Ab Initio Molecular Dynamcis

MolSim2018

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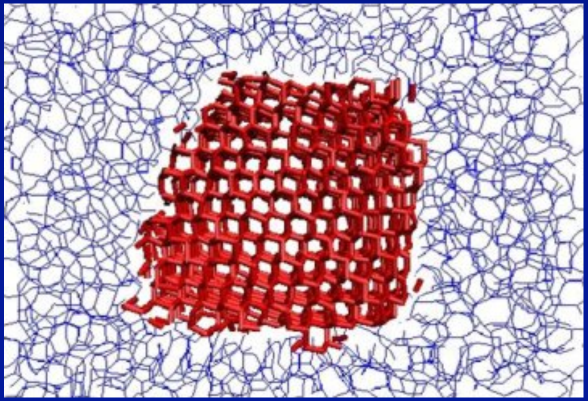
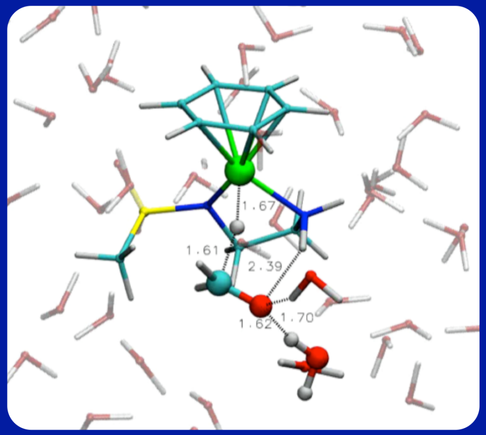




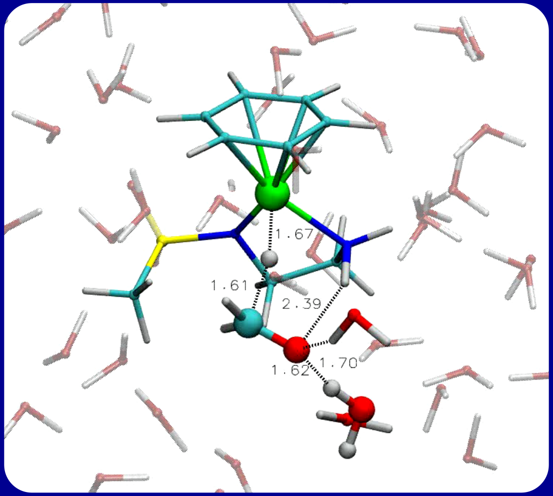
Example: Chemical Processes in Complex Environment

Key Notions

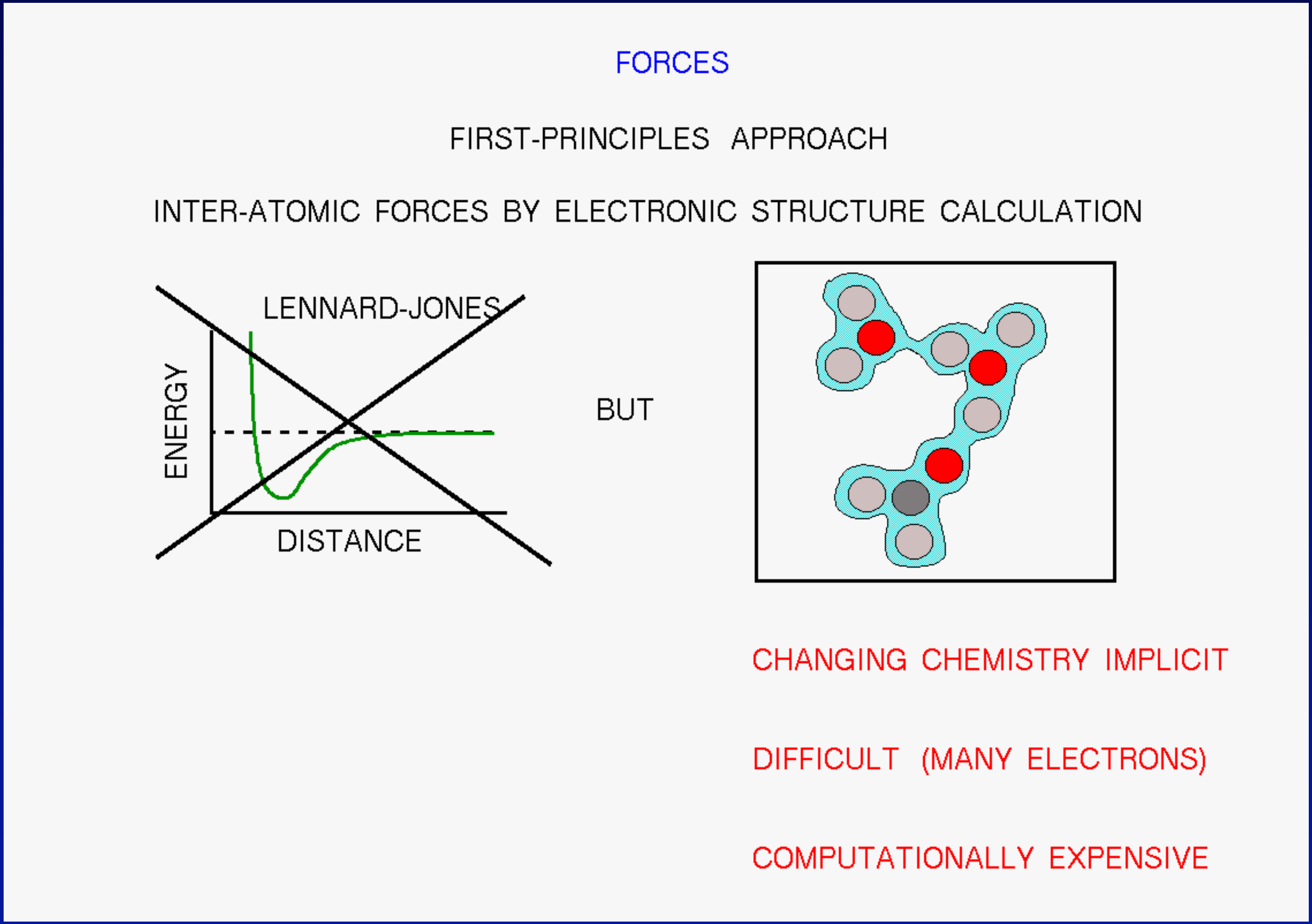
Chemical Transformations <-> Electronic Structure

Temperature <-> Motion & Fluctuations

Condensed Phase <-> Statistical Mechanics Methods



CONTEXT



FORCES

FIRST-PRINCIPLES APPROACH

INTER-ATOMIC FORCES BY ELECTRONIC STRUCTURE CALCULATION

BUT

CHANGING CHEMISTRY IMPLICIT

DIFFICULT (MANY ELECTRONS)

COMPUTATIONALLY EXPENSIVE

METHODS

DFT-Based Molecular Dynamics

ATOMIC NUCLEI + ELECTRONS

Electrons $\xrightarrow[H\psi = E\psi]{}$ Atomic Forces $\xrightarrow[F = m \times a]{}$ Atomic Motion

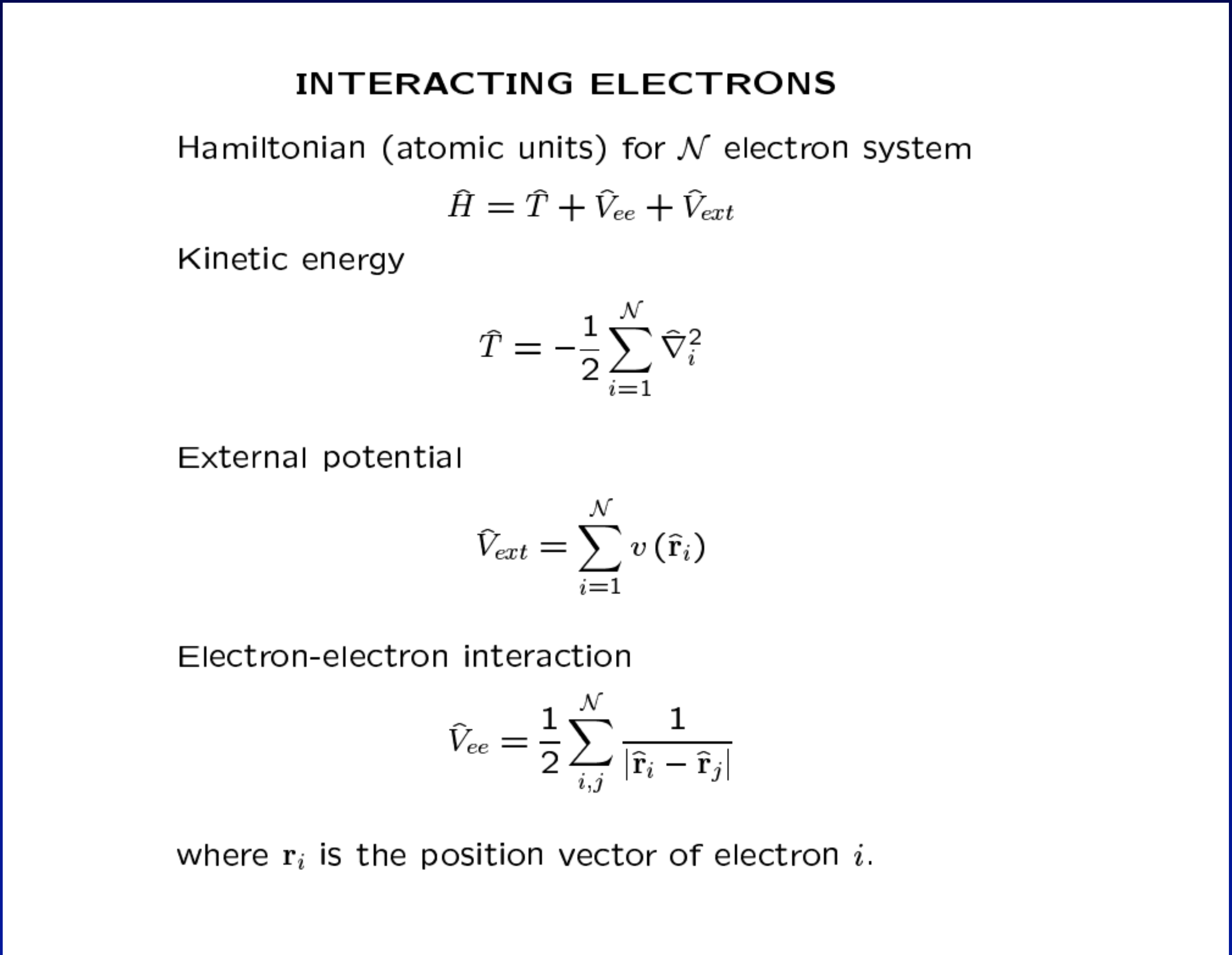
QUANTUM MECHANICS

Density Functional Theory

NEWTON'S EQN

Molecular Dynamics

Density Functional Theory



INTERACTING ELECTRONS

Hamiltonian (atomic units) for $\mathcal{N}$ electron system

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

Kinetic energy

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{\mathcal{N}} \hat{\nabla}_i^2$$

External potential

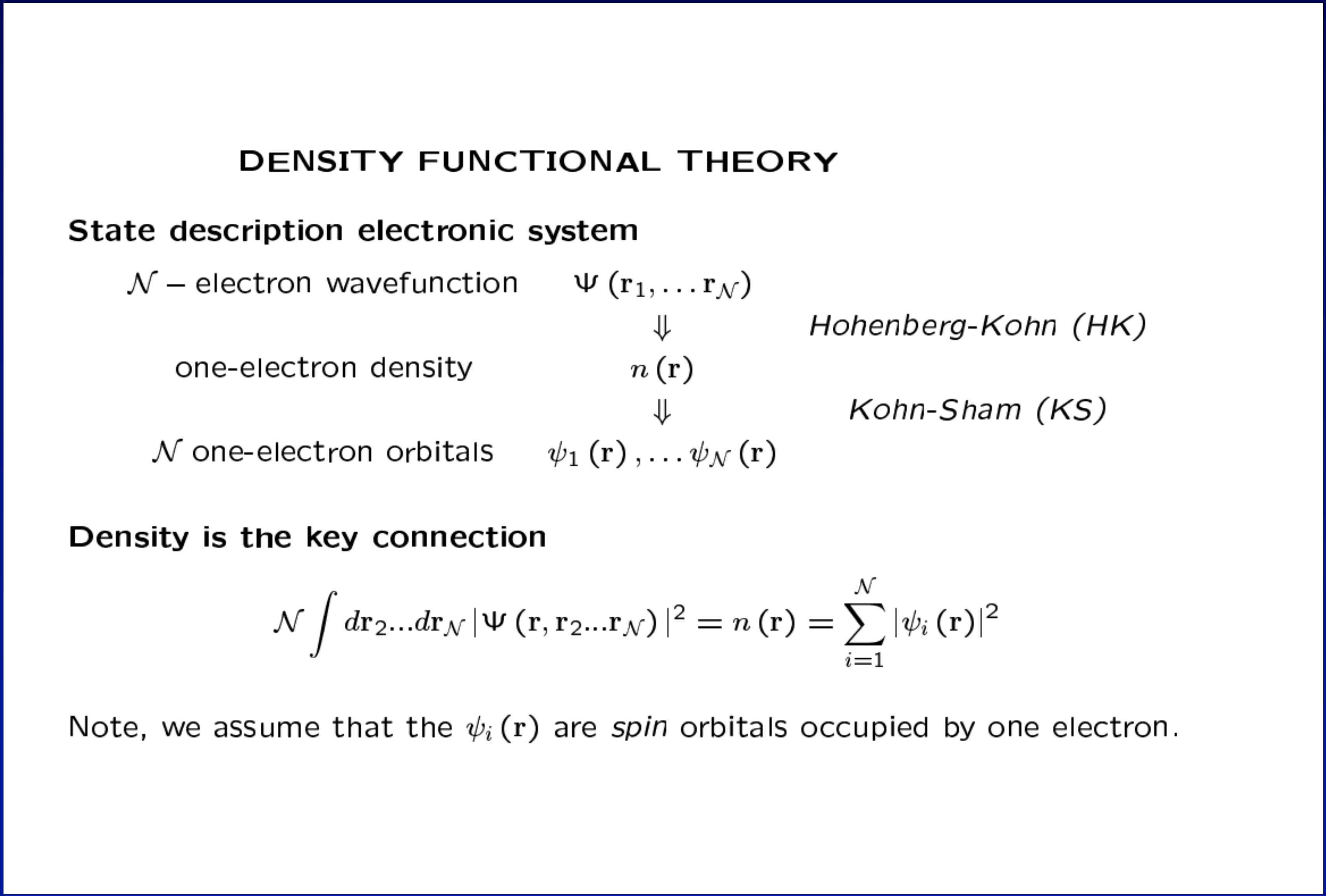
$$\hat{V}_{ext} = \sum_{i=1}^{\mathcal{N}} v\left(\hat{\mathbf{r}}_i\right)$$

Electron-electron interaction

$$\hat{V}_{ee} = \frac{1}{2}\sum_{i,j}^{\mathcal{N}} \frac{1}{\left|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j\right|}$$

where $\mathbf{r}_i$ is the position vector of electron i.

Density Functional Theory



DENSITY FUNCTIONAL THEORY

State description electronic system

$\mathcal{N}$ – electron wavefunction $\Psi\left(\mathbf{r}_1, \ldots \mathbf{r}_{\mathcal{N}}\right)$

$\Downarrow$ *Hohenberg-Kohn (HK)*

one-electron density $n\left(\mathbf{r}\right)$

$\Downarrow$ *Kohn-Sham (KS)*

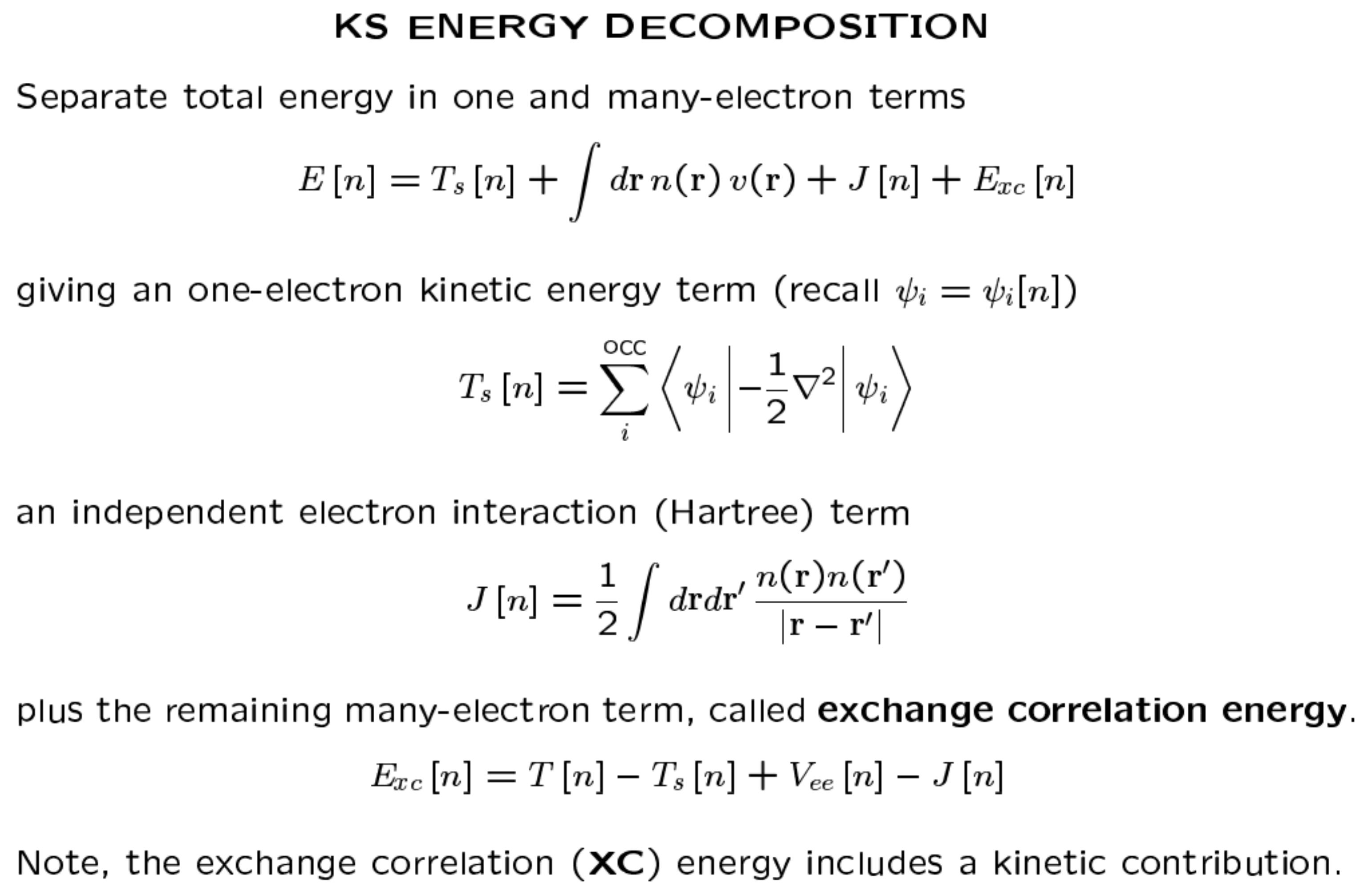
$\mathcal{N}$ one-electron orbitals $\psi_1\left(\mathbf{r}\right), \ldots \psi_{\mathcal{N}}\left(\mathbf{r}\right)$

Density is the key connection

$$\mathcal{N} \int d\mathbf{r}_2 \ldots d\mathbf{r}_{\mathcal{N}} \left|\Psi\left(\mathbf{r}, \mathbf{r}_2 \ldots \mathbf{r}_{\mathcal{N}}\right)\right|^2 = n\left(\mathbf{r}\right) = \sum_{i=1}^{\mathcal{N}} \left|\psi_i\left(\mathbf{r}\right)\right|^2$$

Note, we assume that the $\psi_i\left(\mathbf{r}\right)$ are *spin* orbitals occupied by one electron.

Density Functional Theory



KS ENERGY DECOMPOSITION

Separate total energy in one and many-electron terms

$$E\,[n] = T_s\,[n] + \int d\mathbf{r}\, n(\mathbf{r})\, v(\mathbf{r}) + J\,[n] + E_{xc}\,[n]$$

giving an one-electron kinetic energy term (recall $\psi_i = \psi_i[n]$)

$$T_s\,[n] = \sum_i^{\text{occ}} \left\langle \psi_i \middle| -\frac{1}{2}\nabla^2 \middle| \psi_i \right\rangle$$

an independent electron interaction (Hartree) term

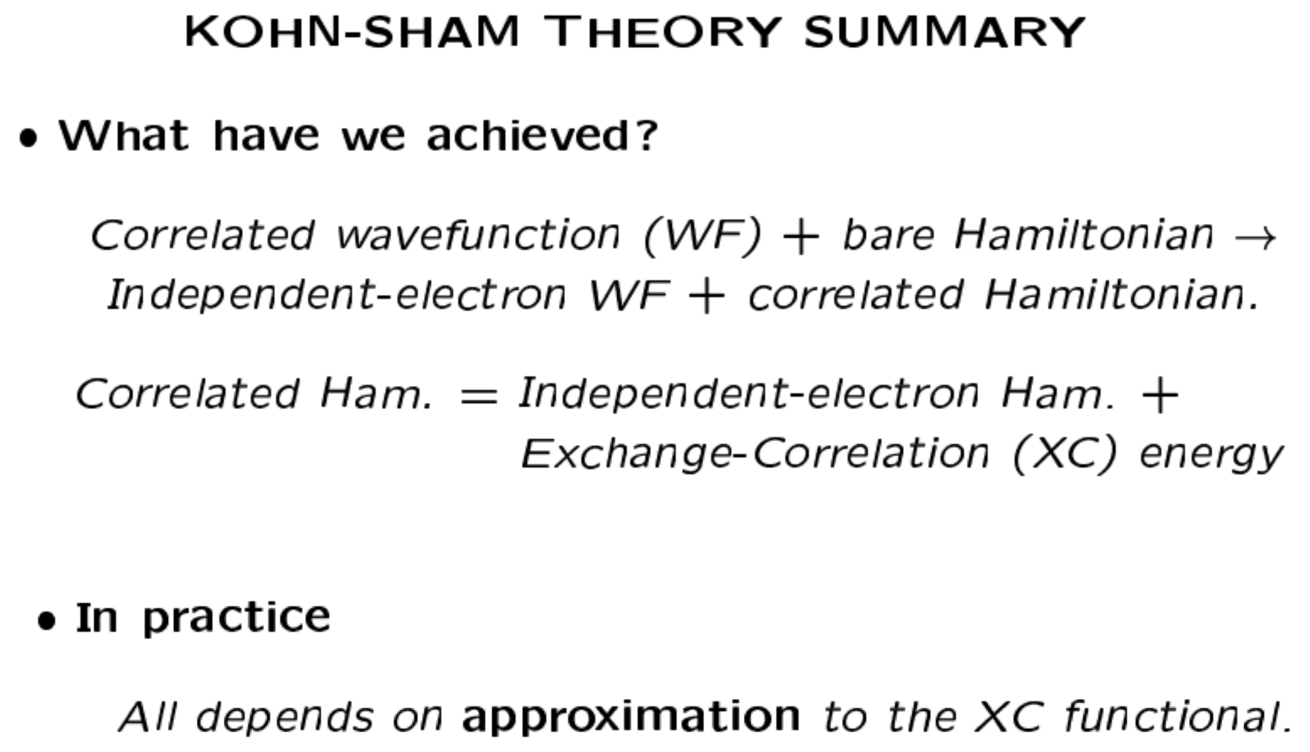
$$J\,[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

plus the remaining many-electron term, called **exchange correlation energy**.

$$E_{xc}\,[n] = T\,[n] - T_s\,[n] + V_{ee}\,[n] - J\,[n]$$

Note, the exchange correlation (**XC**) energy includes a kinetic contribution.

Density Functional Theory



KOHN-SHAM THEORY SUMMARY

- **What have we achieved?**

  Correlated wavefunction (WF) + bare Hamiltonian →
  Independent-electron WF + correlated Hamiltonian.

  Correlated Ham. = Independent-electron Ham. +
  Exchange-Correlation (XC) energy

- **In practice**

  All depends on **approximation** *to the XC functional.*

Density Functional Theory

LOCAL DENSITY APPROXIMATION (LDA)

Approximate XC energy by the integral over a **local XC energy density**

$$E_{xc}^{\mathrm{LDA}}[n] = \int d\mathbf{r}\, F_{xc}(n(\mathbf{r})) = \int d\mathbf{r}\, \epsilon_{xc}(n(\mathbf{r}))\, n(\mathbf{r})$$

$\epsilon_{xc}(n) =$ The exchange correlation energy per electron of the **homogeneous electron gas** at density n

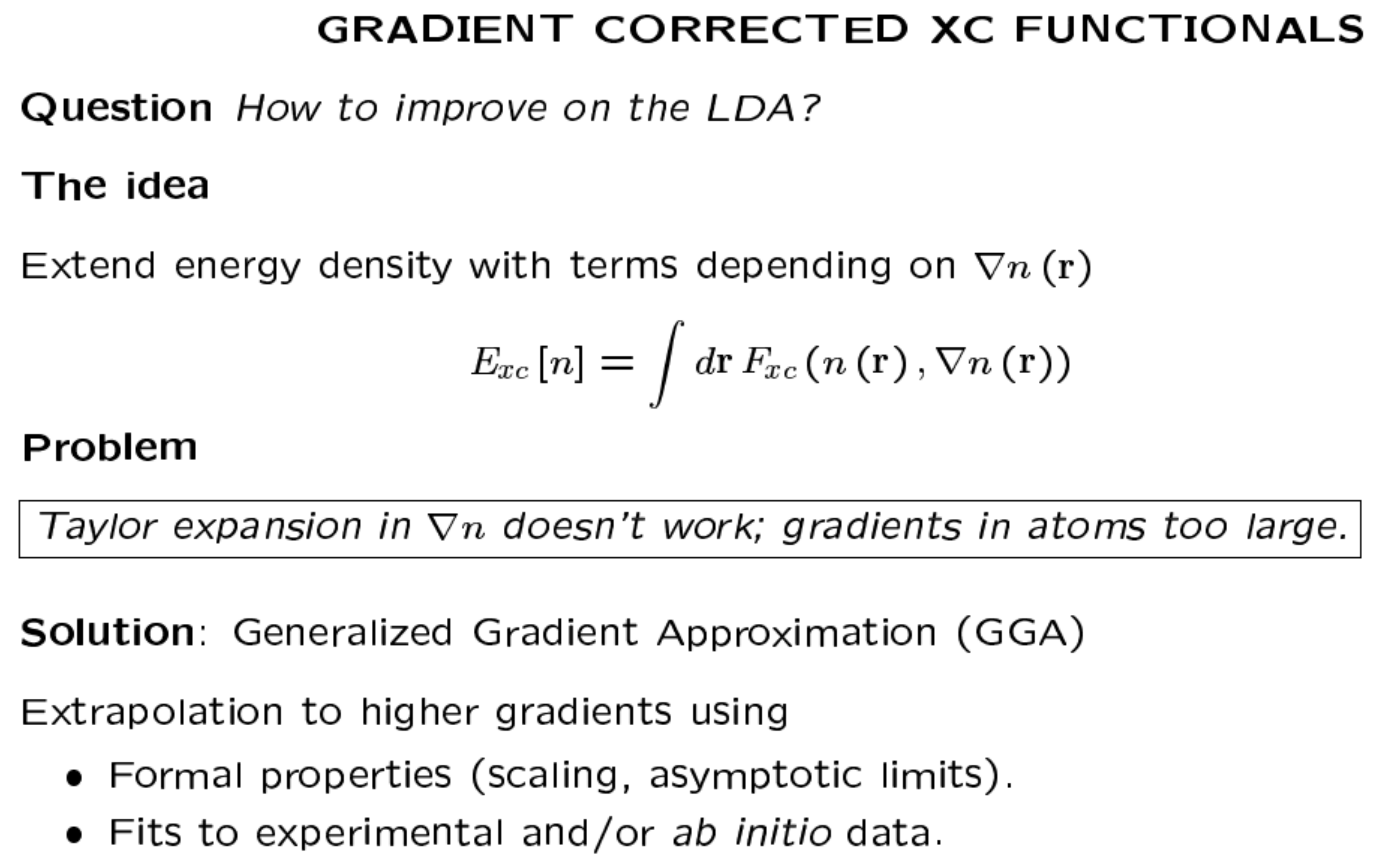
$$\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$$

with $\epsilon_x(n)$ the Dirac exchange density of the homogeneous electron gas

$$\epsilon_x(n) = C_x\, n^{1/3}, \qquad C_x = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

and $\epsilon_c(n)$ obtained from quantum Monte Carlo (Ceperley-Alder).

Density Functional Theory



GRADIENT CORRECTED XC FUNCTIONALS

Question *How to improve on the LDA?*

The idea

Extend energy density with terms depending on $\nabla n(\mathbf{r})$

$$E_{xc}[n] = \int d\mathbf{r}\, F_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

Problem

Taylor expansion in ∇n doesn't work; gradients in atoms too large.

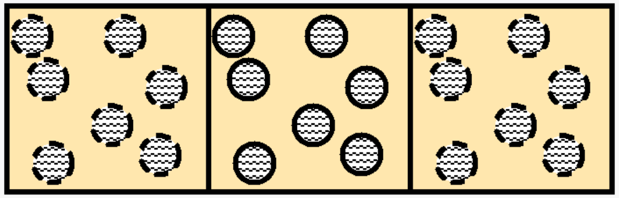
Solution: Generalized Gradient Approximation (GGA)

Extrapolation to higher gradients using

- Formal properties (scaling, asymptotic limits).
- Fits to experimental and/or *ab initio* data.

Plane Waves & Pseudopotentials

Periodic Boundary Conditions



Basis set $\{\varphi_\alpha\}$ of Plane Waves (Ω is the volume of the box)

$$\varphi_\alpha(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{G}_\alpha \cdot \vec{r}}$$

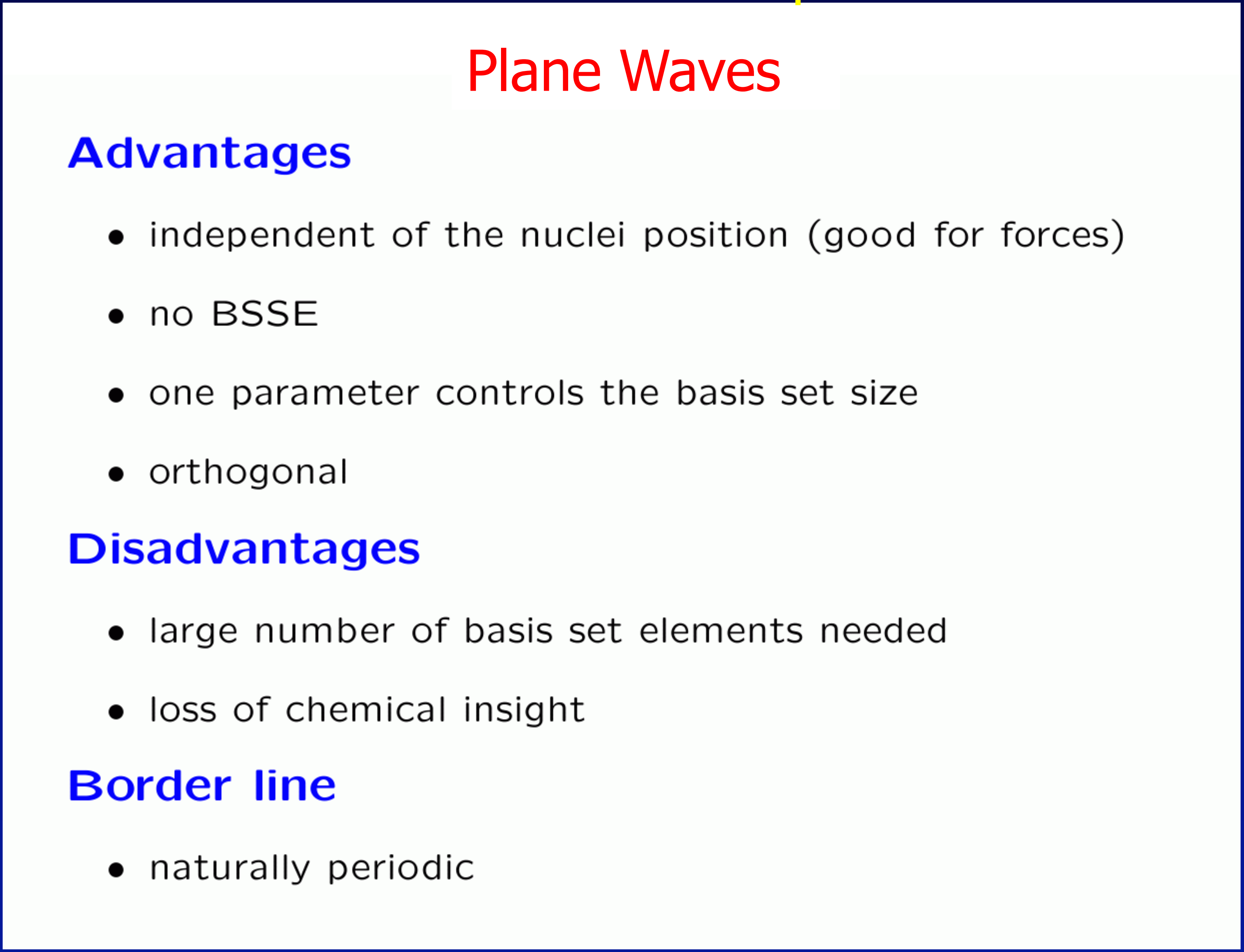
The wavefunctions are expanded as

$$\boxed{\phi_i(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} c_i(\vec{G}) e^{i\vec{G}\cdot\vec{r}}}$$

For an orthorhombic box with lengths L_x, L_y and L_z, the wavevectors $\vec{G}$ are

$$\vec{G} = i \cdot \frac{2\pi}{L_x} \cdot \vec{x} + j \cdot \frac{2\pi}{L_y} \cdot \vec{y} + k \cdot \frac{2\pi}{L_z} \cdot \vec{z}\ ; \text{ with } i, j, k \in \mathbb{Z}$$

Plane Waves & Pseudopotentials



Plane Waves

Advantages

- independent of the nuclei position (good for forces)
- no BSSE
- one parameter controls the basis set size
- orthogonal

Disadvantages

- large number of basis set elements needed
- loss of chemical insight

Border line

- naturally periodic

Plane Waves & Pseudopotentials

Why Pseudopotentials?

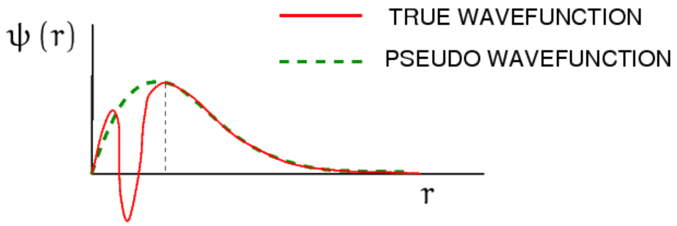
- **Reduction of basis set size**
  effective speedup of calculation

- **Reduction of number of electrons**
  reduces the number of degrees of freedom

- **Inclusion of relativistic effects**
  relativistic effects can be included "partially" into effective potentials

PSEUDO-POTENTIALS

$$V_{\text{e-ion}}(\mathbf{r}) = \sum_\ell v_\ell(\mathbf{r})\,\mathcal{P}_\ell$$



Car-Parrinello Molecular Dynamics

Ions: $\mathbf{R}^N = (\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$

Electrons: $\phi_i(\mathbf{r}, \mathbf{R}^N) = \sum_{\mathbf{G}} c_i(\mathbf{G}, \mathbf{R}^N) e^{i\mathbf{G}\cdot\mathbf{r}}$

Energy: $E(\mathbf{R}^N) = E_{DFT}[n(\mathbf{R})] + E_{ion-ion}(\mathbf{R}) \qquad n(\mathbf{R}) = \sum_i |\phi(\mathbf{r}, \mathbf{R})|^2$

Two options for Molecular Dynamics

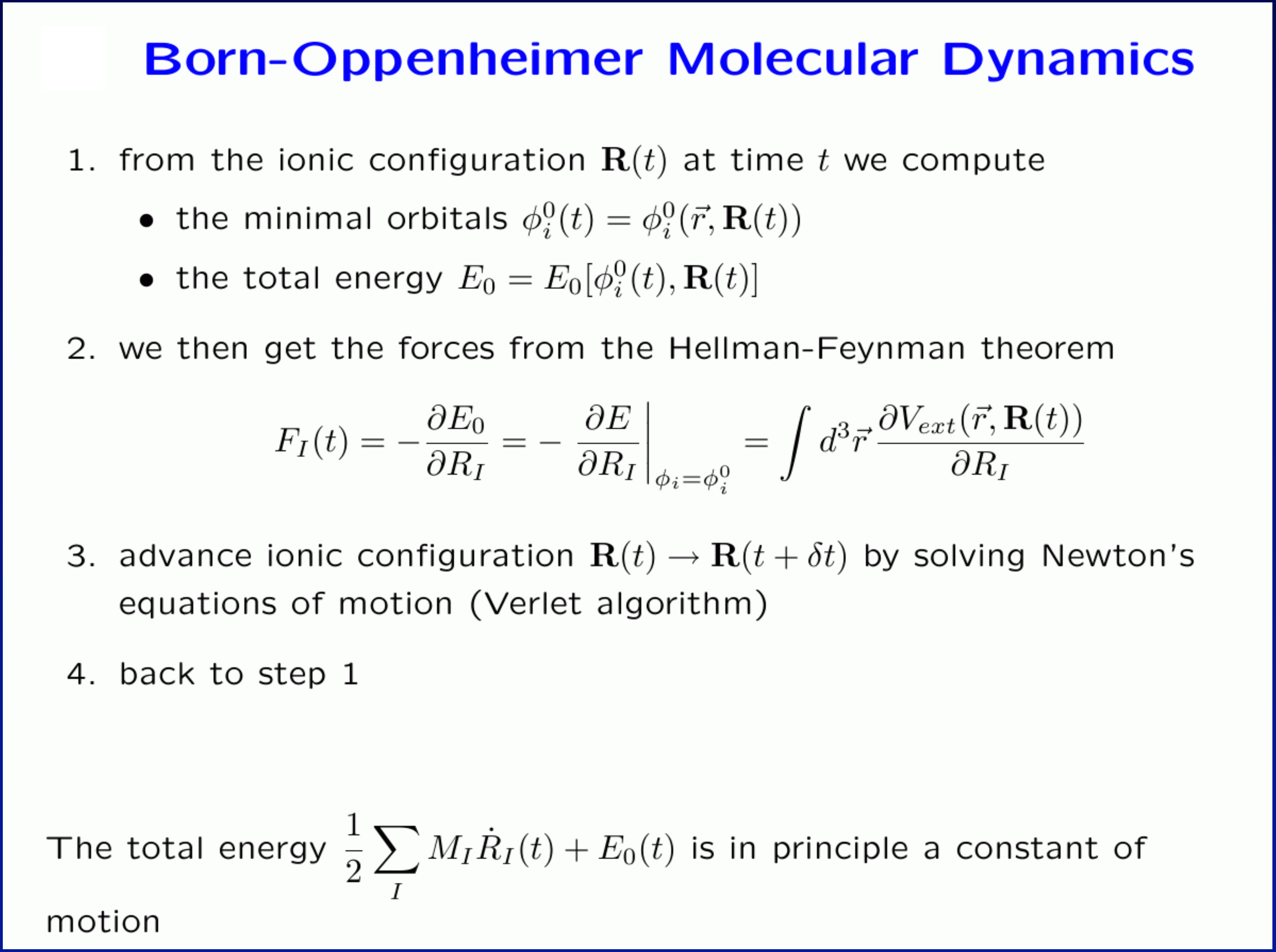
Born-Oppenheimer Molecular dynamics

1. optimize the wavefunction at fixed ionic positions
2. propagate the ions from the Hellmann-Feynman forces

Car-Parrinello Molecular Dynamics combines 1. and 2.

Non Hellmann-Feynman forces

Car-Parrinello Molecular Dynamics



Born-Oppenheimer Molecular Dynamics

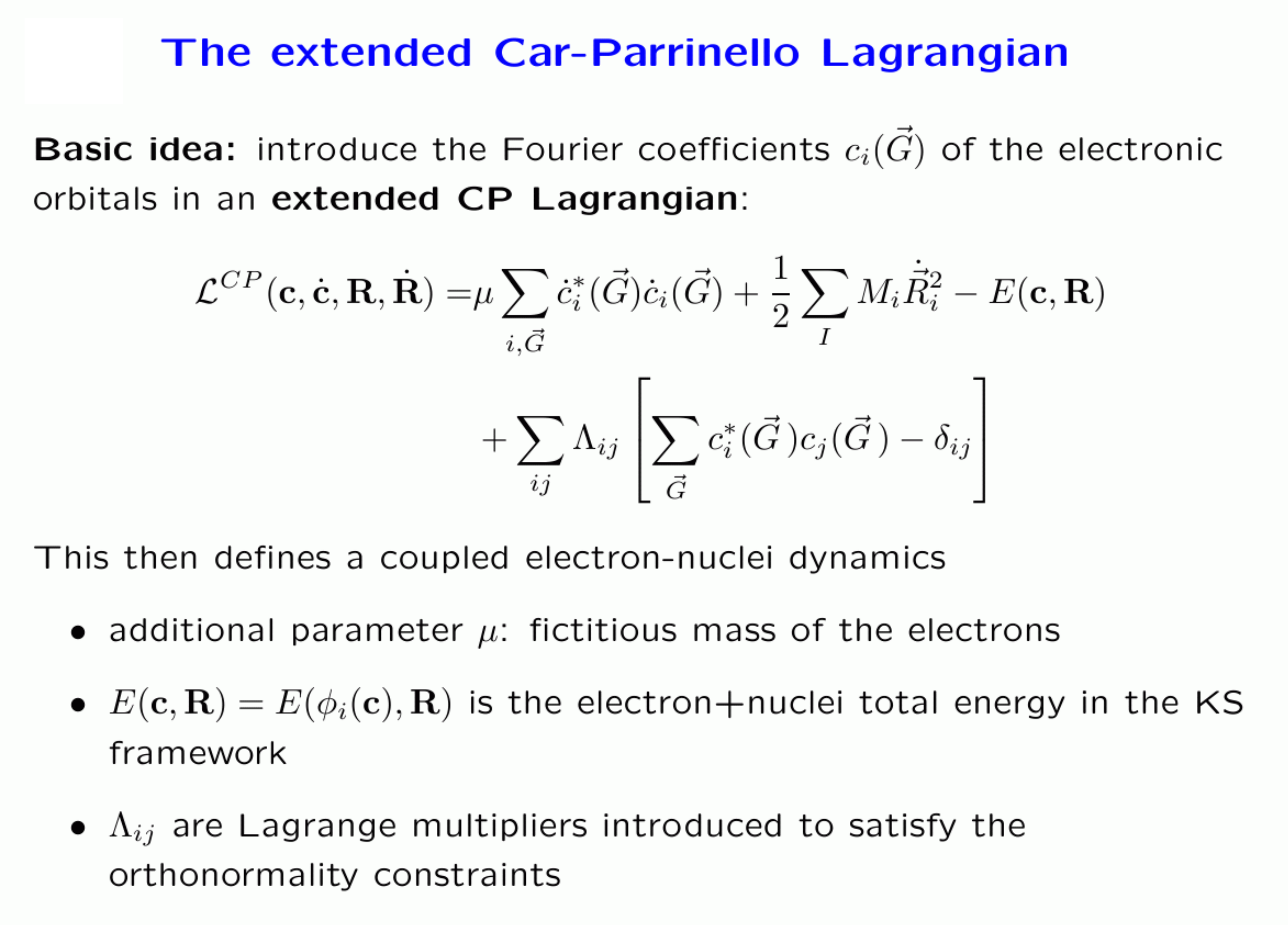
1. from the ionic configuration $\mathbf{R}(t)$ at time t we compute
   - the minimal orbitals $\phi_i^0(t) = \phi_i^0(\vec{r}, \mathbf{R}(t))$
   - the total energy $E_0 = E_0[\phi_i^0(t), \mathbf{R}(t)]$
2. we then get the forces from the Hellman-Feynman theorem

$$F_I(t) = -\frac{\partial E_0}{\partial R_I} = -\left.\frac{\partial E}{\partial R_I}\right|_{\phi_i=\phi_i^0} = \int d^3\vec{r}\,\frac{\partial V_{ext}(\vec{r}, \mathbf{R}(t))}{\partial R_I}$$

3. advance ionic configuration $\mathbf{R}(t) \rightarrow \mathbf{R}(t+\delta t)$ by solving Newton's equations of motion (Verlet algorithm)
4. back to step 1

The total energy $\frac{1}{2}\sum_I M_I \dot{R}_I(t) + E_0(t)$ is in principle a constant of motion

Car-Parrinello Molecular Dynamics



The extended Car-Parrinello Lagrangian

Basic idea: introduce the Fourier coefficients $c_i(\vec{G})$ of the electronic orbitals in an **extended CP Lagrangian**:

$$\mathcal{L}^{CP}(\mathbf{c},\dot{\mathbf{c}},\mathbf{R},\dot{\mathbf{R}}) = \mu \sum_{i,\vec{G}} \dot{c}_i^*(\vec{G})\dot{c}_i(\vec{G}) + \frac{1}{2}\sum_I M_i \dot{\vec{R}}_i^2 - E(\mathbf{c},\mathbf{R})$$

$$+ \sum_{ij} \Lambda_{ij} \left[\sum_{\vec{G}} c_i^*(\vec{G}\,) c_j(\vec{G}\,) - \delta_{ij} \right]$$

This then defines a coupled electron-nuclei dynamics

- additional parameter μ: fictitious mass of the electrons
- $E(\mathbf{c},\mathbf{R}) = E(\phi_i(\mathbf{c}),\mathbf{R})$ is the electron+nuclei total energy in the KS framework
- Λ_{ij} are Lagrange multipliers introduced to satisfy the orthonormality constraints

Car-Parrinello Molecular Dynamics

CP equation of motions

This leads to the coupled set of equations of motions:

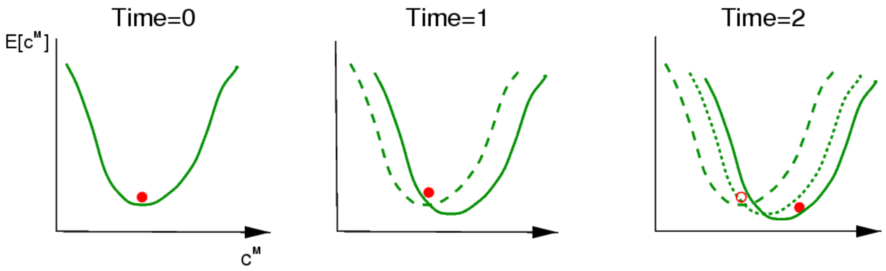
$$\mu \ddot{c}_i(\vec{G}\,) = -\frac{\partial E(\mathbf{c},\mathbf{R})}{\partial c_i^*(\vec{G}\,)} + \sum_j \Lambda_{ij} c_j(\vec{G}\,)$$

$$M_I \ddot{\vec{R}}_I = -\frac{\partial E(\mathbf{c},\mathbf{R})}{\partial \vec{R}_I}$$

WHY DOES IT WORK?

ELECTRONS ALMOST ON BORN-OPPENHEIMER SURFACE

DEVIATION DETERMINED BY MASS ELECTRONS μ



ACTUAL FORCE IN ERROR

AVERAGE FORCE IS CORRECT -> TRUE TRAJECTORY

Car-Parrinello Molecular Dynamics

If the dynamics of $c_i(\vec{G}\,)$'s is fast enough, the electrons respond nearly adiabatically to the change of the potential $E(\mathbf{c},\mathbf{R})$ they feel, due to the ionic motion.

Providing their dynamics is fast, the orbitals are "approximately" minimal and we should stay "close" to the Born-Oppenheimer surface

Advantages

- no self-consistency or loop minimization required
- the Hamiltonian $\mathcal{H}^{CP}$ is better conserved than the classical Hamiltonian of BO dynamics due to minimization errors. We should thus have more stable thermodynamics

Disadvantages

- We are constantly a bit off the BO surface, $E(\mathbf{c},\mathbf{R}) \geq E_0(\mathbf{R})$
- the timestep imposed by the fastest component, which are the electrons, is smaller than in BO dynamics

Car-Parrinello Molecular Dynamics

ACCURACY

BASIS SET

PLANE WAVES $E_{cut} \sim |\mathbf{k}_{max}|^2$

PSEUDO POTENTIALS

NORM-CONSERVING (BHS, Martins-Troullier)

SOFT (Vanderbilt, Bloechl)

DFT FUNCTIONAL

LDA+GGA: ENERGIES ACCURATE WITHIN FEW KCAL/MOL

ELECTRONIC MASS ⟷ MD TIME STEP

SMALL MASS μ + : SMALL DEVIATION FROM BO SURFACE

- : SMALL TIME STEP -> MANY TIME STEPS