t u nh n

Chương 3 c phương p *ab initio*

3.1 p Hartree-Fock

3.2 c m m va o m a ng

3.3 nh ly Hohenberg-Kohn

3.4 c phương nh Kohn-Sham

3.5 c m m trao i tương quan

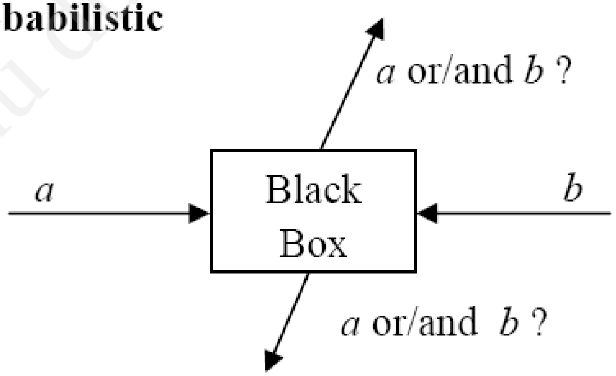
3.1 p Hartree-Fock

3.1.1 Sự phản đối xứng và nguyên lý loại trừ Pauli

Các hạt đồng nhất (Identical particles)

Classically: Two possibilities - <u>Deterministic</u>

Quantum Mechanically: - Probabilistic



Các hạt đồng nhất phải có cùng:

- **Điện tích**
- **Spin**
- **Khối lượng**

Mật xác suất tìm thấy hạt: $dP = |\psi(x_1, x_2)|^2 dx_1 dx_2 = |\psi(x_2, x_1)|^2 dx_1 dx_2$

$\psi(x_2, x_1)$: hàm sóng của hệ hạt 2 và 1

$\psi(x_1, x_2)$: hàm sóng của hệ hạt 1 và 2

⇒ $|\psi(x_1, x_2)|^2 = |\psi(x_2, x_1)|^2$

$\psi(x_1, x_2) = \pm\psi(x_2, x_1)$

Không thể phân biệt được các hạt đồng nhất

Hàm sóng của hệ là tổ hợp tuyến tính:

$$\psi = \psi(x_1, x_2) \pm \psi(x_2, x_1)$$

- : Phản đối xứng, Fermion (spin bán nguyên)

+ : Đối xứng, Boson (spin nguyên)

Hai hạt không tương tác và có spin $n_{1,2}$

$$\psi(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2)$$

$$\psi(x_2, x_1) = \psi_{n_1}(x_2)\psi_{n_2}(x_1)$$

tổ hợp tuyến tính $\psi = \psi_{n_1}(x_1)\psi_{n_2}(x_2) \pm \psi_{n_1}(x_2)\psi_{n_2}(x_1)$

Xét hai electron (Fermion) có cùng spin $n_1 = n_2$

$$\psi = \psi_{n_1}(x_1)\psi_{n_1}(x_2) - \psi_{n_1}(x_2)\psi_{n_1}(x_1) = 0$$

Xét hai electron (Fermion) có spin $n_1 \neq n_2$

$$\psi = \psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\psi_{n_2}(x_1) \neq 0$$

Nguyên lý loại trừ Pauli

Định thức Slater

Ở điều kiện chuẩn hóa hàm sóng:

$$\psi = \frac{1}{\sqrt{2!}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\psi_{n_2}(x_1)\right]$$

$$= \frac{1}{\sqrt{2!}}\begin{vmatrix} \psi_{n_1}(x_1) & \psi_{n_2}(x_1) \\ \psi_{n_1}(x_2) & \psi_{n_2}(x_2) \end{vmatrix}$$

Trường hợp hệ có N hạt đồng nhất không tương tác:

$$\psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{n_1}(x_1) & \psi_{n_2}(x_1) & \dots & \psi_{N}(x_1) \\ \psi_{n_1}(x_2) & \psi_{n_2}(x_2) & \dots & \psi_{N}(x_2) \\ \dots & \dots & \dots & \dots \\ \psi_{n_1}(x_N) & \psi_{n_2}(x_N) & \dots & \psi_{N}(x_N) \end{vmatrix}$$

Materials are composed of nuclei $\{Z_\alpha, M_\alpha, R_\alpha\}$ and electrons $\{r_i\}$ the interactions are known

$$H = -\sum_{\alpha} \frac{\hbar^2 \nabla_\alpha^2}{2M_\alpha} - \sum_{i} \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2} \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy of nuclei

Kinetic energy of electrons

Nucleus-Nucleus interaction

Electron-Nucleus interaction

Electron-Electron interaction

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

Ab-initio (first principles) Method – ONLY Atomic Numbers $\{Z_i\}$ as input parameters

3.1.2 Born-Oppenheimer Approximation

- Hamiltonian of the coupled electron-ion system

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}}.$$

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}),$$

- Difference in time scales of ionic and electronic motions
  - Electrons respond instantaneously to slow ionic motion

$$\frac{m_N}{m_e} \geq \frac{m_p}{m_e} \approx 1839$$

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

- Decoupled Schrödinger equations

$$\begin{aligned}[T_e + V_{ee} + V_{eI}(\{\mathbf{R}_I\})]\Psi_n(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) &= \varepsilon_n(\{\mathbf{R}_I\})\Psi_n(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) \\ [T_I + V_{II} + \varepsilon_n(\{\mathbf{R}_I\})]\chi(\{\mathbf{R}_I\}) &= E\chi(\{\mathbf{R}_I\})\end{aligned}$$

- Adiabatic approximation
  - Electrons quickly respond to changes of nuclei, thus allowing the electronic system to remain in its ground state
  - Ions move on the potential-energy surface of the electronic ground state

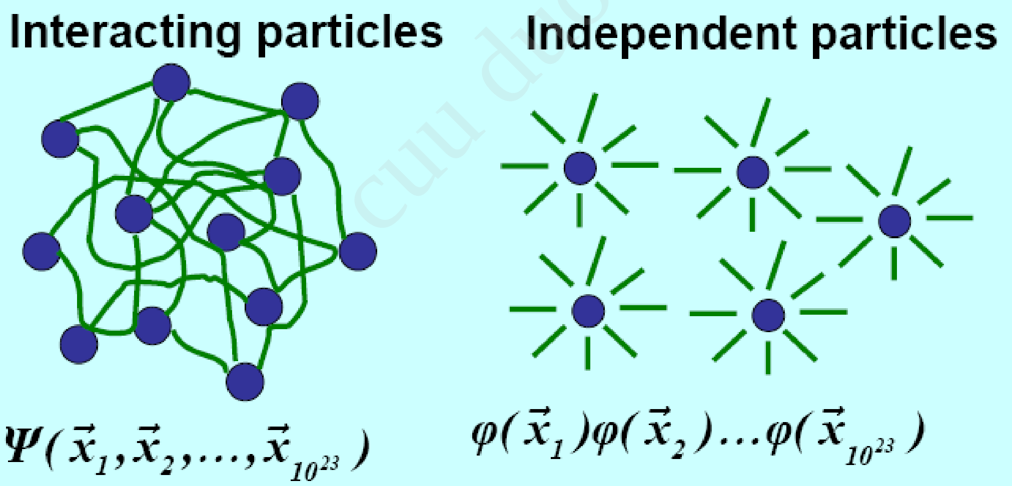
$$\begin{aligned}[T_e + V_{ee} + V_{eI}(\{\mathbf{R}_I\})]\Psi_0(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) &= \varepsilon_0(\{\mathbf{R}_I\})\Psi_0(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) \\ [T_I + V_{II} + \varepsilon_0(\{\mathbf{R}_I\})]\chi(\{\mathbf{R}_I\},t) &= i\hbar\frac{\partial}{\partial t}\chi(\{\mathbf{R}_I\},t)\end{aligned}$$

3.1.3 Xấp xỉ trường trung bình (effective potential)

- We still have to solve *many*-electron problem.
  - Exchange property: Pauli exclusion principle
  - Correlation property: interacting electrons

$$\mathcal{H}\Psi(\{\mathbf{r}_i\}) = \varepsilon\Psi(\{\mathbf{r}_i\})$$

$$\mathcal{H} = -\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + \sum_i V_{\text{ion}}(\mathbf{r}_i) + \frac{e^2}{2}\sum_{j\neq i}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



Idea: consider electrons as independent particles moving in an effective potential

- **Single-particle approach in an effective potential**
  - Exchange and Correlation effects are treated in an average way
  - Hartree approximation
  - Hartree–Fock approximation
  - Density functional theory

3.1.4 Phương pháp Hartree

In the Born–Oppenheimer approximation, the time-independent nonrelativistic. Hamiltonian of the *n*-interacting-particle system is written in atomic units as:

$$\hat{H}^{\mathrm{el}} = \sum_{i=1}^{n} -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{n}\sum_{\alpha}^{M} \frac{Z_A}{r_{i\alpha}} + \frac{1}{2}\sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{1}{r_{ij}}$$

$$= \sum_{i=1}^{n} \left(\hat{T}_i + \hat{V}_{i\alpha} + \frac{1}{2}\hat{V}_{ij} \right)$$

Fock operator $\hat{H}^{el} = \sum_{i=1}^{n} \left(\hat{T}_i + \hat{V}_{i\alpha} + \frac{1}{2}\hat{V}_{ij} \right)$

$$= \sum_{i=1}^{n} \left(\hat{h}_i + \frac{1}{2}\sum_{j\neq i} \hat{V}_j \right) = \sum_{i=1}^{n} \hat{F}_i$$

Hartree product

$$\Psi_n(x_1, x_2, \ldots, x_n) = \Pi_i \phi_i(x_i)$$ n – particle wavefunction

$$= \phi_i(x_1)\phi_j(x_2)\ldots\phi_n(x_n)$$

n occupied spin orbitals of the system:

$$\phi_i(x_i) = \phi_i(r_i)\sigma_i$$

also written as:

$$\phi_i = \phi_i(r_i)\alpha_i$$

$$\bar{\phi}_i = \phi_i(r_i)\beta_i$$

Xấp xỉ **LCAO** (Linear combination of atomic orbitals)

$$\phi_i(x_i) = \sum_j c_{ij}\chi_j(x_i)$$ χ_j basis set.

Hartree energy $E^H[\phi] = \langle \Psi_n \mid \sum_{i=1}^{n} \hat{F}_i \mid \Psi_n \rangle$

$$= \langle \phi_i(x_1) \ldots \phi_n(x_n) \mid \sum_{i=1}^{n} \hat{F}_i \mid \phi_i(x_1) \ldots \phi_n(x_n) \rangle$$

$$= \sum_{i=1}^{n} \left(e_i + \frac{1}{2} \sum_{j \neq i} J_{ij} \right)$$

$$e_i = \langle \phi_i(x_1) \mid \hat{h}_1 \mid \phi_i(x_1) \rangle$$

$$= \int dx_1 \, \phi_i^*(x_1) \hat{h}_1 \phi_i(x_1)$$

$J_{ij} = \langle \phi_i(x_1)\phi_j(x_2) \mid \frac{1}{r_{12}} \mid \phi_i(x_1)\phi_j(x_2) \rangle$ ***: Coulomb integral***

$$= \int \int dx_1 dx_2 \, \phi_i^*(x_1)\phi_i(x_1) \frac{1}{r_{12}} \phi_j^*(x_2)\phi_j(x_2)$$

Giản đồ phương pháp Hartree

Self consistent field **(SCF)**

LCAO

$$\phi_i(x_i) = \sum_j c_{ij}\chi_j(x_i)$$

Xác định các hệ số c_{ij}

$$|\underline{\underline{\mathrm{H}}}^{\mathrm{el}} - E\underline{\underline{S}}| = 0$$

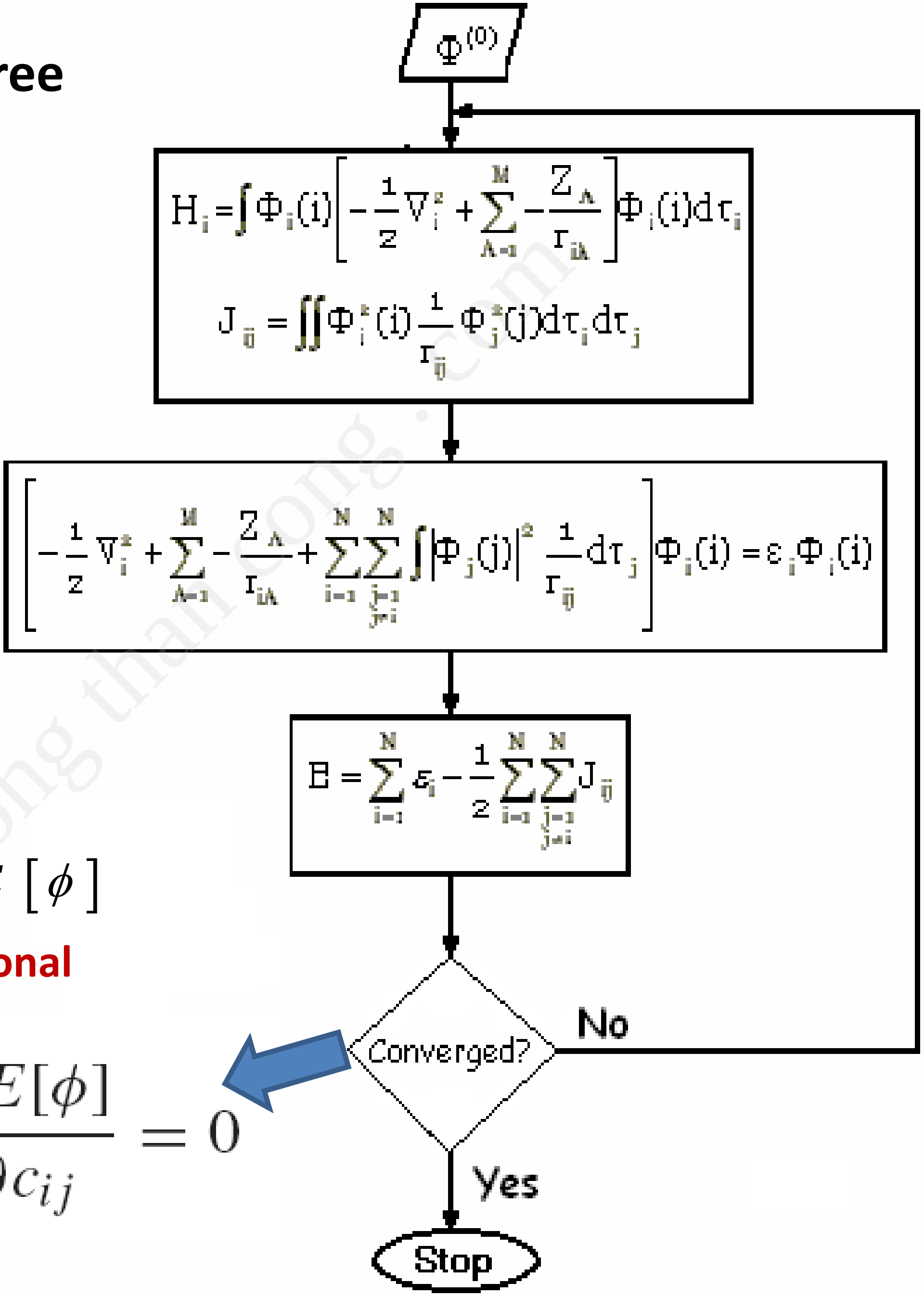
Coulomb integral

$$E = E[\phi]$$

functional

Iterative procedure of SCF

$$\frac{\partial E[\phi]}{\partial c_{ij}} = 0$$



$$\Phi^{(0)}$$

$$H_i = \int \Phi_i(i)\left[-\frac{1}{2}\nabla_i^2 + \sum_{A=1}^{M} -\frac{Z_A}{r_{iA}}\right]\Phi_i(i)\,d\tau_i$$

$$J_{ij} = \iint \Phi_i^*(i)\frac{1}{r_{ij}}\Phi_j^*(j)\,d\tau_i\,d\tau_j$$

$$\left[-\frac{1}{2}\nabla_i^2 + \sum_{A=1}^{M} -\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N}\int|\Phi_j(j)|^2\frac{1}{r_{ij}}\,d\tau_j\right]\Phi_i(i) = \varepsilon_i\Phi_i(i)$$

$$E = \sum_{i=1}^{N}\varepsilon_i - \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\ j\neq i}}^{N} J_{ij}$$

3.1.5 Phương pháp Hartree-Fock

This wavefunction is an antisymmetrised product of one-electron wavefunctions, the so-called ***Slater determinant***

$$\Psi_n(x_1, x_2, \ldots, x_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & \ldots & \phi_n(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & \ldots & \phi_n(x_2) \\ \ldots & \ldots & \ldots & \ldots \\ \phi_1(x_n) & \phi_2(x_n) & \ldots & \phi_n(x_n) \end{vmatrix}$$

Hartree–Fock energy:

$$E^{\mathrm{HF}}[\phi] = \langle \Psi_n \mid \sum_{i=1}^{n} \hat{F}_i \mid \Psi_n \rangle$$

$$= \sum_{i=1}^{n} \left\{ e_i + \frac{1}{2} \sum_{j \neq i} (J_{ij} - K_{ij}) \right\}$$

$\phi_i(x_i) = \phi_i(r_i)\sigma_i$ **spin orbitals**

Two-electron integral

$$K_{ij} = \langle \phi_i(x_1)\phi_j(x_2) \mid \frac{1}{r_{12}} \mid \phi_j(x_1)\phi_i(x_2)\rangle$$

$$= \langle \phi_i(r_1)\sigma_i\phi_j(r_2)\sigma_j \mid \frac{1}{r_{12}} \mid \phi_j(r_1)\sigma_j\phi_i(r_2)\sigma_i\rangle$$

$$= \langle \phi_i(r_1)\phi_j(r_2) \mid \frac{1}{r_{12}} \mid \phi_j(r_1)\phi_i(r_2)\rangle\langle\sigma_i \mid \sigma_j\rangle\langle\sigma_j \mid \sigma_i\rangle$$

$$= \int\int dr_1 dr_2\, \phi_i^*(r_1)\phi_j(r_1)\frac{1}{r_{12}}\phi_j^*(r_2)\phi_i(r_2).\delta_{\sigma_i\sigma_j}\delta_{\sigma_j\sigma_i}$$

$$\hat{K}_j\phi_i(x_1) = \int dx_2\, \phi_j^*(x_2)\phi_i(x_2)\frac{1}{r_{ij}}\phi_i(x_1)$$ ***Exchange integral***

Hạn chế của phương pháp Hartree-Fock

The Hartree-Fock wavefunction does not include these correlation effects because it describes the electrons as moving in the average potential field of all the other electrons. The instantaneous influence of electrons that come close together at some point is not taken into account.

Các phương pháp tiến bộ :

Configuration Interaction **(CI)**

Density Functional Theory (DFT)