

# Quantum Chemistry Learning Progress Report #2

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## 1 Summary

In this week, basic ideas of Hatree-Fock approximation was learned. Also, principles of configuration interaction, rules of matrix elements were learned.

## 2 Modern Quantum Chemistry p. 53-74 [1]

### 2.1 Hatree-Fock Approximation

According to the variational method, the ground state of an  $N$ -electron system could be expressed by a single Slater determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle$$

By minimizing  $E_0$  with respect to the choice of spin orbitals, one can derive Hatree-Fock equation

$$f(i)\chi(\mathbf{x}_i) = \varepsilon\chi(\mathbf{x})$$

Where  $f(i)$  is a one-electron operator called Fock operator

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{\text{HF}}(i)$$

Note that  $v^{\text{HF}}(i)$  is the average potential of  $i$ th electron.  $v^{\text{HF}}(i)$  depends on its eigenfunctions, which means HF equation is non-linear and must be solved iteratively. The procedure for solving the Hatree-Fock equation is called **self-consistent-field (SCF)** method.

Generally, in practice, the Hartree-Fock equation is solved by introducing a finite set of spatial basis functions  $\{\phi_\mu|\mu = 1, 2, \dots, K\}$ . Using a basis set of  $K$  spatial functions leads to a set of  $2K$  spin orbitals. In these  $2K$  spin orbitals, the  $N$  spin orbitals with the lowest energies are called the **occupied** or **hole** spin orbitals. The remaining  $2K - N$  orbitals are called **virtual**, **unoccupied**, or **particle** spin orbitals.

## 2.2 The Minimal Basis H<sub>2</sub> Model

The model is called **MO-LCAO** description of H<sub>2</sub>. Basically, it means the molecular orbitals (MOs) are formed as a linear combination of atomic orbitals (LCAO). For two hydrogen atoms 1 and 2, we have two corresponding atomic orbital  $\phi_1$  and  $\phi_2$ . Since the value of  $\phi_1$  and  $\phi_2$  depends on  $\mathbf{r}$ ,  $R_1$ , and  $R_2$ , let

$$\phi \equiv \phi_1(\mathbf{r} = R_1)$$

$$\phi \equiv \phi_2(\mathbf{r} = R_2)$$

The exact 1s orbital of a hydrogen atom centered at  $R$  has the form

$$\phi(\mathbf{r} - R) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta|\mathbf{r}-R|}$$

Where  $\zeta$  is the orbital exponent. This is an example of Slater orbitals. The 1s Gaussian orbital has the form

$$\phi(\mathbf{r} - R) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha|\mathbf{r}-R|}$$

Where  $\alpha$  is the Gaussian orbital exponent. It should be mentioned that  $\phi_1$  and  $\phi_2$  could be normalized, but they will not be orthogonal since the overlap exists

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

$S_{12}$  would depend on the distance  $R_{12} = |R_1 - R_2|$  such that

$$S_{12} = \begin{cases} 1 & R_{12} = 0 \\ 0 & R_{12} = \infty \end{cases}$$

From the two localized atomic orbitals  $\phi_1$  and  $\phi_2$  by symmetric and antisymmetric combination, two **delocalized** MOs could be formed.

Gerade symmetry MO (symmetric)

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2)$$

Ungerade symmetric MO (antisymmetric)

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2)$$

It could easily be proved that  $\phi_1$  and  $\phi_2$  are orthonormal (Exercise 2.6)

$$\langle \psi_1 | \psi_1 \rangle = \langle \psi_2 | \psi_2 \rangle = 1$$

$$\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle = 0$$

This is the simplest example of the general techniques of expanding a set of spatial molecular orbitals in a set of known spatial basis functions

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

Using only two basis functions for  $H_2$  is an example of a minimal basis set and an obvious choice for the two functions  $\phi_1$  and  $\phi_2$  which are the 1s atomic orbitals of the atoms. The correct linear combinations for this simple choice are determined by symmetry, and one need not solve the Hartree-Fock equation. Thus, for  $H_2$  molecule, given two spatial orbitals  $\psi_1$  and  $\psi_2$ , 4 spin orbitals could be formed

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

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

$$\chi_3(\mathbf{x}) = \psi_2(\mathbf{r})\alpha(\omega)$$

$$\chi_4(\mathbf{x}) = \psi_2(\mathbf{r})\beta(\omega)$$

The **Hartree-Fock ground state** in this model is the single determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$

Using bar to denote spin orbitals with different spin

$$\chi_1 \equiv \psi_1 \quad \chi_2 \equiv \bar{\psi}_1$$

$$\chi_3 \equiv \psi_2 \quad \chi_4 \equiv \bar{\psi}_2$$

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$$

## 2.3 Excited Determinants

Recalled that the Hartree-Fock ground state

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle$$

is the best approximation to the ground state. From  $2K$  orbitals, pick  $N$  orbitals, there are

$$\binom{2K}{N} = \frac{2K!}{N!(2K-N)!}$$

combinations. This is the same number of different single determinants that one can form from  $N$  electrons and  $2K$  spin orbitals. **The Hartree-Fock ground state is just one of these.** These determinants could be taken to represent approximate excited states of the system, or be used in linear combination with  $|\Psi_0\rangle$  for a more accurate description of the ground state or any excited state of the system.

A **singly excited determinants** is one in which an electron has been promoted to a virtual spin orbital  $\chi_r$  from occupied  $\chi_a$  in ground state  $|\Psi_0\rangle$ .

$$|\Psi_a^r\rangle = |\chi_1\cdots\chi_r\chi_b\cdots\chi_N\rangle$$

Similarly, a doubly excited determinant is

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\cdots\chi_r\chi_s\cdots\chi_N\rangle$$

While the excited determinants are not accurate representations of the excited states of the system, they are important as  $N$ -electron basis functions for an expansion of the exact  $N$ -electron states of the system.

## 2.4 Form of the Exact Wave Function and Configuration Interactions

Suppose we have a complete set of functions  $\{\chi_i(x)\}$ . Any function  $\Phi(x_1)$  of a single variable can be exactly expanded as

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1)$$

Expansion of 2 variables

$$\Phi(x_1, x_2) = \sum_i a_i(x_2) \chi_i(x_1) = \sum_{ij} b_{ij} \chi_i(x_1) \chi_j(x_2)$$

Since  $\Phi$  required to be antisymmetric, let

$$\begin{aligned} \Phi(x_1, x_2) &= \sum_i \sum_{j>i} b_{ij} [\chi_i(x_1) \chi_j(x_2) - \chi_j(x_1) \chi_i(x_2)] \\ &= \sum_{i<j} 2^{1/2} b_{ij} |\chi_i \chi_j\rangle \end{aligned}$$

Thus, an arbitrary antisymmetric function could be expanded in terms of all unique determinants formed from a complete set of one-variable functions. Therefore, the exact wave function for the ground and excited states of our  $N$ -electron problem can be written as a linear combination of all possible  $N$ -electron Slater determinants formed from a complete set of spin orbitals  $\{\chi_i\}$ .

Since all possible determinants can be described by reference to the Hartree-Fock determinants, the exact wave function for any state of the system could be rewrite as

$$|\Phi\rangle = c_0 |\Psi_0\rangle + \sum_{ra} c_a^r |\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} + \dots$$

The exact energies of the ground and excited states of the system are the eigenvalues of  $\mathbf{H}$  where

$$\mathbf{H}_{ij} = \langle \Psi_j | \mathbf{H} | \Psi_i \rangle, |\Psi_i\rangle \in \{|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, \dots\}$$

Every  $|\Psi_j\rangle$  can be defined by specifying a “configuration” of spin orbitals from which it is formed, this procedure is called configuration interaction “**CI**”. The lowest eigenvalue of  $\mathbf{H}$ , denoted by  $\mathcal{E}_0$ , is the exact non-relativistic ground state energy of the system within the Born-Oppenheimer approximation. Define the correlation energy

$$E_{\text{corr}} = \mathcal{E}_0 - E_0$$

Above procedures could not be implemented due to the infinite basis sets. However, diagonalizing  $\mathbf{H}$  formed from  $\binom{2K}{N}$  set of determinants leads to solutions that are exact within the one-electron subspace spanned by the  $2K$  spin orbitals, or equivalently, within the  $N$ -electron subspaces spanned by the  $\binom{2K}{N}$  determinants. This procedure is called **full CI**.

Consider the case of  $N = 2$  and  $2K = 4$ , there are totally 6 combinations

**Ground**

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$$

**Singly excited**

$$|\Psi_1^2\rangle = |2\bar{1}\rangle$$

$$|\Psi_1^{\bar{2}}\rangle = |\bar{2}1\rangle$$

$$|\Psi_1^2\rangle = |12\rangle$$

$$|\Psi_1^{\bar{2}}\rangle = |1\bar{2}\rangle$$

**Doubly excited**

$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle$$

Within the space spanned by the minimal basis set, the exact wave functions will be linear combinations of these six determinants. The Hartree-Fock ground state has two electrons in gerade orbital and is of  $g$  symmetry. The singly excited determinants are ungerade orbitals,  $u$  symmetry. The doubly excited determinants is gerade orbital  $g$  symmetry. Notice that the ground state wave function  $|\Phi_0\rangle$  (different from Hartree-Fock ground state) is in  $g$  symmetry, then

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_{12}^{34}|\Phi_{12}^{34}\rangle$$

The exact value could be found by diagonalizing

$$\mathbf{H} = \begin{bmatrix} \langle\Psi_0^{2\bar{2}}|\mathcal{H}|\Psi_0^{2\bar{2}}\rangle & \langle\Psi_0|\mathcal{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \\ \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathcal{H}|\Psi_0\rangle & \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathcal{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \end{bmatrix}$$

**2.5 Minimal Basis H<sub>2</sub> MAtrix Elements**

The Hamiltonian for any two-electron system is

$$\begin{aligned} \mathcal{H} &= \left( -\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left( -\frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + r_{12}^{-1} \\ &= h(1) + h(2) + r_{12}^{-1} \end{aligned}$$

Separate total Hamiltonian into one- and two-electron parts

$$\mathcal{O}_1 = h(1) + h(2)$$

$$\mathcal{O}_2 = r_{12}^{-1}$$

First consider  $\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle$

$$\langle\Psi_0|h(1)|\Psi_0\rangle = \frac{1}{2} \int d\mathbf{x}_1 \chi_1(\mathbf{x}_1) h(\mathbf{r}_1) \chi_1(\mathbf{x}_1) + \frac{1}{2} \int d\mathbf{x}_1 \chi_2(\mathbf{x}_1) h(\mathbf{r}_1) \chi_2(\mathbf{x}_1)$$

By the same procedure with  $h(2)$ , then

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \int d\mathbf{x}_1 \chi_1(\mathbf{x}_1) h(\mathbf{r}_1) \chi_1(\mathbf{x}_1) + \int d\mathbf{x}_1 \chi_2(\mathbf{x}_1) h(\mathbf{r}_1) \chi_2(\mathbf{x}_1)$$

Note that the expression is one-electron integral. Introducing notation

$$\langle ij | \rangle = \langle \chi_i | h | \chi_j \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

Then

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle$$

Next, consider  $\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle$ . Since  $r_{12} = r_{21}$ , we can interchange variables, therefore

$$\begin{aligned} \langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_2^*(\mathbf{x}_2) r_{12}^{-1} \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) \\ &\quad - \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_2^*(\mathbf{x}_2) r_{12}^{-1} \chi_2(\mathbf{x}_1) \chi_1(\mathbf{x}_2) \end{aligned}$$

Introducing

$$\langle ij | kl \rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

Then we have

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \langle 12 | 12 \rangle - \langle 12 | 21 \rangle$$

Thus, the Hartree-Fock ground state energy is

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle$$

## 2.6 Notations for One- and Two-Electron Integrals

Recall the definition of notation for two-electron integral over spin orbitals, then it is clear that

$$\begin{aligned} \langle ij | kl \rangle &= \langle ji | lk \rangle \\ \langle ij | kl \rangle &= \langle kl | ij \rangle^* \end{aligned}$$

Introduce a special symbol for an antisymmetrized two-electron integral

$$\begin{aligned} \langle ij || kl \rangle &= \langle ij | kl \rangle - \langle ij | lk \rangle \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} (1 - \mathcal{P}_{12}) \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) \end{aligned}$$

Where  $\mathcal{P}_{12}$  is an operator which interchanges the coordinates of electron 1 and 2. Note that

$$\langle ii || kk \rangle = 0$$

Another notation: chemist's notation

$$[ij | kl] = \langle ik | jl \rangle$$

## 2.7 General Rules for Matrix Elements (Proved in Next Section)

Declare two types of operators.

First: a sum of one-electron operators

$$\mathcal{O}_1 = \sum_{i=1}^N h(i)$$

$h(i)$  is any operator involving only the  $i$ th electron.

Second: a sum of two-electron operators

$$\mathcal{O}_2 = \sum_{i=1}^N \sum_{j>i}^N v(i,j) \equiv \sum_{i<j} v(i,j)$$

$v(i,j)$  depends on  $i$ th and  $j$ th electron. The coulomb interaction between two electrons is

$$v(i,j) = r_{ij}^{-1}$$

Consider determinants  $|K\rangle$ ,  $|L\rangle$ , and operator  $\mathcal{O}$ . The goal is to find  $\langle K|\mathcal{O}|L\rangle$  in following three cases.

**Case 1**  $|K\rangle = |L\rangle$

$$|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$$

**Case 2** When the two determinants differ by one spin orbital

$$|L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$$

**Case 3** When two two determinants differ by two spin orbitals

$$|L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$$

**Rules for  $\mathcal{O}_1$**

**Case 1**  $|K\rangle = |L\rangle$ ,  $|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_1|K\rangle = \sum_m^N [m|h|m] = \sum_m^N \langle m|h|m\rangle$$

**Case 2**  $|L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = [m|h|p] = \langle m|h|p\rangle$$

**Case 3**  $|L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = 0$$

**Rules for  $\mathcal{O}_2$**

**Case 1**  $|K\rangle = |L\rangle, |K\rangle = |\cdots \chi_m \chi_n \cdots\rangle$

$$\langle K | \mathcal{O}_2 | K \rangle = \frac{1}{2} \sum_m^N \sum_n^N = [mm|nn] - [mn|nm] = \frac{1}{2} \sum_m^N \sum_n^N \langle mn || mn \rangle$$

**Case 2**  $|L\rangle = |\cdots \chi_p \chi_n \cdots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = \sum_n^N [mp|nn] - [mn|np] = \sum_n^N \langle mn || pn \rangle$$

**Case 3**  $|L\rangle = |\cdots \chi_p \chi_q \cdots\rangle$

$$\langle K | \mathcal{O}_2 | L \rangle = [mp|nq] - [mq|np] = \langle mn || pq \rangle$$

The rules are same for the Hartree-Fock ground state.

## References

- [1] A. Szabo and N. S. Ostlund, *Modern quantum chemistry: introduction to advanced electronic structure theory*. Courier Corporation, 2012.