Molecular Dynamics

$$\mathbf{R}(t)$$

dynamics, spectroscopy

$$\langle A \rangle \approx \frac{1}{T} \int_0^T A(\mathbf{R}(t)) \; dt$$

Equilibrium statistical mechanics

Some History of MD

- MANIAC operational at Los Alamos in 1952
- Metropolis, Rosenbluth, Rosenbluth and Teller: Metropolis Monte Carlo method (for equilibrium systems) in 1953.
- Alder and Wainwright (Livermore 1956): dynamics of hard spheres.
- Vineyard (Brookhaven 1959-60): radiation damage in copper.
- Rahman (Argonne 1964): liquid argon.
- Car and Parrinello (Sissa1985): *ab-initio* MD

A Tutorial on Molecular Dynamics (MD)

- For an interacting n-particle system, the equation of motion of the system is *N* coupled equations.

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i(\vec{r}_1, \cdots, \vec{r}_N)$$

- Note: The force depends on positions only. The total energy of the system is conserved (in a microcanonical evolution).

A Tutorial on Molecular Dynamics (MD)

- We follow the evolution of the system, which is composed of N classical particles.

- Each particle interacts simultaneously with every other particle, and can experience an additional external potential.

- This is a *many-body* problem. What does it differ from the dynamics of the electronic system?
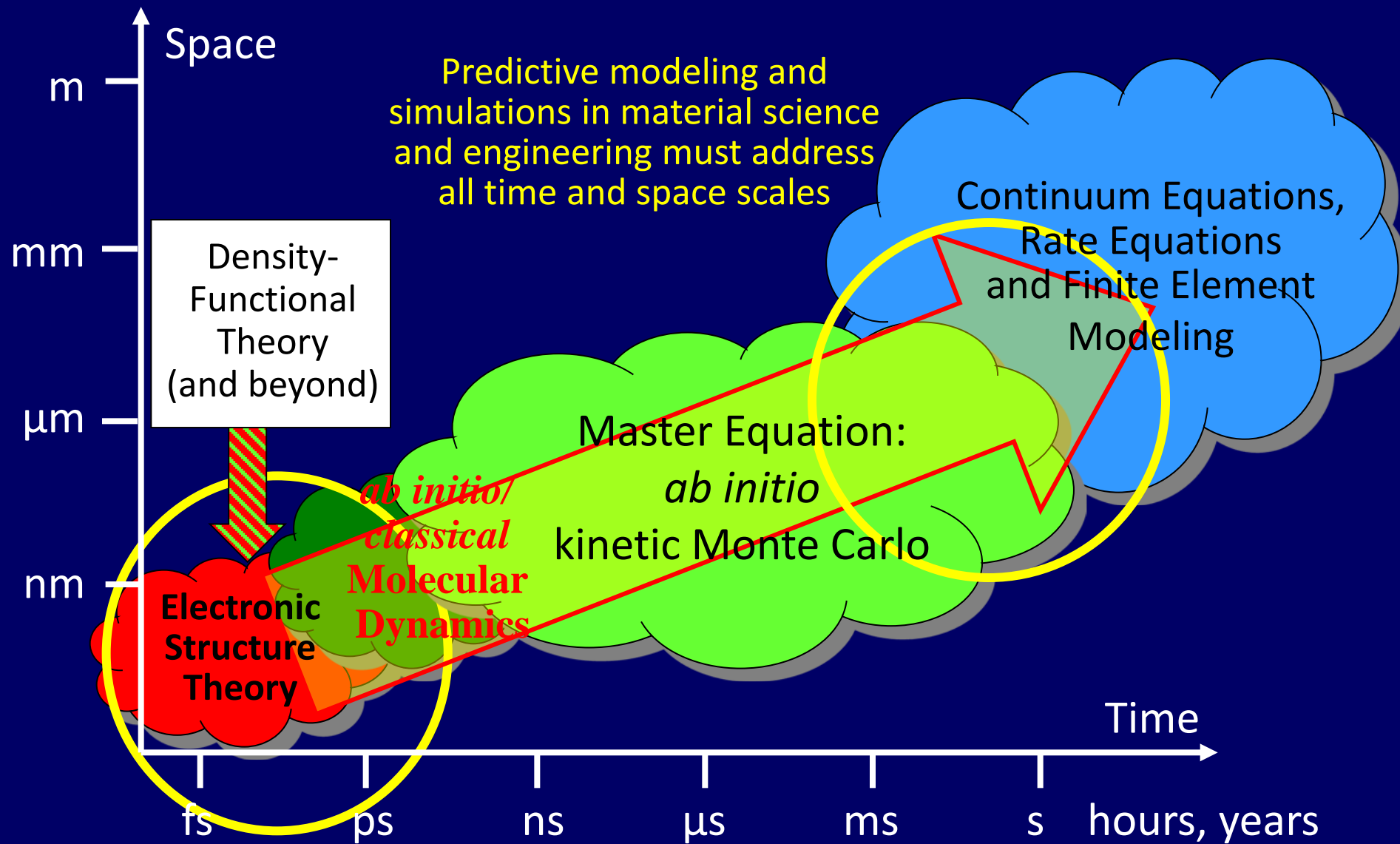
Phase Space

- If we have N particles, we need to specify positions and velocities for all of them ($6N$ variables) to uniquely identify the dynamics of the system.

- One point in a $6N$-dimensional space (the phase space) represents the dynamical system.

Three Goals of MD

- **Ensemble averages** (thermodynamics)

- **Real-time evolution** (chemistry)

- **Ground-state** of the optimized structures

   a). Structure of low-symmetry systems: liquids, amorphous solids, defects, surfaces.

   b). Ab-initio approach: bond-breaking and charge transfer; structure of a complex in non trivial systems such as biomolecules.

Limitations of MD

- **Time scales** (< nano seconds)

- **Length scales** (<1 um)

- **Accuracy of forces**

- **Classical nuclei**

Thermodynamical Averages

Under hypothesis of **ergodicity**, we can assume that the temporal average along a trajectory is equal to the ensemble-average over the phase space.

$$\langle A \rangle = \int A \exp(-\beta E) d\vec{r}^N d\vec{p}^N \Big/ \int \exp(-\beta E) d\vec{r}^N d\vec{p}^N$$

$$\bar{A} = \frac{1}{T} \int_0^T A(t)\, dt \quad \Rightarrow \quad \langle A \rangle = \bar{A}$$

- Let's do straightforward integration of the equations of motion (in a microcanonical ensemble with constant N, V and E).

- The trajectory in the phase space spans states belonging to the microcanonical ensemble.

- A long trajectory generates an excellent sample of microstates.

Computational Experiment with MD

- **Initialize**: select positions and velocities

- **Integrate**: compute all forces, and determine new positions

- **Equilibrate**: let the system reach equilibrium (*i.e.* lose memory of initial conditions)

- **Average**: accumulate quantities of interest

Initialization: Maxwell-Boltzmann Distribution

$$n(v) \propto \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 \exp\left(\frac{-mv^2}{2k_B T} \right)$$
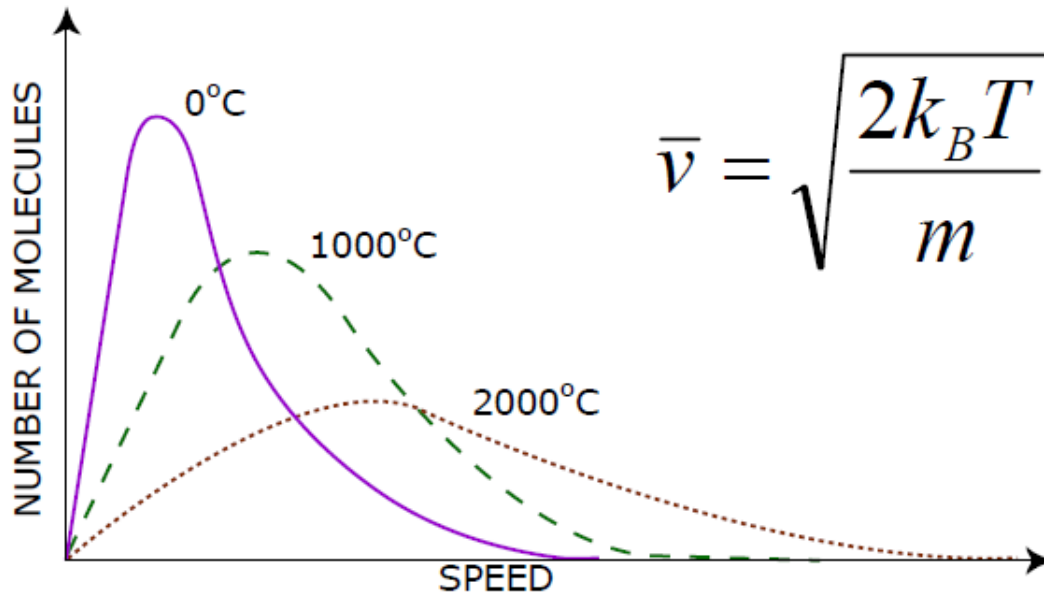
$$\bar{v} = \sqrt{\frac{2k_B T}{m}}, \quad v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

Integrate

- **Use an integrator**: Verlet, leapfrog Verlet, velocity Verlet, Gear predictor-corrector

- **Robust, long-term conservation** of the constant of motion, time-reversible, constant volume in phase space

- **Choose thermodynamic ensemble** (microcanonical NVE, or canonical NVT using a thermostat, isobaric-isothermic NPT with a barostat…)

Integrator: The Verlet algorithm

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 + (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

$$\mathbf{r}(t - \Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 - (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

Adding the two expressions gives

$$\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)$$

$$\mathbf{a}(t) = -(1/m)\nabla V(\mathbf{r}(t)) \qquad \mathbf{v}(t) = \frac{\mathbf{r}(t + \Delta t) - \mathbf{r}(t - \Delta t)}{2\Delta t}$$

$$\langle A \rangle \approx \frac{1}{N}\sum_{i=1}^{N} A(\vec{r}_n)$$

A Case Study of MD

Polymer interaction with a metal oxide surface

1. Cleave, relax Al2O3 surface, and then increase the surface area

2. Build an amorphous cell of *p*-nitro styrene polymer

3. Add the polymer to the surface

5. Optimize the layer system and run molecular dynamics

6. Calculate the interaction energy

Why *ab Initio* MD ?

- Chemical processes

- Poorly known interatomic interactions, *e.g*., at high Pressure and/or Temperature

- Properties depending explicitly on electronic states: IR spectra, Raman scattering, and NMR chemical shift

- Bonding properties of complex systems

Categories of *ab initio* MD

- **Born-Oppenheimer Molecular Dynamics**
  – move on a PES, the electronic structure calculation converges at each time point

- **Car-Parrinello Molecular Dynamics**
  – propagate the electronic structure *as well as* the nuclei using an extended *Lagrangian*

A General View of qMD

- Quantum Molecular Dynamics (qMD): any MD method that derives forces on nuclei from quantum-mechanical electrons.

- Using Hellman-Feynman forces on the ions (Born-Oppenheimer Molecular Dynamics)

- Most qMD methods were developed/implemented within the framework of DFT
  - Why? Electron correlation effects included, computational efficiency (relatively speaking)
  - All limitations (excited states, spin issues, hydrogen problem, van der Waals interaction, etc. etc.) of the ground-state DFT apply

- qMD simulations pioneered by Car and Parrinello in 1985 under the DFT framework are the most effective techniques to compute the dynamic properties of materials from electronic structure equations.

- Four important advances:
  - Optimization methods instead of variational equations
  - Equation of motion (instead of matrix diagonalization)
  - Fast Fourier Transform (FFT) instead of matrix operations
  - Trace of the occupied subspace instead of eigenvectors operations

- Car and Parrinello combined these features into a unified algorithm for electronic states, self-consistency and nuclear movement

Born-Oppenheimer MD

● Electronic quantum adiabatic evolution and classical ionic dynamics

Effective Hamiltonian :

$$\mathbf{H_I} = \mathbf{H_I^O}(\{\vec{R_I}, \dot{\vec{R_I}}\}) + \mathbf{F}(\{\vec{R_I}\})$$

$H^o_I \rightarrow$ includes ionic K.E. and ion-ion interaction

2nd term $\rightarrow$ Free energy of an inhomogeneous electron gas
in the fixed configuration of ions at positions ($\mathbf{R_I}$)

Electronic ground state – electron density $\rho(r)$ that minimizes
$F(\{\mathbf{R_I}\})_{min}$

Born-Oppenheimer Potential Energy Surface

$$U_{BO}\left(\{\vec{R_I}\}\right) = \min_{\rho(\vec{r})} E\left(\rho(\vec{r}), \{\vec{R_I}\}\right)$$

Born-Oppenheimer MD

Electronic density $\rho(r) = \sum_i f_i |\psi_i(\vec{r})|^2$; $f_i \rightarrow$ occupation number

$E_{eI} \rightarrow$ Electron-Ion coupling term includes local and nonlocal components

Kohn-Sham Hamiltonian operator

$$\frac{\delta E_{KS}}{\delta \psi_i^*(\mathbf{r})} = f_i H_{ks} \psi_i(\mathbf{r})$$
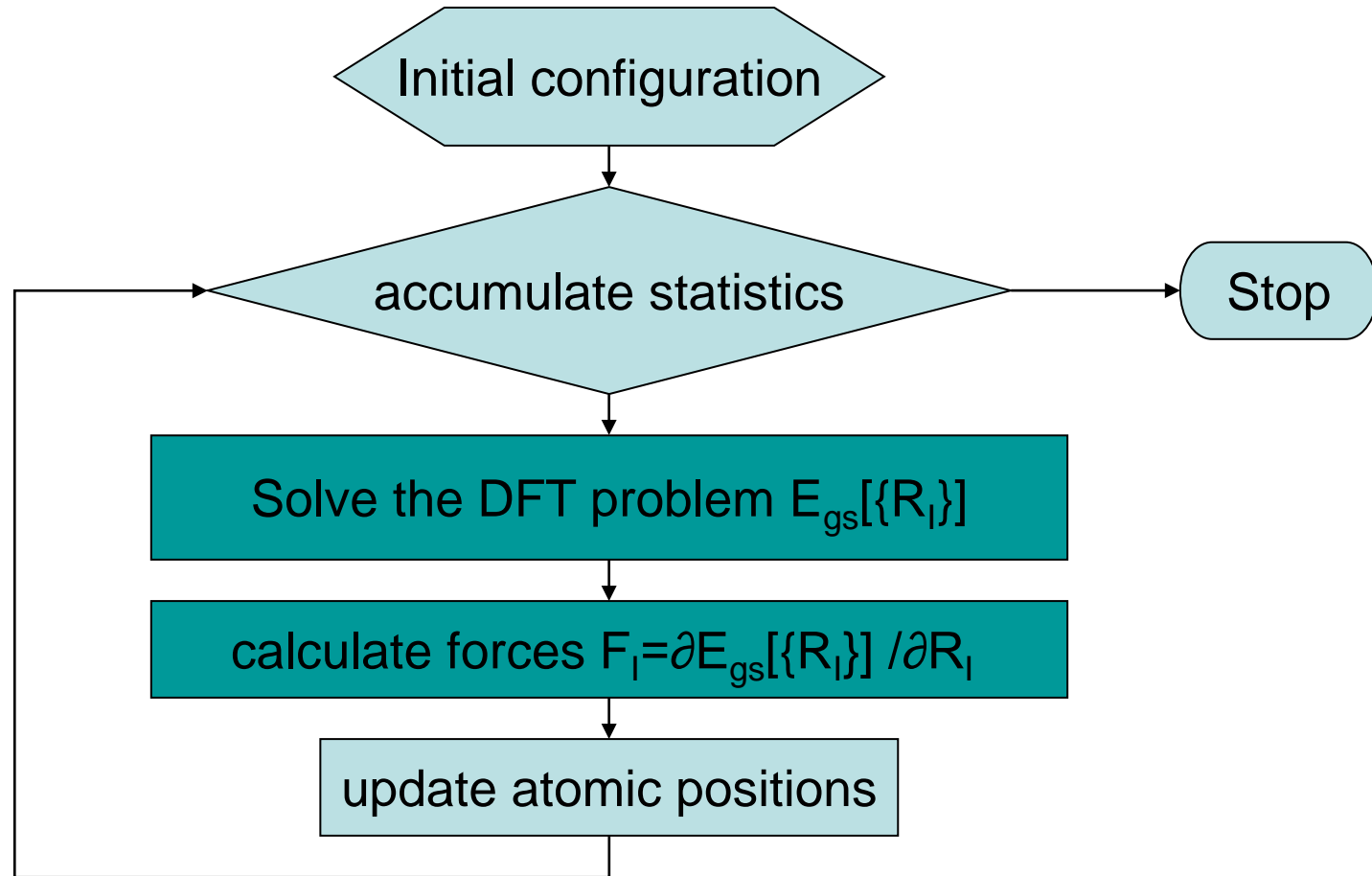
Time evolution of electronic variables

$$H_{ks}(t) \psi_i^{ks}(\mathbf{r}, t) = \varepsilon_i(t) \psi_i^{ks}(\mathbf{r}, t)$$

Time dependence of H_{ks} $\leftarrow$ slow ionic evolution govern by Newton's equations

$$M_I \ddot{\vec{R}}_I = \vec{F}_I = [\frac{\partial U_{ks}}{\partial R_I}]$$

U_{ks} = minimum of E_{ks} w.r.t. ψ_i

Born-Oppenheimer Molecular Dynamics

Initial configuration

accumulate statistics → Stop

Solve the DFT problem $E_{gs}[\{R_I\}]$

calculate forces $F_I = \partial E_{gs}[\{R_I\}] / \partial R_I$

update atomic positions

Pros & Cons of BOMD

Advantages

- True Electronic Adiabatic Evolution on the BO PES

Disadvantages

- Need to solve the self-consistent electronic-structure problem at each time step

- Minimization algorithms require ~ 10 iterations to converge to the BO forces

- Poorly converged electronic minimization → damping of the ionic motion

Computationally demanding procedure

Car-Parrinello MD

CP fictitious Lagrangian (for both ions and electrons)

$$L_{CP} = \mu \sum_i \int |\dot{\psi}_i(\mathbf{r})|^2 \, d\vec{r} + \frac{1}{2} \sum_I M_I \dot{\vec{R}}_I^2 - E_{ks}[\{\psi_i\}, \vec{R}_I]$$
$$+ \sum_{i,j} \Lambda_{ij} \left(\int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\vec{r} - \delta_{ij} \right)$$

- (fictitious) kinetic energy for the electrons

- Kinetic energy of the nuclei

- Potential energy of the electrons AND of the ions

- Final term ensures the orthonormality of the electronic wavefunctions

CP Equations of Motion

Equations of motion from L_{cp} :

$$\frac{d}{dt}\frac{\partial L_{cp}}{\partial \dot{q}_i} - \frac{\partial L_{cp}}{\partial q_i} = 0$$

$$\mu\ddot{\psi}_i(\mathbf{r},t) = -\frac{\delta E_{ks}}{\delta \psi_i^*(\mathbf{r})} + \sum_j \Lambda_{ij}\psi_j(\mathbf{r})$$

$$= -f_i H_{ks}\psi_i(\mathbf{r},t) + \sum_j \Lambda_{ij}\psi_j(\mathbf{r})$$

Electronic time evolution

$$M_I\ddot{R}_I = -\frac{\partial E_{ks}}{\partial R_I}\big|_\rho$$

Ionic time evolution

$$N_{ij}(t) = \int \psi_i^*(\mathbf{r},t)\psi_j(\mathbf{r},t)d\mathbf{r} = \delta_{ij}$$

Constraint equation

Car-Parrinello Molecular Dynamics

Initial configuration

Solve the DFT problem $E_{gs}[\{R_I\}, \{\psi_i\}]$

accumulate statistics → Stop

ionic forces $F_I = - \partial E_{tot}[\{R_I\}] / \partial R_I$

electronic forces $F_i = - \partial E_{tot}[\{R_I\}, \{\psi_i\}] / \partial \psi_i^*$

update atomic positions R_I

update wave functions ψ_i
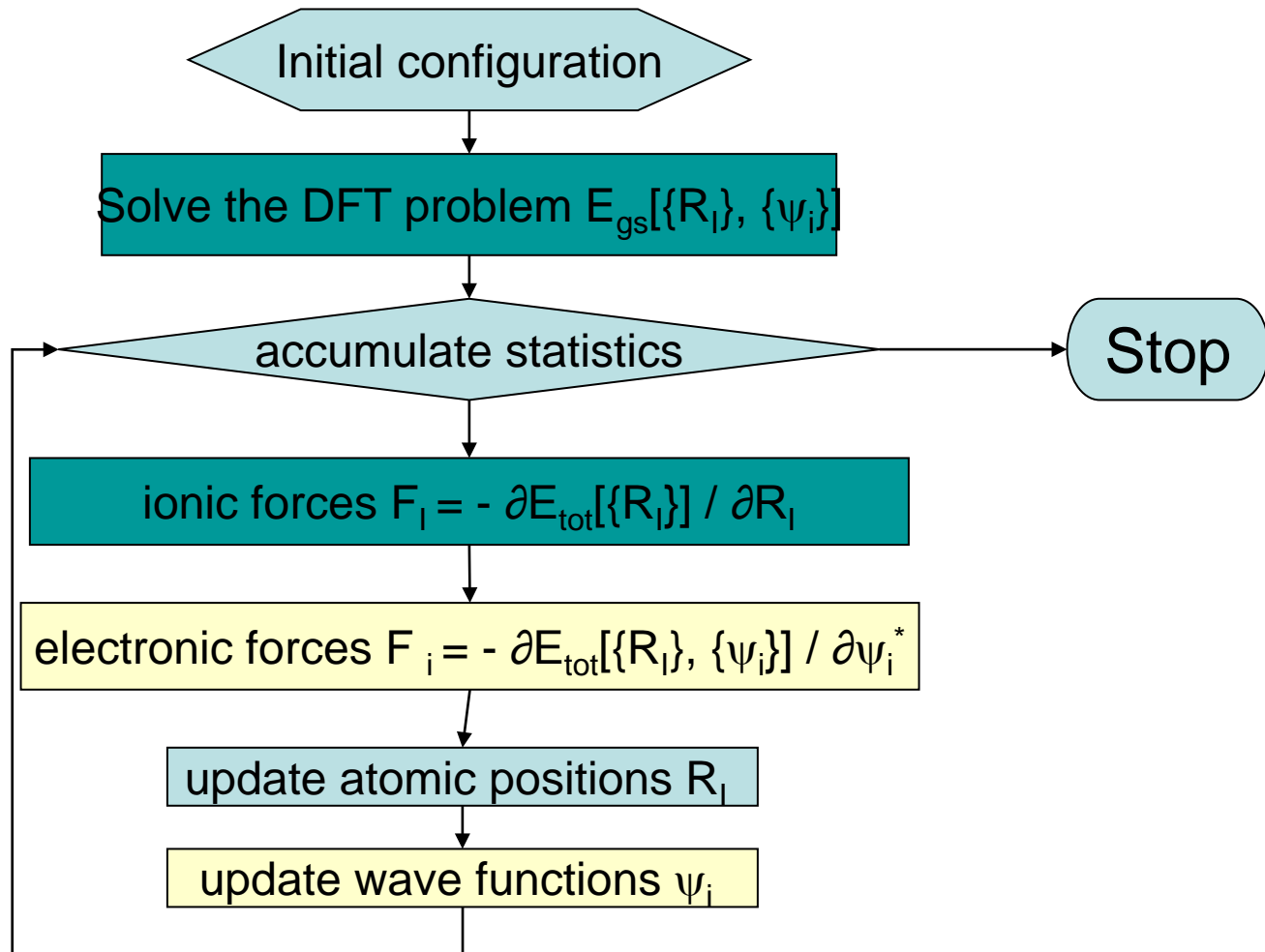
Dynamic Simulations

Quantum Dynamics
- Ab initio potential
- Both nuclear and electronic (and thus MANY) degrees of freedom
- Chemical reactions
- Few atoms
- Accessible length scale ~5 Å
- Accessible time scale ~ 10 fs

Ab initio **MD**
- On-the-fly potential
- Electronic degrees of freedom
- Formation and breaking of bonds
- ~100 atoms
- Accessible length scale ~ 20 Å
- Accessible time scale ~ 10 ps

Classical MD
- Hardwired potential
- No electronic degrees of freedom
- No chemical reaction
- ~100,000 atoms
- Accessible length scale ~100 Å
- Accessible time scale ~ 10 ns

Difficulties in the CP method

- The behavior of the fictitious Lagrangian has to be examined with great care. The method works well for system with an electronic energy gap.
  - Characteristics electronic oscillations are of the order of E_{gap}/μ. If these frequencies are much higher than the typical nuclear vibrational frequencies then the electrons will follow the nuclei adiabatically ➔ total energy of the physical system is conserved (does not include the fictitious kinetic energy of the electrons)
  - **Careful choice of the electrons' fictitious mass μ to ensure adiabaticity**, typically $\mu = 400 m_e$,
- Time step Δt must be short
  - Δt is determined by the fictitious electronic degrees of freedom: time step must be smaller than in typical simulations for nuclei alone, typically **0.05 fs**
  - Fictitious mass and time step are not completely decoupled and have to be carefully checked to ensure meaningful calculations
- Vanishing gaps and metallic systems are difficult to treat with the straightforward application of the CP method
  - energy transfer from ions to electrons
  - Need of thermostats to pump energy out of the fictitious system