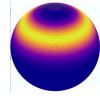


Vietnam Academy of Science and Technology
Ho Chi Minh City Institute of Physics



QuantumLab-HCMIP

Electronic structure theory for molecules and materials

Lecture 02: Orbitals and basis functions

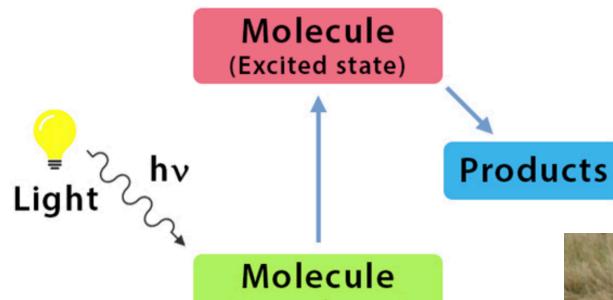
Trần Nguyên Lân, Ph.D

Email: lantrann@gmail.com, tnlan@hcmip.vast.vn

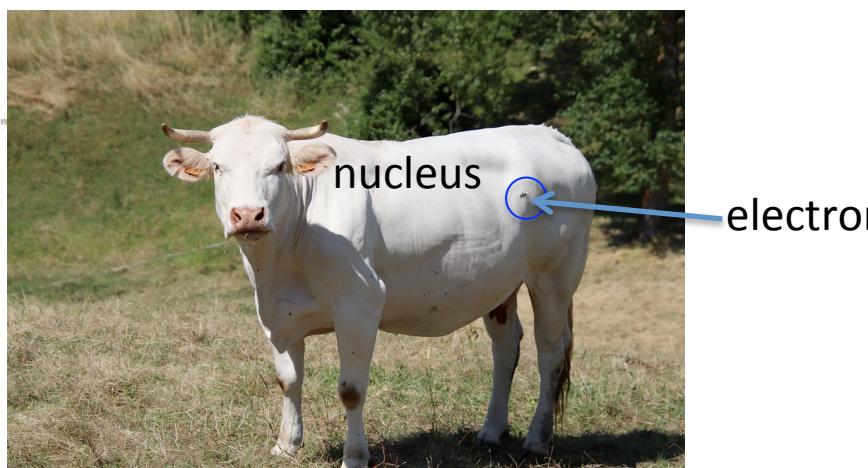
Website: <https://lantrann.github.io/QuantumLab-HCMIP/>

Reminding lecture 01

- Electronic structure theory: why and what?
- Born-Oppenheimer approximation
- Variational principle



$$E_0 \leq E[\tilde{\vec{0}}] = \frac{\langle \tilde{\vec{0}} | \hat{H} | \tilde{\vec{0}} \rangle}{\langle \tilde{\vec{0}} | \tilde{\vec{0}} \rangle}$$



Outline

- Slater determinant
- LCAO approximation
- Atomic basis sets

Slater determinant

Definition 1: an *orbital* is a wave-function for a single particle.

In molecules: molecular orbitals, in materials: crystalline orbitals

Definition 2: an *spatial orbital* is the function of the position vector \mathbf{r} and describes the spatial distribution of an electron.
Orthonormal condition:

$$\int d\mathbf{r} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij} \quad \text{with } i = 1, 2, \dots, K$$

Definition 3: a *spin orbital* is wave-function describe both its spatial distribution and spin function

$$\chi(\mathbf{x}) = \psi(\mathbf{r}) f(\omega)$$

with $\mathbf{x} = \{\mathbf{r}; \omega\}$ and

$$f(\omega) = \begin{cases} \alpha : \text{spin up} (\uparrow) \\ \beta : \text{spin down} (\downarrow) \end{cases}$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1; \quad \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$



Note: if we have K spatial orbitals,
we will have $2K$ spin orbitals!

Slater determinant

$$\int \psi_i^\alpha(\mathbf{r})\psi_j^\alpha(\mathbf{r})d\mathbf{r} = \int \psi_i^\beta(\mathbf{r})\psi_j^\beta(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Exercise 2.1 Given a set of K orthonormal spatial functions, $\{\psi_i^\alpha(\mathbf{r})\}$, and another set of K orthonormal functions, $\{\psi_i^\beta(\mathbf{r})\}$, such that the first set is not orthogonal to the second set, i.e.,

$$\int d\mathbf{r} \psi_i^{\alpha*}(\mathbf{r})\psi_j^\beta(\mathbf{r}) = S_{ij} \quad i = 1, 2, \dots, K$$

where \mathbf{S} is an overlap matrix, show that the set $\{\chi_i\}$ of $2K$ spin orbitals, formed by multiplying $\psi_i^\alpha(\mathbf{r})$ by the α spin function and $\psi_i^\beta(\mathbf{r})$ by the β spin function, i.e.,

$$\left. \begin{array}{l} \chi_{2i-1}(\mathbf{x}) = \psi_i^\alpha(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) = \psi_i^\beta(\mathbf{r})\beta(\omega) \end{array} \right\} i = 1, 2, \dots, k$$

is an orthonormal set.

Show that: $\int \chi_i(\mathbf{x})\chi_j(\mathbf{x})d\mathbf{x} = \delta_{ij}$

From textbook 2

Slater determinant

$$\int \chi_i^*(\mathbf{x}) \chi_j(\mathbf{x}) d\mathbf{x} = \begin{cases} \int \psi_i^{\alpha*}(\mathbf{r}) \alpha(\omega) \psi_j^\alpha(\mathbf{r}) \alpha(\omega) d\mathbf{r} d\omega \\ \int \psi_i^{\alpha*}(\mathbf{r}) \alpha(\omega) \psi_j^\beta(\mathbf{r}) \beta(\omega) d\mathbf{r} d\omega \\ \int \psi_i^{\beta*}(\mathbf{r}) \beta(\omega) \psi_j^\alpha(\mathbf{r}) \alpha(\omega) d\mathbf{r} d\omega \\ \int \psi_i^{\beta*}(\mathbf{r}) \beta(\omega) \psi_j^{\beta*}(\mathbf{r}) \beta(\omega) d\mathbf{r} d\omega \end{cases}$$
$$= \begin{cases} \langle \alpha | \alpha \rangle \int \psi_i^{\alpha*}(\mathbf{r}) \psi_j^\alpha(\mathbf{r}) d\mathbf{r} & \delta_{ij} \\ \langle \alpha | \beta \rangle \int \psi_i^{\alpha*}(\mathbf{r}) \psi_j^\beta(\mathbf{r}) d\mathbf{r} & 0 \\ \langle \beta | \alpha \rangle \int \psi_i^{\beta*}(\mathbf{r}) \psi_j^\alpha(\mathbf{r}) d\mathbf{r} & 0 \\ \langle \beta | \beta \rangle \int \psi_i^{\beta*}(\mathbf{r}) \psi_j^{\beta*}(\mathbf{r}) d\mathbf{r} & \delta_{ij} \end{cases} = \delta_{ij} \delta_{\alpha\beta}$$

Slater determinant

For simplicity, we consider non-interacting systems: $\hat{H} = \sum_i \hat{h}_i$

Hamiltonian \hat{h}_i will have sets of eigenfunctions $\{\chi_j\}$ and eigenvalues $\{\varepsilon_j\}$

$$\hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i);$$

We have the Schrodinger equation for the whole system of N electrons:

$$\hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

So what are the form of Ψ and E ?

Slater determinant

For simplicity, we consider non-interacting systems: $\hat{H} = \sum_i \hat{h}_i$

Hamiltonian \hat{h}_i will have sets of eigenfunctions $\{\chi_j\}$ and eigenvalues $\{\varepsilon_j\}$

$$\hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i);$$

We have the Schrodinger equation for the whole system of N electrons:

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

So what are the form of Ψ and E ?

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

$$E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

Prove :

$$\begin{aligned} & (h_1 + h_2 + \dots + h_N) \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) \\ &= h_1 \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + h_2 \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \dots + h_N \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) \\ &= \varepsilon_i \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \varepsilon_j \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \dots + \varepsilon_k \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) \end{aligned}$$

Such a many-electron wave-function is the **Hartree product** $\Psi^{\text{Hartree}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$

Uncorrelated or independent wave-function

Slater determinant

For simplicity, we consider non-interacting systems: $\hat{H} = \sum_i \hat{h}_i$

Hamiltonian \hat{h}_i will have sets of eigenfunctions $\{\chi_j\}$ and eigenvalues $\{\varepsilon_j\}$

$$\hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i);$$

We have the Schrodinger equation for the whole system of N electrons:

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

So what are the form of Ψ and E ?

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

$$E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

Prove :

$$(h_1 + h_2 + \dots + h_N) \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

$$= h_1 \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + h_2 \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \dots + h_N \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

$$= \varepsilon_i \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \varepsilon_j \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N) + \dots + \varepsilon_k \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)$$

Such a many-electron wave-function is the **Hartree product** $\Psi^{\text{Hartree}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$

Uncorrelated or independent wave-function

From the Hartree product, the probability to find electron 1 at a given position is independent of the position of electron 2.

Not true in practice!

Slater determinant

Pauli exclusion principle: A many-electron wave-function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x} = (\mathbf{r}, \omega)$ of any two electrons

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

Slater determinant

Pauli exclusion principle: A many-electron wave-function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x} = (\mathbf{r}, \omega)$ of any two electrons

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

From wikipedia:

The Pauli exclusion principle is the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) **cannot** occupy the same quantum state within a quantum system simultaneously.

Does the Hartree product satisfy the Pauli principle?

Slater determinant

Pauli exclusion principle: A many-electron wave-function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x} = (\mathbf{r}, \omega)$ of any two electrons

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

From wikipedia:

The Pauli exclusion principle is the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) **cannot** occupy the same quantum state within a quantum system simultaneously.

Does the Hartree product satisfy the Pauli principle? **NO!**

Consider a two-electron system:

$$\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)$$

$$\Psi_{21}^{HP}(\mathbf{x}_2, \mathbf{x}_1) = \chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1)$$

$$\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \Psi_{21}^{HP}(\mathbf{x}_2, \mathbf{x}_1)$$

Slater determinant

Pauli exclusion principle: A many-electron wave-function must be antisymmetric with respect to the interchange of the coordinate $\mathbf{x} = (\mathbf{r}, \omega)$ of any two electrons

$$\Phi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$$

From wikipedia:

The Pauli exclusion principle is the quantum mechanical principle which states that two or more identical fermions (particles with half-integer spin) **cannot** occupy the same quantum state within a quantum system simultaneously.

Does the Hartree product satisfy the Pauli principle? **NO!**

Consider a two-electron system:

$$\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)$$

$$\Psi_{21}^{HP}(\mathbf{x}_2, \mathbf{x}_1) = \chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1)$$

$$\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \Psi_{21}^{HP}(\mathbf{x}_2, \mathbf{x}_1)$$

Taking a linear combination of Ψ_{12}^{HP} and Ψ_{21}^{HP} :

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = a[\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1)]$$

we have:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

Let's find a?

Satisfy the Pauli principle!

Slater determinant

Normalized condition:

$$a^2 \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2) \Psi(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 = 1$$

$$\Leftrightarrow a^2 \int [\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) - \Psi_{21}^{HP}(\mathbf{x}_1, \mathbf{x}_2)]^* [\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) - \Psi_{21}^{HP}(\mathbf{x}_1, \mathbf{x}_2)] d\mathbf{x}_1 d\mathbf{x}_2 = 1$$

$$\Leftrightarrow a^2 \left[\int \Psi_{12}^{HP*}(\mathbf{x}_1, \mathbf{x}_2) \Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \int \Psi_{21}^{HP*}(\mathbf{x}_1, \mathbf{x}_2) \Psi_{21}^{HP}(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \right]$$

$$- a^2 \left[\int \Psi_{12}^{HP*}(\mathbf{x}_1, \mathbf{x}_2) \Psi_{21}^{HP}(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \int \Psi_{21}^{HP*}(\mathbf{x}_1, \mathbf{x}_2) \Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \right] = 1$$

$$\Leftrightarrow 2a^2 = 1 \Rightarrow a = \frac{1}{\sqrt{2}}$$

Taking a linear combination of Ψ_{12}^{HP} and Ψ_{21}^{HP} :

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = a [\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1)]$$

we have:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$$

Let's find a?

Satisfy the Pauli principle!

Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

This is called **Slater determinant**. Now, generalize to a N -electron system

Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

This is called **Slater determinant**. Now, generalize to a N -electron system

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \dots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \dots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \dots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$


2K (spin-orbitals)

↑
N (electrons)
↓

Note 1: interchanging coordinates of two electrons corresponds to interchanging two rows, changing the sign of determinant => **Slater determinants satisfy the Pauli principle!**

Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

This is called **Slater determinant**. Now, generalize to a N -electron system

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \dots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \dots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \dots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

Note 1: interchanging coordinates of two electrons corresponds to interchanging two rows, changing the sign of determinant => **Slater determinants satisfy the Pauli principle!**

Short-hand notation:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)\rangle = |\chi_i\chi_j\dots\chi_k\rangle$$

The anti-symmetry for the short-hand notation

$$|\dots\chi_m\dots\chi_n\dots\rangle = -|\dots\chi_n\dots\chi_m\dots\rangle$$

Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)] = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix}$$

This is called **Slater determinant**. Now, generalize to a N -electron system

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \dots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \dots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \dots & \chi_k(\mathbf{x}_N) \end{vmatrix}$$

2K (spin-orbitals)

Short-hand notation:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\dots\chi_k(\mathbf{x}_N)\rangle = |\chi_i\chi_j\dots\chi_k\rangle$$

The anti-symmetry for the short-hand notation

$$|\dots\chi_m\dots\chi_n\dots\rangle = -|\dots\chi_n\dots\chi_m\dots\rangle$$

Read more in Book 02 (pages 52-53) for the physical meaning of exchange effects!!!

Note 1: interchanging coordinates of two electrons corresponds to interchanging two rows, changing the sign of determinant => **Slater determinants satisfy the Pauli principle!**

Note 2:

- The anti-symmetry of fermionic wave-functions introduces **exchange effects**.
- The motion of two parallel (same) spins is correlated
- The motion of two opposite spins remains uncorrelated

Homework 1

Exercise 2.5 Consider the Slater determinants

$$|K\rangle = |\chi_i \chi_j\rangle$$

$$|L\rangle = |\chi_k \chi_l\rangle$$

Show that

$$\langle K | L \rangle = \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}$$

Note that the overlap is zero unless: 1) $k = i$ and $l = j$, in which case $|L\rangle = |K\rangle$ and the overlap is unity and 2) $k = j$ and $l = i$ in which case $|L\rangle = |\chi_j \chi_i\rangle = -|K\rangle$ and the overlap is minus one.

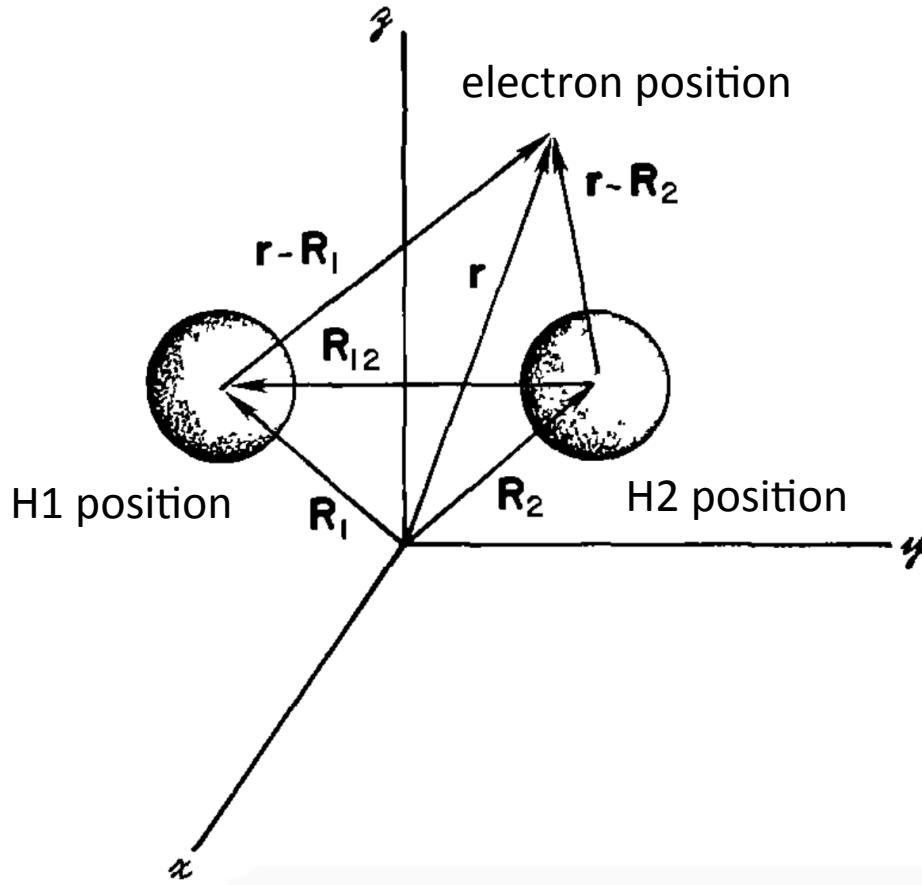
Outline

- Slater determinant
- **LCAO approximation**
- Atomic basis sets

LCAO approximation

LCAO: linear combination of atomic orbitals

Consider H₂ where H has only 1s orbital.



Atomic orbitals (AOs):

$$\phi_1 = \phi_1(\mathbf{r} - \mathbf{R}_1)$$

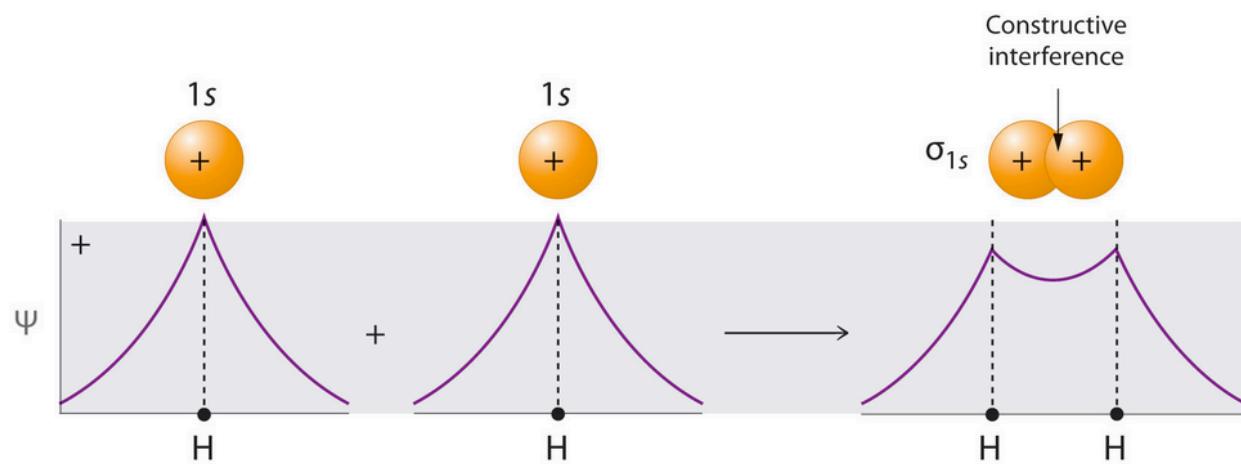
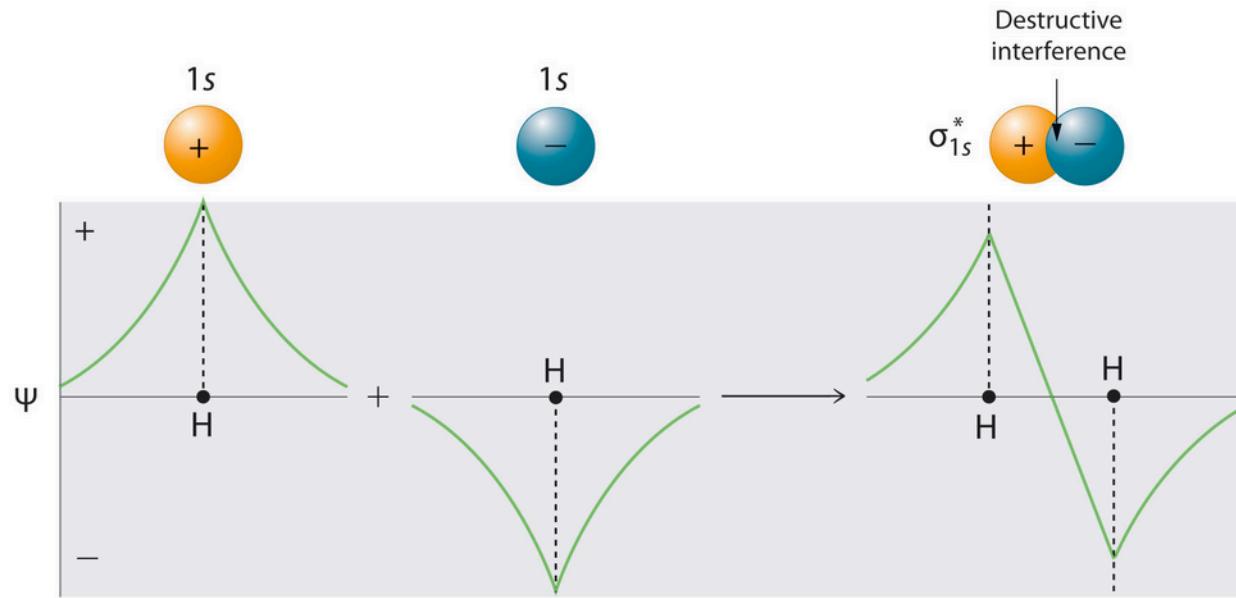
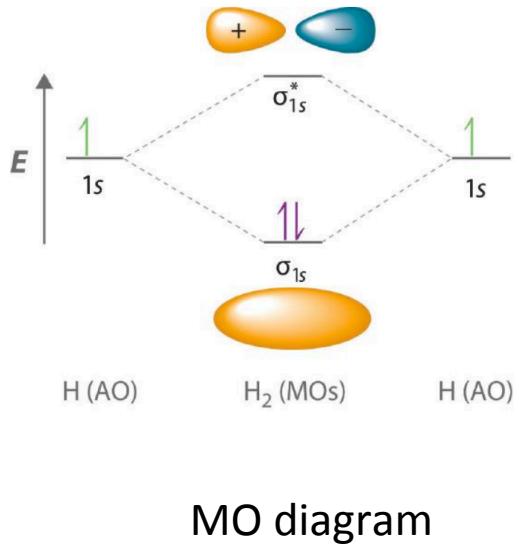
$$\phi_2 = \phi_2(\mathbf{r} - \mathbf{R}_2)$$

Overlap between them:

$$S_{12} = \int \phi_1^*(\mathbf{r} - \mathbf{R}_1) \phi_2(\mathbf{r} - \mathbf{R}_2) d\mathbf{r}$$

$$S_{12} = \begin{cases} 1 & \text{if } R_{12} = |\mathbf{R}_1 - \mathbf{R}_2| = 0 \\ 0 & \text{if } R_{12} \rightarrow \infty \end{cases}$$

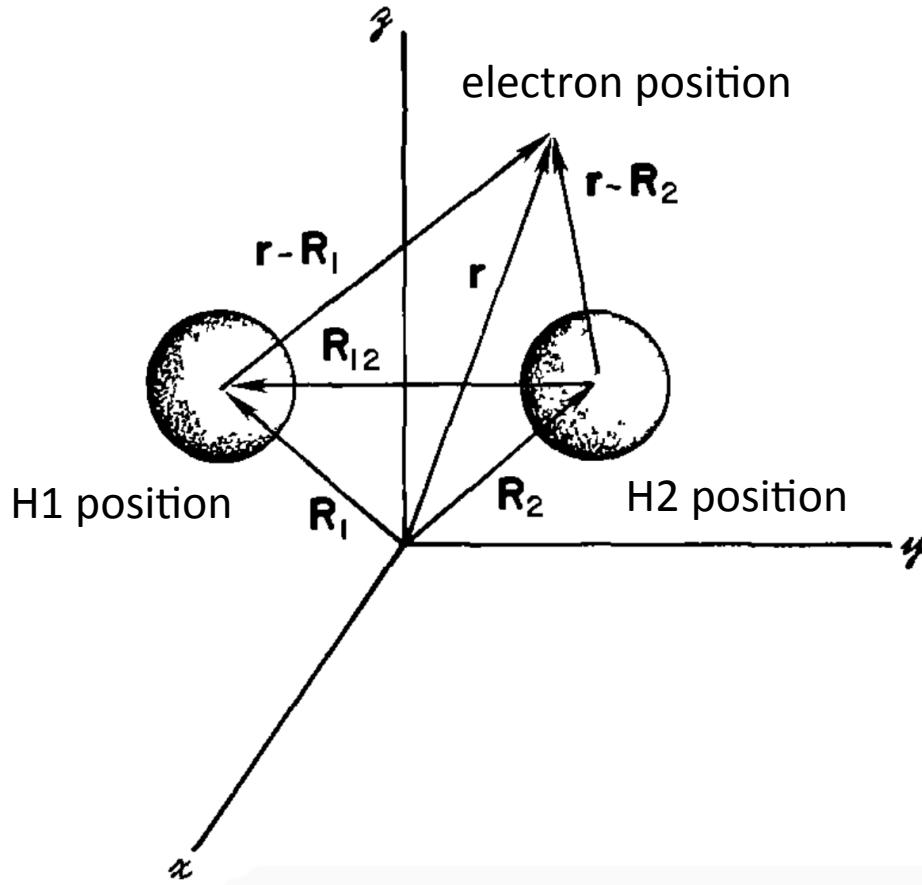
Remind [in Lecture 01]



LCAO approximation

LCAO: linear combination of atomic orbitals

Consider H₂ where H has only 1s orbital.



Atomic orbitals (AOs):

$$\phi_1 = \phi_1(\mathbf{r} - \mathbf{R}_1)$$

$$\phi_2 = \phi_2(\mathbf{r} - \mathbf{R}_2)$$

Overlap between them:

$$S_{12} = \int \phi_1^*(\mathbf{r} - \mathbf{R}_1) \phi_2(\mathbf{r} - \mathbf{R}_2) d\mathbf{r}$$

$$S_{12} = \begin{cases} 1 & \text{if } R_{12} = |\mathbf{R}_1 - \mathbf{R}_2| = 0 \\ 0 & \text{if } R_{12} \rightarrow \infty \end{cases}$$

Spatial molecular orbitals (MOs) are the linear combination of AOs (LCAO):

$$\psi_1 = a[\phi_1 + \phi_2] \quad - \text{ bonding}$$

$$\psi_2 = b[\phi_1 - \phi_2] \quad - \text{ anti-bonding}$$

LCAO approximation

LCAO: linear combination of atomic orbitals

Spin MOs ($\leq 2K$)

$$\chi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

:

$$\chi_{2k-1}(\mathbf{x}) = \psi_k(\mathbf{r})\alpha(\omega)$$

$$\chi_{2k}(\mathbf{x}) = \psi_k(\mathbf{r})\beta(\omega)$$



$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K c_{i\mu} \phi_{\mu}(\mathbf{r})$$

Spatial MOs ($\leq K$)

Generalize to K AOs

Atomic orbitals (AOs):

$$\phi_1 = \phi_1(\mathbf{r} - \mathbf{R}_1)$$

$$\phi_2 = \phi_2(\mathbf{r} - \mathbf{R}_2)$$

Overlap between them:

$$S_{12} = \int \phi_1^*(\mathbf{r} - \mathbf{R}_1) \phi_2(\mathbf{r} - \mathbf{R}_2) d\mathbf{r}$$

$$S_{12} = \begin{cases} 1 & \text{if } R_{12} = |\mathbf{R}_1 - \mathbf{R}_2| = 0 \\ 0 & \text{if } R_{12} \rightarrow \infty \end{cases}$$

Spatial molecular orbitals (MOs) are the linear combination of AOs (LCAO):

$$\psi_1 = a[\phi_1 + \phi_2] \quad - \text{ bonding}$$

$$\psi_2 = b[\phi_1 - \phi_2] \quad - \text{ anti-bonding}$$

LCAO approximation

LCAO: linear combination of atomic orbitals

Spin MOs ($\leq 2K$)

$$\chi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega)$$

$$\chi_2(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega)$$

:

$$\chi_{2k-1}(\mathbf{x}) = \psi_k(\mathbf{r})\alpha(\omega)$$

$$\chi_{2k}(\mathbf{x}) = \psi_k(\mathbf{r})\beta(\omega)$$



$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K c_{i\mu} \phi_{\mu}(\mathbf{r})$$

Spatial MOs ($\leq K$)

How to get these coefficients?

Generalize to K AOs

How to get these functions?

Atomic orbitals (AOs):

$$\phi_1 = \phi_1(\mathbf{r} - \mathbf{R}_1)$$

$$\phi_2 = \phi_2(\mathbf{r} - \mathbf{R}_2)$$

Overlap between them:

$$S_{12} = \int \phi_1^*(\mathbf{r} - \mathbf{R}_1) \phi_2(\mathbf{r} - \mathbf{R}_2) d\mathbf{r}$$

$$S_{12} = \begin{cases} 1 & \text{if } R_{12} = |\mathbf{R}_1 - \mathbf{R}_2| = 0 \\ 0 & \text{if } R_{12} \rightarrow \infty \end{cases}$$

Spatial molecular orbitals (MOs) are the linear combination of AOs (LCAO):

$$\psi_1 = a[\phi_1 + \phi_2] \quad - \text{ bonding}$$

$$\psi_2 = b[\phi_1 - \phi_2] \quad - \text{ anti-bonding}$$

Outline

- Slater determinant
- LCAO approximation
- **Atomic basis sets**

Credit: David Sherrill, Georgia Tech, USA

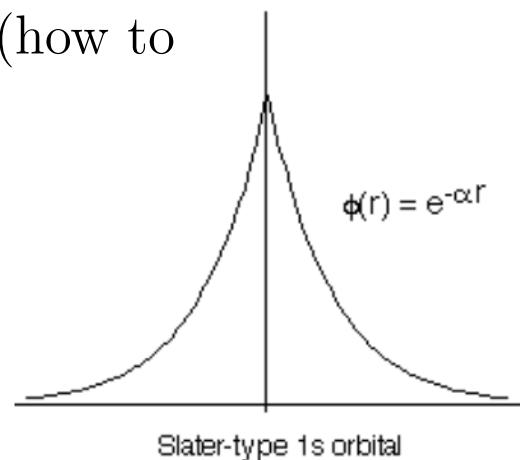
Atomic basis sets

Slater-Type Orbitals (STO's)

$$\phi_{abc}^{STO}(x, y, z) = N x^a y^b z^c e^{-\zeta r}$$

r : relative to nuclear position $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}$

- N is a normalization constant
- a, b, c control angular momentum, $L = a + b + c$
- ζ (zeta) controls the width of the orbital (large ζ gives tight function, small ζ gives diffuse function)
- These are H-atom-like, at least for 1s; however, they lack radial nodes and are not pure spherical harmonics (how to get 2s or 2p, then?)
- Correct short-range and long-range behavior



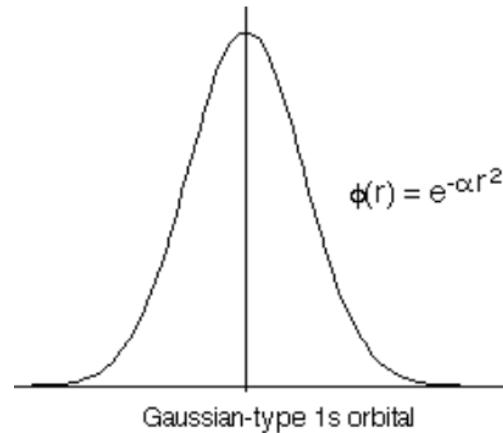
Atomic basis sets

Gaussian-Type Orbitals (GTO's)

$$\phi_{abc}^{GTO}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2}$$

\mathbf{r} : relative to nuclear position
 $\mathbf{r} \rightarrow \mathbf{r} - \mathbf{R}$

- Again, a, b, c control angular momentum, $L = a + b + c$
- Again, ζ controls width of orbital
- No longer H-atom-like, even for 1s
- Much easier to compute (Gaussian product theorem)
- Almost universally used by quantum chemists



Atomic basis sets

Exercise :

The normalized 1s Gaussian-type functions, centered at \mathbf{R}_A and \mathbf{R}_B , have the form:

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) = (2\alpha / \pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2}$$

$$\phi_B(\beta, \mathbf{r} - \mathbf{R}_B) = (2\beta / \pi)^{3/4} e^{-\beta|\mathbf{r} - \mathbf{R}_B|^2}$$

The product of two functions is:

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\beta, \mathbf{r} - \mathbf{R}_B) = K_{AB} \phi_p(p, \mathbf{r} - \mathbf{R}_p)$$

Let's find K_{AB} , p , and \mathbf{R}_p

Atomic basis sets

Exercise :

The normalized 1s Gaussian-type functions, centered at \mathbf{R}_A and \mathbf{R}_B , have the form:

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) = (2\alpha / \pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2}$$

$$\phi_B(\beta, \mathbf{r} - \mathbf{R}_B) = (2\beta / \pi)^{3/4} e^{-\beta|\mathbf{r} - \mathbf{R}_B|^2}$$

The product of two functions is:

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\beta, \mathbf{r} - \mathbf{R}_B) = K_{AB} \phi_p(p, \mathbf{r} - \mathbf{R}_p)$$

Let's find K_{AB} , p , and \mathbf{R}_p

Solution :

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\beta, \mathbf{r} - \mathbf{R}_B) = (2\alpha / \pi)^{3/4} (2\beta / \pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} e^{-\beta|\mathbf{r} - \mathbf{R}_B|^2}$$

$$\text{consider } \exp = -\alpha|\mathbf{r} - \mathbf{R}_A|^2 - \beta|\mathbf{r} - \mathbf{R}_B|^2$$

$$= -\alpha(r^2 + R_A^2 - 2\mathbf{r}\mathbf{R}_A) - \beta(r^2 + R_B^2 - 2\mathbf{r}\mathbf{R}_B) = -(\alpha + \beta) \left(r^2 - 2\mathbf{r} \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta} + \frac{\alpha R_A^2 + \beta R_B^2}{\alpha + \beta} \right)$$

$$\boxed{\text{let } p = \alpha + \beta \text{ and } R_p = \frac{\alpha R_A + \beta R_B}{\alpha + \beta}}$$

$$\exp = -p \left(r^2 - 2\mathbf{r}\mathbf{R}_p + R_p^2 - \left(\frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right)^2 + \frac{(\alpha + \beta)(\alpha R_A^2 + \beta R_B^2)}{(\alpha + \beta)^2} \right) = -p \left(|\mathbf{r} - \mathbf{R}_p|^2 + \frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2 \right)$$

constant

Atomic basis sets

Exercise :

GTOs are convenient
for compute!
Most people use them

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\alpha, \mathbf{r} - \mathbf{R}_B) = (2\alpha/\pi)^{3/4} (2\beta/\pi)^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2} e^{-p|\mathbf{r} - \mathbf{R}_p|^2}$$

$$= \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi} \right)^{3/4} \left(\frac{2(\alpha+\beta)}{\pi} \right)^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2} e^{-p|\mathbf{r} - \mathbf{R}_p|^2}$$

$$K_{AB} = \left(\frac{2\alpha\beta}{(\alpha+\beta)\pi} \right)^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2}$$

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\alpha, \mathbf{r} - \mathbf{R}_B) = K_{AB} \left(2p/\pi \right)^{3/4} e^{-p|\mathbf{r} - \mathbf{R}_p|^2} = K_{AB} \phi_p(p, \mathbf{r} - \mathbf{R}_p)$$

Solution :

$$\phi_A(\alpha, \mathbf{r} - \mathbf{R}_A) \phi_B(\alpha, \mathbf{r} - \mathbf{R}_B) = (2\alpha/\pi)^{3/4} (2\beta/\pi)^{3/4} e^{-\alpha|\mathbf{r} - \mathbf{R}_A|^2} e^{-\beta|\mathbf{r} - \mathbf{R}_B|^2}$$

$$\text{consider } \exp = -\alpha|\mathbf{r} - \mathbf{R}_A|^2 - \beta|\mathbf{r} - \mathbf{R}_B|^2$$

$$= -\alpha(r^2 + R_A^2 - 2\mathbf{r}\mathbf{R}_A) - \beta(r^2 + R_B^2 - 2\mathbf{r}\mathbf{R}_B) = -(\alpha + \beta) \left(r^2 - 2\mathbf{r} \frac{\alpha\mathbf{R}_A + \beta\mathbf{R}_B}{\alpha + \beta} + \frac{\alpha R_A^2 + \beta R_B^2}{\alpha + \beta} \right)$$

$$\text{let } p = \alpha + \beta \text{ and } R_p = \frac{\alpha R_A + \beta R_B}{\alpha + \beta}$$

$$\exp = -p \left(r^2 - 2\mathbf{r}\mathbf{R}_p + R_p^2 - \left(\frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right)^2 + \frac{(\alpha + \beta)(\alpha R_A^2 + \beta R_B^2)}{(\alpha + \beta)^2} \right) = -p \left(|\mathbf{r} - \mathbf{R}_p|^2 + \frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2 \right)$$

constant

Atomic basis sets

Contracted Gaussian-Type Orbitals (CGTO's)

- *Problem:* STO's are more accurate, but it takes longer to compute integrals using them
- *Solution:* Use a linear combination of enough GTO's to mimic an STO
- *Unfortunate:* A combination of n Gaussians to mimic an STO is often called an “STO-nG” basis, even though it is made of CGTO's...

$$\phi_{abc}^{CGTO}(x, y, z) = N \sum_{i=1}^n c_i x^a y^b z^c e^{-\zeta_i r^2}$$

Atomic basis sets

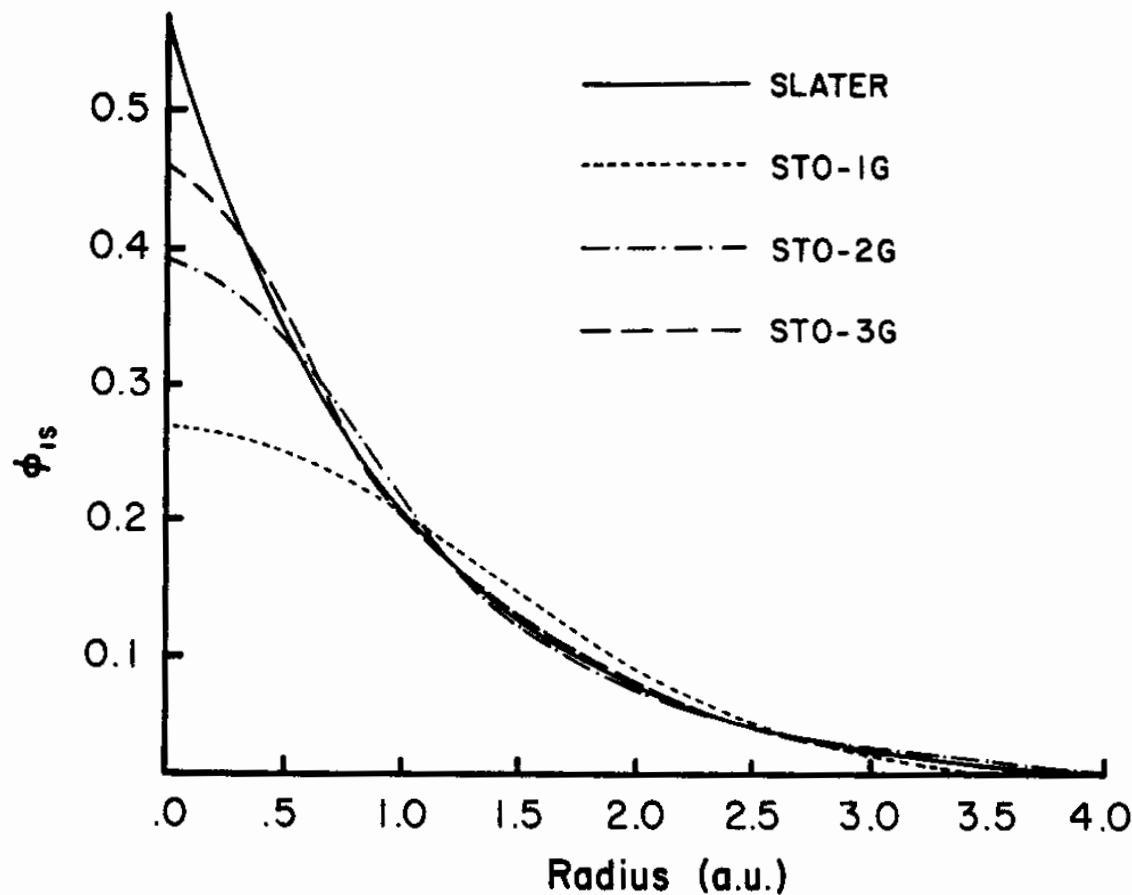


Figure 3.3 Comparison of the quality of the least-squares fit of a 1s Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.

Figure from Szabo and Ostlund, Modern Quantum Chemistry.

Atomic basis sets

Example:

Anatomy of a Basis Set: H atom, STO-3G

A basis set of Contracted Gaussian-Type Orbitals (CGTO's) needs to specify the exponents (ζ_i 's) and the contraction coefficients (c_i 's). These are given below in the format used by the Gaussian program (exponents first)

H 0

S 3 1.00

3.42525091 0.154328970

0.623913730 0.535328140

0.168855400 0.444634540

Discussions

- For Hartree-product wave-functions, total energy is a sum of orbital energies:

$$\hat{H} = \sum_i \hat{h}_i ; \quad \hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i); \quad \hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$
$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \dots \chi_k(\mathbf{x}_N) \quad E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

What about Slater-determinant wave-functions?

- Can contracted Gaussian-type orbitals be used for crystalline materials?

Discussions

- For Hartree-product wave-functions, total energy is a sum of orbital energies:

$$\hat{H} = \sum_i \hat{h}_i ; \quad \hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i); \quad \hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$
$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \dots \chi_k(\mathbf{x}_N) \quad E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

What about Slater-determinant wave-functions?

=>> you'll see it next time

- Can contracted Gaussian-type orbitals be used for crystalline materials?

Discussions

- For Hartree-product wave-functions, total energy is a sum of orbital energies:

$$\hat{H} = \sum_i \hat{h}_i ; \quad \hat{h}_i \chi_j(\mathbf{x}_i) = \varepsilon_j \chi_j(\mathbf{x}_i); \quad \hat{H} \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$
$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \dots \chi_k(\mathbf{x}_N) \quad E = \varepsilon_i + \varepsilon_j + \dots + \varepsilon_k$$

What about Slater-determinant wave-functions?

=>>> you'll see it next time

- Can contracted Gaussian-type orbitals be used for crystalline materials?

=>>> See textbook 01 (and internet) about plane wave

Homework 2: write what you understand about
plane wave basis sets

