Electrochemistry project, Chemistry Department, November 2006

Ab-initio Molecular Dynamics Simulation

Outline

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  - Total energy concepts
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- Ab-initio total energy calculation
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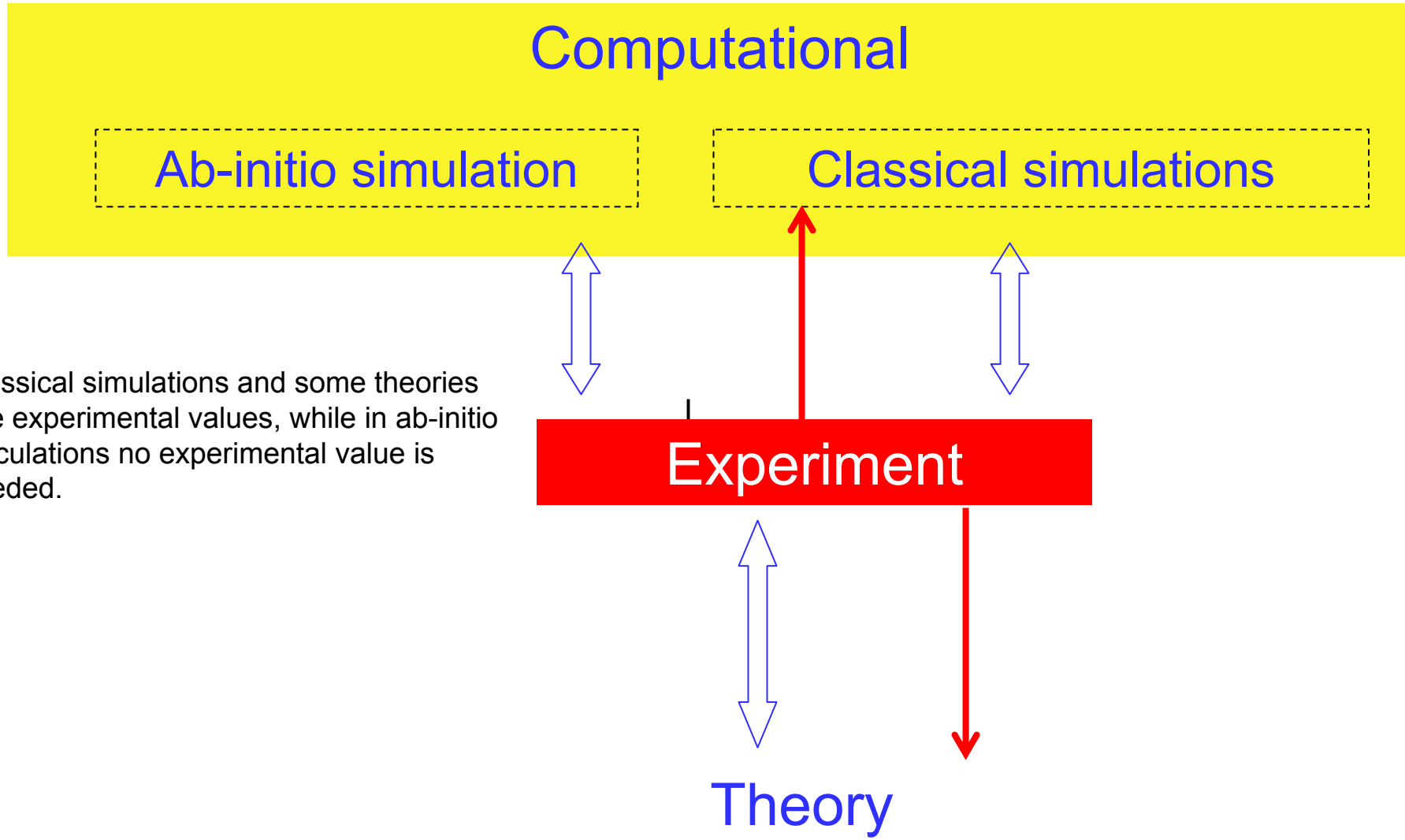
- Implementation to total energy calculation
- Ionic relaxation (Geometry optimization)

Ab-initio concepts



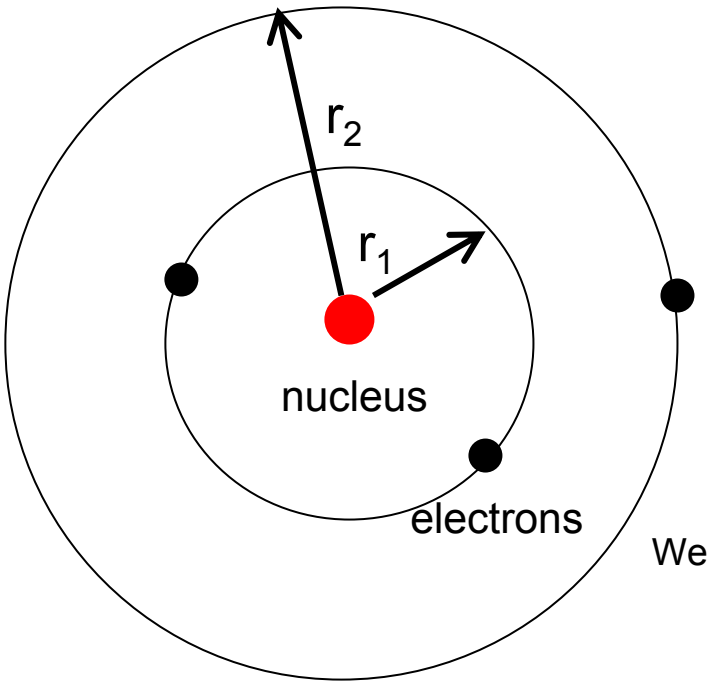
Classical simulations and some theories use experimental values, while in ab-initio calculations no experimental value is needed.

Ab-initio -> No experimental data in needed as an input for the calculation

Total energy concepts

Assumption: T=0K (no kinetics energy for nucleus)

- Total energy of an atom in gas phase
  - ❖ Classical view



$$E_{tot}^{atom} = E_{e-ion} + E_{e-e}$$

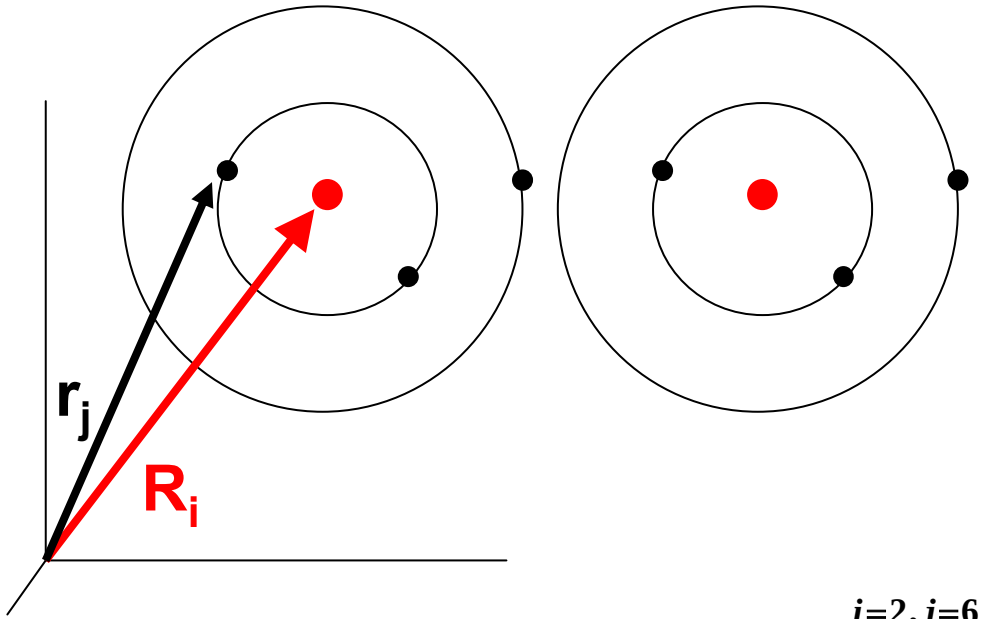
$$E_{tot}^{atom} = -e_0 V_{e-ion} - e_0 V_{e-e}$$

$$E_{tot}^{atom} = \sum_{i=1}^{3} \frac{-z}{|r_i|} + \sum_{i>j=1} \frac{1}{|r_i - r_j|}$$

We use atomic unit: $e_0 = 1, \quad \frac{1}{4\pi\varepsilon\varepsilon_0} = 1$

Total energy $E_{tot}^{atom} < 0$: The require energy to take apart all electrons from the nucleus

- Total energy of a molecule in gas phase

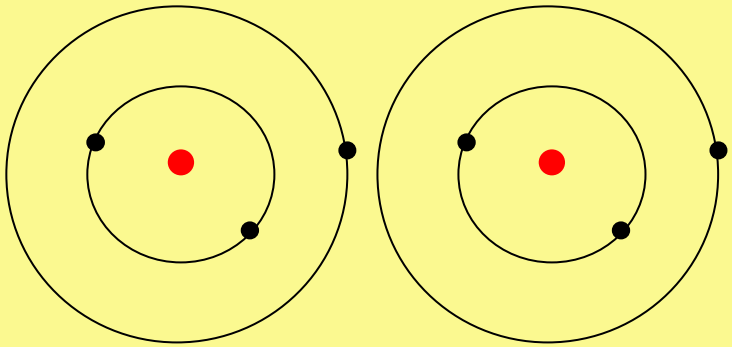


$$E_{tot}^{mol} = E_{e-ion} + E_{e-e} + E_{ion-ion}$$

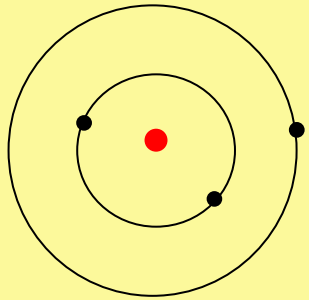
$$E_{tot}^{mol} = -e_0 V_{e-ion} - e_0 V_{e-e} + z e_0 V_{ion-ion}$$

$$E_{tot}^{mol} = \sum_{i=1,j=1}^{i=2,j=6} \frac{-z}{|R_i - r_j|} + \sum_{i,j=1}^{6} \frac{1}{|r_i - r_j|} + \sum_{i>j=1}^{i=2,j=2} \frac{-z^2}{|R_i - R_j|}$$

Total energy $E_{tot}^{mol} < 0$: The require energy to take apart all electrons AND nucleus



$$E_{tot}^{mol}$$



$$E_{tot}^{atom}$$

What is $\Delta E = E_{tot}^{mol} - E_{tot}^{atom}$

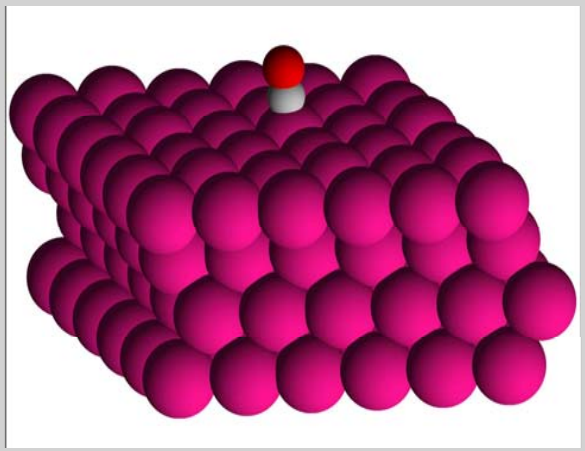
It is the binding energy of a molecule: the require energy to take apart two atoms of a molecule

Adsorption energy

Definition: The require energy to take apart the adsorbate from the surface

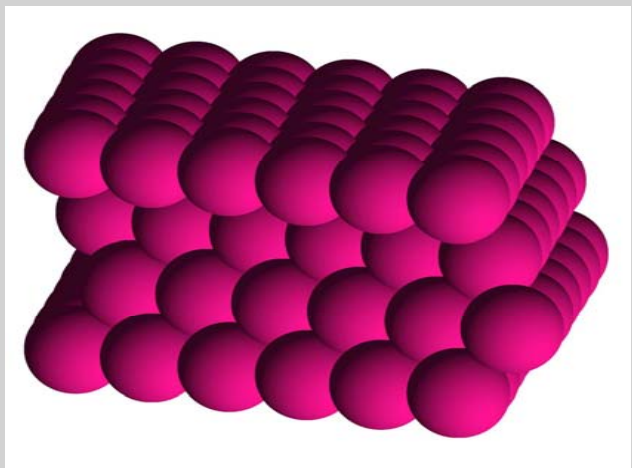
Example: CO adsorption on Pt

CO/Pt



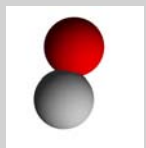
$E_{tot}^{slab+CO}$

Clean Pt slab



E_{tot}^{slab}

CO in gas phase



E_{tot}^{CO}

Project Objective

Hydrogen and CO adsorption energies on Pt(111), Pt(110) and Pt(100)

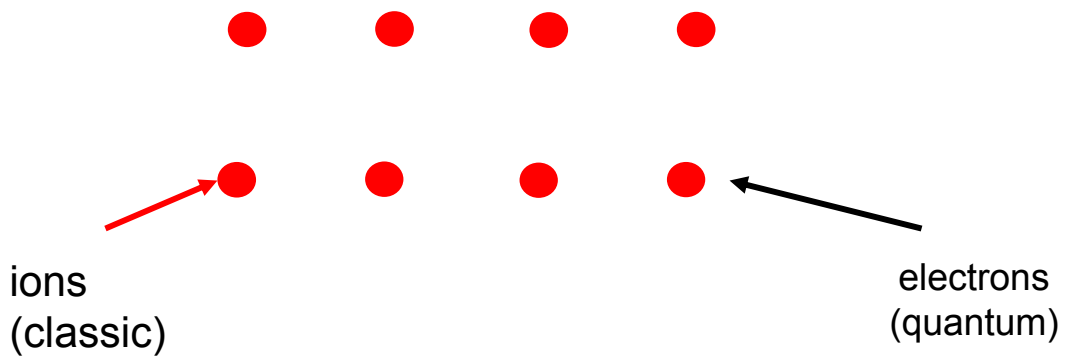
Ab-initio total energy calculation of a system of nucleons and electrons

- The electrons and ions are very small therefore quantum consider is needed

Approximation 1: ions are much bigger compare to electrons -> ions as classical particles

. Electrons -> Quantum particles -> Wavefunction -> Charge density n(r) -> Schrödinger eq.

Nucleons -> Classical particles -> Point charge -> Newton (coulomb) law



Schrödinger equation for system of electrons

$$\tilde{H}\Psi = E\Psi$$

where Ψ is the total wavefunction of the system.

Kohn-Sham orbitals

$$\Psi = \varphi_1\varphi_2 \ldots \varphi_N$$

The charge density is given by

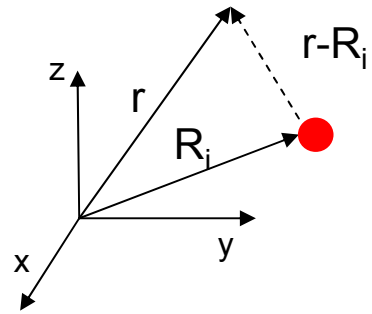
$$n(r) = \sum_{i=1}^{N} |\varphi_i|^2$$

H is the Hamiltonian.

$$\tilde{H} = \tilde{T} + V_{e-e} + V_{ext}$$

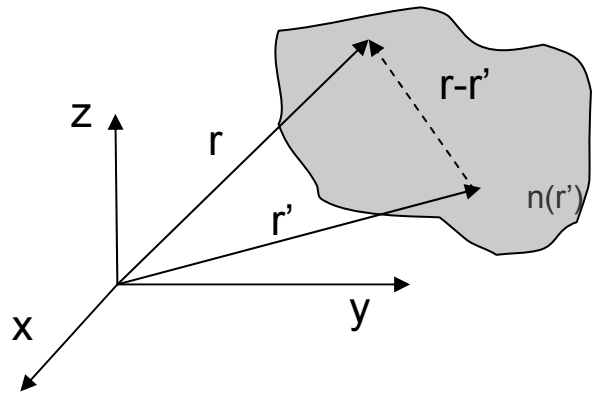
V_{ext} is the interaction with an external potential. In our case the external potential is just electron-proton interaction:

$$V_{ext}[n] = \sum_{i=1}^{N} \frac{z}{|r - R_i|}$$

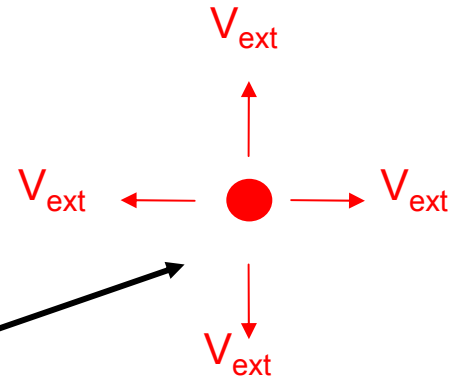


R_i is the position of ions.

$V_{e\text{-}e}$ is electron-electron coulomb interaction:



$$V_{e-e}[n] = \int \frac{n(r')dr'}{|r - r'|}$$



Charge density
of electrons n(r)

$$\mathbf{H} = T + V_{e\text{-}e} + V_{ext}$$

X ✓ ✓

T is the kinetic energy of electrons of the <u>interacting system</u>.

The bad news is that there no solution for T and Ψ therefore there is no solution for Schrödinger equation.

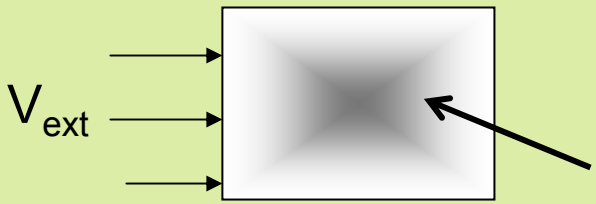
Density Functional Theory (DFT)

Theory1: External potential is a unique functional of the density n(r). That means if we have a system of electrons, the ground state density $n_0(r)$ corresponding to an external potential (like the potential from the protons) V_{ext} can not be reproduced using any other potential V'_{ext}.

Theory 2: The correct ground state density $n_0(r)$ minimizes the total energy functional.

Interacting particles (electrons)

$\mathbf{H} = T + V_{e\text{-}e} + V_{ext}$

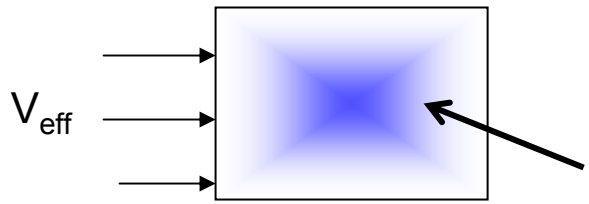


electrons
at ground state $n_0(r)$

DFT

Non interacting particles

$\mathbf{H_s} = T_s + V_{eff}$



non-interacting
particles n(r)

if $E_{tot}=E_{min} \rightarrow n=n_0(r)$

Based on the DFT many body problem of fully interacting particles in an external potential V_{ext} is simply replaced by a system of non-interacting particles in a effective potential V_{eff} giving the same ground state charge density $n_0(r)$.

T_s is now the kinetic operator of a non-interacting system with N particles which can be easily given by:

$$T_s = \sum_{i=1}^{N} \frac{-\hbar^2 \, d^2}{2m \, dr^2}$$

The effective potential V_{eff} is:

$$V_{eff} = V_{e\text{-}e} + V_{ext} + \mathbf{V_{xc}}$$

$\mathbf{V_{xc}}$: The extra term which contains all the energy contribution which were not taking into account in the transition from the interacting system to the non-interacting system. V_{xc} is called exchange-correlation potential

The exchange-correlation potential can be expressed as:

$$V_{xc}[n] = \frac{dE_{xc}[n]}{dn}$$

where $E_{xc}[n]$ is the exchange-corralation energy.

The above DFT is formally exact, but it is impossible to find a exact from for Vxc

The most common approach is the Local Density Approximation LDA

$$E_{xc}[n] = \int \varepsilon_{xc}(n) n(r) dr$$

where $\varepsilon_{xc}(n)$ is the energy of a homogeneous electron gas and it is known. Therefore the $E_{xc}[n]$ and hence $V_{xc}[n]$ are all known.

Various approximations have been introduced in the course of the years to improve LDA. The Generalized Gradient Approximation (GGA) is one of those approximations which is more or less commonly accepted to be an improvement over LDA.

In GGA approximation the Vxc depends not only on charge density n(r) but also on the magnitude of the gradient of the charge density $|\nabla n|$

Vxc [n] → in GGA approximation → $V_{xc}[n, |\nabla n|]$

Implementation to total energy calculation

$$E_{tot} = E_{el} + E_{ion-ion}$$

In order to calculate to E_{el} we need to solve the following Schrödinger equation.

$$H_s \Psi = E_{el} \Psi$$

$$(T_s + V_{e-e}[n] + V_{ext}[n] + V_{XC}[n])\varphi_i = E\varphi_i \quad i = 1, 2, .., N$$

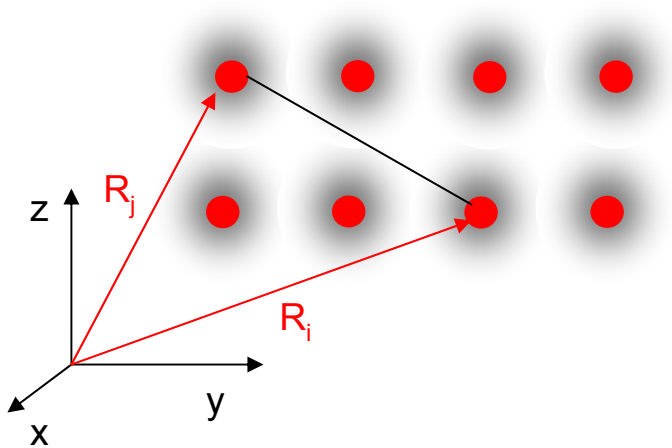
$$n(r) = \sum_{i=1}^{N} |\varphi_i|^2$$

The effective potential depends on the density, the density depends on Kohn-Sham orbitals (φ_i) and Kohn-Sham orbitals depends on the effective potential!!

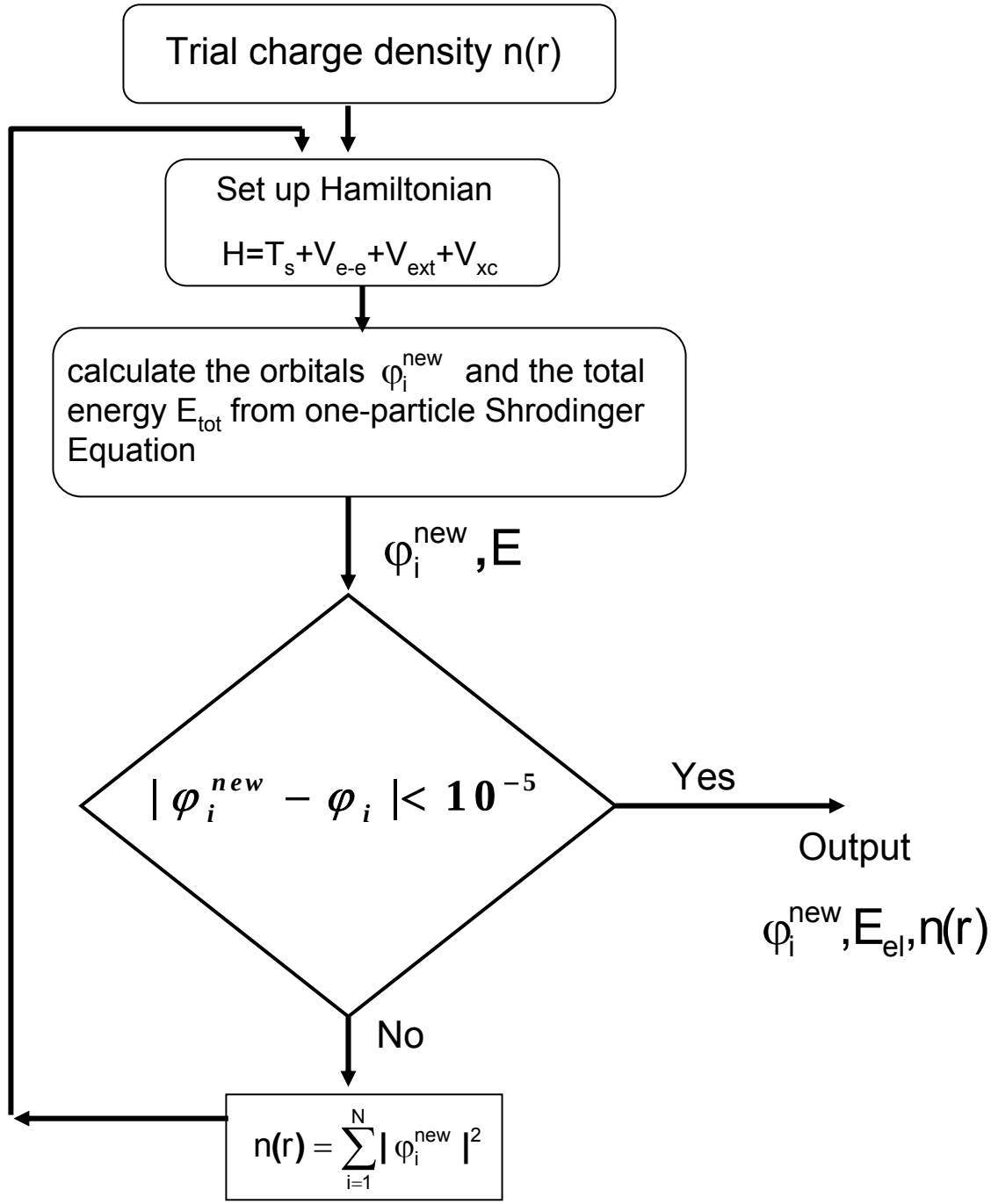
Ion-ion interaction term

$$E_{tot} = E_{el} + E_{ion-ion}$$

where $E_{ion\text{-}ion}$ is just the coulomb interaction between ions



$$E_{ion} = \sum_{i,j,i\neq j} \frac{Z^2}{|R_i - R_j|^2}$$


Trial charge density n(r)
Set up Hamiltonian
$H=T_s+V_{e-e}+V_{ext}+V_{xc}$
calculate the orbitals φ_i^{new} and the total energy E_{tot} from one-particle Shrodinger Equation
φ_i^{new}, E
$|\varphi_i^{new} - \varphi_i| < 10^{-5}$
Yes
Output
$\varphi_i^{new}, E_{el}, n(r)$
No
$n(r) = \sum_{i=1}^{N} |\varphi_i^{new}|^2$

Basis set-Plane wave

In this section we are going to briefly explain how we can solve the Kohn-Sham equation and obtain the wavefunctions and energies. If we multiply both sides of the Kohn-Sham Eq.? by $\varphi^*_i(r)$ and take an integral from both sides we gets:

$$\frac{-\hbar^2}{2m}\int \varphi_i^*(r).\frac{d^2}{dr^2}\varphi_i(r).dr + \int \varphi_i^*(r)\left(V_{e-e}[n] + V_{ext}[n] + V_{xc}[n]\right)\varphi_i(r)dr = \varepsilon_i \int \varphi_i^*(r)\varphi_i(r)dr$$

One way to solve the Kohn-Sham equation is to expand the wavefunction φ_i in a plane wave basis set. Using plane wave as a basis set has some advantages and some disadvantage. The advantage of using the plane wave is that it which help us to simplify the above Kohn-Sham equation.

$$\varphi_i(r) = \sum_{k=1}^{\infty} C_{i,k}.\exp(ik.r)$$

where mathematically the sum is over a infinite number of plane wave but of course in practice we see that it already converges for a large number of plane wave. By substituting this equation into the above Shrodinger equation and using the following mathematical principal:

$$\int \exp(ik\cdot r).\exp(ik'\cdot r)dr = \delta_{kk'}$$

We end up with a matrix with N_{max} x N_{max} elements where N_{max} is the number of the plane waves.
N_{max} depends very much to the size of your system. i.e. number of atoms in your system and also the elements you use. it can be as big as 1e+5 number of plane waves. In order to get φi and εi from the matrix we need to diagonal it which of course needs a powerful computer or even several computers working as parallel.

Reminding: When φ_i and ε_i are calculated in the next iteration a new charge density should be constructed and again a new matrix should be diagonalized. Usually 10-30 iterations in needed to get the total energy of the system self consistently.

- The calculated total energy in this way depends very strongly on the position of the tions.
- The position of the atoms is given by you, and it is not precise enough.
- Therefore the total energy calculation will be absolutely wrong

Solution

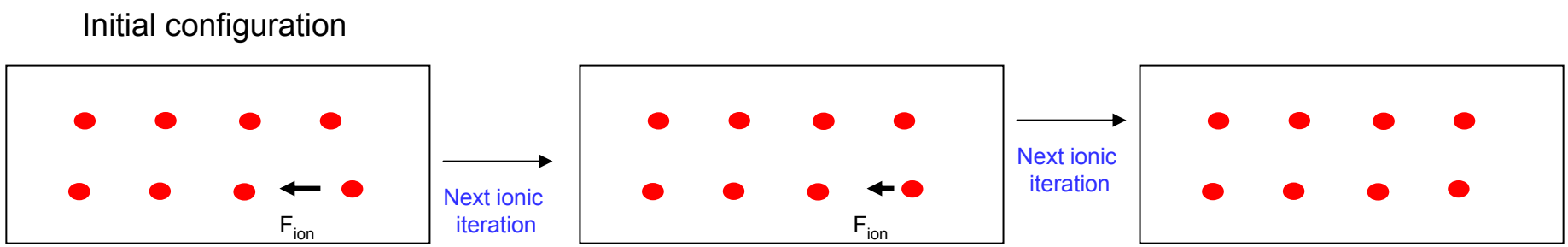
Geometry optimization

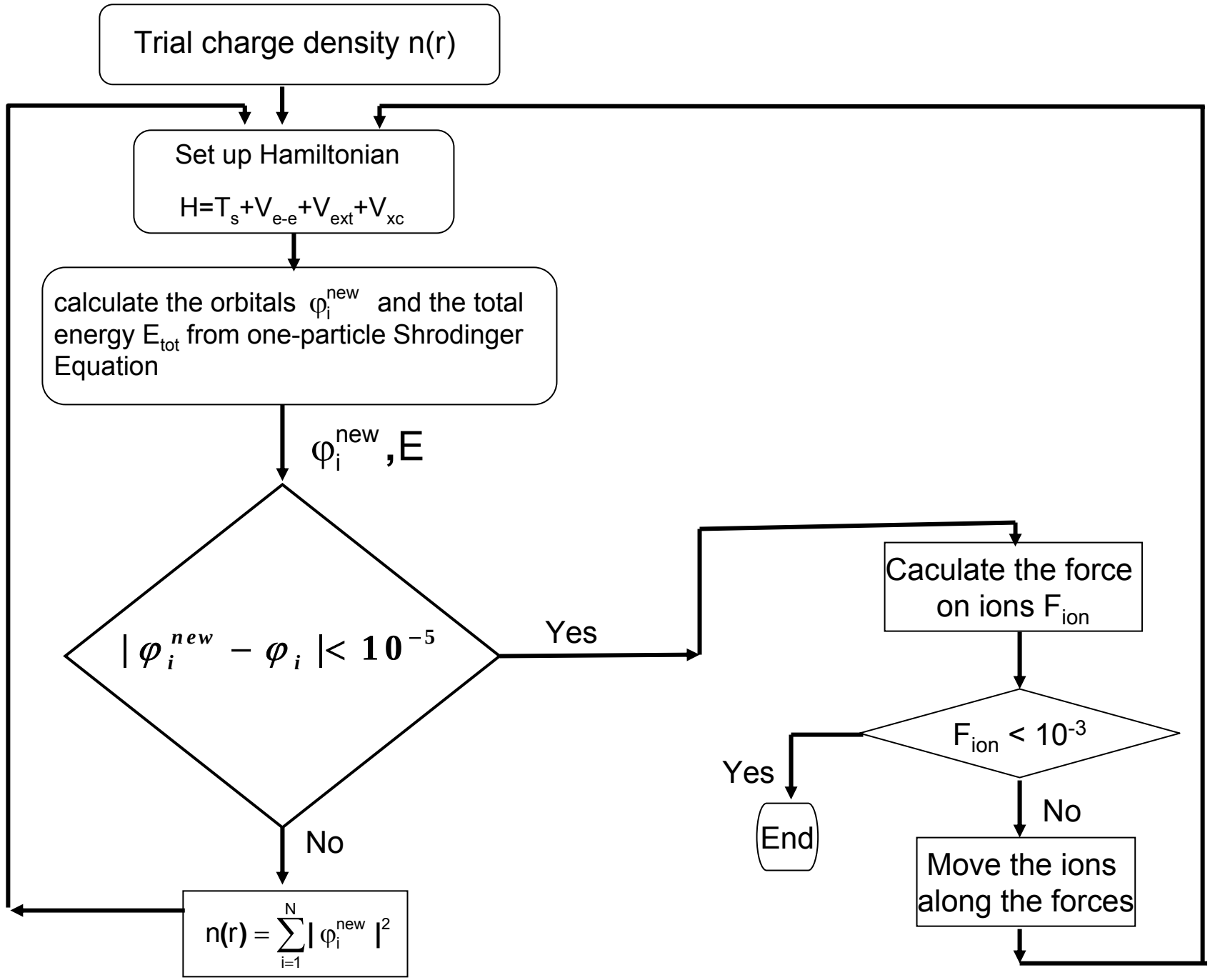
➢ It is possible to calculate the force on each ion from the total energy calculation 

$$F_i = \frac{dE_{tot}}{dR_i}$$

➢ we can move the ions a little bit along the forces and redo the total energy calculation

➢ we repeat the above calculation until the total force on ions becomes almost zero




Trial charge density n(r)
Set up Hamiltonian
H=T_s+V_e-e+V_ext+V_xc
calculate the orbitals φ_i^new and the total energy E_tot from one-particle Shrodinger Equation
φ_i^new ,E
| φ_i^new − φ_i |< 10^−5
Yes
No
n(r) = Σ_{i=1}^{N} | φ_i^new |^2
Caculate the force on ions F_ion
F_ion < 10^-3
Yes
End
No
Move the ions along the forces

References:

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