

# Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

Alexander Yu. Sokolov

## Week 7-8: Advanced electronic structure theory

### IV. SLATER DETERMINANTS AND THE HARTREE-FOCK APPROXIMATION

1) We need to make sure that the many-electron wavefunction written as a product of spin-orbitals is by construction antisymmetric with respect to the permutation of any two electrons. When we considered an example of a helium atom in the  $^3S$  state, it was easy to construct an antisymmetric wavefunction because there were only two spin-orbitals. In general, for a two-electron system we can write a wavefunction in the antisymmetric form as:

$$|\Psi(1,2)\rangle = \frac{1}{\sqrt{2}}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)] \quad (1)$$

The prefactor  $\frac{1}{\sqrt{2}}$  is necessary to satisfy the normalization condition  $\langle\Psi|\Psi\rangle = 1$ . We can rewrite this equation in a more compact form:

$$|\Psi(1,2)\rangle = \mathcal{A}(1,2)\psi_1(1)\psi_2(2) \quad (2)$$

where  $\mathcal{A}(1,2)$  is the **antisymmetrizer operator** that makes the resulting wavefunction antisymmetric with respect to the permutation of the electrons 1 and 2. It also includes the normalization prefactor.

2) We can generalize Eq. (2) for a system with  $N$  electrons:

$$|\Psi(1,\dots,N)\rangle = \mathcal{A}(1,\dots,N) \prod_i^N \psi_i(i) \quad (3)$$

As in the previous case, the antisymmetrizer operator  $\mathcal{A}(1,\dots,N)$  contains the normalization prefactor and is used to make sure that  $|\Psi(1,\dots,N)\rangle$  is antisymmetric with respect to the permutation of any two electrons.

3) Realizing that Eq. (3) is the definition of a determinant, we can write the wave-

function as:

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} \quad (4)$$

This form of the wavefunction is called the **Slater determinant**. We can easily verify that Eq. (4) reduces to Eq. (1) for the two-electron system. Interestingly, Eq. (4) demonstrates one of the postulates of quantum mechanics: each electron is associated with every orbital, i.e. electrons are *indistinguishable*.

4) Since a determinant is uniquely defined by its diagonal, we can represent the wavefunction more compactly as  $|\Psi\rangle = |\psi_1 \psi_2 \dots \psi_{N-1} \psi_N\rangle$ . In this notation, the normalization prefactor is implied.

5) Slater determinant is a very convenient mathematical object for representing electronic wavefunctions. Permutation of two rows or two columns of the Slater determinant is equivalent to permuting two orbitals or two electrons, resulting in a sign change. If two columns or two rows are the same, the Slater determinant is zero. Thus, Slater determinant naturally satisfies Pauli principle for any  $N$ -electron system.

6) In the **Hartree-Fock approximation**, the electronic wavefunction is chosen to be a Slater determinant. Using this form of the wavefunction, we can derive an expression for the Hartree-Fock energy. We recall that

$$E = \sum_i^N \langle \Psi | \hat{h}_i | \Psi \rangle + \sum_{i>j}^N \langle \Psi | \frac{1}{r_{ij}} | \Psi \rangle \quad (5)$$

Thus, each term on the r.h.s. of the energy expression can be written as an expectation value  $\langle \Psi | \hat{O} | \Psi \rangle$  where  $\hat{O} = \hat{h}_i$  or  $\hat{O} = \frac{1}{r_{ij}}$ . Each term  $\langle \Psi | \hat{O} | \Psi \rangle$  can be written as:

$$\frac{1}{N!} \int \begin{vmatrix} \psi_1^*(1) & \psi_1^*(2) & \cdots & \psi_1^*(N) \\ \psi_2^*(1) & \psi_2^*(2) & \cdots & \psi_2^*(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N^*(1) & \psi_N^*(2) & \cdots & \psi_N^*(N) \end{vmatrix} \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (6)$$

This is equal to:

$$\frac{1}{N!} \int \begin{matrix} \psi_1^*(1) \psi_2^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \\ -\psi_2^*(1) \psi_1^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \\ -\psi_1^*(1) \psi_3^*(2) \psi_2^*(3) \cdots \psi_N^*(N) \\ \vdots \end{matrix} \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (7)$$

where there are  $N! - 3$  more possibilities. The first term in this expansion is

$$\frac{1}{N!} \int \psi_1^*(1) \psi_2^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (8)$$

The second term is

$$\frac{1}{N!} \int -\psi_2^*(1) \psi_1^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (9)$$

Since determinants change sign upon interchange of two columns, we get:

$$\frac{1}{N!} \int \psi_2^*(1) \psi_1^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \hat{O} \begin{vmatrix} \psi_1(2) & \psi_1(1) & \cdots & \psi_1(N) \\ \psi_2(2) & \psi_2(1) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(2) & \psi_N(1) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (10)$$

Since 1 and 2 are just integration variables, we can switch them:

$$\frac{1}{N!} \int \psi_2^*(2) \psi_1^*(1) \psi_3^*(3) \cdots \psi_N^*(N) \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (11)$$

Thus, the second term is the same as the first term in Eq. (8). Analogously, all of the other  $N! - 2$  permutations have the same value, so the integral  $\langle \Psi | \hat{O} | \Psi \rangle$  becomes

$$\int \psi_1^*(1) \psi_2^*(2) \psi_3^*(3) \cdots \psi_N^*(N) \hat{O} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \cdots & \psi_1(N) \\ \psi_2(1) & \psi_2(2) & \cdots & \psi_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(1) & \psi_N(2) & \cdots & \psi_N(N) \end{vmatrix} d1 d2 \dots dN \quad (12)$$

We can make an important observation: *the spin-orbitals that are not being operated by an operator must be occupied by the same electron on the left and on the right of Eq. (12) or the integral  $\langle \Psi | \hat{O} | \Psi \rangle$  will be identically zero, due to orthonormality of the spin-orbitals.*

We first assume that  $\hat{O} = \hat{h}_i$ . The only non-zero term in Eq. (12) is:

$$\begin{aligned} \langle \Psi | \hat{h}_i | \Psi \rangle &= \int \psi_1^*(1) \psi_2^*(2) \cdots \psi_N^*(N) \hat{h}_i \psi_1(1) \psi_2(2) \cdots \psi_N(N) d1 d2 \dots dN \\ &= \int \psi_1^*(1) \psi_1(1) d1 \cdots \int \psi_i^*(i) \hat{h}_i \psi_i(i) di \cdots \int \psi_N^*(N) \psi_N(N) dN \\ &= \int \psi_i^*(i) \hat{h}_i \psi_i(i) di = \int \psi_i^*(1) \hat{h}_1 \psi_i(1) d1 = \langle i | \hat{h} | i \rangle \end{aligned} \quad (13)$$

We now assume that  $\hat{O} = \frac{1}{r_{ij}}$  ( $i > j$ ). The non-zero terms in Eq. (12) are:

$$\begin{aligned} &\int \psi_1^*(1) \cdots \psi_j^*(j) \cdots \psi_i^*(i) \cdots \psi_N^*(N) \frac{1}{r_{ij}} \begin{bmatrix} \psi_1(1) \cdots \psi_j(j) \cdots \psi_i(i) \cdots \psi_N(N) \\ -\psi_1(1) \cdots \psi_i(j) \cdots \psi_j(i) \cdots \psi_N(N) \end{bmatrix} d1 \dots dN \\ &= \int \psi_1^*(1) \psi_1(1) d1 \cdots \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_i(i) \psi_j(j) di dj \cdots \int \psi_N^*(N) \psi_N(N) dN \\ &\quad - \int \psi_1^*(1) \psi_1(1) d1 \cdots \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_j(i) \psi_i(j) di dj \cdots \int \psi_N^*(N) \psi_N(N) dN \\ &= \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_i(i) \psi_j(j) di dj - \int \psi_i^*(i) \psi_j^*(j) \frac{1}{r_{ij}} \psi_j(i) \psi_i(j) di dj \\ &= \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{12}} \psi_i(1) \psi_j(2) d1 d2 - \int \psi_i^*(1) \psi_j^*(2) \frac{1}{r_{12}} \psi_j(1) \psi_i(2) d1 d2 \\ &= \langle ij | ij \rangle - \langle ij | ji \rangle \end{aligned} \quad (14)$$

Using these results, we can write the Hartree-Fock energy expression as:

$$E = \sum_i^N \langle i | \hat{h} | i \rangle + \sum_{i>j}^N (\langle ij | ij \rangle - \langle ij | ji \rangle) \quad (15)$$

7) Let us compare the energy (15) with the energy obtained in the Hartree approximation. We see that the Hartree energy is equal to the first two terms in the Hartree-Fock energy expression. However, the third term in Eq. (15) that depends on  $\langle ij | ji \rangle$  does not appear in the Hartree approximation. This term is called the **exchange energy** and the integrals  $\langle ij | ji \rangle$  are called **exchange integrals**. While the Coulomb integrals  $\langle ij | ij \rangle$  can be interpreted as the energy of Coulomb repulsion between electron densities  $|\psi_i(1)|^2$  and  $|\psi_j(2)|^2$ , the exchange integrals do not have a simple intuitive interpretation. They can be expressed as:

$$\langle ij | ji \rangle = \int \psi_i^*(1) \psi_j(1) \frac{1}{r_{12}} \psi_i(2) \psi_j^*(2) d1 d2 \quad (16)$$

Since  $i > j$ , the products  $\psi_i^*(1) \psi_j(1)$  involve pairs of different spin-orbitals, i.e. the exchange interaction involves electrons that are delocalized between  $\psi_i$  and  $\psi_j$ . Whereas the Coulomb repulsion described by the integrals  $\langle ij | ij \rangle$  always raises the energy (destabilization), the exchange energy involves a negative sign, thus lowering the energy (stabilization).

8) The appearance of the exchange term in the Hartree-Fock energy expression is due to indistinguishability of the electrons in the Hartree-Fock theory. In general, the *exchange interaction is a quantum mechanical effect that only occurs between identical particles*. For example, exchange interaction between two electrons with opposite spins is zero. Thanks to the exchange interaction, the Hartree-Fock energies are much closer to the exact electronic energies than those obtained from the Hartree approximation. For most of the molecular systems near equilibrium geometries, the Hartree-Fock energy is equal to  $\sim 99\%$  of the exact electronic energy. For this reason, the Hartree-Fock theory plays an important role in electronic structure theory. It provides a foundation for how we understand chemistry and chemical bonding. In addition, it is often used as the first step towards more accurate approximations.

9) The Hartree-Fock energy is often expressed as

$$E = \sum_i^N \langle i | \hat{h} | i \rangle + \sum_{i>j}^N \langle ij || ij \rangle \quad (17)$$

where  $\langle ij || ij \rangle$  are called the **antisymmetrized two-electron integrals**, which are defined in general as:

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle \quad (18)$$

Realizing that  $\langle ii || ii \rangle = 0$ , we can also write the energy using an unrestricted summation as:

$$E = \sum_i^N \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^N \langle ij || ij \rangle \quad (19)$$

10) The two-electron integrals  $\langle pq | rs \rangle$  and  $\langle pq || rs \rangle$  have the following symmetry properties:

$$\begin{aligned} \langle pq || rs \rangle &= -\langle pq || sr \rangle = -\langle qp || rs \rangle = \langle qp || sr \rangle \\ &= \langle rs || pq \rangle = -\langle sr || pq \rangle = -\langle rs || qp \rangle = \langle sr || qp \rangle \end{aligned} \quad (20)$$

$$\begin{aligned} \langle pq | rs \rangle &= \langle rq | ps \rangle = \langle ps | rq \rangle = \langle rs | pq \rangle \\ &= \langle qp | sr \rangle = \langle qr | sp \rangle = \langle sp | qr \rangle = \langle sr | qp \rangle \end{aligned} \quad (21)$$

The notation  $\langle pq | rs \rangle$  and  $\langle pq || rs \rangle$  is called the **Physicists' notation**. In some literature, the so-called **Chemists' notation** is used where the two-electron integrals are represented as  $(pq | rs)$ . There exists a simple relationship between the two types of notation:

$$(pq | rs) = \int \psi_p^*(1) \psi_q(1) \frac{1}{r_{12}} \psi_r^*(2) \psi_s(2) d1 d2 = \langle pr | qs \rangle \quad (22)$$

## V. THE HARTREE-FOCK EQUATIONS

1) We have demonstrated that the Hartree-Fock energy can be evaluated using the one- and two-electron integrals that involve spin-orbitals  $|\psi_i\rangle$ . But how can we determine  $|\psi_i\rangle$ ? According to the variational principle, the best approximation to the exact wavefunction is given by the Hartree-Fock wavefunction that has the

lowest energy. Thus, we need to find spin-orbitals that minimize the Hartree-Fock energy. An important condition is that the spin-orbitals should remain orthonormal during the minimization. We can perform such constrained minimization by using the Lagrange's method of undetermined multipliers. In this method, we construct a functional that is equal to the Hartree-Fock energy plus an additional term that specifies the orthonormality constraint:

$$\mathcal{L} = E - \sum_{ij}^n \varepsilon_{ij} (S_{ij} - \delta_{ij}) \quad (23)$$

In Eq. (23)  $\varepsilon_{ij}$  are the Lagrange multipliers and  $S_{ij} = \langle \psi_i | \psi_j \rangle$  is the overlap between two spin-orbitals.

2) Enforcing the variational condition  $\delta \mathcal{L} = 0$ , we arrive at the equations that prescribe which spin-orbitals minimize the Hartree-Fock energy:

$$\hat{f} |\psi_i\rangle = \varepsilon_i |\psi_i\rangle \quad (24)$$

According to these equations (which are called the **Hartree-Fock equations**), the optimal spin-orbitals must be the eigenfunctions of the one-electron operator  $\hat{f}$  called the **Fock operator**:

$$\hat{f}(1) = \hat{h}(1) + \sum_j^N (\hat{J}_j(1) - \hat{K}_j(1)) \quad (25)$$

Each eigenfunction  $|\psi_i\rangle$  is assigned an eigenvalue  $\varepsilon_i$  called **orbital energy**. The first term of the Fock operator is the familiar core Hamiltonian. The last two terms  $\hat{J}_j$  and  $\hat{K}_j$  are called the **Coulomb and exchange operators**, respectively.

3) The Coulomb operator is defined as:

$$\hat{J}_j(1) = \int \psi_j^*(2) \psi_j(2) \frac{1}{r_{12}} d2 \quad (26)$$

This operator describes a one-electron potential obtained by averaging the Coulomb interaction  $\frac{1}{r_{12}}$  of electron 1 and 2 over the space and spin coordinates of electron 2, weighted by the probability  $|\psi_j(2)|^2 d2$  that electron 2 occupies the volume element  $d2$  at the position  $\mathbf{x}_2$ . By summing over all  $j \neq i$ , one obtains the total averaged potential acting on the electron in  $\psi_i(1)$ , arising from the  $N - 1$  electrons in the other spin-orbitals.

4) The exchange operator can be defined in terms of its action on a spin-orbital  $|\psi_i\rangle$ :

$$\hat{K}_j(1)\psi_i(1) = \int \psi_j^*(2)\psi_i(2)\frac{1}{r_{12}}d2\psi_j(1) \quad (27)$$

This operator has a somewhat strange form and does not have a simple classical interpretation like the Coulomb operator. We see that the action of  $\hat{K}_j(1)$  involves an exchange of electrons 1 and 2. Unlike the *local* Coulomb operator, the exchange operator is *nonlocal*, since there does not exist a simple potential  $\hat{K}_j(1)$  uniquely defined at a local point in space  $\mathbf{x}_1$ . The result of operating  $\hat{K}_j(1)$  on  $\psi_i(1)$  depends on the value of  $\psi_i$  throughout all space, not just  $\mathbf{x}_1$ , as evident from Eq. (27). Both  $\hat{J}_j(1)$  and  $\hat{K}_j(1)$  are called *integral operators*, that is their action involves integration over the coordinates of the electron 2.

5) Note that although the spin-orbitals  $|\psi_i\rangle$  must be the eigenfunctions of the Fock operator, the Fock operator itself depends on the spin-orbitals  $|\psi_i\rangle$  via the operators  $\hat{J}_j$  and  $\hat{K}_j$ . This demonstrates the *self-consistent* nature of the Hartree-Fock equations: changing the spin-orbitals leads to a modified Fock operator, which gives rise to a new set of spin-orbitals as its eigenfunctions. In practice, the Hartree-Fock equations are solved by starting with an initial set of spin-orbitals  $|\psi_i\rangle$  (also known as the *guess*) and optimizing the spin-orbitals by updating the Fock operator and solving the eigenvalue problem (24) at every iteration. This process is called the *self-consistent field* method (SCF).

6) According to the Hartree-Fock equations, electron on the spin-orbital  $|\psi_i\rangle$  interacts with electrons on other spin-orbitals only through an averaged (*mean-field*) one-electron potential described by the Fock operator (and not directly through the Coulomb operator  $\frac{1}{r_{12}}$ ). For this reason, the Hartree-Fock theory is often referred to as the *mean-field* or *independent-electron* approximation.

7) The Hartree-Fock equations can be solved efficiently if we formulate the eigenvalue problem (24) in the matrix form. Multiplying both sides of Eq. (24) by  $\langle\psi_j|$ , we obtain:

$$f_{ji} = \langle\psi_j|\hat{f}|\psi_i\rangle = \epsilon_i\delta_{ij} , \quad (28)$$

Thus, the solution of the Hartree-Fock equations  $|\psi_i\rangle$  (the “optimal” spin-orbitals) must diagonalize the Fock operator matrix  $f_{ij}$ . The matrix elements  $f_{ij}$  can be



expressed as:

$$f_{ji} = \langle \psi_j | \hat{h} | \psi_i \rangle + \sum_k^N \langle \psi_j | \hat{J}_k | \psi_i \rangle - \sum_k^N \langle \psi_j | \hat{K}_k | \psi_i \rangle \quad (29)$$

where

$$\langle \psi_j | \hat{J}_k | \psi_i \rangle = \int \psi_j^*(1) \psi_i(1) \frac{1}{r_{12}} \psi_k^*(2) \psi_k(2) d1d2 = \langle jk | ik \rangle \quad (30)$$

$$\langle \psi_j | \hat{K}_k | \psi_i \rangle = \int \psi_j^*(1) \psi_k(1) \frac{1}{r_{12}} \psi_k^*(2) \psi_i(2) d1d2 = \langle jk | ki \rangle \quad (31)$$

Thus, we obtain:

$$f_{ji} = \langle j | \hat{h} | i \rangle + \sum_k^N \langle jk | ik \rangle . \quad (32)$$

8) Solving the Hartree-Fock equations allows us to assign an orbital energy  $\epsilon_i$  for each spin-orbital  $\psi_i$ . Since a Slater determinant is uniquely specified by a set of  $N$  spin-orbitals that appear on its diagonal, the Hartree-Fock wavefunction can be graphically represented using a molecular orbital diagram with energy levels corresponding to the orbital energies and the spin-up/spin-down arrows as their occupations.