

The method of ab initio molecular dynamics

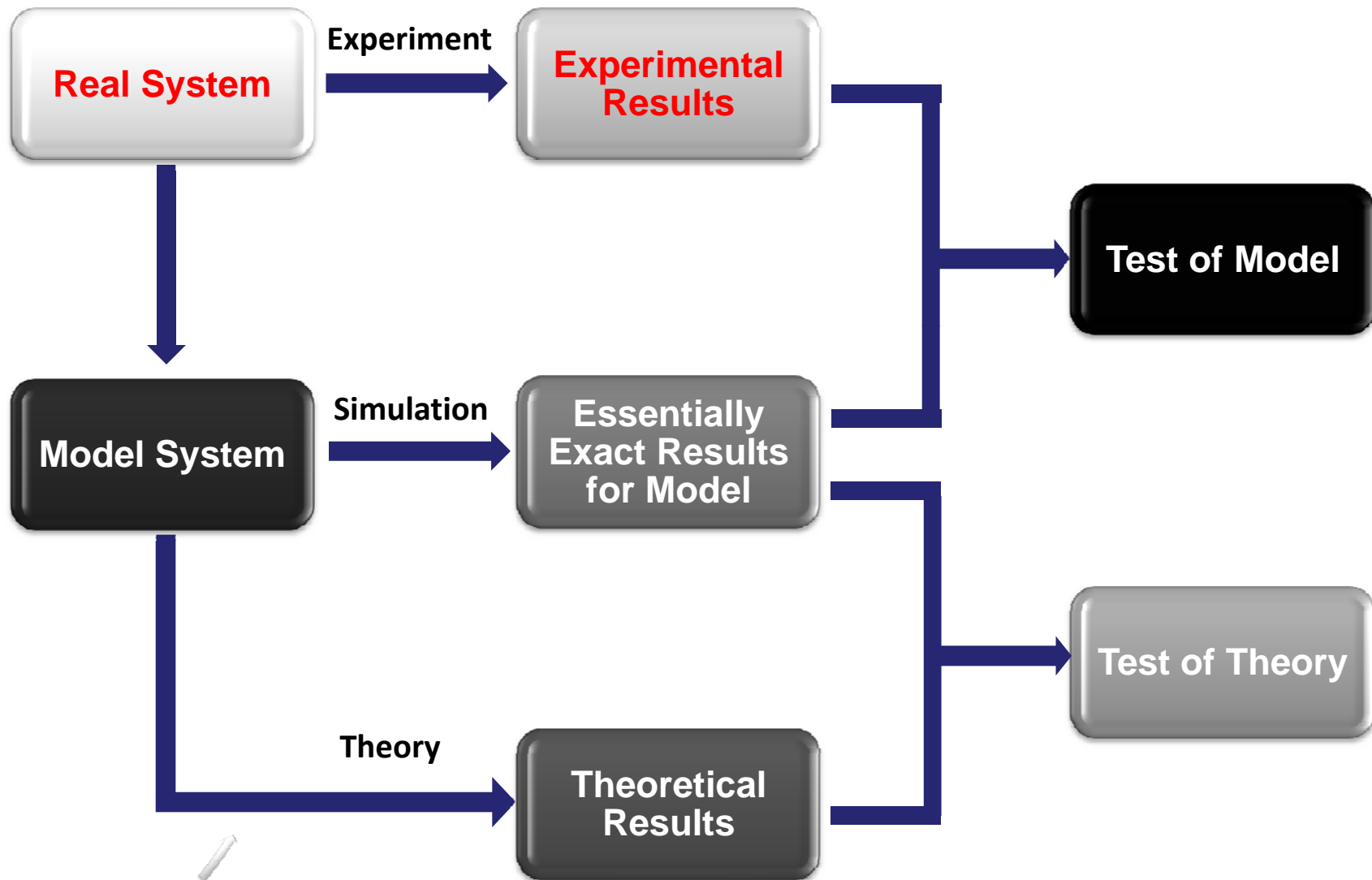
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Molecular Simulations:



Basic methods:

Molecular dynamics: Generate configurations from dynamical evolution of atoms

Monte Carlo: Generate configurations using random numbers

Molecular Dynamics

$$\begin{aligned}M_I \ddot{\mathbf{R}}(t) &= F_I(t) \\ &= -\nabla_I V(\{\mathbf{R}_I(t)\})\end{aligned}$$

➤ How do you get V?

Construct Global potential energy surface from QM calculations. If 10 points are used along each degree of freedom \rightarrow Total number of calculation would be $\sim 10^{3N}$!

Reduction of dimensionality

Write the full many-body potential in the following form

$$V(\{\mathbf{R}_I\}) = \sum_I^N v_1(\mathbf{R}_I) + \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K}^N v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \dots$$

The one-body term can be set to zero. Ignore v_3 and higher order terms.

$$V(\{\mathbf{R}_I\}) = \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J)$$

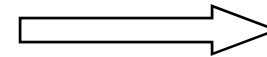
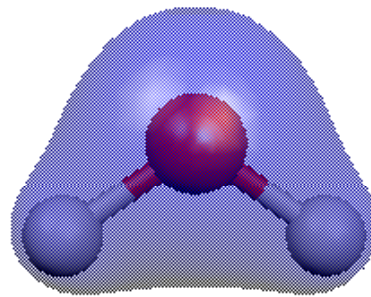
v_2 = Pair interaction potential. Find it from quantum electronic structure calculations.

For better results, $v_2 \rightleftarrows v_2^{\text{effective}}$...Empirical pair potential

Pair Potential Approach

- Solves dimensionality bottleneck problem in constructing the global potential energy surface.
- But
 1. Fails to describe processes where electronic degrees of freedom play active roles.
 2. Same pair potential is used in all thermodynamic conditions (usually not accurate)
 3. Cooperative or many-body effects can be important
- Systems where these are **not** issues \implies Use empirical pair potentials (MM) \implies **Classical simulations**

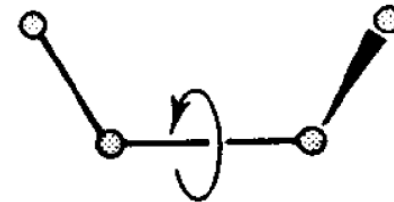
Empirical Force
Fields



- **Ignores electronic degrees of freedom**
- **Calculates energy as a function of nuclear positions only**
- Many of the molecular force fields in use today can be interpreted in terms of a relatively simple five-component picture of the intra and inter-molecular interactions.

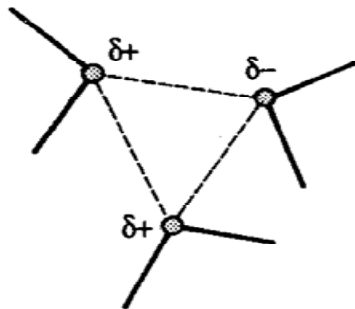
$$V(\mathbf{r}^N) =$$

Bond stretching + Bond bending + Bond rotation (torsion)

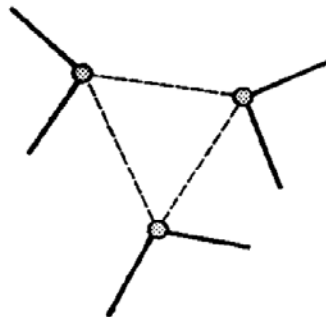


+ Non-bonded interactions

Electrostatic



van der Waals



Ref. A. R. Leach, *Molecular Modelling*, Addison Wesley Longman (1998)

Ab initio Molecular Simulations

- Empirical pair potentials
 1. Fail to describe processes where electronic degrees of freedom play active roles.
 2. Same pair potentials are used in all thermodynamic conditions (usually not accurate)
 3. Cooperative or many-body effects can be important
- Systems where these are significant issues, calculate the full-many-body potential from quantum mechanical calculation by considering the system at the level of electrons, protons, neutrons (QM).

⇒ Ab initio simulations ⇒ 10^5 times more expensive computationally

Structure of current lecture

QM (dynamical perspective)

- Molecular dynamics under quantum many body potential
 - Ehrenfest molecular dynamics
 - Born-Oppenheimer molecular dynamics
 - Car-Parrinello molecular dynamics
- Quantum many-body potential is obtained from quantum electronic structure calculations

References

- D. Marx and J. Hutter, *Ab Initio Molecular Dynamics: Theory and Implementation*, Cambridge University Press (2009)
- A. Messiah, *Quantum Mechanics*, Vol. I, John Wiley & Sons

Unifying QM with molecular dynamics

Say, \mathbf{R}_I = nuclear coordinates
 \mathbf{r}_i = electronic coordinate

Ref. D. Marx and J. Hutter, *Ab Initio Molecular Dynamics*, Cambridge Univ Press, 2009.

The Hamiltonian Operator,

$$\begin{aligned} H &= - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I < J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\ &= - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \end{aligned}$$

Dynamical evolution of the system given by time dependent Schrödinger equation (TDSE)

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = H \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$$

Goal:

- To carry out classical dynamics of nuclei in **QM potential**
 - > Separate nuclear and electronic contributions to the total wave function $\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$.

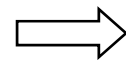
The simplest possible form is a product ansatz

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \Psi(\mathbf{r}_i, t)\chi(\mathbf{R}_I, t)$$

Then ,

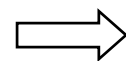
$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}_i, t)\chi(\mathbf{R}_I, t) = \left[- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e} \right] \Psi(\mathbf{r}_i, t)\chi(\mathbf{R}_I, t)$$

Multiply by $\psi(\{\mathbf{r}_i\}, t)$ and
integrate over $\{\mathbf{r}_i\}$



Equation of motion for
 $\chi(\{\mathbf{R}_I\}, t)$

Multiply by $\chi(\{\mathbf{R}_I\}, t)$ and
integrate over $\{\mathbf{R}_I\}$



Equation of motion for
 $\psi(\{\mathbf{r}_i\}, t)$

Time dependent self-consistent field equations (TDSCF)

$$i\hbar \frac{\partial \chi}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi + \left\{ \int d\mathbf{r} \Psi^* H_e \Psi \right\} \chi$$

$$H_e = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}$$

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + \left\{ \int d\mathbf{R} \chi^* \left(- \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + V_{n-e} \right) \chi \right\} \Psi(\mathbf{r}_i, t)$$

- Both electrons and nuclei move quantum mechanically in time-dependent effective potentials which are obtained self-consistently.
- The simple product ansatz produces mean field description of the coupled nuclear and electronic dynamics.

Classical dynamics of nuclei and quantum dynamics of electrons

- Task of approximating the nuclei as classical point particles. How? See Messiah, Vol I , Chapter-6

- Rewrite the nuclear wave function in the form

$\chi = A(\mathbf{R}_I, t)e^{\frac{iS(\mathbf{R}_I, t)}{\hbar}}$ in terms of an amplitude factor A and a phase S which are both considered to be real.

- Next Step: Use the above form in TDSCF equations and separate the real and imaginary parts.

Time evolution of nuclear state in terms of S and A

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \int d\mathbf{r} \Psi^* H_e \Psi = \hbar^2 \sum_I \frac{1}{2M_I} \frac{\nabla_I^2 A}{A}$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I} (\nabla_I A) (\nabla_I S) + \sum_I \frac{1}{2M_I} A (\nabla_I^2 S) = 0$$

Note: Nuclear density $P(\mathbf{r}) = \chi^* \chi = A^2$

On multiplication by $2A > \frac{\partial}{\partial t} A^2 + \nabla \sum_I \frac{1}{M_I} A^2 \nabla S = 0$

Which can be written as $\frac{\partial}{\partial t} P + \sum_I \nabla J_I = 0$

Where $J_I = P \mathbf{v}_I$ and $\mathbf{v}_I = \frac{\nabla S}{M_I}$

- Take classical limit of equation of S

$$\frac{\partial S}{\partial t} + \sum_I \frac{M_I}{2} \mathbf{v}_I^2 + \int d\mathbf{r} \Psi^* H_e \Psi = 0$$

- Take gradient

$$\frac{\partial}{\partial t} \nabla S + \nabla \sum_I \frac{M_I}{2} \mathbf{v}_I^2 + \nabla \int d\mathbf{r} \Psi^* H_e \Psi = 0$$

$$M_I \frac{d\mathbf{v}_I}{dt} = -\nabla \int d\mathbf{r} \Psi^* H_e \Psi = -\nabla V$$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \int d\mathbf{r} \Psi^* H_e \Psi$$

- **What about $\psi(\{ r_i \}, t)$?**

Its TDSCF equation still contains the nuclear wave function $X(\{ R_I \}, t)$!

Calculation of electronic wave function for classical nuclei

- Classical limit:

$$|\chi(\mathbf{R}_I, t)|^2 = \prod \delta(\mathbf{R} - \mathbf{R}_I(t))$$

$$\int d\mathbf{R} \chi^* \mathbf{R}_I \chi \rightarrow \mathbf{R}_I(t)$$

- TDSCF equation for $\psi(\{\mathbf{r}_i\}, t)$ then becomes

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \Psi \\ &= \mathcal{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \end{aligned}$$

- Electrons evolve self-consistently as the classical nuclei are propagated. The above approach of solving Newton equation for nuclei and simultaneously time dependent Schrödinger equation for electrons is called *Ehrenfest molecular dynamics*.

Ehrenfest Molecular Dynamics

1. The electronic Hamiltonian H_e depends parametrically on the classical nuclear positions $\{ R_I \}$ at time t .
2. The feedback between the classical and quantum degrees of freedom is incorporated in both directions although in a mean field sense.
3. Its a hybrid or mixed quantum-classical approach because only the nuclei are taken as classical particles whereas the electrons are treated quantum mechanically (QM).
4. Like real time classical evolution of nuclei, electronic subsystem also evolves in real time according to time dependent Schrödinger equation.

Born - Oppenheimer Molecular Dynamics

- We restrict the wave function ψ to be the ground state adiabatic wave function ψ_0 of H_e at each instant of time according to

$$H_e \psi_0 = E_0 \psi_0, \quad E_0 \equiv E_0(\{R_I\})$$

$$M_I \ddot{R}_I(t) = -\nabla_I \min_{\psi_0} \langle \psi_0 | H_e | \psi_0 \rangle$$

- The nuclei move on the ground state Born-Oppenheimer potential energy surface. This is called the *Born-Oppenheimer molecular dynamics (BOMD)*.
- This should be a good approximation if the energy difference between ψ_0 and first excited state ψ_1 is large everywhere compared to the thermal energy $k_B T$.

Born - Oppenheimer Molecular Dynamics

1. $E_0(\{R_I\})$ or the ground state Born – Oppenheimer potential energy surface is obtained by solving the time independent electronic Schrödinger equation.
2. The task of solving nuclear motion can be decoupled from the task of computing quantum potential energies through electronic structure calculations.
3. Intrinsic time dependence of ψ is ignored. It is assumed that electrons follow adiabatically the classical nuclear motion.
4. The time dependence of the electronic structure is dictated by its parametric dependence on the classical dynamics of the nuclei which it just follows.

Born - Oppenheimer Molecular Dynamics

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{ \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle \}$$

$$\mathcal{H}_e \Psi_0 = E_0 \Psi_0$$

Let us focus on the electronic part for effective one-particle Hamiltonians, e.g. Hartree–Fock, Kohn-Sham

Say, Φ_i = one-electron wave function

$$\psi_0 = \frac{1}{\sqrt{N!}} \det \{ \phi_i \}$$

Variational minimization of $\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$ subject to the constraint that one-particle wave functions are orthonormal leads to HF theory. The above constrained minimization can be cast into Lagrange's formalism

$$\mathcal{L} = -\langle \psi_0 | H_e | \psi_0 \rangle + \sum_{i,j} \Lambda_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

Where, Λ_{ij} are the associated Lagrange multipliers that are necessary to take care of the constraints.

Effective one-electron equations

Unconstrained variation of the Lagrangian \mathcal{L} with respect to the orbitals with

$\frac{\delta \mathcal{L}}{\delta \phi_i} = 0$ leads to the well known **Hartree Fock (HF)** equation –

$$H_e^{HF} \phi_i = \sum_j \Lambda_{ij} \phi_j$$

On unitary transformation, $H_e^{HF} \phi_i = \varepsilon_i \phi_i$

Where, $H_e^{HF} = H_1 + \sum_j (2J_j - K_j)$, $H_1 = -\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|R_I - r|}$

A similar equation is obtained if **Kohn-Sham** density functional theory is used: $H_e^{KS} \phi_i = \sum_j \Lambda_{ij} \phi_j$

Where, $H_e^{KS} = -\frac{1}{2} \nabla^2 + V(r) + \int \frac{\rho(r')}{|r - r'|} dr' + V_{xc}[\rho]$

Relook at Ehrenfest and Born Oppenheimer Molecular Dynamics

Ehrenfest MD

1. Time step for integration is dictated by the intrinsic dynamics of the electrons. Since electrons move much faster than nuclei, the largest possible time step is that which allows us to integrate the electronic equation of motion properly.
2. The electronic wave function is propagated by applying the Hamiltonian to an initial wave function.

BOMD

1. The electronic problem is treated within the time independent Schrödinger equation. No electron dynamics whatsoever. This means the equations of motion can be integrated on the time scale of nuclear motion, i.e. by using a larger time step.
2. Electronic structure problem has to be solved self-consistently at each molecular dynamics step.

Best things:

- i. Use large time steps.
- ii. Avoid solving electronic structure problem at every time.

} Car – Parrinello molecular dynamics

Car-Parrinello Molecular Dynamics

- The Car-Parrinello approach takes direct advantages of the quantum mechanical adiabatic time scale separation of fast electronic (quantum) and slow nuclear (classical) motion.
- The two-component quantum-classical system is mapped into a two-component purely classical problem with two separate energy scales at the expenses of losing the intrinsic time dependence of the electronic sub-systems.
- The central quantity $\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$ is a function of $\{ R_I \}$. It is also considered to be a functional of $\{ \phi_i \}$, where $\psi_0 = \frac{1}{\sqrt{N!}} \det\{\phi_i\}$
- In classical mechanics, the forces on the nuclei are obtained by taking the derivative of Lagrangian with respect to nuclear coordinates.
- Given suitable Lagrangian, the functional derivative with respect to orbitals, which are interpreted as classical fields, yield forces on the orbitals.

Car – Parrinello Lagrangian

$$\mathcal{L}^{CP} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2}_{\text{kinetic energy}} + \underbrace{\sum_i \mu_i \langle \dot{\psi}_i | \dot{\psi}_i \rangle - \langle \Psi_0 | H_e | \Psi_0 \rangle}_{\text{potential energy}} + \underbrace{\sum_{i,j} \Lambda_{ij} (\langle \psi_i | \psi_i \rangle - \delta_{ij})}_{\text{constraints}}$$

where, and μ is the fictitious mass.

The corresponding classical equations of motion are given by

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad ; \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\psi}_i^*} = \frac{\partial \mathcal{L}}{\partial \psi_i^*}$$

$$\text{Nuclear Motion : } M_I \ddot{\mathbf{R}}_I = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi | H_e | \Psi \rangle$$

Orbital Motion

$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^*} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^*} \{constraints\}$$

$$\mu_i \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^*} \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle + \sum_j \Lambda_{ij} \psi_j$$

For the case of Kohn–Sham DFT , the above equations read:

$$M_I \ddot{R}_I(t) = -\nabla \langle \psi_0 | H_e^{KS} | \psi_0 \rangle$$

$$\mu \ddot{\phi}(t) = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j$$

Which are known as *Car-Parrinello equations of motion*.

R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471(1985)

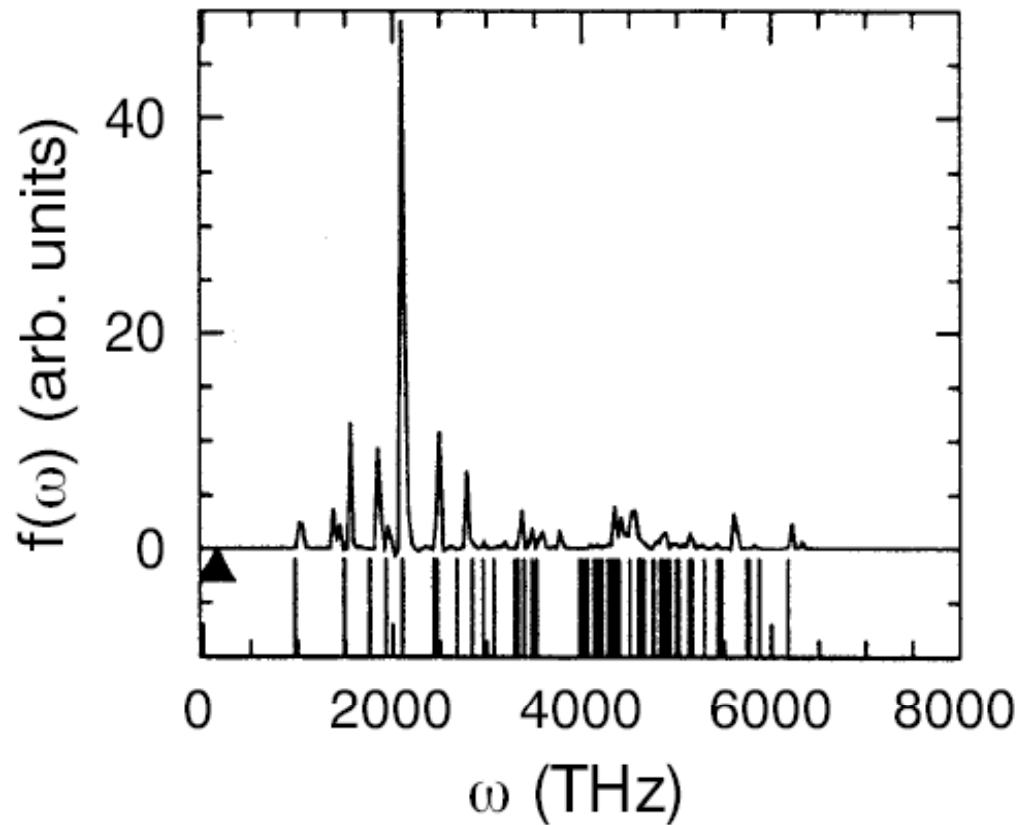
Car-Parrinello molecular dynamics

- The nuclei move in time at a physical temperature $\propto \sum_I M_I \dot{R}_I^2$
- We can assign a fictitious temperature $\propto \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle$ to the orbitals, i.e. to the electronic degrees of freedom.
- When electrons are ‘cold’, $\sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle$ is very small.
So that, $\mu \ddot{\phi}_i \sim 0 \implies 0 = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j$
which is the KS equation for electronic orbitals.
- For low electronic fictitious temperature, the electronic subsystem remains close to the exact BO surface.
- A ground state wave function optimized for the initial configuration will stay close to its ground state during time evolution as long as it is kept at low fictitious temperature.

Running Car-Parrinello molecular dynamics

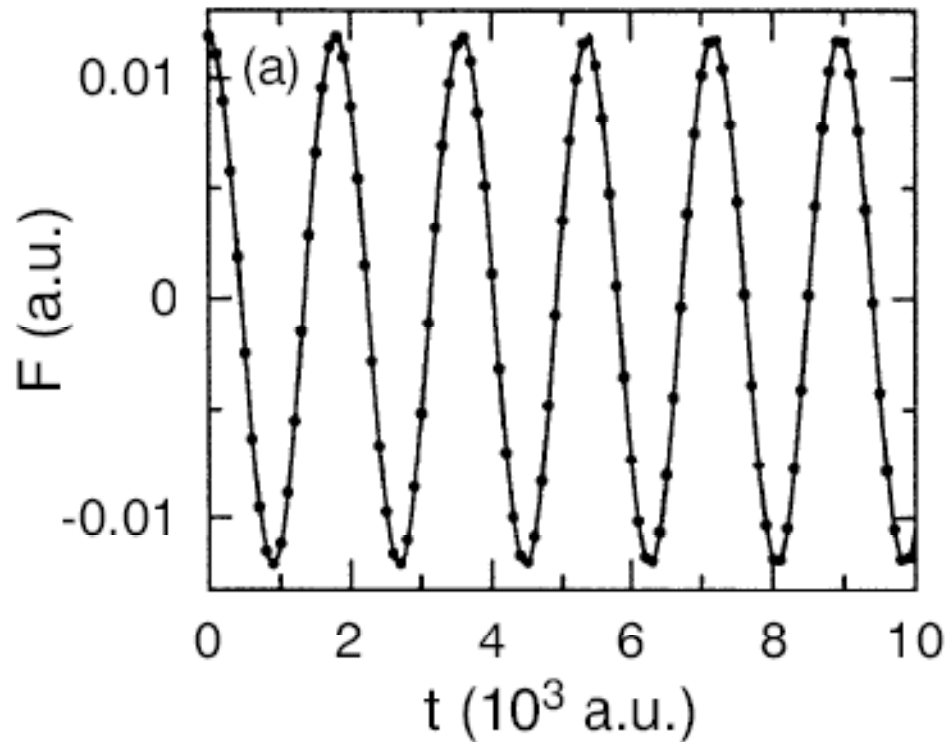
- The main task is to separate in practice the nuclear and electronic motion such that the fast electronic subsystem stays cold also for long times but still follows the slow nuclear motion adiabatically.
- The nuclei must themselves be kept at a much higher temperature.
- This can be achieved via decoupling of the two subsystems. Decoupling is possible if the power spectra of both subsystems do not have substantial overlap of their vibrational density of states . This would prevent energy leakage from hot nuclei to cold electrons.
- The above requirements can be achieved by proper choice of parameters such as fictitious mass, time step etc.

An example of vibrational density of states from CPMD simulation – Silicon atom on a periodic lattice



[D. Marx and J. Hutter, *Ab Initio Molecular Dynamics: Theory and Implementation*, Cambridge University Press (2009)]

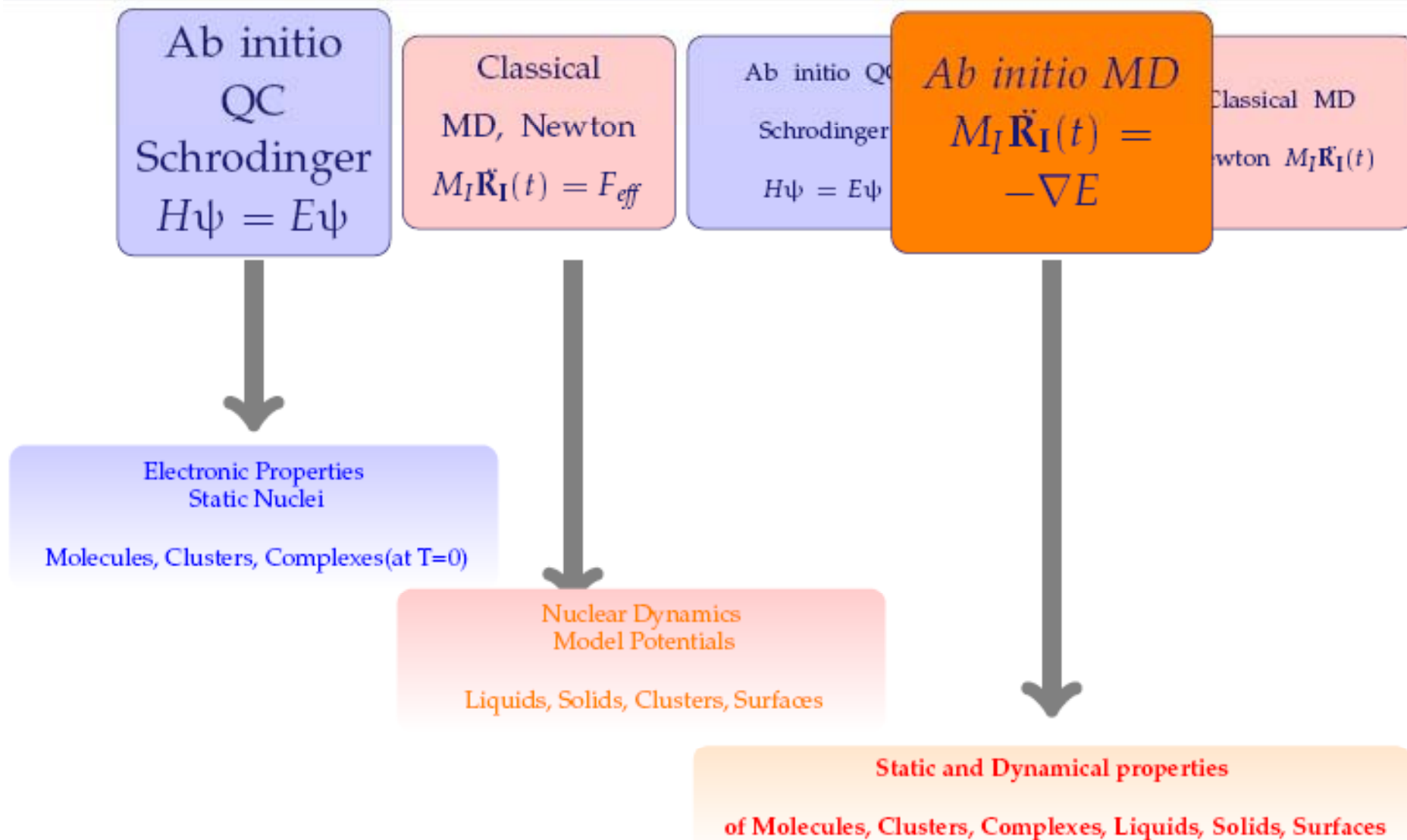
Comparison of Forces Obtained from Car-Parrinello and Born-Oppenheimer Molecular Dynamics



[D. Marx and J. Hutter, *Ab Initio Molecular Dynamics: Theory and Implementation*, Cambridge University Press (2009)]

Summary

Comparison of Methods



Summary

(QM) Dynamical Simulation Methods:

- **Born-Oppenheimer molecular dynamics:**

$$M_I \ddot{R}_I(t) = -\nabla_I \min_{\{\Psi_i\}} \langle \Psi_0 | H_e | \Psi_0 \rangle$$

$$0 = -H_e \phi_i + \sum_j \Lambda_{ij} \phi_j ; \Psi_0 = \det \{ \phi_i \}$$

- **Ehrenfest Molecular Dynamics :**

$$M_I \ddot{R}_I(t) = -\nabla_I \langle \Psi | H_e | \Psi \rangle$$

$$i\hbar \dot{\Psi}(t) = H_e \Psi$$

- **Car- Parrinello Molecular Dynamics**

$$M_I \ddot{R}_I(t) = -\nabla_I \langle \Psi_0 | H_e | \Psi_0 \rangle$$

$$\mu_i \ddot{\phi}_i(t) = -H_e \phi_i + \sum_j \Lambda_{ij} \phi_j ; \Psi_0 = \det \{ \phi_i \}$$