

Problem session (4)

15/04/11 Yuki NAKAGAWA

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The time independent Schrödinger equation for a particle of mass m moving in one dimension with energy E in a system that does not change with time (for instance, its volume remains constant) is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi + V(x)\Psi = E\Psi \quad (\text{Eq. 1})$$

The total energy E is the sum of potential energy and kinetic energies. The first term must be related to the kinetic energy of the particle; $\hbar = \frac{h}{2\pi}$ is a convenient modification of Planck's constant with the value 1.055×10^{-34} Js. The factor $V(x)$ is the potential energy of the particle at the point x . Wavefunction Ψ which is the solution of the Schrödinger equation describes all physical information (for instance, energy, existence probability of particle, and so on). The Schrödinger equation is very useful to consider atom and molecule. However, we cannot solve the Schrödinger equation exactly without only a few example (H, He⁺, H₂⁺, single-electron atoms and molecules).

How we describe the structure of many-electron atoms and molecules?

To describe the structure, we need to use approximation. One of the most approximation is molecular orbital theory (MO theory). Almost all modern computational work makes use of MO theory. In MO theory, the concept of atomic orbital is extended to that of 'molecular orbital', which is a wavefunction that spreads over all the atoms in a molecule.

Question: Please solve the molecular orbital ϕ of molecule A-B using MO theory.

Answer: With atomic orbital of A (χ_A) and B (χ_B), molecular orbital ϕ is

$$\phi = C_A \chi_A + C_B \chi_B \quad (\text{Eq. 2})$$

If atomic orbitals are real function, expectation value of energy ε is

$$\varepsilon = \frac{\int \phi \hat{H} \phi d\tau}{\int \phi^2 d\tau} \quad (\text{Eq. 3})$$

In Eq. 3, coefficients C_A and C_B follow variation principle.

$$\frac{d\varepsilon(C_A, C_B)}{dC_A} = 0 \quad \text{and} \quad \frac{d\varepsilon(C_A, C_B)}{dC_B} = 0$$

The first step is to express the two integrals in Eq. 3 in terms of the coefficients. The denominator is

$$\int \phi^2 d\tau = \square$$

because the individual atomic orbitals are normalized ($\int \chi_A^2 d\tau = 1$ and $\int \chi_B^2 d\tau = 1$) and the overlap integral is S ($S = \int \chi_A \chi_B d\tau$).

With the integrals written as $\int \chi_A \hat{H} \chi_A d\tau = \alpha_A$, $\int \chi_B \hat{H} \chi_B d\tau = \alpha_B$, $\int \chi_A \hat{H} \chi_B d\tau = \int \chi_B \hat{H} \chi_A d\tau = \beta$.

The numerator is

$$\int \phi \hat{H} \phi d\tau = \square$$

At this point we can write the complete expression for ε as

$$\varepsilon = \frac{\square}{\square} \quad (\text{Eq. 4})$$

Its minimum is found by differentiation with respect to the two coefficients and setting the results equal to 0. After some straightforward work we obtain

$$\frac{d\varepsilon(C_A, C_B)}{dC_A} = \square \quad (\text{Eq. 5})$$

$$\frac{d\varepsilon(C_A, C_B)}{dC_B} = \square \quad (\text{Eq. 6})$$

We must find values of C_A and C_B that satisfy the conditions

$$\begin{pmatrix} \alpha_A - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha_B - \varepsilon \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0 \quad (\text{Eq. 7})$$

which are the secular equations. To solve the secular equation for the coefficients we need to know the energy ε of the orbital. The secular equations (Eq. 7) have a solution if secular determination is 0. That is

$$\begin{vmatrix} \alpha_A - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha_B - \varepsilon \end{vmatrix} = \square$$

$$\square = 0 \quad (\text{Eq. 8})$$

We can make the Hückel approximation that $S = 0$. This quadratic equation for ε has the solutions

$$\varepsilon = \frac{\square \pm \sqrt{\square}}{2}$$

$$= \frac{\square \pm \square \sqrt{1 + \frac{4\square}{\square}}}{2}$$

$$\approx \frac{\square \pm \square \left(1 + \frac{2\square}{\square}\right)}{2} \quad \left(\sqrt{1+x} = 1 + \frac{1}{2}x \right)$$

$$\varepsilon = \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}, \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B} \quad (\alpha_A - \alpha_B > 0) \quad (\text{Eq. 9})$$

The upper energy $\varepsilon = \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}$ gives the coefficients $C_B = \frac{\beta}{\alpha_A - \alpha_B} C_A$.

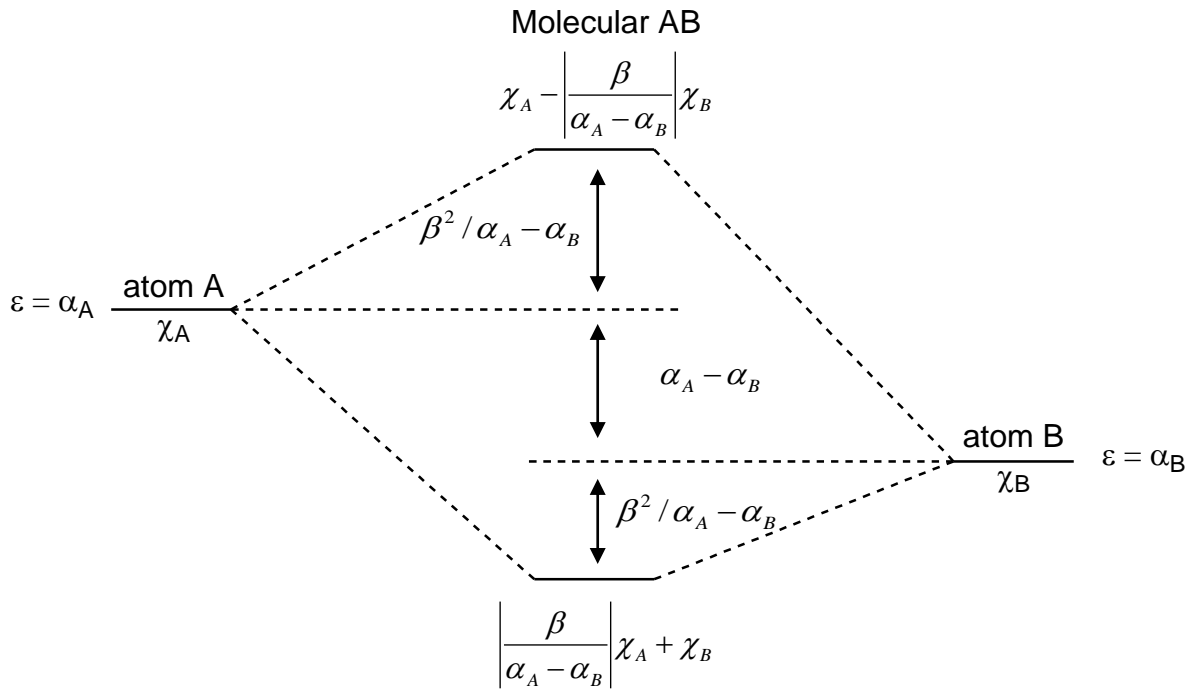
As a result, antibonding orbital ϕ is

$$\phi = C_A \left(\chi_A + \frac{\beta}{\alpha_A - \alpha_B} \chi_B \right) \quad (-1 < \frac{\beta}{\alpha_A - \alpha_B} < 0)$$

On the other hand, the lower energy $\varepsilon = \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B}$ gives the coefficients $C_A = -\frac{\beta}{\alpha_A - \alpha_B} C_B$.

As a result, bonding orbital ϕ is

$$\phi = C_B \left(-\frac{\beta}{\alpha_A - \alpha_B} \chi_A + \chi_B \right) \quad (-1 < \frac{\beta}{\alpha_A - \alpha_B} < 0)$$

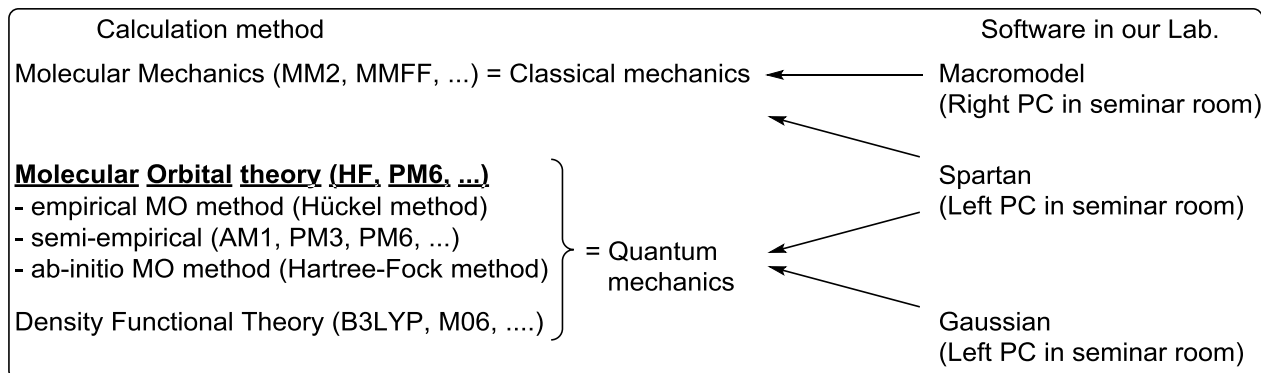


Problem session (4) -Answer-

15/04/11 Yuki NAKAGAWA

Topics -Molecular orbital theory and Hartree-Fock method-

0. Introduction



Contents

1. Schrödinger equation
2. Molecular Orbital theory
3. The variation principle (Question in this time)
4. Slater determinant -the Pauli principle-
5. Self-Consistent Field
6. Hartree-Fock equation

1. Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed an equation for finding the wavefunction of any system. The time independent Schrödinger equation for a particle of mass m moving in one dimension with energy E in a system that does not change with time (for instance, its volume remains constant) is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi + V(x)\Psi = E\Psi \quad (\text{Eq. 1})$$

Eq. 1 is also written as

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

The total energy E is the sum of potential energy and kinetic energies. The first term must be related to the kinetic energy of the particle; $\hbar = \frac{h}{2\pi}$ is a convenient modification of Planck's constant with the value 1.055×10^{-34} Js. The factor $V(x)$ is the potential energy of the particle at the point x . Wavefunction Ψ which is the solution of the Schrödinger equation describes all physical information (for instance, energy, existence probability of particle, and so on).

For example, we think about a particle in a one-dimensional box model.

$$\left(\begin{array}{ll} 0 \leq x \leq a, & V(x) = 0 \\ x < 0, \quad a \leq x, & V(x) = \infty \end{array} \right)$$

If we determine wavefunction of the particle

$$\Psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \quad (0 \leq x \leq a, n = 1, 2, 3, \dots),$$

the Schrödinger equation is

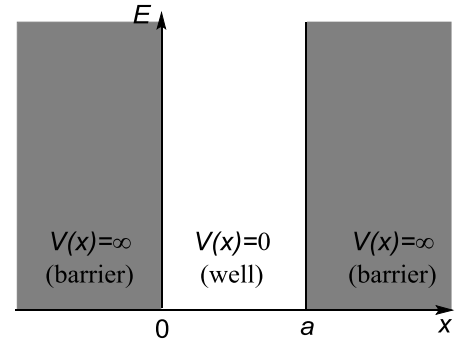


Fig. 1 one-dimensional box model

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left\{ \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \right\} \\ &= -\frac{\hbar^2}{2m} \left\{ -\frac{n^2 \pi^2}{a^2} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \right\} \\ &= \frac{\hbar^2 \pi^2}{2ma^2} n^2 \Psi(x) \end{aligned} \quad (\text{Eq. 2})$$

Therefore, energy E is

$$E_n = \frac{\hbar^2}{8ma^2} n^2 \quad (n = 1, 2, 3, \dots) \quad (\text{Eq. 3})$$

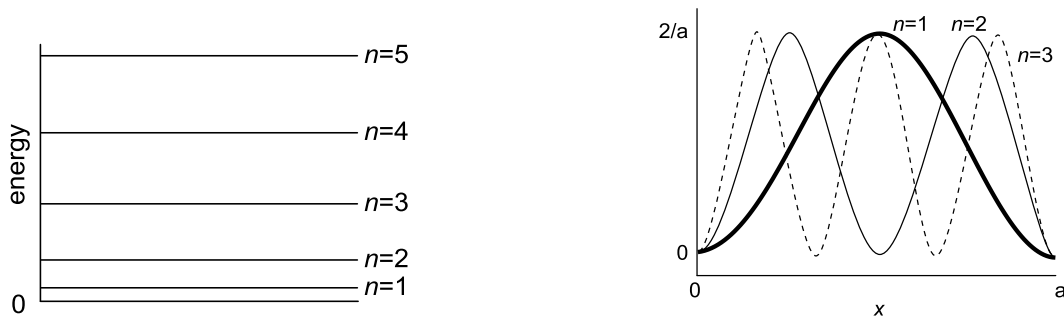


Fig. 2 quantum number and energy level and distribution of existence probability of a particle

The Schrödinger equation is very useful to consider atom and molecule. However, we cannot solve the Schrödinger equation exactly without only a few examples (H, He⁺, H₂⁺, single-electron atoms and molecules).

Example of unsolved Schrödinger equation (He atom)

$$\left(-\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 \right) \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

kinetic energies of electron 1 and 2

$$+ \left(-k_0 \frac{2e^2}{r_1} - k_0 \frac{2e^2}{r_2} + k_0 \frac{e^2}{r_{12}} \right) \Psi(1,2) = E\Psi(1,2) \quad (\text{Eq. 4})$$

Coulomb energies between electron 1 and 2

$$\nabla_i^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad k_0 = \frac{1}{4\pi\epsilon_0} = 8.9876 \times 10^9 [Nm^2 / A^2 s^2]$$

We cannot solve the term of $k_0 \frac{e^2}{r_{12}}$

the nuclei move relatively slowly and may be treated as stationary while the electrons move in their field. (the nuclear kinetic energy is neglected)

Born-Oppenheimer approximation

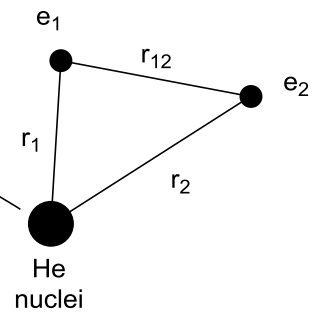


Fig. 3 He atom

How we describe the wavefunctions of many-electron molecules (atoms)?

2. Molecular orbital theory

In molecular orbital theory, the concept of atomic orbital is extended to that of ‘molecular orbital’, which is a wavefunction that spreads over all the atoms in a molecule. That is to say that electrons do not belong to particular bonds but spread throughout the entire molecular. In this theory, an approximation is used as a technique for calculating wavefunction of molecular orbital:

Molecular orbital ϕ is formed from a linear combination of atomic orbitals χ_n .

$$\phi = C_A \chi_A + C_B \chi_B + C_C \chi_C + \dots = \sum_n C_n \chi_n \quad (\text{Eq. 5})$$

C_n : coefficients

The approximation is called an LCAO-MO.

Example of LCAO-MO

We consider hydrogen molecule (H_2). H_2 molecule includes two hydrogen atoms. We name two hydrogen atoms: one is H_A , the other is H_B . Each of 1s atomic orbital of H_A and H_B is χ_{1sA} and χ_{1sB} .

Molecular orbital ϕ is described as

$$\phi_1 = C_A \chi_{1sA} + C_B \chi_{1sB} = C(\chi_{1sA} + \chi_{1sB})$$

and

$$\phi_2 = C'_A \chi_{1sA} - C'_B \chi_{1sB} = C'(\chi_{1sA} - \chi_{1sB})$$

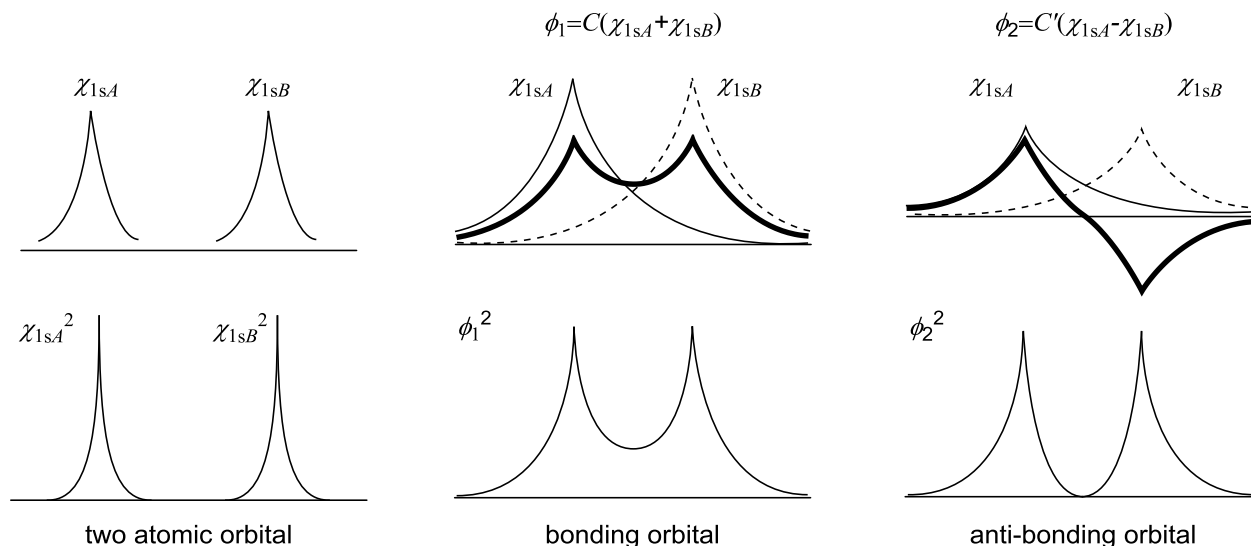


Fig. 4 orbital of hydrogen atom (H) and orbital of hydrogen molecule (H₂)

The wavefunctions of many-electron molecules are described by LCAO-MO. However, we have a new problem. We don't know about appropriate coefficients C_n .

3. The variation principle

A more systematic way of finding the coefficients in the linear combinations used to build molecular orbitals is provided by the variation principle which is proved in the following justification:

If an arbitrary wavefunction ϕ is used to calculate the energy $\langle E \rangle$, the value calculated is never less than the true energy E_0 .

$$\langle E \rangle = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0 \quad (\text{Eq. 6})$$

This principle is the basis of all modern molecular structure calculations. The arbitrary wavefunction is called the trial wavefunction. The principle implies that, **if we vary the coefficients in the trial wavefunction until the lowest energy is achieved (by evaluating the expectation value of the**

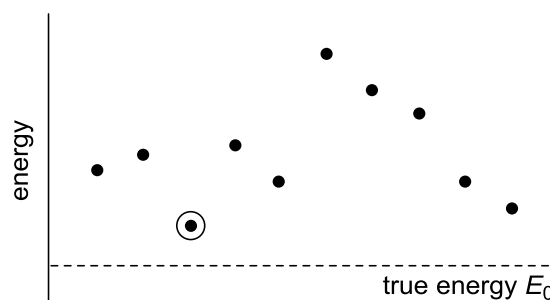


Fig. 5 The variation principle

Hamiltonian for each wavefunction), then those coefficients will be the best for the particular form of trial function. We might get a lower energy if we use a more complicated wavefunction (for example, by taking linear combination of several atomic orbitals on each atom), but we shall have the optimum (minimum energy) molecular orbital that can be built from the chosen basis set, the given set of atomic orbitals.

We can write the expectation value of energy ε using a wavefunction $\phi(\lambda)$, which is

$$\varepsilon(\lambda) = \frac{\int \phi^*(\lambda) \hat{H} \phi(\lambda) d\tau}{\int \phi^*(\lambda) \phi(\lambda) d\tau} \quad (\text{Eq. 7})$$

The condition of the minimum the expectation value of energy $\varepsilon(\lambda)$ is

$$\frac{d\varepsilon(\lambda)}{d\lambda} = 0$$

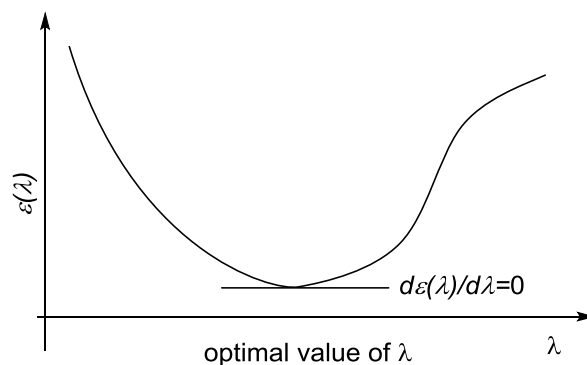


Fig. 6 Condition of the variation principle

Question. Please solve the molecular orbital ϕ of heteronuclear diatomic molecule A-B using MO theory.

Answer.

With atomic orbital of A (χ_A) and B (χ_B), molecular orbital ϕ is

$$\phi = C_A \chi_A + C_B \chi_B \quad (\text{Eq. 8})$$

If atomic orbitals are real function, the expectation value of energy ε is

$$\varepsilon = \frac{\int \phi \hat{H} \phi d\tau}{\int \phi^2 d\tau} \quad (\text{Eq. 9})$$

In Eq. 9, coefficients C_A and C_B follow variation principle.

$$\frac{d\varepsilon(C_A, C_B)}{dC_A} = 0 \quad \text{and} \quad \frac{d\varepsilon(C_A, C_B)}{dC_B} = 0 \quad (\text{Eq. 10})$$

The first step is to express the two integrals in Eq. 9 in terms of the coefficients. The denominator is

$$\begin{aligned} \int \phi^2 d\tau &= \int (C_A \chi_A + C_B \chi_B)^2 d\tau \\ &= C_A^2 \int \chi_A^2 d\tau + C_B^2 \int \chi_B^2 d\tau + 2C_A C_B \int \chi_A \chi_B d\tau \\ &= C_A^2 + C_B^2 + 2C_A C_B S \end{aligned} \quad (\text{Eq. 11})$$

because the individual atomic orbitals are normalized ($\int \chi_A^2 d\tau = 1$ and $\int \chi_B^2 d\tau = 1$) and the overlap integral is S ($S = \int \chi_A \chi_B d\tau$).

With the integrals written as $\int \chi_A \hat{H} \chi_A d\tau = \alpha_A$, $\int \chi_B \hat{H} \chi_B d\tau = \alpha_B$, $\int \chi_A \hat{H} \chi_B d\tau = \int \chi_B \hat{H} \chi_A d\tau = \beta$.

The numerator is

$$\begin{aligned} \int \phi \hat{H} \phi d\tau &= \int (C_A \chi_A + C_B \chi_B) \hat{H} (C_A \chi_A + C_B \chi_B) d\tau \\ &= C_A^2 \int \chi_A \hat{H} \chi_A d\tau + C_A C_B \int \chi_A \hat{H} \chi_B d\tau + C_B C_A \int \chi_B \hat{H} \chi_A d\tau + C_B^2 \int \chi_B \hat{H} \chi_B d\tau \\ &= C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B \end{aligned} \quad (\text{Eq. 12})$$

At this point we can write the complete expression for ε as

$$\varepsilon = \frac{C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B}{C_A^2 + C_B^2 + 2C_A C_B S} \quad (\text{Eq. 13})$$

Its minimum is found by differentiation with respect to the two coefficients and setting the results equal to 0. After some straightforward work we obtain

$$\begin{aligned} \frac{d\varepsilon(C_A, C_B)}{dC_A} &= \frac{d}{dC_A} \left(\frac{C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B}{C_A^2 + C_B^2 + 2C_A C_B S} \right) \\ &= \frac{d}{dC_A} (C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B) (C_A^2 + C_B^2 + 2C_A C_B S)^{-1} \\ &= (C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B)' (C_A^2 + C_B^2 + 2C_A C_B S)^{-1} + \\ &\quad (C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B) \left\{ (C_A^2 + C_B^2 + 2C_A C_B S)^{-1} \right\}' \\ &= (2C_A \alpha_A + 2C_B \beta) (C_A^2 + C_B^2 + 2C_A C_B S)^{-1} + \\ &\quad (C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B) \cdot -(C_A^2 + C_B^2 + 2C_A C_B S)' (C_A^2 + C_B^2 + 2C_A C_B S)^{-2} \\ &= \frac{2C_A \alpha_A + 2C_B \beta}{C_A^2 + C_B^2 + 2C_A C_B S} - \frac{(C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B)(2C_A + 2C_B S)}{(C_A^2 + C_B^2 + 2C_A C_B S)^2} \\ &= \frac{2C_A \alpha_A + 2C_B \beta}{C_A^2 + C_B^2 + 2C_A C_B S} - \frac{C_A^2 \alpha_A + 2C_A C_B \beta + C_B^2 \alpha_B}{C_A^2 + C_B^2 + 2C_A C_B S} \cdot \frac{2C_A + 2C_B S}{C_A^2 + C_B^2 + 2C_A C_B S} \\ &= \frac{2C_A \alpha_A + 2C_B \beta}{C_A^2 + C_B^2 + 2C_A C_B S} - \frac{\varepsilon(2C_A + 2C_B S)}{C_A^2 + C_B^2 + 2C_A C_B S} \\ &= \frac{2\{(\alpha_A - \varepsilon)C_A + (\beta - \varepsilon S)C_B\}}{C_A^2 + C_B^2 + 2C_A C_B S} \end{aligned} \quad (\text{Eq. 14})$$

$$\frac{2\{(\alpha_A - \varepsilon)C_A + (\beta - \varepsilon S)C_B\}}{C_A^2 + C_B^2 + 2C_A C_B S} = 0$$

$$\therefore (\alpha_A - \varepsilon)C_A + (\beta - \varepsilon S)C_B = 0 \quad (\text{Eq. 15})$$

$$\frac{d\varepsilon(C_A, C_B)}{dC_B} = \frac{2\{(\alpha_B - \varepsilon)C_B + (\beta - \varepsilon S)C_A\}}{C_A^2 + C_B^2 + 2C_A C_B S} \quad (\text{Eq. 16})$$

$$\therefore (\alpha_B - \varepsilon)C_B + (\beta - \varepsilon S)C_A = 0 \quad (\text{Eq. 17})$$

We must find values of C_A and C_B that satisfy the conditions

$$\begin{pmatrix} \alpha_A - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha_B - \varepsilon \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0 \quad (\text{Eq. 18})$$

which are the secular equations. To solve the secular equation for the coefficients we need to know the energy ε of the orbital. The secular equations (Eq. 18) have a solution if secular determination is 0. That is

$$\begin{vmatrix} \alpha_A - \varepsilon & \beta - \varepsilon S \\ \beta - \varepsilon S & \alpha_B - \varepsilon \end{vmatrix} = (\alpha_A - \varepsilon)(\alpha_B - \varepsilon) - (\beta - \varepsilon S)^2$$

$$(1 - S^2)\varepsilon^2 + \{2\beta S - (\alpha_A + \alpha_B)\}\varepsilon + \alpha_A \alpha_B - \beta^2 = 0 \quad (\text{Eq. 19})$$

We can make the Hückel approximation that $S = 0$. This quadratic equation for ε has the solutions

$$\begin{aligned} \varepsilon &= \frac{(\alpha_A + \alpha_B) \pm \sqrt{(\alpha_A + \alpha_B)^2 - 4(\alpha_A \alpha_B - \beta^2)}}{2} \\ &= \frac{(\alpha_A + \alpha_B) \pm \sqrt{(\alpha_A - \alpha_B)^2 + 4\beta^2}}{2} \\ &= \frac{(\alpha_A + \alpha_B) \pm (\alpha_A - \alpha_B) \sqrt{1 + \frac{4\beta^2}{(\alpha_A - \alpha_B)^2}}}{2} \\ &\approx \frac{(\alpha_A + \alpha_B) \pm (\alpha_A - \alpha_B) \left(1 + \frac{2\beta^2}{(\alpha_A - \alpha_B)^2}\right)}{2} \quad \left(\sqrt{1+x} = 1 + \frac{1}{2}x\right) \\ \varepsilon &= \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}, \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B} \quad (\alpha_A - \alpha_B > 0) \quad (\text{Eq. 20}) \end{aligned}$$

The upper energy $\varepsilon = \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}$ gives the coefficients

$$C_B = \frac{\beta}{\alpha_A - \alpha_B} C_A \quad (\because (\alpha_A - \varepsilon)C_A + \beta C_B = 0).$$

As a result, antibonding orbital ϕ is

$$\phi = C_A \left(\chi_A + \frac{\beta}{\alpha_A - \alpha_B} \chi_B \right) \quad (-1 < \frac{\beta}{\alpha_A - \alpha_B} < 0) \quad (\text{Eq. 21})$$

On the other hand, the lower energy $\varepsilon = \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B}$ gives the coefficients

$$C_A = -\frac{\beta}{\alpha_A - \alpha_B} C_B \quad (\because (\alpha_B - \varepsilon)C_B + \beta C_A = 0).$$

As a result, bonding orbital ϕ is

$$\phi = C_B \left(-\frac{\beta}{\alpha_A - \alpha_B} \chi_A + \chi_B \right) \quad (-1 < \frac{\beta}{\alpha_A - \alpha_B} < 0) \quad (\text{Eq. 22})$$

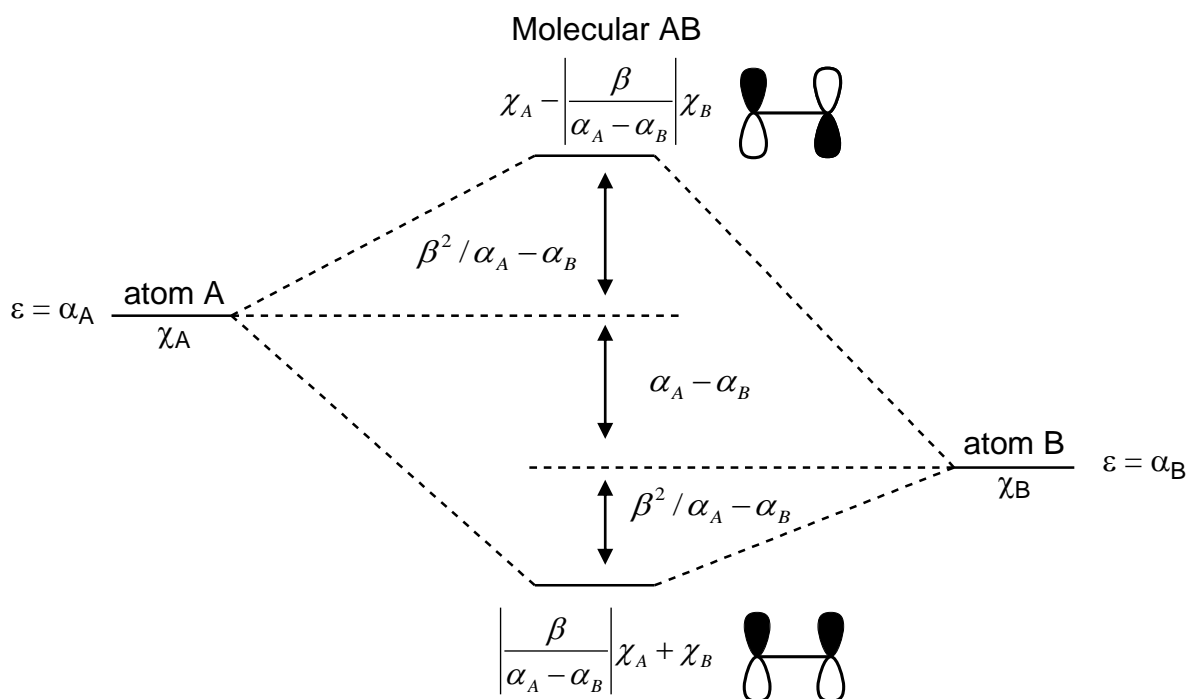


Fig. 7 bonding orbital and anti-bonding orbital

$\int \chi_A \hat{H} \chi_A d\tau = \alpha_A$, $\int \chi_B \hat{H} \chi_B d\tau = \alpha_B$ are Coulomb integrals. These can be interpreted as the energy of the electron when it occupies A (for α_A) or B (for α_B).

$\int \chi_A \hat{H} \chi_B d\tau = \int \chi_B \hat{H} \chi_A d\tau = \beta$ are resonance integrals.

These affect the bond strength.

$\int \chi_A \chi_B d\tau = S$ is overlap integral. This integral indicates two atomic orbitals on different atoms overlap.

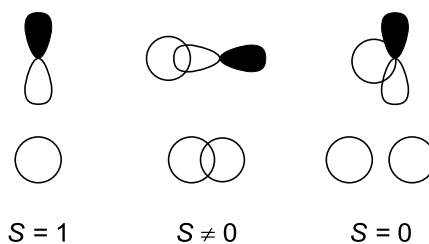


Fig.8 overlap integral S

Hückel approximations (empirical MO method) are

- All overlap integrals S are set equal to zero.
- All resonance integrals β between non-neighbors are set equal to zero
- All remaining resonance integrals are set equal to β

The Hückel method is severe approximation to consider the wavefunction of molecule.

How we calculate more detail wavefunction? —————> Hartree-Fock equation (one method)

Before studying about Hartree-Fock equation, we must know about two important concepts.

One is Slater determinant. The other is Self-Consistent Field.

4. Slater determinant -The Pauli principle-

An electron in a molecule has α spin or β spin. Previous calculation we considered ignore spin of electrons.

Now, when we consider spin of electrons for calculating wavefunction, we cannot avoid a principle which describes spin of electrons. The principle is the Pauli principle.

Lithium, for instance, has three electrons. The first two occupy a 1s orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the 1s orbital because that configuration is forbidden by the Pauli exclusion principle:

No more than two electrons may occupy any given orbital, and if two do occupy one orbital, han their spins must be paired.

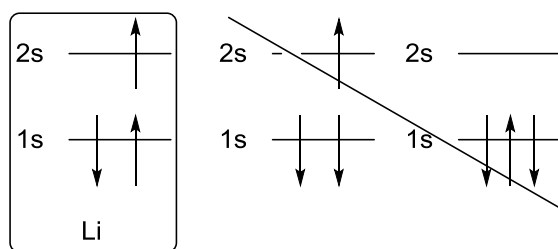


Fig. 9 the Pauli exclusion principle

The Pauli exclusion principle is a special case of a general statement called the Pauli principle:

When the labels of any two identical fermions are exchanged, the total wavefunction changes sign; when the labels of any two identical bosons are exchanged, the sign of the total wavefunction remains the same. (The electron is fermion)

By ‘total wavefunction’ is meant the entire wavefunction, including the spin of the particles. To see that the Pauli principle implies the Pauli exclusion principle, we consider the wavefunction for two electrons $\Psi(1, 2)$. The Pauli principle implies that it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function:

$$\Psi(1,2) = -\Psi(2,1) \quad (\text{Eq. 23})$$

Suppose the two electrons in an atom occupy an orbital $\Psi(1, 2)$, then in the orbital approximation the overall wavefunction is $\psi(1)\psi(2)$.

$$\begin{aligned} \Psi &= \psi(1)\psi(2) \\ \hat{H}_1\psi(1) &= E_1\psi(1), \quad \hat{H}_2\psi(2) = E_2\psi(2) \\ \hat{H}_{all}\Psi &= \hat{H}_{all}(\psi(1)\psi(2)) = (\hat{H}_1 + \hat{H}_2)(\psi(1)\psi(2)) = \psi(2)\hat{H}_1\psi(1) + \psi(1)\hat{H}_2\psi(2) \\ &= \psi(2)E_1\psi(1) + \psi(1)E_2\psi(2) = (E_1 + E_2)\psi(1)\psi(2) = E_{all}\Psi \end{aligned}$$

To apply the Pauli principle, we must deal with the total wavefunction including spin. There are several possibilities for two spins: both α , denoted $\alpha(1)\alpha(2)$, both β , denoted $\beta(1)\beta(2)$, and one α the other β , denoted either $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$.

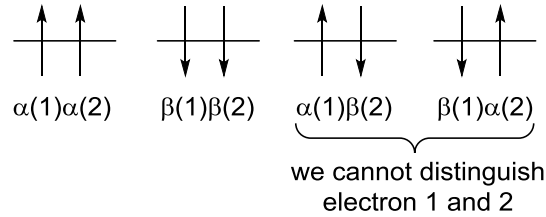


Fig. 10 spin orbital

Because we cannot tell which electron is α and which is β , in the last case it is appropriate to express the spin states as the (normalized) linear combination.

$$\begin{aligned} \sigma_+(1,2) &= \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} \\ \sigma_-(1,2) &= \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} \end{aligned} \quad (\text{Eq. 24})$$

These combinations allow one spin to be α and the other β with equal probability. The total wavefunction of the system is therefore the orbital part and one of four spin states:

$$\begin{aligned} \Psi(1,2, \alpha_1, \alpha_2) &= \psi(1)\psi(2)\alpha(1)\alpha(2) \\ \Psi(1,2, \beta_1, \beta_2) &= \psi(1)\psi(2)\beta(1)\beta(2) \\ \Psi(1,2, \alpha, \beta) &= \psi(1)\psi(2)\sigma_+(1,2) \quad \text{or} \quad \psi(1)\psi(2)\sigma_-(1,2) \end{aligned} \quad (\text{Eq. 25})$$

The Pauli principle says that for a wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = \frac{1}{\sqrt{2}} \{ \alpha(2)\beta(1) + \beta(2)\alpha(1) \} = \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) + \beta(1)\alpha(2) \} = \sigma_+(1,2) \quad (\text{Eq. 26})$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$:

$$\sigma_-(2,1) = \frac{1}{\sqrt{2}} \{ \alpha(2)\beta(1) - \beta(2)\alpha(1) \} = -\frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \} = -\sigma_-(1,2) \quad (\text{Eq. 27})$$

This combination does change sign (it is ‘antisymmetric’). The product also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that Pauli exclusion principle. The exclusion principle (but not the more general Pauli principle) is irrelevant when the orbital occupied by the electrons are different, and both electrons may then have, but need not have, the same spin state. In each case the overall wavefunction must still be antisymmetric overall and must satisfy the Pauli principle itself.

A final point in this connection is that the acceptable product wavefunction $\psi(1)\psi(2)\sigma_-(1,2)$ can be expressed as a determinant:

$$\begin{aligned} \Psi(1,2,\alpha,\beta) &= \psi(1)\psi(2)\sigma_-(1,2) \\ &= \frac{1}{\sqrt{2}} \{ \psi(1)\alpha(1)\psi(2)\beta(2) - \psi(2)\alpha(2)\psi(1)\beta(1) \} \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix} \end{aligned} \quad (\text{Eq. 28})$$

Any acceptable wavefunction for a closed-shell species can be expressed as a Slater determinant, as such determinants are known. In general, for N electrons in orbitals ψ_a, ψ_b, \dots

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & \dots & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & \dots & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_b(2)\alpha(2) & \psi_b(3)\alpha(3) & \dots & \psi_b(N)\alpha(N) \\ \vdots & \vdots & \vdots & \dots & \vdots \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & \dots & \psi_z(N)\beta(N) \end{vmatrix} \quad (\text{Eq. 29})$$

5. Self-Consistent Field

The central difficulty of the Schrödinger equation is the presence of the electron-electron interaction terms. The potential energy V in Schrödinger equation of all the electrons in an N -electron atom is

$$V = -k_0 \sum_i^N \frac{Ze^2}{r_i} + \frac{1}{2} k_0 \sum_{i,j=1}^N \frac{e^2}{r_{ij}}, \quad i \neq j \quad \left(N = 2(\text{He}), \quad V_{\text{He}} = -k_0 \sum_i^2 \frac{2e^2}{r_i} + \frac{1}{2} k_0 \frac{e^2}{r_{12}} \right) \quad (\text{Eq. 30})$$

$$-k_0 \sum_i^N \frac{Ze^2}{r_i} : \text{Attraction to the nucleus}, \quad \frac{1}{2} k_0 \sum_{i,j=1}^N \frac{e^2}{r_{ij}} : \text{Repulsion between electrons}$$

The first term is the total attractive interaction between the electrons and the nucleus. The second term is the total repulsive interaction between the electrons; r_{ij} is the distance between electrons i and j . The factor of one-half prevents double-counting of electron pair repulsions (1 interacting with 2 is the same as 2 interacting with 1). It is hopeless to expect to find analytical solutions of a Schrödinger equation with such a complicated potential energy term, but computational techniques are available that give very detailed and reliable numerical solutions for the wavefunction and energies. The techniques were originally introduced by D. R. Hartree and then modified by V. Fock to take into account the Pauli principle. In broad outline, the Hartree-Fock self-consistent field (HF-SCF) procedure is as follow.

In the Ne atom, for instance, the orbital approximation suggests configuration $1s^2 2s^2 2p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now we consider one of the $2p$ electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. This equation has the form

$$\underbrace{\hat{H}(1)\psi_{2p}(1)}_{\text{solvable}} + \underbrace{V(\text{other electrons})}_{\text{unsolvable}} \psi_{2p}(1) - \underbrace{V(\text{exchange correction})}_{\text{unsolvable}} \psi_{2p}(1) = E_{2p} \psi_{2p}(1) \quad (\text{Eq. 31})$$

Although the equation is for an electron in the $2p$ orbital, it depends on the wavefunctions of all the other occupied orbitals in the atom, and similar equations can be written for them too.

$$\hat{H}(2)\psi_{2p}(2) + V(\text{other electrons}) \psi_{2p}(2) - V(\text{exchange correction}) \psi_{2p}(2) = E_{2p} \psi_{2p}(2) \quad (\text{Eq. 32})$$

$$\hat{H}(1)\psi_{2s}(1) + V(\text{other electrons}) \psi_{2s}(1) - V(\text{exchange correction}) \psi_{2s}(1) = E_{2s} \psi_{2s}(1) \quad (\text{Eq. 33})$$

The various terms are as follows:

- The first term on the left is the contribution of the kinetic energy and the attraction of electron to nucleus.
- The second term takes into account the potential energy of the electron of interest due to the electrons in the other occupied orbitals.
- The third term is an exchange correction that takes account the spin correlation effects.

There is no hope of solving Eq. 31~33 analytically. However, it can be solved numerically if we guess an approximate form of the wavefunctions of all the orbitals except 2p. The procedure is then repeated for the other orbitals in the atom, the 1s, 2s orbitals. This sequence of calculations gives the form of 2p, 2s, 1s orbitals and in general, they will differ from the set used initially to start the calculation. These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals is obtained. The recycling continues until the orbital and energies obtained are insignificantly different from those used at start of the current cycle. The solutions are then ‘self-consistent’ and accepted as solution of the problem.

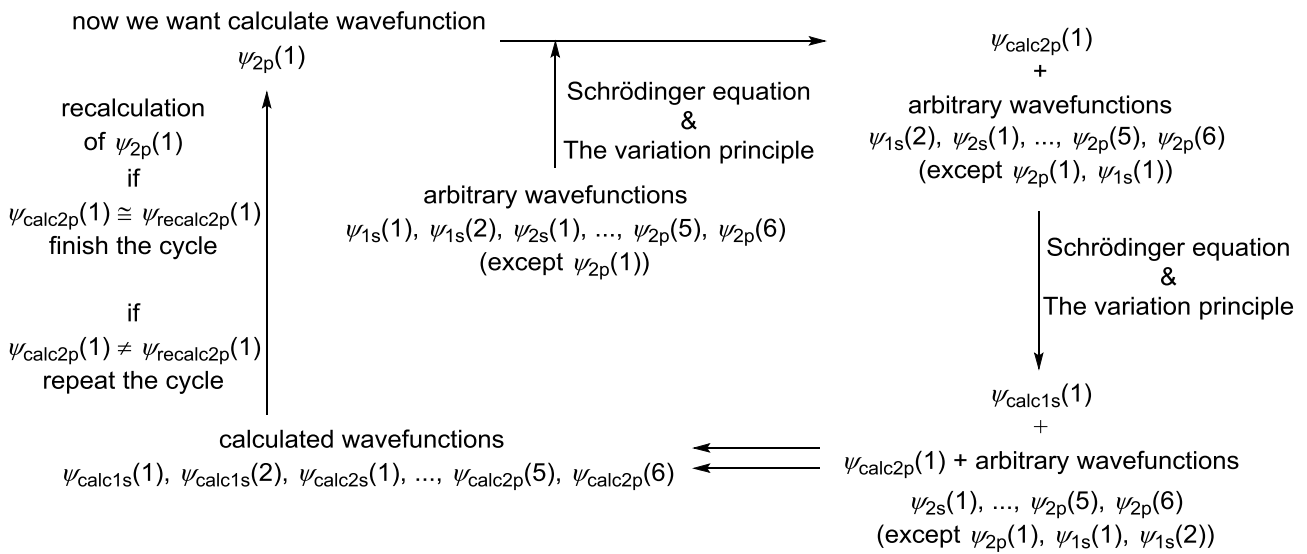


Fig. 11 Self-Consistent Field

6. Hartree-Fock equation

If we consider overall wavefunction Ψ of N -electron molecule, the Schrödinger equation is

$$\hat{H}_{all}\Psi = E_{all}\Psi$$

$$\hat{H}_{all} = -\frac{\hbar^2}{2m_e}\nabla^2 - k_0\sum_{i,j}^N\frac{Z_j e^2}{r_{ij}} + \frac{1}{2}k_0\sum_{i,i'=1}^N\frac{e^2}{r_{ii'}}, \quad i \neq i' \quad (\text{Eq. 34})$$

$-\frac{\hbar^2}{2m_e}\nabla^2$: kinetic energies of all electron, $-k_0\sum_{i,j}^N\frac{Z_j e^2}{r_{ij}}$: attraction to all nucleus,

$\frac{1}{2}k_0\sum_{i,i'=1}^N\frac{e^2}{r_{ii'}}$: repulsion between all electrons without itself.

Now, we describe Ψ as Slater determinant with molecular orbitals including spin $\psi_{\mu,\sigma}(i)$:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{a,\alpha}(1) & \psi_{a,\alpha}(2) & \psi_{a,\alpha}(3) & \dots & \psi_{a,\alpha}(N) \\ \psi_{a,\beta}(1) & \psi_{a,\beta}(2) & \psi_{a,\beta}(3) & \dots & \psi_{a,\beta}(N) \\ \psi_{b,\alpha}(1) & \psi_{b,\alpha}(2) & \psi_{b,\alpha}(3) & \dots & \psi_{b,\alpha}(N) \\ \vdots & \vdots & \vdots & \dots & \vdots \\ \psi_{z,\beta}(1) & \psi_{z,\beta}(2) & \psi_{z,\beta}(3) & \dots & \psi_{z,\beta}(N) \end{vmatrix} \quad (\text{Eq. 35})$$

The expectation value of energy $\langle E_{\text{all}} \rangle$ is

$$\langle E_{\text{all}} \rangle = \frac{\int \Psi \hat{H}_{\text{all}} \Psi d\tau}{\int \Psi^2 d\tau} \quad (\text{Eq. 36})$$

When we apply the variation principle for Eq. 36, we derive Hartree-Fock equation as follow:

$$\begin{aligned} \hat{f}\psi_{\mu,\sigma}(i) &= \varepsilon_{i'} \psi_{\mu,\sigma}(i) \\ \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - k_0 \sum_{i,j} \frac{Z_j e^2}{r_{ij}} + \sum_{i \neq i'} \left(\hat{J}_{\mu,\sigma}(i') - \hat{K}_{\mu,\sigma}(i') \right) \right] \psi_{\mu,\sigma}(i) &= \varepsilon_{i'} \psi_{\mu,\sigma}(i), \quad (\mu = a, b, \dots, z), (\sigma = \alpha, \beta) \end{aligned} \quad (\text{Eq. 37})$$

$$-\frac{\hbar^2}{2m_e} \nabla_i^2 - k_0 \sum_{i,j} \frac{Z_j e^2}{r_{ij}} : \text{kinetic energies and attraction to all nucleus}$$

$$\begin{aligned} \hat{J}_{\mu,\sigma}(i') \psi_{\mu,\sigma}(i) &= \left[\int \psi_{\mu,\sigma}(i')^* k_0 \frac{e^2}{r_{i'i}} \psi_{\mu,\sigma}(i') d\tau_2 \right] \psi_{\mu,\sigma}(i) \\ &: \text{Coulomb operator (repulsion between electrons)} \end{aligned} \quad (\text{Eq. 38})$$

$$\begin{aligned} \hat{K}_{\mu,\sigma}(i') \psi_{\mu,\sigma}(i) &= \left[\int \psi_{\mu,\sigma}(i')^* k_0 \frac{e^2}{r_{i'i}} \psi_{\mu,\sigma}(i') d\tau_2 \right] \psi_{\mu,\sigma}(i) \\ &: \text{Exchange operator (the Pauli principle)} \end{aligned} \quad (\text{Eq. 39})$$

Especially, the sum of the Coulomb operator is

$$\sum_{i \neq i'} \hat{J}_{\mu,\sigma}(i') = \sum_{i \neq i'} \int \psi_{\mu,\sigma}(i')^* k_0 \frac{e^2}{r_{i'i}} \psi_{\mu,\sigma}(i') d\tau_2 = \sum_{i \neq i'} \int k_0 \frac{e^2 |\psi_{\mu,\sigma}(i')|^2}{r_{i'i}} d\tau_2 \quad (\text{Eq. 40})$$

This term means that the effect of other electrons is accounted for in a mean-field. Therefore, the n-body system is replaced by a 1-body problem.

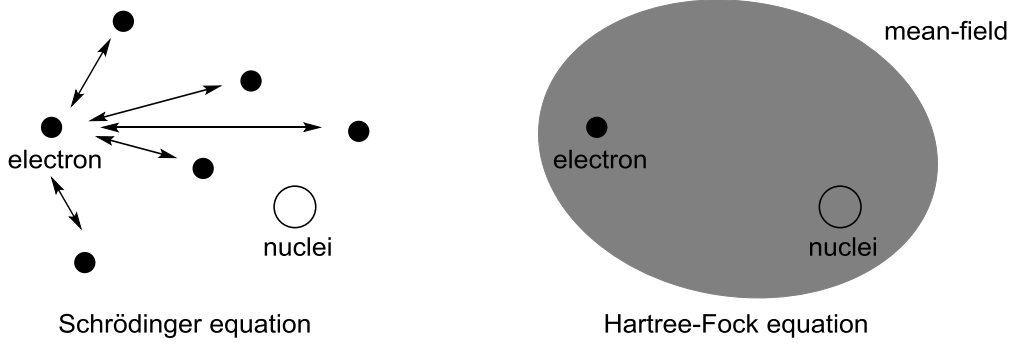


Fig. 12 mean-field of Hartree-Fock equation

However, Fock operator \hat{f} contains the other wavefunctions like $\psi_{\mu,\sigma}(i')$. So, we cannot also solve Hartree-Fock equation analytically. If we solve the Hartree-Fock equation, we must use self-consistent field method. Furthermore, arbitrary molecular orbitals $\psi_{\mu,\sigma}(i')$ is found with LCAO-MO theory.

$$\psi_{\mu,\sigma}(i') = \sum_{l=a}^m C_{l,\mu,\sigma} \chi_l = C_{a,\mu,\sigma} \chi_a + C_{b,\mu,\sigma} \chi_b + \dots + C_{m,\mu,\sigma} \chi_m \quad (\text{Eq. 41})$$

As a result, to solve Hartree-Fock equation is to calculate coefficient C_l using SCF.

$$\hat{f}_i \sum_{l=a}^m C_{l,\mu,\sigma} \chi_l(i) = \epsilon_{ii'} \sum_{l=a}^m C_{l,\mu,\sigma} \chi_l(i) \quad (\text{Eq. 42})$$

$$\begin{pmatrix} F_{11} - \epsilon_i & F_{12} - \epsilon_i S_{12} \\ F_{21} - \epsilon_i S_{21} & F_{22} - \epsilon_i \end{pmatrix} \begin{pmatrix} C_{i,1} \\ C_{i,2} \end{pmatrix} = 0 \quad (\text{Eq. 43}) \quad \begin{pmatrix} \alpha_A - \epsilon & \beta - \epsilon S \\ \beta - \epsilon S & \alpha_B - \epsilon \end{pmatrix} \begin{pmatrix} C_{i,1} \\ C_{i,2} \end{pmatrix} = 0 \quad (\text{Eq. 18})$$

$$F_{ii} = \int \chi_i \hat{f} \chi_i d\tau, \quad F_{ii'} = \int \chi_i \hat{f} \chi_{i'} d\tau = \int \chi_{i'} \hat{f} \chi_i d\tau$$

Eq. 42 is written as follow:

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix} \begin{pmatrix} C_{i,1} \\ C_{i,2} \end{pmatrix} = \begin{pmatrix} \epsilon_i & 0 \\ 0 & \epsilon_i \end{pmatrix} \begin{pmatrix} 1 & S_{12} \\ S_{21} & 1 \end{pmatrix} \begin{pmatrix} C_{i,1} \\ C_{i,2} \end{pmatrix} \quad (\text{Eq. 44})$$

We generalize Eq. 44:

$$\begin{pmatrix} F_{11} & F_{12} & \dots & F_{1m} \\ F_{21} & F_{22} & \dots & F_{2m} \\ \vdots & \vdots & \dots & \vdots \\ F_{m1} & F_{m2} & \dots & F_{mm} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1m} \\ C_{21} & C_{22} & \dots & C_{2m} \\ \vdots & \vdots & \dots & \vdots \\ C_{m1} & C_{m2} & \dots & C_{mm} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1m} \\ S_{21} & S_{22} & \dots & S_{2m} \\ \vdots & \vdots & \dots & \vdots \\ S_{m1} & S_{m2} & \dots & S_{mm} \end{pmatrix} \begin{pmatrix} C_{11} & C_{12} & \dots & C_{1m} \\ C_{21} & C_{22} & \dots & C_{2m} \\ \vdots & \vdots & \dots & \vdots \\ C_{m1} & C_{m2} & \dots & C_{mm} \end{pmatrix} \begin{pmatrix} \epsilon_1 & 0 & \dots & 0 \\ 0 & \epsilon_2 & \dots & 0 \\ \vdots & \vdots & \dots & \vdots \\ 0 & 0 & \dots & \epsilon_m \end{pmatrix} \quad (\text{Eq. 45})$$

F C S C ϵ

We obtain Eq. 45 as $FC=SC\epsilon$ (Hartree-Fock-Roothaan equation)

C : basis-sets (STO-3G, 3-21G, 6-31G, 6-311G, ...)

$$\text{Overall wavefunction } \Psi = \frac{\text{sum of the all wavefunction of molecular orbital including spin}}{\psi_{a,\alpha}(1) + \dots + \dots + \dots + \psi_{b,\beta}(N)}$$

$$\text{II}$$

$$\sum_{l=1}^m C_l \chi_l$$

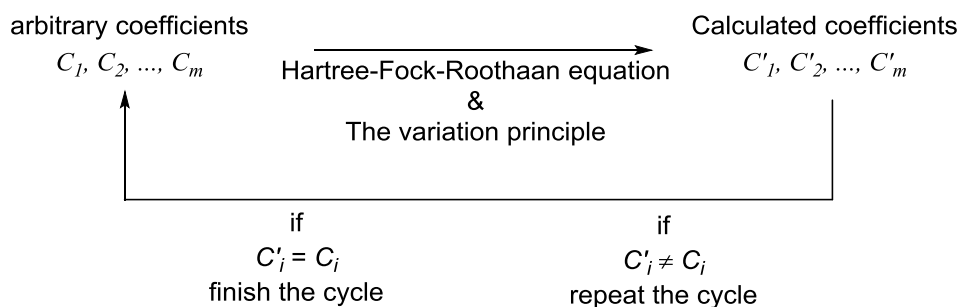


Fig. 13 Hartree-Fock-Roothaan equation

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Appendix

-Basis sets-

Minimal basis sets

STO-3G: This basis sets have only atomic orbitals which each atom has.

H: 1s, C: 1s, 2s, 2p_x, 2p_y, 2p_z

Split-valence basis sets (3-21G, 6-31G, 6-311G, ...): This basis sets have two or three (or more) basis sets for each atomic orbital.

3-21G, 6-31G: H: 1s, 1s', C: 1s, 2s, 2s', 2p_x, 2p_y, 2p_z, 2p_x', 2p_y', 2p_z'

6-311G: H: 1s, 1s', 1s'', C: 1s, 2s, 2s', 2s'', 2p_x, 2p_y, 2p_z, 2p_x', 2p_y', 2p_z', 2p_x'', 2p_y'', 2p_z''

-Semi-empirical method-

Semi-empirical method use approximation to solve Hatree-Fock equation.

Approximation of PM6: 1. All overlap integrals S are set equal to zero.

2. Coulomb integrals and resonance integrals don't solve directly.

PM6 method replaces these integral with experimental parameter*.

*Stewart, J. J. P. *J Mol Model*, **2007**, *13*, 1173.

-Density Functional Theory-

Density functional theory focuses on the electron density ρ .

$$\rho(r) = \sum_{m,occupied} |\psi_m(r)|^2$$

In this theory, the Schrödinger equation is modified which is known as Kohn-Sham equations.

$$\left[-\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{r_A} + V^{eff} \right] \psi_k = \epsilon_k \psi_k$$

$$V^{eff} = V^{Coulomb} + V^{XC}$$

If we know true V^{XC} , the Kohn-Sham equation is equal the Schrödinger equation. However, we cannot know true V^{XC} . Thus, parameter V^{XC} determines the accuracy of DFT calculation.

Exchange correlation functional (V^{XC}) consist exchange functional and correlation functional.

Exchange functional: B, mPW, PW91, S, ... (spin correlation effects)

Correlation functional: LYP, VWN, ... (electron-electron interaction effects)

Hybrid functional: B3LYP, M06, B3PW91, B3B86, ...

If we know true V^{XC} , the Kohn-Sham equation is equal the Schrödinger equation.

