Lecture on First-principles Computation (1): General Introduction

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About the lecturer

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  (Room 506, Building of Key Laboratory of
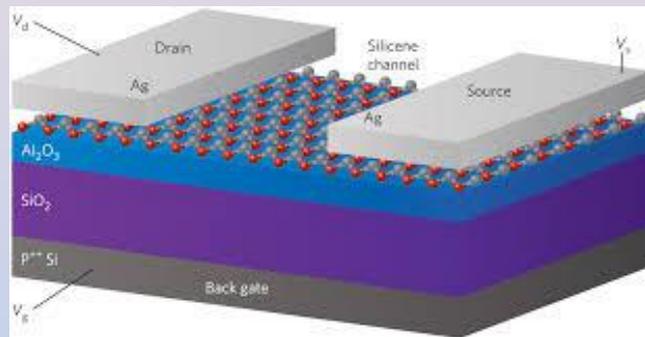 Quantum Information)

- Slides: http://lqcc.ustc.edu.cn/renxg

The triangle of scientific research:
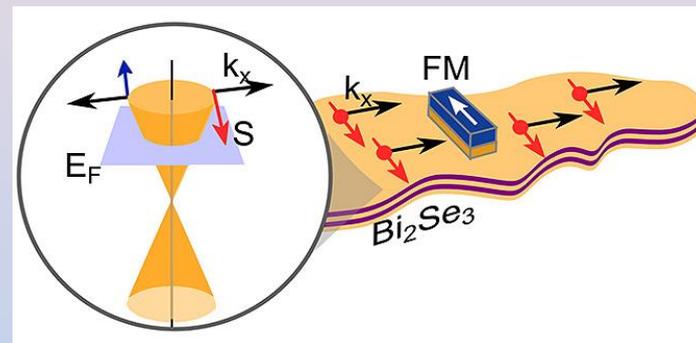# "computation" plays an increasingly important role
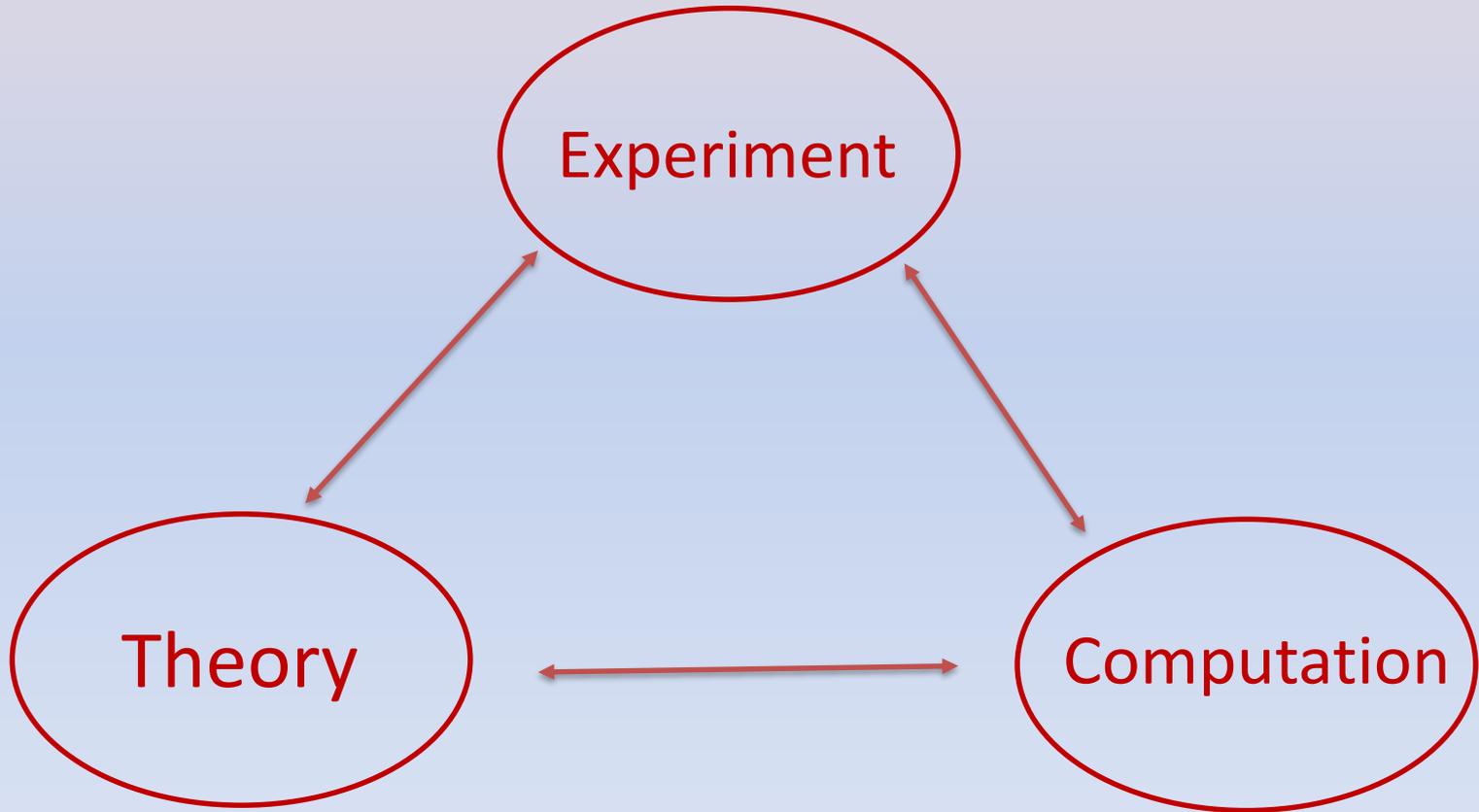
Novel functional materials are the key to address the energy and environmental challenges
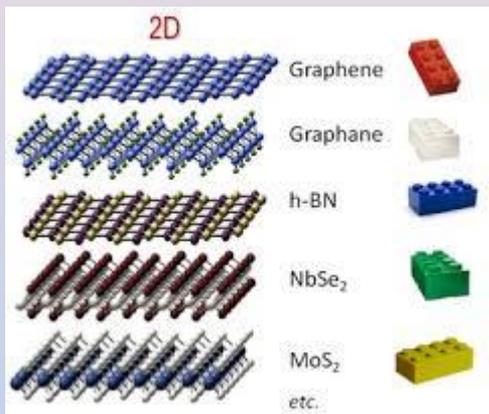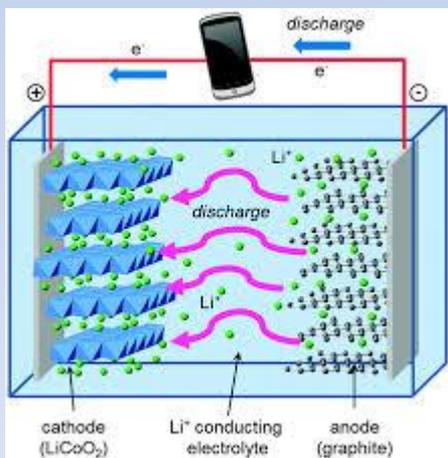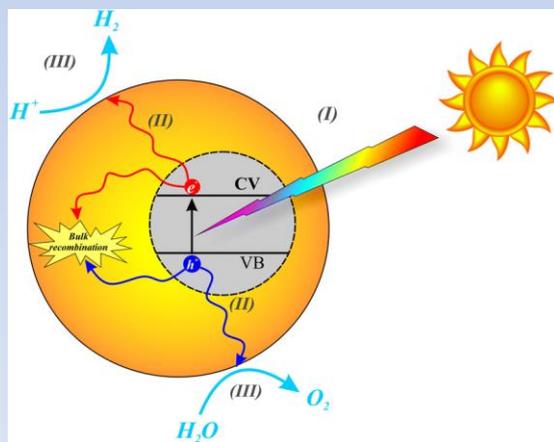

2D materials

Silicene-based transistor

Topological materials

Li-ion battery

Photocatalysis for water splitting
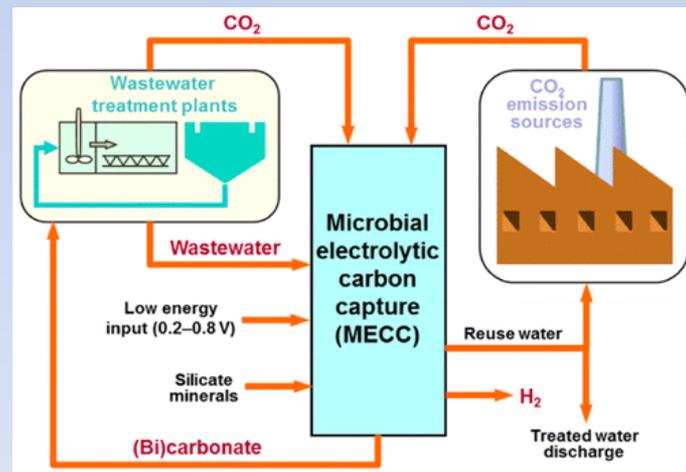
CO_2 capture/conversion

Materials simulations and novel materials design

Atomic composition & structure → Electronic structure → Physical & chemical Properties
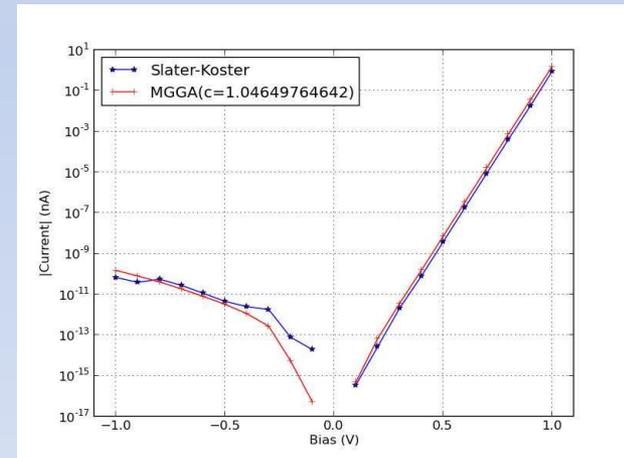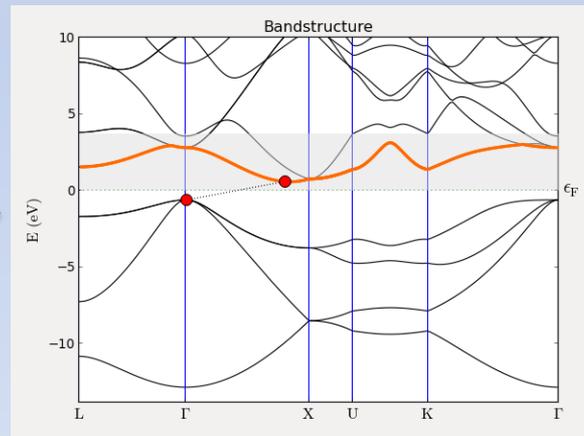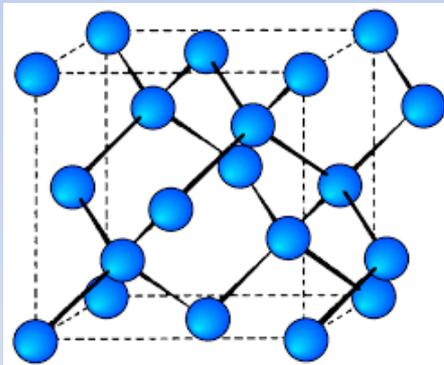
Si crystal structure

Si band structure

I-V curve

Materials design → ?

First-principles computation of molecules and condensed matter

Some key features of "first-principles computation"

- Materials are described as a collection of positively charged nuclei and negatively charged electrons

- The electronic degree of freedom is treated quantum mechanically

- Computer simulations are heavily relied upon

- Material-specific properties are accessible

- Quantitative predictions can often be achieved

Why bother to learn first-principles methods?

- First-principles computations play an increasingly important role in chemistry, condensed-matter physics, materials science, and even biology.

- The discovery and/or design of novel materials is the key to solve the energy and environmental problems that the human society is facing. First-principles computations, especially high throughput computations can help to significantly reduce the time and cost for designing and discovering novel materials.

- To understand better what have been computed, it is necessary to understand the methodologies behind the computations.

Materials genome project:
the materials innovation infrastructure

First principles computations
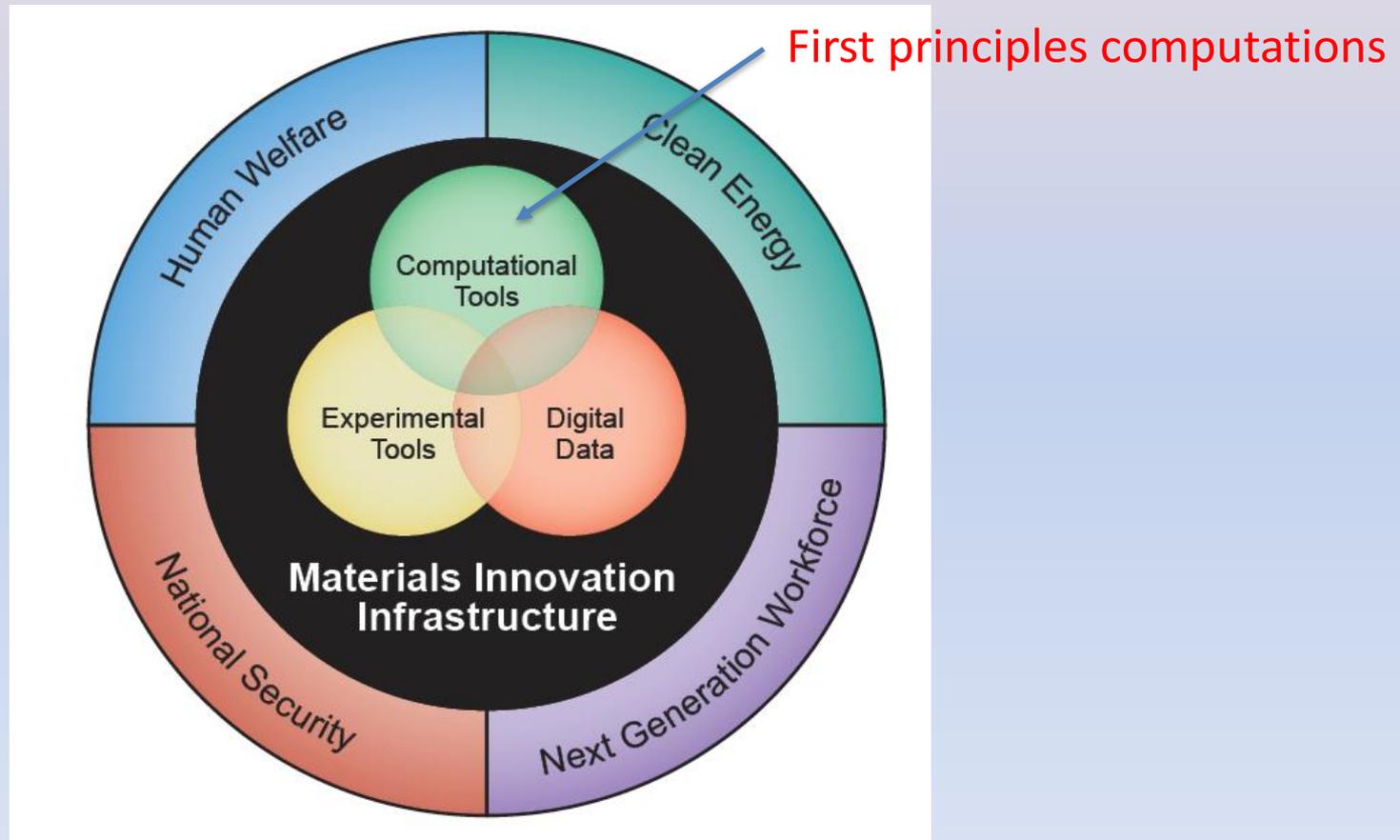
From the presentation by Dr. Cyrus Wadia,
http://www.whitehouse.gov/mgi

Many-body interacting Hamiltonian for condensed matter physics, chemistry, and materials science

$$\hat{H} = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j}^{N_e} \frac{e^2}{|r_i - r_j|}$$

The electron part

$$-\sum_{\alpha=1}^{N_{nul}} \frac{\nabla_\alpha^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha \neq \beta}^{N_{nul}} \frac{Z_\alpha Z_\beta e^2}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}$$

The nuclei part

$$-\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_{nul}} \frac{Z_\alpha e^2}{|r_i - \boldsymbol{R}_\alpha|}$$

The electron-nuclei attraction

The Schrödinger equation:

$$\hat{H}\Psi_{\boldsymbol{k}}(\{r_i\}, \{\boldsymbol{R}_\alpha\}) = E_k \Psi_{\boldsymbol{k}}(\{r_i\}, \{\boldsymbol{R}_\alpha\})$$
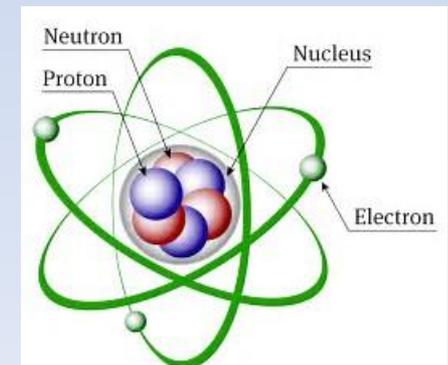
Dirac's remarks (1929)

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.
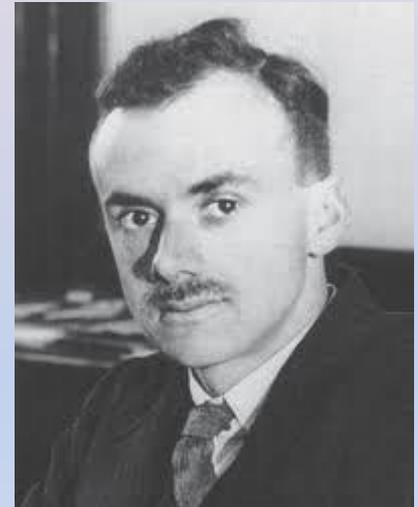
The Born-Oppenheimer approximation

$$\widehat{H}^e = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j}^{N_e} \frac{e^2}{|r_i - r_j|} + \sum_i^{N_e} V^{ext}_{\{R_\alpha, Z_\alpha\}}(r_i)$$

$$V^{ext}_{\{R_\alpha, Z_\alpha\}}(r) = -\sum_{\alpha=1}^{N_{nul}} \frac{Z_\alpha e^2}{|r - R_\alpha|}$$ is the external potential due to the nuclei.

Often the nuclear potential is treated classically.

The "*external*" potential contains the information about the positions and species of the constituted atoms, and hence specifies the actual systems, may they be atoms, molecules, solids, surfaces, clusters, nanostructure ……

The Born-Oppenheimer approximation is not always valid, but it is an useful approximation in many situations. Here we simply assume its validity.

The *ab-initio* electronic many-body Hamiltonian

$$\hat{H}^e = -\sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_i^{N_e} V_{\{\boldsymbol{R}_i, Z_i\}}^{ext}(\boldsymbol{r}_i)$$

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

The ground state and excited states of the electronic Hamiltonian determine most properties of materials. The solution of the electronic Hamiltonian is often called the "*electronic structure*".

Despite the considerable simplification that the Born-Oppenheimer approximation brings, the computational challenge remains. The exact solution of the interacting many-body Hamiltonian is not accessible even numerically for *O(N)*>10.

Further simplification/approximation is a must!

Materials' properties are largely determined by their electronic structures

- Ground state ➡️
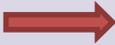
  Cohesive energies, lattice constants, bulk moduli, elastic coefficients, phonon spectra, magnetic ordering, static electric/magnetic susceptibility, structural phase transition, etc.

- Excited States ➡️

  Specific heat, Pauli spin susceptibility, photoemission spectra, optical adsorption spectra, energy gaps, transport properties, thermodynamic phase transition, etc.

  The key in first-principle computations is to calculate the electronic structure of materials.

Side remark: the role of nuclear motions

- The motions of nuclei need to considered for dynamical problems, e.g., crystal growth, atom/molecules hoping on surfaces, phase transition, chemical reaction, ion mobility, diffusion of impurities, etc.

- The motion of electrons occurs at microscopic scales (10^{-9} m in length, 10^{-15} s in time). However, to understand certain properties of composite materials (e.g., the hardness of an alloy), we need to go to mesoscopic or even macroscopic scales. In these case, a multi-scale modeling is often necessary.

Different ways to approximately treat the many-body Hamiltonian

- Model Hamiltonian approaches

- Mean-field methods

- Density-functional theory (DFT)

- Many-body perturbation theory (MBPT)

- Quantum chemistry (wave-function based) methods

- Quantum Monte Carlo (MC) methods

- …...

What will be covered in this course

- Basic concepts and method of condensed matter (solid state) physics (2 weeks)

- Density-Functional Theory (8 weeks)
  concepts, approximation, implementation, application

- Many-body Perturbation Theory and Green Function Theory (4 weeks）

- Dynamical Mean-Field Theory (DMFT) (1 week)
  LDA+DMFT and its application in real materials

- Summery (1 week)

Reference books

1. Richard M. Martin, *"Electronic Structure: Basic Theory and Practical Methods"*, (Cambridge 2004)

2. Kieron Burke, *"The ABC of DFT"*,

3. Alexander L. Fetter and John Dirk Walecka, "Quantum Theory of Many-Particle Systems" (Dover, 2003)

Basic knowledge of quantum mechanics

For a quantum system in its eigenstate $|\Phi\rangle$, the value of an physical quantity measured experimentally corresponds to the expectation value of the corresponding operator with respect to the state in question.

$$O = \langle\Phi|\hat{O}|\Phi\rangle, \langle\Phi|\Phi\rangle = 1$$

For example, the electron density operator

$$\hat{n}(\boldsymbol{r}) = \sum_{i}^{N_e} \delta(\boldsymbol{r} - \boldsymbol{r}_i)$$

The electron density:

$$n(\boldsymbol{r}) = \left\langle\Phi\left|\sum_{i}^{N_e} \delta(\boldsymbol{r} - \boldsymbol{r}_i)\right|\Phi\right\rangle = N_e \int d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_{N_e}\left|\Phi(\boldsymbol{r}, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_{N_e})\right|^2$$

From now on, we set $N_e = N$ for simplicity.

Basic knowledge of quantum mechanics

For a quantum system in its eigenstate $|\Phi\rangle$, the value of an physical quantity measured experimentally corresponds to the expectation value of the corresponding operator with respect to the state in question.

$$O = \langle\Phi|\hat{O}|\Phi\rangle, \langle\Phi|\Phi\rangle = 1$$

The ground-state energy of the electronic system:

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

$$E_0 = \langle\Phi_0|\hat{H}^e|\Phi_0\rangle = \langle\hat{T} + \hat{V}_{ee}\rangle + \langle\hat{V}_{ext}\rangle$$

$$= \langle\hat{T} + \hat{V}_{ee}\rangle + \int v_{ext}(\boldsymbol{r})n(\boldsymbol{r})d\boldsymbol{r}$$

Note: $\hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(\boldsymbol{r}_i), n(r) = \langle\Phi_0|\sum_i^N \delta(\boldsymbol{r} - \boldsymbol{r}_i)|\Phi_0\rangle$

The Hartree approximation

The evaluation of $\langle \Phi_0 | \hat{T} + \hat{V}_{ee} | \Phi_0 \rangle$ is too difficult (intractable) for a true many-body wave function.

To simply the problem, D. Hartree introduced the following approximation in 1927:

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N) = \varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)\cdots\varphi_N(\boldsymbol{r}_N)$$

Douglas Hartree

i.e., the particles are viewed as independent of one another

Now the ground-state energy:

$$E_0 = \langle \Phi | \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} | \Phi \rangle$$

$$= \sum_{n=1}^{N} \left\langle \varphi_n \left| -\frac{\nabla^2}{2m} \right| \varphi_n \right\rangle + \frac{1}{2} \sum_{m \neq n}^{N} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{|\varphi_n(\boldsymbol{r})|^2 |\varphi_m(\boldsymbol{r})|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + \int v_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r}$$

The Hartree approximation

$$E = \sum_{n=1}^{N} \left\langle \varphi_n \left| -\frac{\nabla^2}{2m} \right| \varphi_n \right\rangle + \frac{1}{2} \sum_{m \neq n}^{N} \iint d\boldsymbol{r} d\boldsymbol{r}' \frac{|\varphi_n(\boldsymbol{r})|^2 |\varphi_m(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + \int v_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) d\boldsymbol{r}$$

$$n(\boldsymbol{r}) = \sum_{n=1}^{N} |\varphi_n(\boldsymbol{r})|^2 = \sum_{n=1}^{N} \varphi_n^*(\boldsymbol{r}) \varphi_n(\boldsymbol{r})$$

Minimizing $E = E[\varphi_n]$ with respect to $\varphi_n^*(\boldsymbol{r})$ under the constraint that $\langle \varphi_n | \varphi_m \rangle = \delta_{nm}$,

$$\frac{\delta}{\delta \varphi_n^*} \left\{ E[\varphi_n] - \sum_{n,m} \epsilon_{nm} [\langle \varphi_n | \varphi_m \rangle - \delta_{nm}] \right\} = 0$$

one obtains the Hartree equation:

$$\left[-\frac{\nabla^2}{2m} + \sum_{m \neq n}^{N} \int d\boldsymbol{r}' \frac{|\varphi_m(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{ext}(\boldsymbol{r}) \right] \varphi_n(\boldsymbol{r}) = \sum_m \epsilon_{nm} \varphi_m(\boldsymbol{r})$$

The *canonical* Hartree equation

The Hartree equation:

$$\left[-\frac{\nabla^2}{2m} + \sum_{m \neq n}^{N} \int d\boldsymbol{r}' \frac{|\varphi_m(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{ext}(\boldsymbol{r}) \right] \varphi_n(\boldsymbol{r}) = \sum_m \epsilon_{nm} \varphi_m(\boldsymbol{r})$$

We can define a unitary transformation U such that

$$U_{n'n} \, \epsilon_{nm} \, U_{mm'} = \tilde{\epsilon}_{n'} \delta_{m'n'}$$

and introduce $\quad \tilde{\varphi}_m(\boldsymbol{r}) = \sum_{m'} U_{mm'} \, \varphi_{m'}(\boldsymbol{r})$, then   "Canonicalization"

$$\left[-\frac{\nabla^2}{2m} + \sum_{m \neq n}^{N} \int d\boldsymbol{r}' \frac{|\tilde{\varphi}_m(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} + v_{ext}(\boldsymbol{r}) \right] \tilde{\varphi}_n(\boldsymbol{r}) = \tilde{\epsilon}_n \tilde{\varphi}_n(\boldsymbol{r})$$

This equation is called the *canonical* Hartree equation.