北京航空航天大學
BEIHANG UNIVERSITY

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Introduction to First-Principles Method

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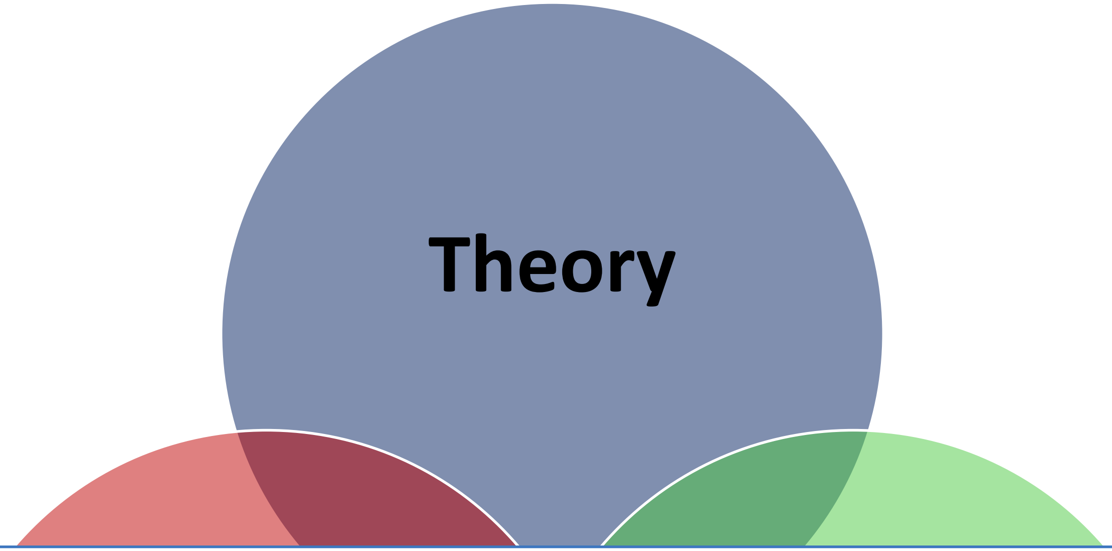
Computer Modeling & Simulation

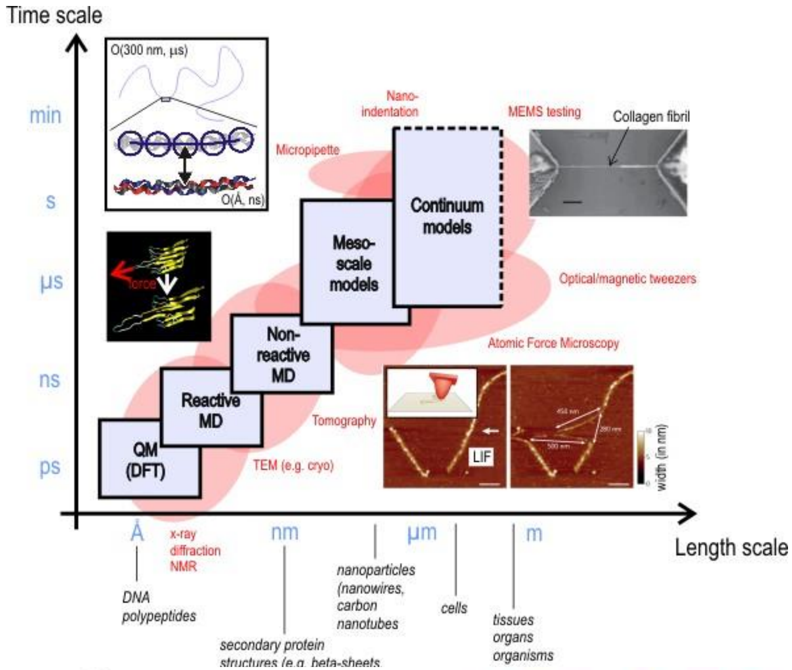


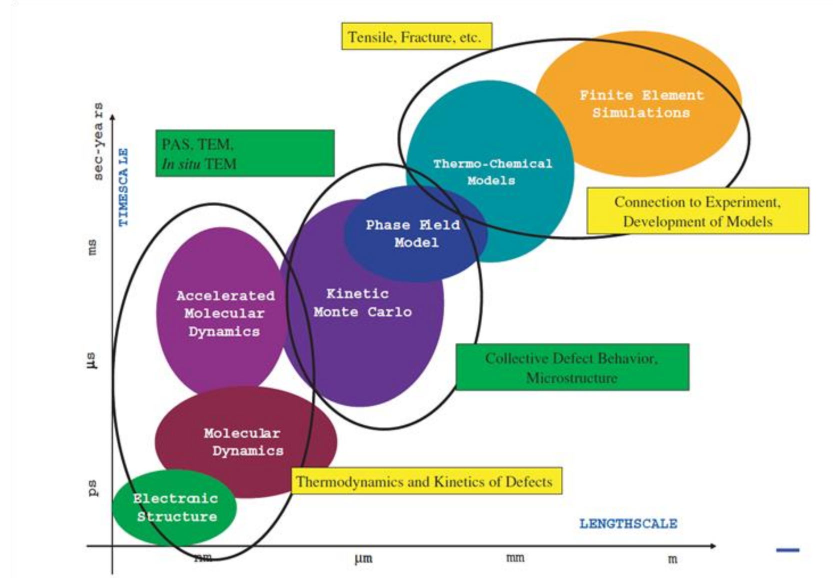
Computer modeling & simulation” has emerged as an indespensable method for scientific research of materials in parallel to experiment and theory.

Outline

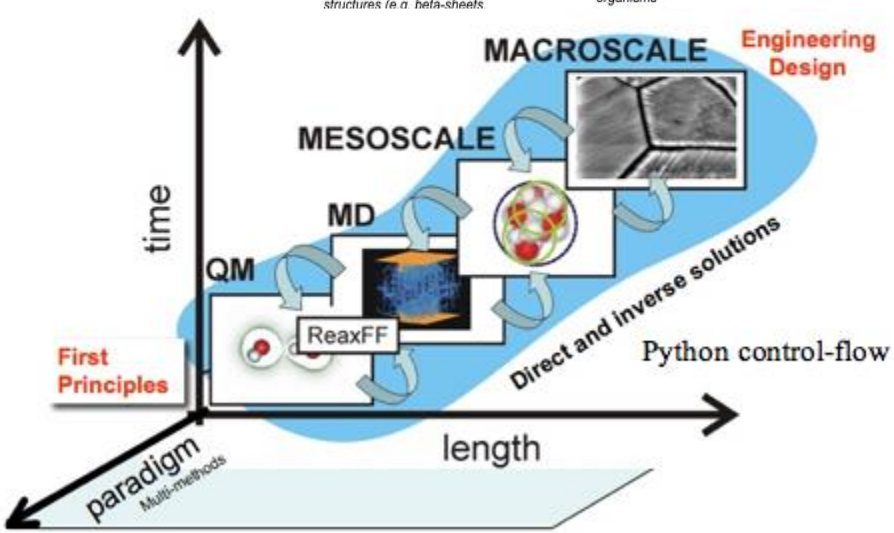
- Introduction (first principles)
- Introduction (history of first principles)
- Basic principles
  - calculation of total energy
  - electron-electron interaction (DFT-LDA)
  - Bloch's theorem – periodic system
  - electron-ion interaction (pseudopotential)
- Supercell technique
- Computational procedure
- Future

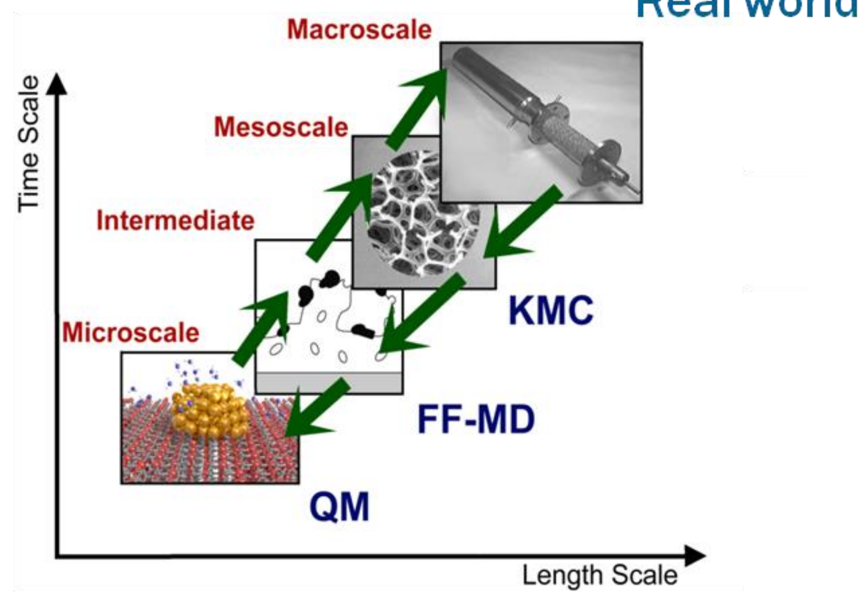
Multiscale Modeling & Simulation : Conceptual framework



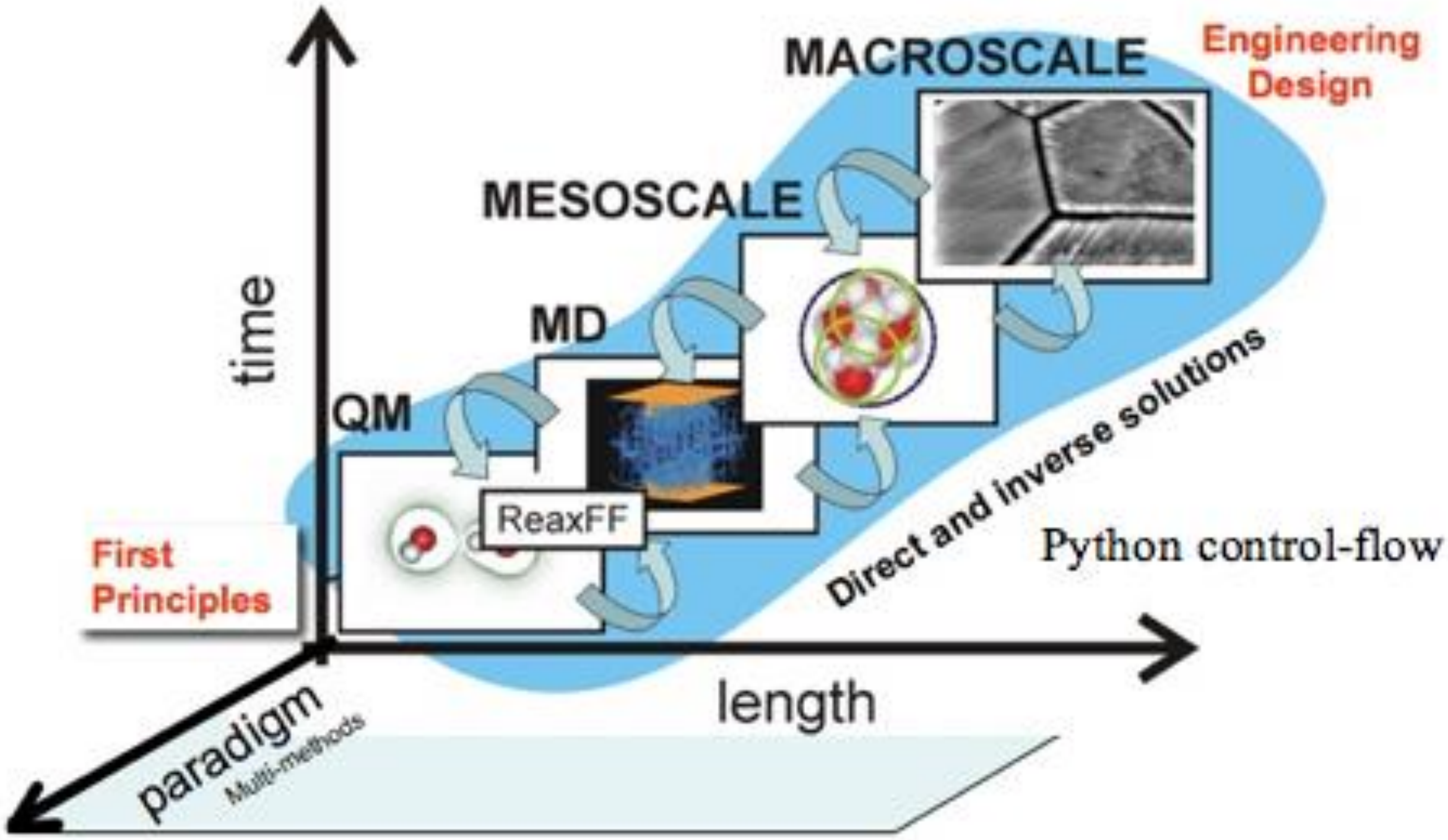


Real world





First-principles method



First-principles method

Solve quantum mechanic Schrodinger equation to obtain Eigen value and Eigen function, and thus the electronic structure.

- The charm: only atomic number and crystal structure as input, which can determine precisely the structure and the properties of the real materials.

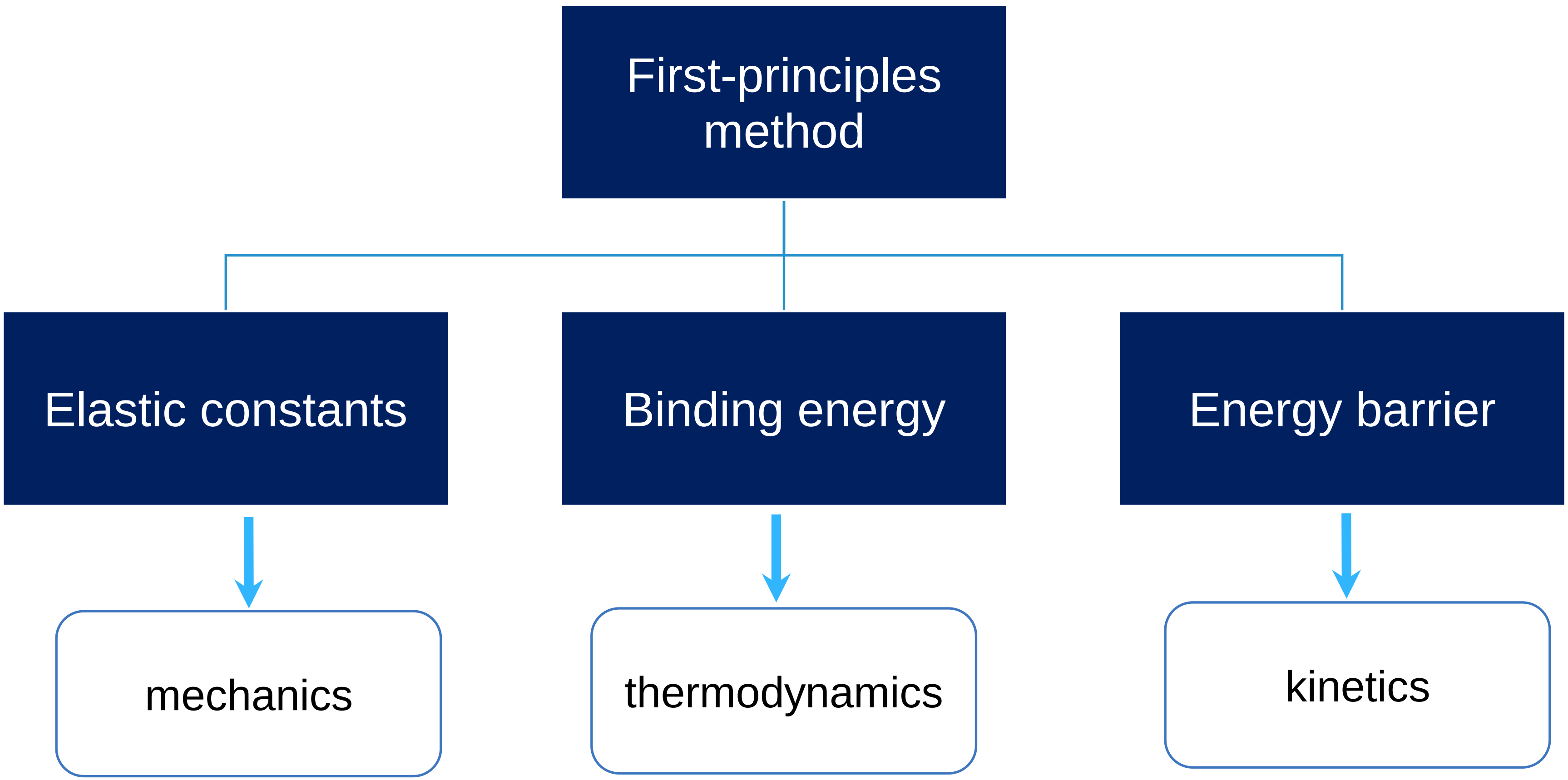
- first principles - physics, materials

  Density functional theory

- *ab initio* -quantum chemistry

  Hartree-Fork self-consistent field

A connection between atomic and macroscopic levels
（不同尺度之间的联系）



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Development of quantum theory in the past 100 years
过去100年量子理论的历史

1920s-1930s	The foundation for most of the theories
1960s	Accurate band structures
1970s	Surfaces and interfaces
1980s	Structural and vibrational properties
1990s	Applications to complex and novel materials

Materials physics Slow!

Atomic physics Fast!

Difficulties in solving the Schrödinger equation

- **Dirac** (1929):

  The difficulty is only that the exact application of quantum theory leads to equations much too complicated to be soluble.

- Large number of strongly interacting atoms in a solid

Schrödinger equation:

Simple to write, yet hard to solve equation

- Calculation in the past 100 years:
  Physical models and theories to simplify of the equations

first principles

Origin: the first mover

✓ Newton's first law: an object either remains at rest or continues to move at a constant velocity, unless acted upon by a net force.

✓ If all the objects were at rest at the start of the universe, yet they moved later. What is the origin of their movement?

✓ Newton believes this is moved by the God, "the first mover".

✓ The first mover should base on one principle, called "first principle"

Quantum mechanics theory – first principle

✓ quantum mechanics reflects structure of atom & molecule and thus the properties of matter, such theory approximates the principle that reflects nature of the universe.

first principles

According to the interaction between nucleus and electrons based on quantum mechanics principles, first principles method finds the solution to the Schrodinger equation through series of approximations and simplifications.

1D Schrodinger equation

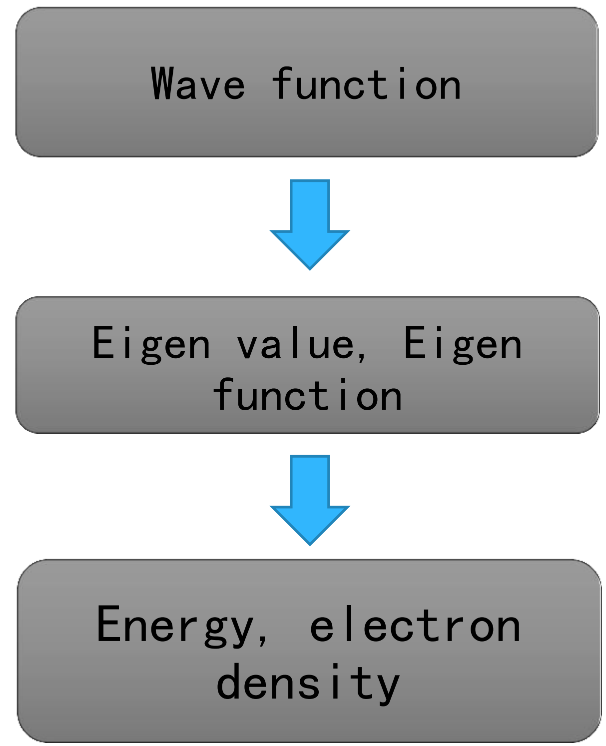
$$-\frac{\hbar^2}{2\mu}\frac{\partial^2 \psi(x,t)}{\partial x^2} + U(x,t)\psi(x,t) = i\hbar\frac{\partial \psi(x,t)}{\partial t}$$

3D Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + U(x,y,z)\psi = i\hbar\frac{\partial \psi}{\partial t}$$

Stationary Schrodinger equation

$$-\frac{\hbar^2}{2\mu}\nabla^2 \psi + U\psi = E\psi$$



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Total energy

Nearly all physical properties are related to total energies or to differences between total energies.

- Equilibrium lattice constant: energy minimum
- surfaces, interfaces and defects, nanostucture: structure that minimize the total energy
- force: derivative of energy with respect to a position
- stress: derivative of energy with respect to a strain
- elastic constant: second derivative of energy

If total energies can be calculated, any physical properties that can be related to a total energy or a difference between total energies can be determined computationally.

Total energy calculations

First-principles methods

- compute the total energy of a system of electrons and nuclei
- a subsequent minimization of the energy with respect to the electronic and nuclear coordinates.

Technique: constructing a Hamiltonian

- kinetic energy of particles
- Coulomb interactions between all the particles

Total-energy calculations: simplifications and approximations needed

- many-body system: nuclei and electrons
- computation: formidable

The basic approximation: Separation of electron and nucleus

Electrons respond essentially instantaneously to the motion of the nuclei

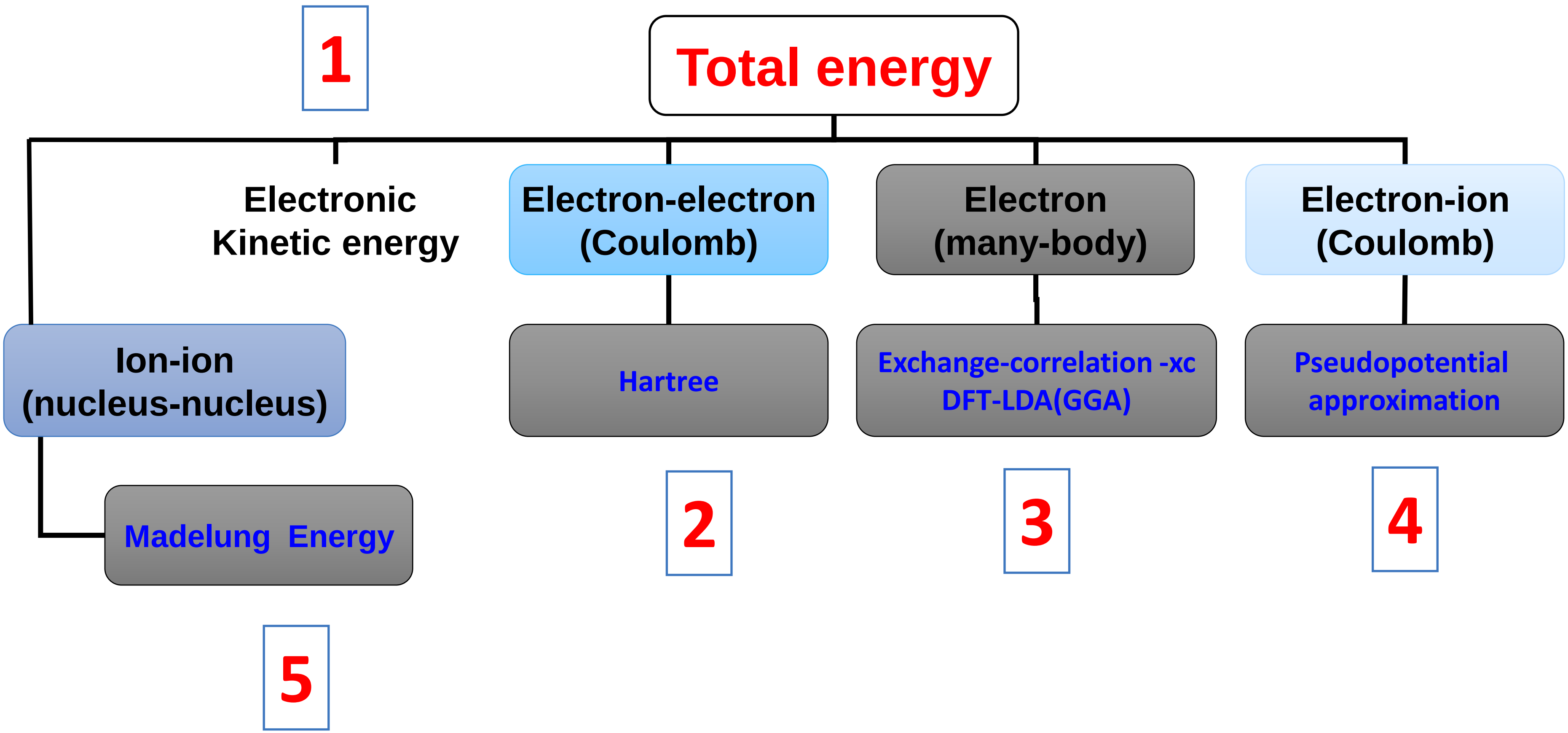
- - *Electron and nucleus: large difference in mass*

Separate of electronic and nuclear coordinates in the many-body wave function

Born-Oppenheimer approximation
(Adiabatic principle)

Total energy calculation

- Five parts consist of total energy



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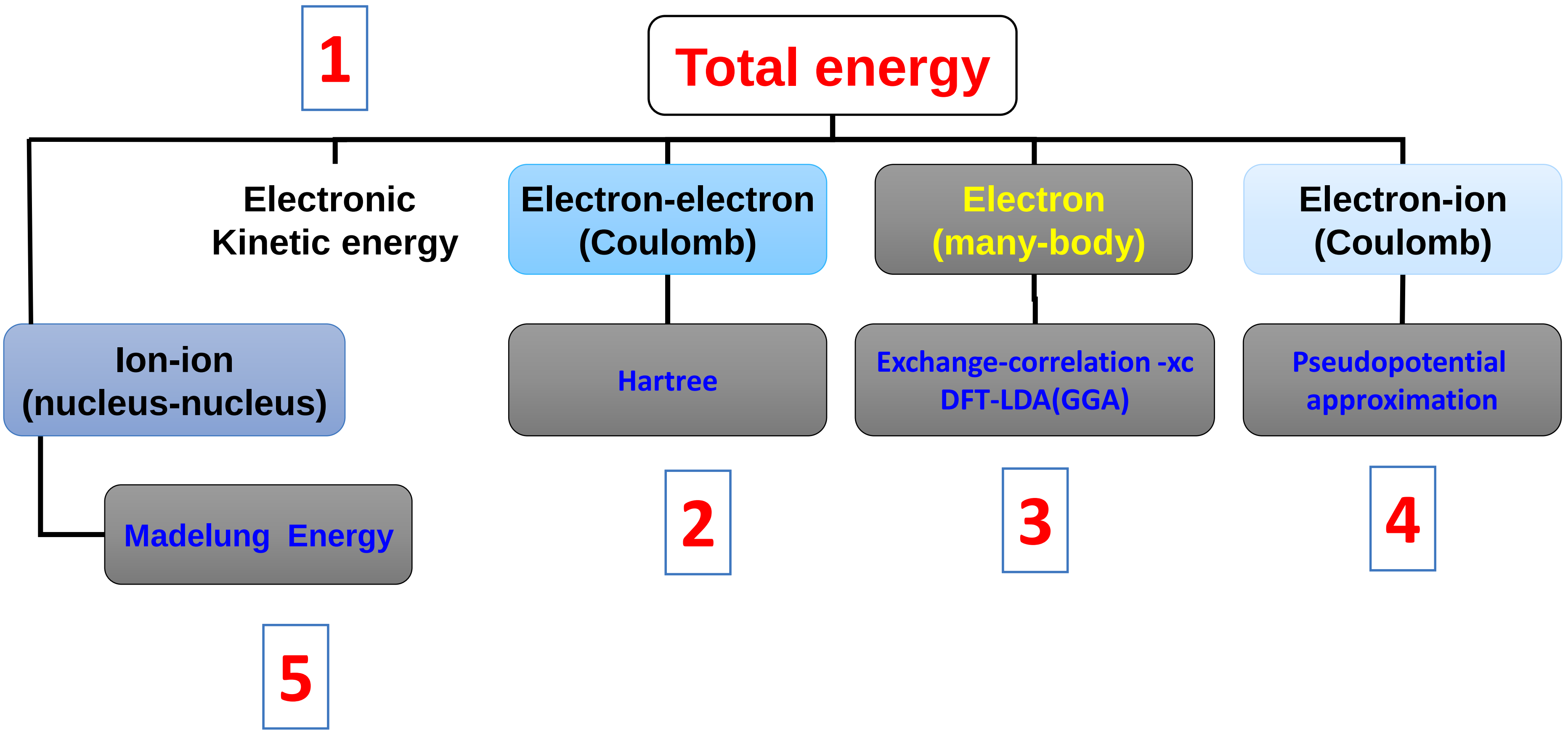

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Electron-electron interaction: Density functional theory

Exchange-correlation

- exchange: energy reduction due to a spatial separation between the electrons with the same spin
- correlation: energy reduction due to a spatial separation between the electrons with the opposite spin

Density Functional Theory (DFT)

- strongly interacting electron gas → a single particle moving in an effective potential
- (one-electron or mean-field approximation)
- Hohenberg and Kohn (1964), Kohn and Sham (1965)

Density functional theory

Total energy: *a unique functional of electron density*

The minimum value of the total energy functional is the ground-state energy of the system, and the density that yields this minimum value is the exact single-particle ground-state density.

(Hohenberg and Kohn, 1964)

How to replace the many-electron problem by an exactly equivalent set of self-consistent one-electron equations.

(Kohn and Sham, 1965)

Density functional theory formulations

- **Kohn-Sham equation** (Redberg a.u.)

$$\left[-\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \varepsilon_i \psi_i(r)$$

$$V_{eff}(r) = V_{ion}(r) + V_H(r) + \mu_{xc}(r)$$

$$V_H(r) = \int \frac{2n(r')}{|r - r'|} dr^3 \quad \text{(Hartree potential)}$$

$$\mu_{xc}(r) = \frac{\delta E_{xc}(n)}{\delta n} \quad \text{(exchange - correlation potential)}$$

$$n(r) = \sum_i^{occ} |\psi_i(r)|^2 \quad \text{(electron density)}$$

Local density approximation

- **Exchange-correlation energy:** exchange-correlation energy per electron in a homogeneous electron gas with the same density as the electron gas at point r.

$$\varepsilon_{xc}(r) = \varepsilon_{xc}^{\text{hom}}[n(r)]$$

$$E_{xc}(n) = \int \varepsilon_{xc}(r) n(r) dr^3$$

$$\mu_{xc}(r) = \varepsilon_{xc}(r) + n(r)\frac{\delta\varepsilon_{xc}}{\delta n}$$

LDA examples

Perdew-Zunger type

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c, \quad \varepsilon_x = -\frac{0.4582?2}{r_s}$$

$$\varepsilon_c = \begin{cases} \dfrac{-0.1423?2}{1+1.0529\sqrt{r_s}+0.3334\sqrt{r_s}} & r_s ?1 \\ (-0.0480+0.0311\ln r_s - 0.0116 r_s \\ \qquad +0.0020 r_s \ln r_s)?2 & r_s < 1 \end{cases}$$

$$\mu_{xc} = \varepsilon_{xc} + \rho\frac{\delta\varepsilon_{xc}}{\delta\rho} = \varepsilon_{xc} - \frac{r_s}{3}\frac{d\varepsilon_{xc}}{dr_s}$$

Wigner type

$$\varepsilon_{xc} = \varepsilon_x + \varepsilon_c, \quad \varepsilon_x = -\frac{0.4582\times 2}{r_s}$$

$$\varepsilon_c = -\frac{0.88}{r_s + 7.8}$$

$$\mu_{xc} = \varepsilon_{xc} - \frac{r_s}{3}\frac{d\varepsilon_{xc}}{dr_s}$$

Charge density at point r $\rho(\vec{r})$, $r_s = \left[\frac{3}{4\pi}\rho^{-1}\right]^{\frac{1}{3}}$

Generalized Gradient Approximation (GGA)

LDA fails in situations where the density undergoes rapid changes.

GGA: *considering the gradient of the electron density*

$$\varepsilon_{xc}(r) = \varepsilon_{xc}[n(r), \nabla n(r)]$$

- A commonly used functional: PW91
  - (Perdew and Yang,1992)

Total energy formulations

$$E_{total} = T(n) + \int V_{ion}(r)n(r)dr^3 + \frac{1}{2}\int V_H(r)n(r)dr^3 + E_{xc}(n) + E_{i-i}$$

$$= \sum_i^{occ} \int \psi_i^*(r)\left(-\nabla^2\right)\ \psi_i(r)dr^3 + \int V_{ion}(r)n(r)dr^3$$

$$+ \frac{1}{2}\int\int \frac{2n(r)n(r')}{|r-r'|} dr^3 dr'^3 + \int \varepsilon_{xc}(r)n(r)dr^3 + E_{i-i}$$

Difficulties after DFT

DFT: Many-body → an effective single-particle interaction

Computation: *a formidable task*

- *infinite* number of noninteracting electrons in a static potential of an *infinite* number of nuclei or ions.

Two difficulties

- a wave function must be calculated for each of the *infinite* number of electrons in the system
- since each electronic wave function extends over the entire solid, the basis set required to expand each wave function is *infinite*.

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Bloch's theorem

Bloch's theorem: in a periodic solid, each electronic wave function can be written as the product of a cell-periodic part and a wavelike part

$$\psi(\vec{r}) = \exp(i\vec{k}\cdot\vec{r})\ u(\vec{r})$$

$$\psi(\vec{r}+\vec{R}) = \exp(i\vec{k}\cdot\vec{R})\ \psi(\vec{r})$$

Real space, reciprocal space

$$a_i \cdot b_j = 2\pi\delta_{ij} = \begin{cases} 2\pi & i=j \\ 0 & i \neq j \end{cases}$$

Wave function can be calculated only in a **primitive cell**

k points sampling

Bloch theorem:

wave vector *k* can be calculated only in the *first Brillouin zone*

However, *still Infinite number of k points are needed.*

The electronic wave functions at *k* points that are very close together will be almost identical, hence it is possible to represent the electronic wave functions over a region of *k* space by the wave functions at a single *k* point.

-- Monkhorst-Pack sampling method:
uniform sampling

Plane wave basis set

$$\psi\left(\vec{r}\right) = \exp(i\vec{k}\cdot\vec{r})\ u(\vec{r})$$

Fourier expansion

$$u(r) = C_{i,G} \exp[iG\cdot r]$$

$$\Downarrow$$

$$\psi(r) = C_{i,k+G} \exp[i(k+G)\cdot r]$$

Kinetic energy cutoff

- In principles, an *infinite* plane-wave basis sets are required to expand the electronic wave functions.

- The coefficients for the PW with small kinetic energy are typically important than those with large kinetic energy.

$$\textit{kinetic energy} \quad \frac{\hbar^2}{2m}\left|k+G\right|^2$$

- **Kinetic energy cutoff:** PW basis set can be truncated to include only plane waves that have kinetic energies less than some particular cutoff energy.

Plane-wave representation of KS equation

Secular equation

$$\sum_{G'}\left[\frac{\hbar^2}{2m}\left|k+G\right|^2\delta_{G,G'}+V_{ion}(G-G')+V_H(G-G')+V_{xc}(G-G')\right]C_{i,k+G'}=\varepsilon_i C_{i,k+G}$$

Kinetic energy, potential: *Fourier transforms*

$$H_{k+G,k+G'}$$

Solution: *diagonalization of a Hamiltonian matrix*

Now system computationally tractable?

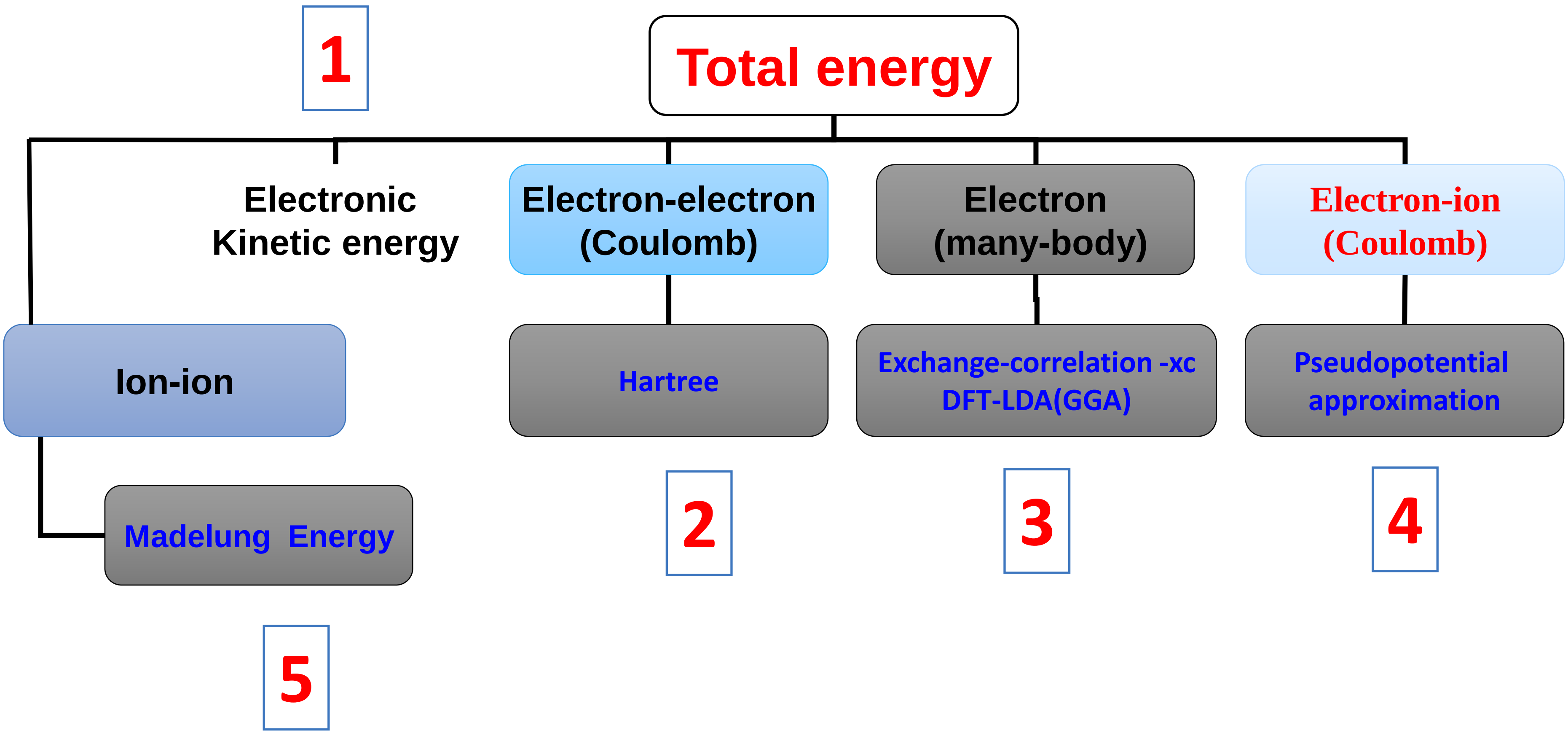
No.

- Matrix size is still intractable large for systems that contain both valence and core electrons.

A severe problem, but can be overcome by use of ***the pesudopotential approximation.***

Total energy calculation

- Five parts consists of total energy



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Separation of valence and core electrons

Most physical properties of solids are dependent on the **valence electrons** to a much greater extent than on the core electrons.

Core region: large number of PWs needed.

- Tightly bound core orbital and the rapid WF oscillations of the valence electrons in the core region.

Electron (core+valence) - nucleus system

→ valence electron-ion (nucleus+core) system

- Only valence electrons are taken into account
- **Pseudopotential approximation**

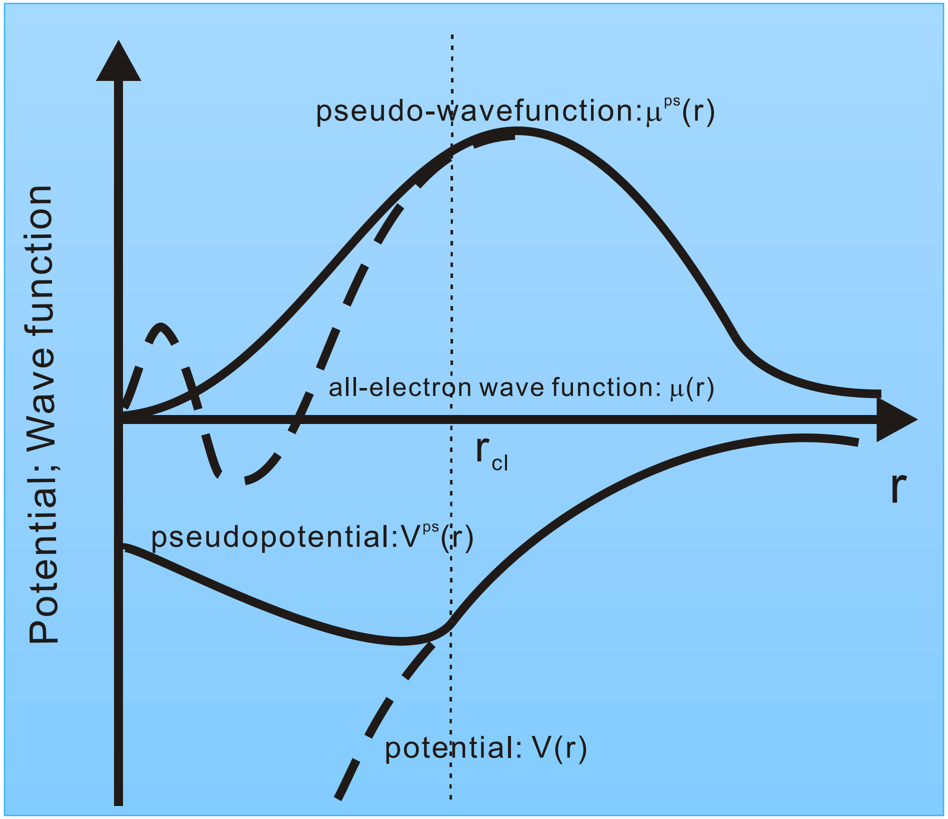
Pseudopotential approximation

Phillips (1958); Heine and Cohen (1970); Yin and Cohen (1982)

- Nucleus-electron → ion-valence electron

PP approximation

- Strong ionic potential → weak pseudopotential
- True valence wave functions (with radial nodes) → pseudo wave function (without nodes)



Norm-conserved pseudopotential

- outside the core region: $u_l^{PS}(r) = u_l^{AE}(r)$

- pseudo wave functions and real wave functions should be identical (both spatial dependences and absolute magnitudes) so that the two wave functions generate identical charge densities.

- inside the core region: $\int_0^{r_{cl}} \left| u_l^{PS}(r) \right|^2 dr = \int_0^{r_{cl}} \left| u_l^{AE}(r) \right|^2 dr$

  - integral the squared amplitudes of real and pseudo wave function are identical.

- The same eigen value: $\varepsilon^{PS} = \varepsilon^{AE}$

Ultrasoft pseudopotential

Large energy cutoff for PW basis set

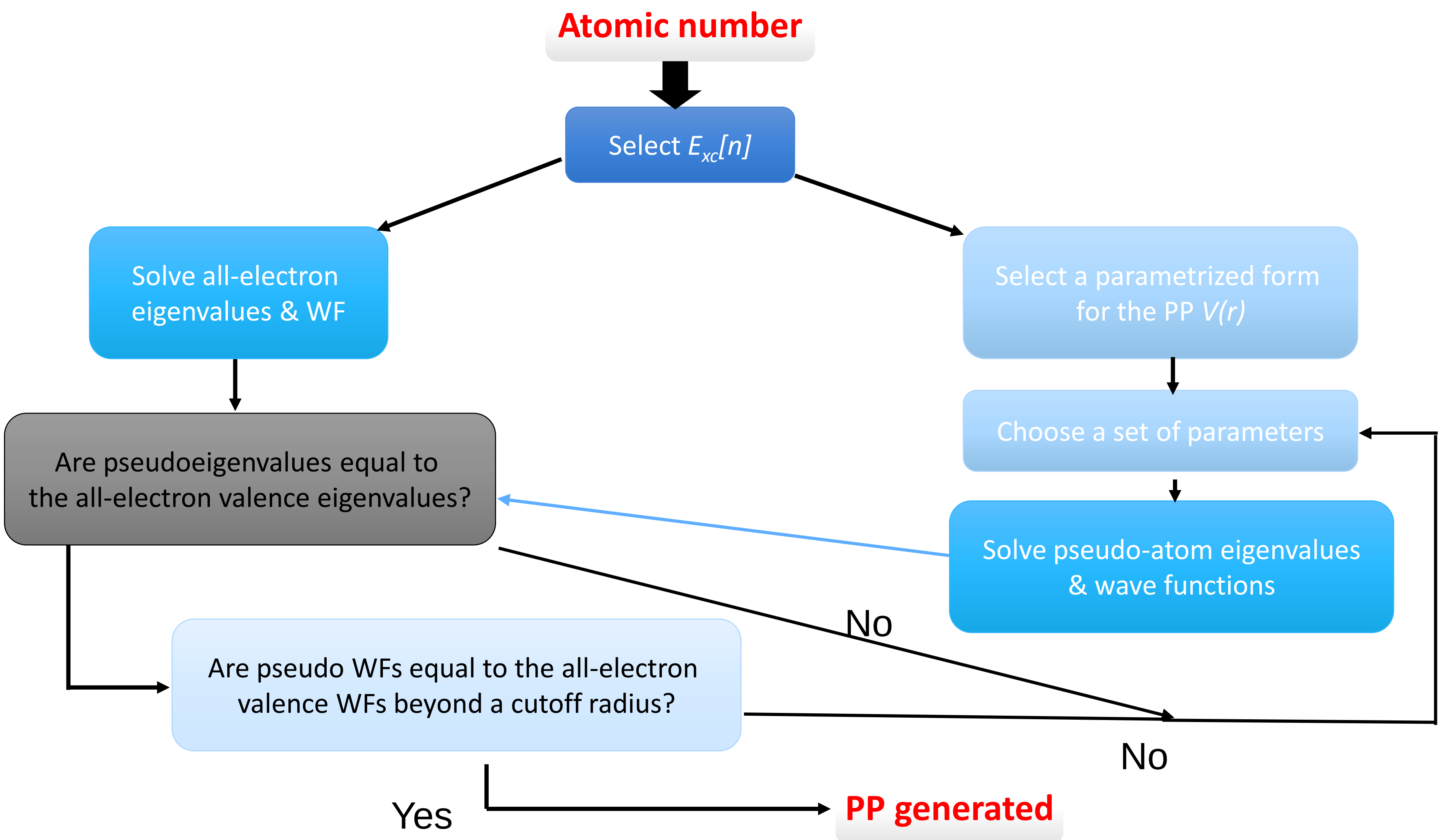
- first-row elements and TM (tightly bound orbital)

Vanderbilt (1990): Relaxing the norm conservation of the pseudopotential.

Wave function: expanded using a much smaller PW basis set.

Charge deficiency: modification needed

Construct a pseudopotential (isolated atom)



Advantages of Pseudopotential Method

- Much fewer plane waves basis states
- Removal of the core electrons: fewer electronic WFs
- Total energy: a thousand times smaller than that of all-electron system. Accuracy increases!

✓ Only total energy differences are meaningful!

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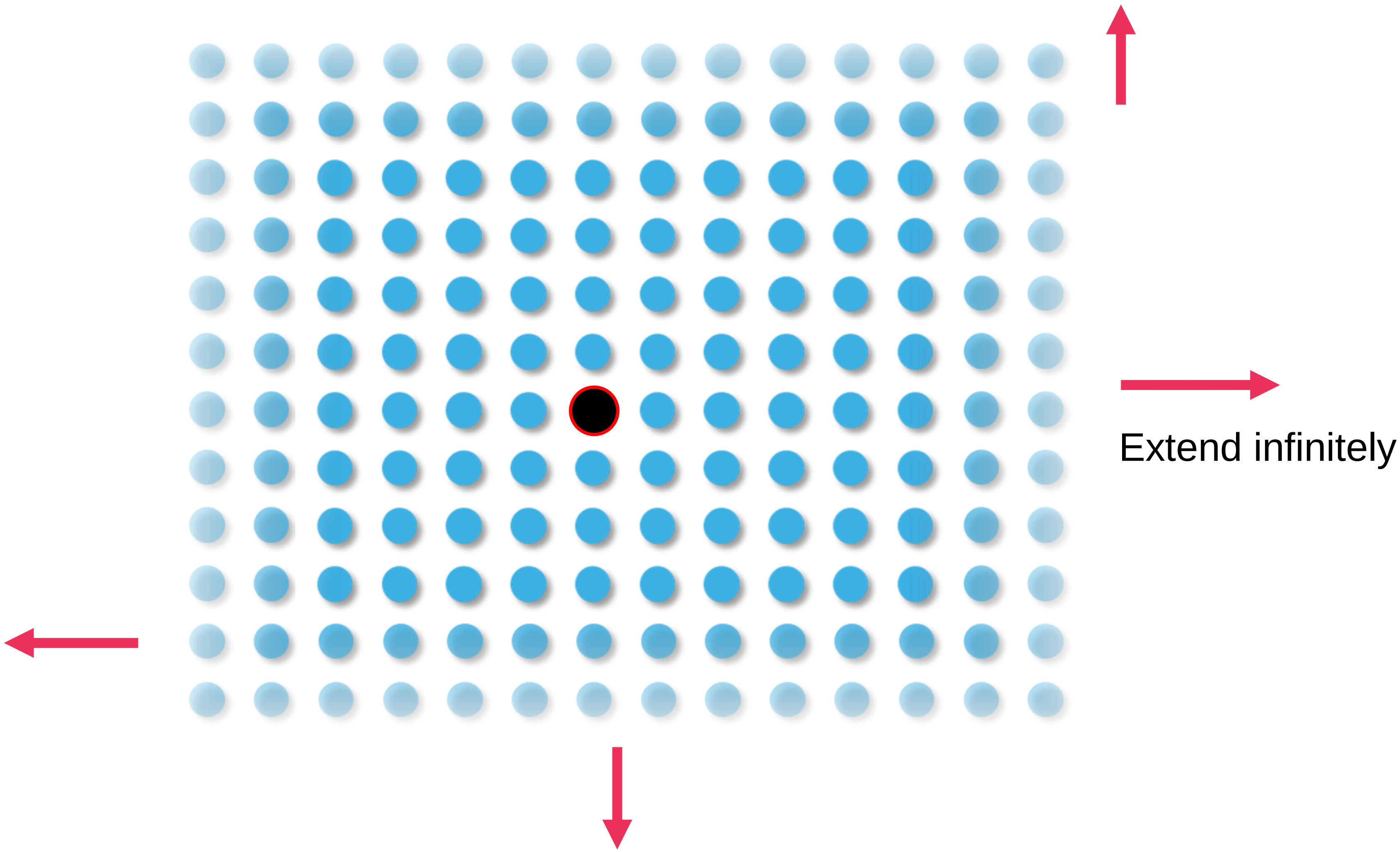
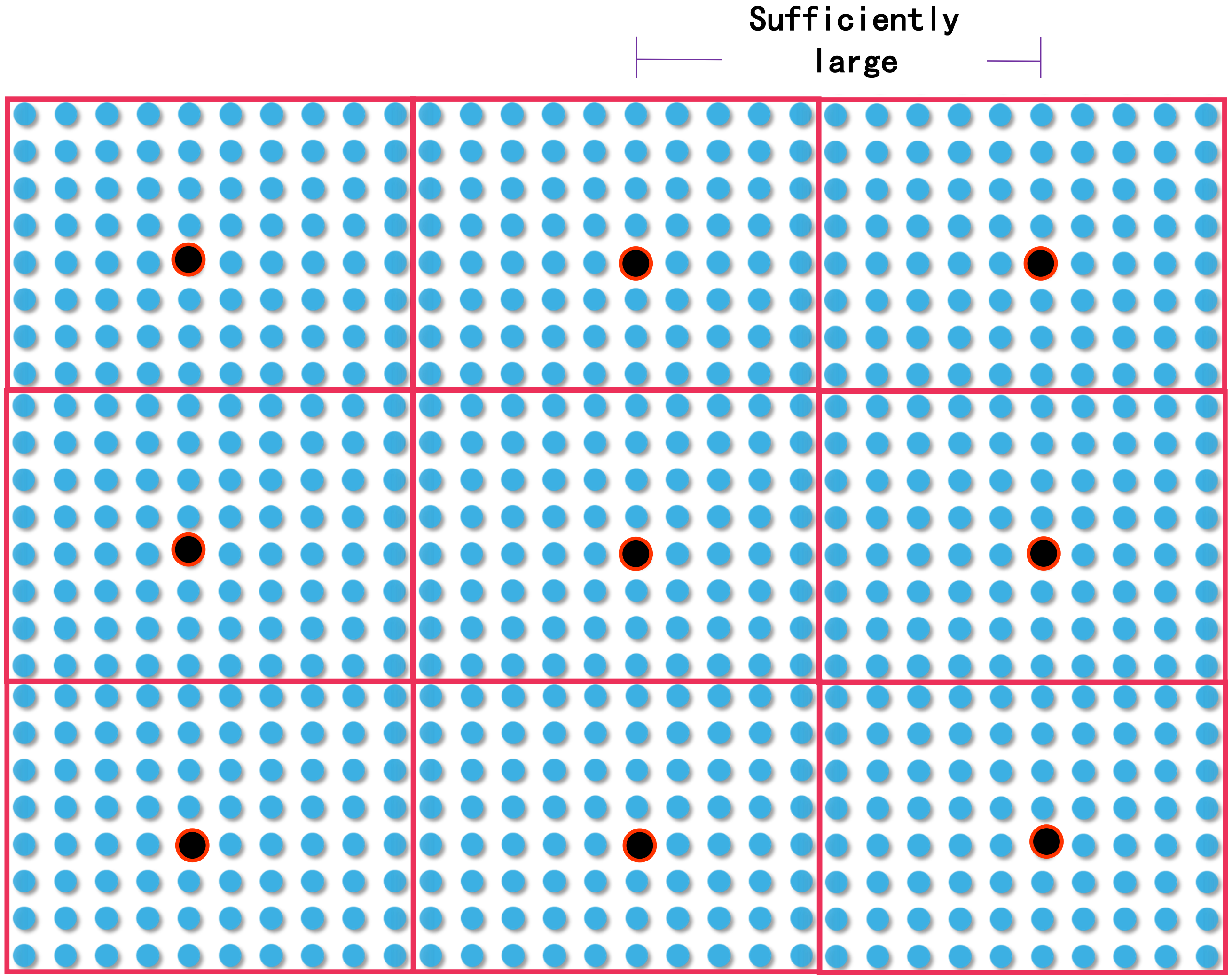
Supercell approximation for aperiodic system
(defect system)

Concept of supercell

point defect: vacancy/impurity (H/He)

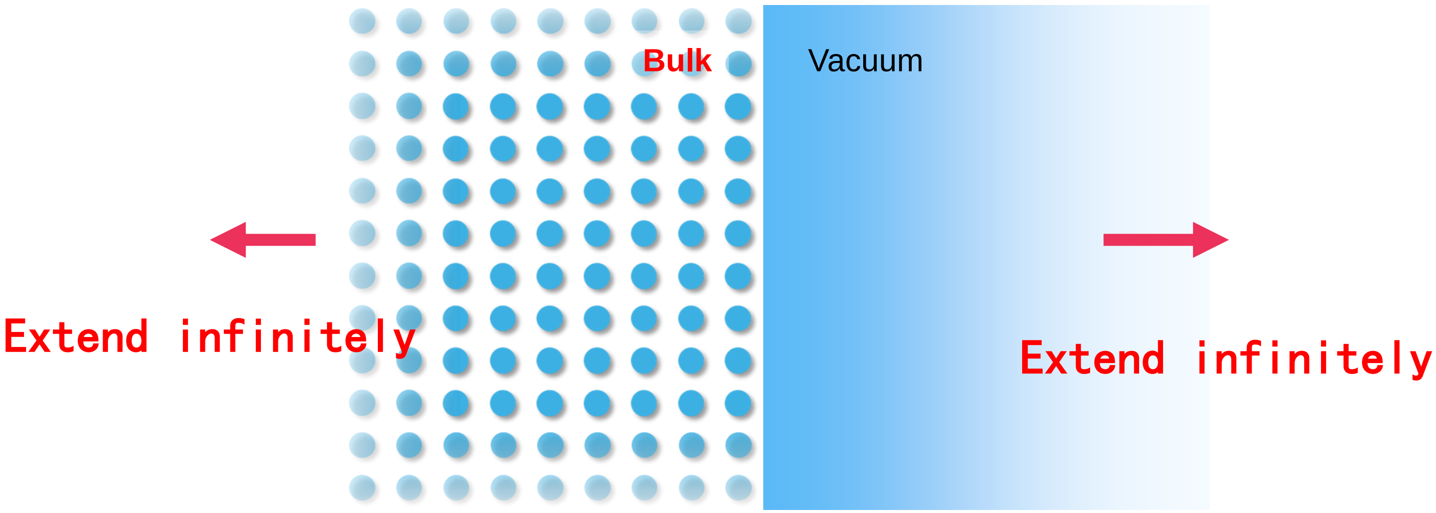


Equivalent unit cell for computation: supercell

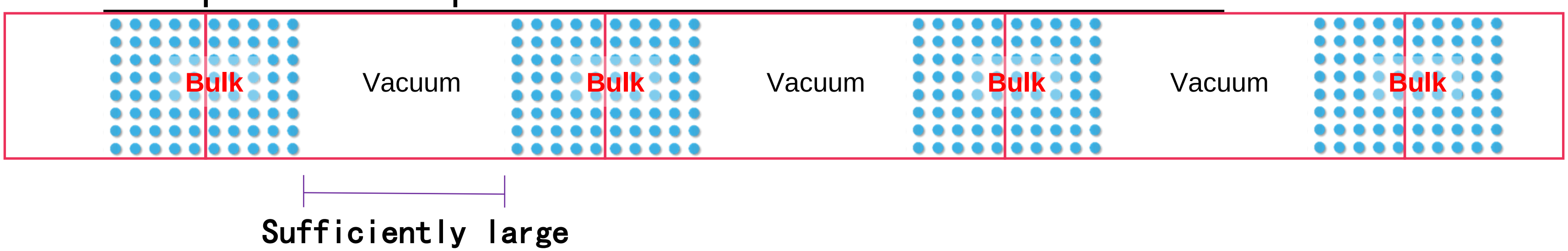


Surface: slab supercell

Ideal surface model



Computational supercell



Supercell: sufficiently large distance

Nonperiodic systems: supercell approximation

Bloch theorem: periodic system only

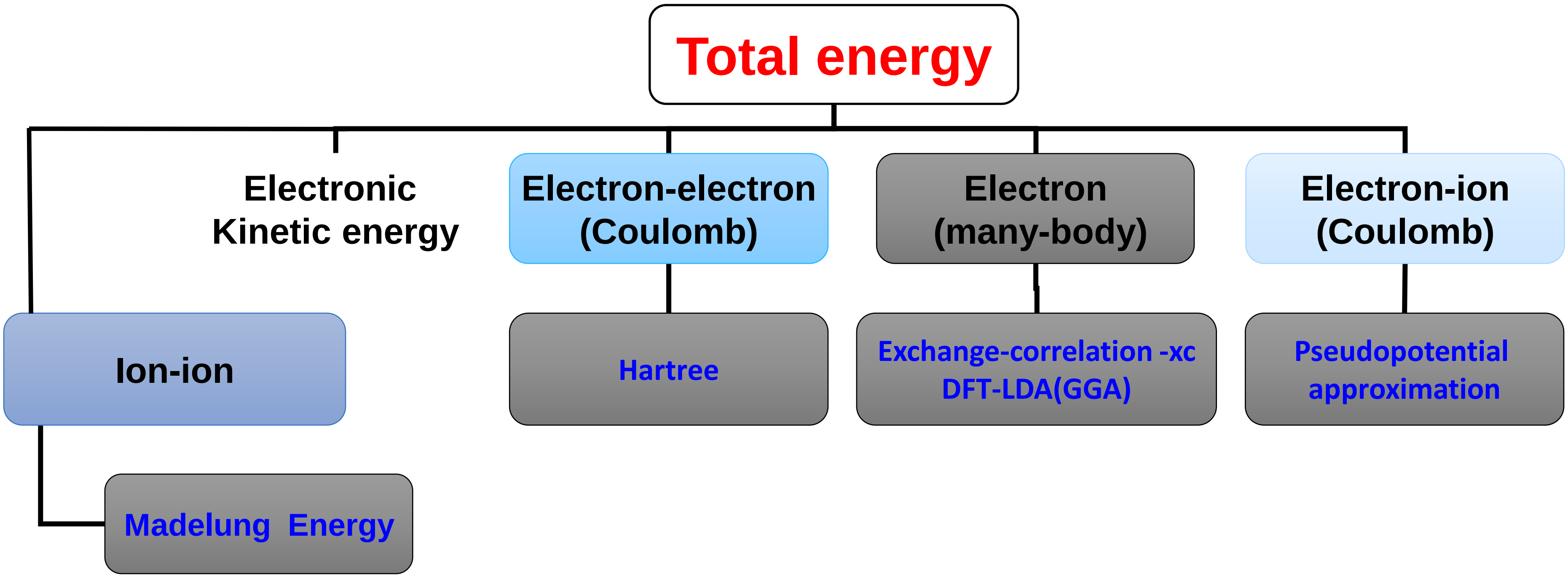
Defect or surface etc: not applicable

Supercell approximation: containing an array of defects, rather than a single defect.

Independence of defects: supercell volume

Total energy calculation

- Five parts consists of total energy



Now computation tractable?

Answer is still No.

Conventional matrix diagonalization technique vs. alternative methods

Efficient computational **algorithms** minimizing Kohn-Sham energy functional needed

- Car-Parrinello Molecular Dynamics (CPMD)
- Steepest decent (SD)
- Conjugate-gradient (CG)
- RMM-DIIS (Residual Minimization - Direct Inversion in the Iterative Subspace)

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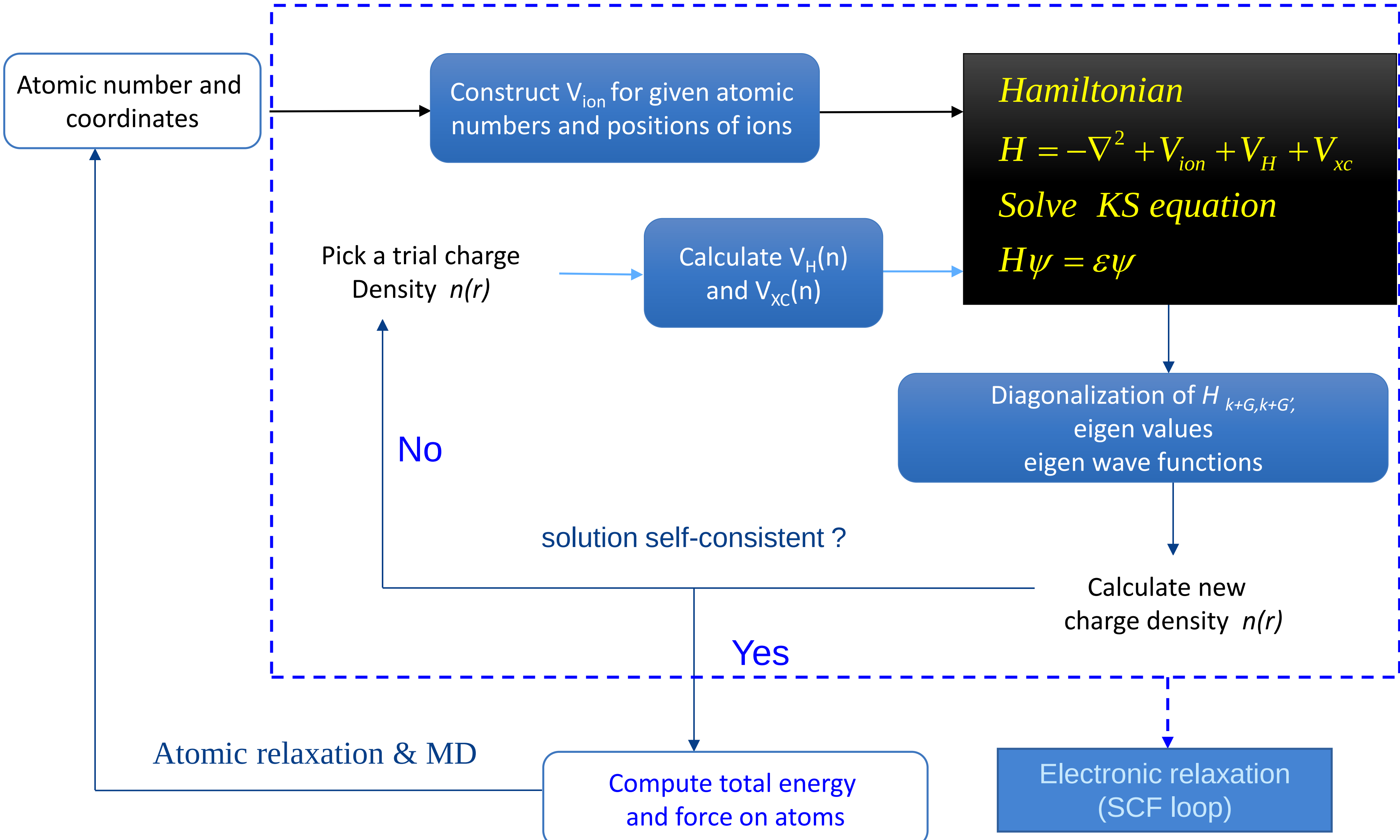
Computational procedure of FP-PP method



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Future …

First-principles pseudopotential method represents a significant fraction of the foundation of the field. Its maturity in the past few decades has given us a useful tool for understanding real materials.

There is every reason to believe that the successes will continue.

by M. L. Cohen

Major software for first-principles calculations

Periodic, DFT, Plane-wave basis set

- VASP: cms.mpi.univie.ac.at/vasp
- CASTEP: www.accelrys.com
- WIEN2K: www.wien2k.at
- ABINIT: www.abinit.org
- PWSCF: www.pwscf.org
- CPMD: www.cpmd.org

Periodic/molecule, DFT(and/or Hartree-Fock), atomic basis set

- DMol: www.accelrys.com
- ADF: www.scm.com
- Crystal03: www.crystal.unito.it
- Siesta: www.uam.es/departamentos/ciencias/fismateriac/siesta

Molecule, DFT (and/or Hartree-Fock), All-electron, atomic basis set

- Gaussian03: www.gaussian.com
- GAMESS: www.msg.ameslab.gov/GAMESS

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Thanks for your attention!