(\vec{r}, t)|^2$$



# Essential Quantum Mechanics

- The central equation(s) of Quantum Mechanics is(are) the Schrödinger's Equation(s)
- In the general, time-dependent form:

$$\hat{H}\Psi(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t)$$



- Wavefunctions which are 'stationary states' (the PDF is not time dependent) are described by the time-independent SE:

$$\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r})$$



# Essential Quantum Mechanics

- For atomistic simulation, we typically have many atoms, each with many electrons, so the wavefunction depends on *all* the atomic and electronic coordinates (and time):

$$\Psi(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, t)$$

- This many-body wavefunction is a non-trivial (and unknown) coupling between all the particles in our system
- Too hard to deal with directly, so start making approximations...



# Essential Quantum Mechanics



- The Born-Oppenheimer approximation (1927)
  - Nuclei are *much* more massive than electrons and move much slower (by  $\sim 10^3$ - $10^5$  times)
  - So we can consider the nuclei to be fixed at some particular time  $t$  and solve the Time-Independent Schrödinger Equation for the electronic system in an external potential created by the nuclei:

$$\Psi(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, t)$$



$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$$



# Essential Quantum Mechanics

- Born-Oppenheimer Molecular Dynamics
  - Solve the TISE for the electronic system to get a total electronic energy as a function of the nuclear coordinates
  - Then evolve the nuclear system with the electronic energy acting as a potential i.e.

$$E(\vec{R}_I) \rightarrow \vec{F}_I = \frac{\partial E(\vec{R}_I)}{\partial \vec{R}_I}$$

- And repeat...
- Can also apply all of our techniques from classical atomistic simulation to get structures, dynamics, mechanical properties ...



# Basics of DFT

- First attempt, guess many-particle wave function is a linear combination of products (Slater Determinant) of single-particle wave functions (Hartree & Fock, 1935)
  - First practical implementation in 1969 (Gaussian 70)
  - Led to Nobel Prize in Chemistry (1998) for John Pople  $\geq O(n^4)$
  - Computationally demanding
  - So limited to relatively small numbers of atoms (~10-100)
- H-F methods are often referred to as ‘wave function theory’
  - Even with the H-F ansatz, the many-particle wave function is still too complicated for practical use, so we make further simplifications...



# Basics of DFT

- Hohenberg-Kohn Theorems (1964)
  - All of the terms in the Hamiltonian that appears in the TISE can be expressed (uniquely) as functionals of the electron density
  - The energy of the system is variational with respect to the density
- Kohn-Sham Method (1965)
  - Instead of the the many-body system of interacting electrons, define a set of 'KS-orbitals' (c.f. wavefunctions) of fictitious, non-interacting electrons moving in an effective potential:

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_H(n(\vec{r})) + V_{XC}(n(\vec{r}))$$

- Then the orbitals which satisfy the K-S Equations (c.f. Schrödinger Eq) give the same density as the interacting system!
- All the electron-electron interactions are included in the exchange-correlation potential
- NB: effective potential depends on the density, which depends on the potential



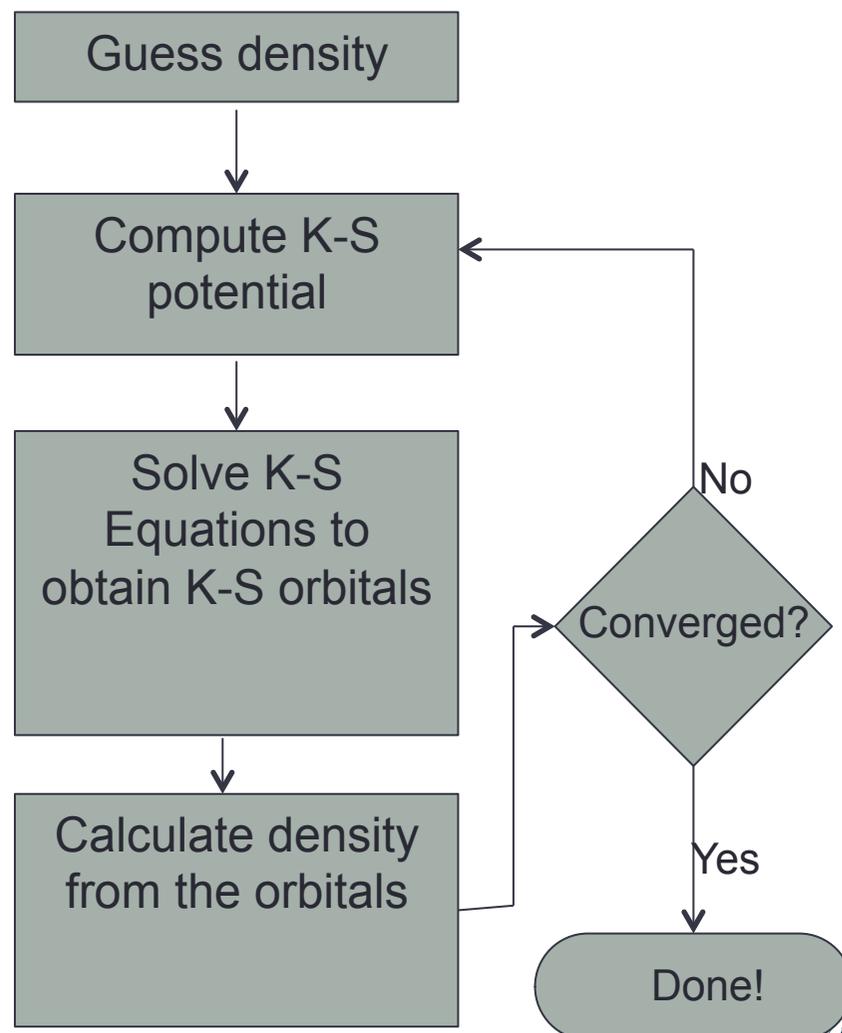
# DFT: Approximations and Theory

- KS-DFT Algorithm:
  - a.k.a. Self-Consistent Field approach (SCF)

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_H(n(\vec{r})) + V_{XC}(n(\vec{r}))$$

$$\left[ -\frac{1}{2} \nabla^2 + V_{KS}(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$$



# Basics of DFT

- Many implementation choices to be made in how the KS orbitals are represented and different methods for solving the KS equations
  - Usually expanded in terms of a basis set:
    - Plane Waves (VASP, CASTEP, Quantum ESPRESSO, ABINIT)
    - Localised Functions e.g. Gaussians, Wavelets (CRYSTAL, ADF, BigDFT)
    - Numerical Basis (CONQUEST, SIESTA)
    - Combinations (CP2K, GPAW)
- Over 70(!) are listed on [http://en.wikipedia.org/wiki/List\\_of\\_quantum\\_chemistry\\_and\\_solid-state\\_physics\\_software](http://en.wikipedia.org/wiki/List_of_quantum_chemistry_and_solid-state_physics_software)



# Basics of DFT

- Performance:
  - Often cubic scaling  $O(N^3)$  with number of basis functions
    - Especially with Plane Wave basis sets
  - Due to matrix diagonalisation required to solve K-S equations
- Growing number of 'linear scaling'  $O(N)$  codes which take advantage of localised basis functions
  - Still a huge prefactor compared with classical MD



# Basics of DFT

- Example – molecular dynamics of forsterite ( $\text{Mg}_2\text{SiO}_4$ )
  - Using ARCHER and CP2K 2.6
- Classical MD
  - Morse-type pair potentials + SPME Electrostatics
  - 28,000 atoms, NPT, 1fs timestep
  - 1 ps = 2 mins on 24 cores
- *Ab-initio* MD
  - Production-quality basis sets
  - 28 atoms, NPT, 0.5 fs timestep
  - 1 ps = 36 mins on 48 cores – over 10,000 times slower!



# Basics of DFT

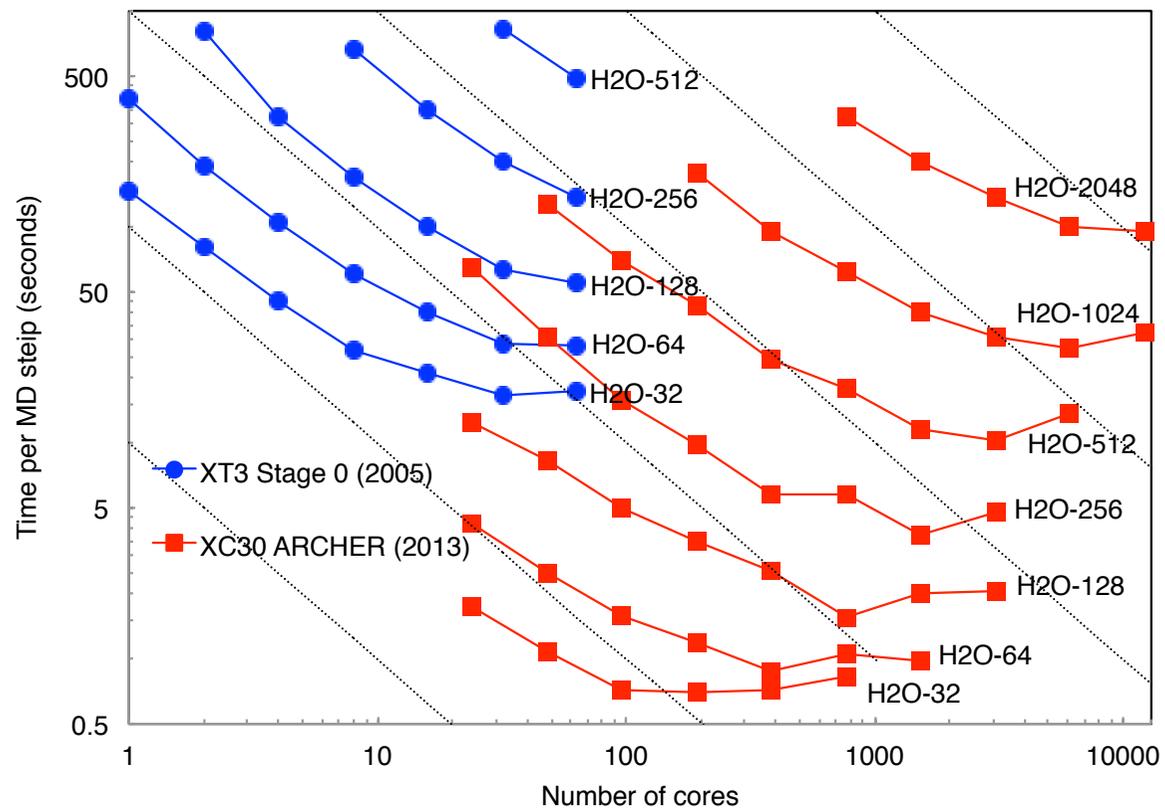


Figure 1. Performance of H2O-32 up to H2O-2048 benchmarks on Cray XT3 (2005) and Cray XC30 (2013)



# Summary

- With care:
  - “First-principles methods may be used for subtle, elegant and accurate computer experiments and insight into the structure and behaviour of matter.”, K. Refson



# Summary

- Without care:
  - “First-principles results may be worthless nonsense”, K. Refson



# Summary

- *Ab initio* MD offers the ability to calculate dynamics based on forces which are not parameterised for particular systems
  - No transferability problem compared to classical MD
- The approximations involved are mathematical, rather than physical
  - Bonding, charge transfer, polarisation emerge from the model rather than being imposed
- Even with efficient DFT codes, still several orders of magnitude slower than classical MD
  - Forces smaller system sizes, finite size effects?
- Possible to couple DFT and classical – QM/MM
  - DFT only for an ‘active region’, rest of system uses forcefield

