Notes on Electronic Structure Theory

Francesco A. Evangelista

Emory University

Updated on February 26, 2019

Contents

Chapter 1

Hückel Theory

1.1 Foundation of the Hückel MO Method

Hückel molecular orbital theory is one of the simplest methods to determine the energy of π electrons in conjugated organic molecules. This approach neglects the σ electrons and makes several simplifications in the treatment of the π electrons.

■ **Example 1.1.1**
ethylene (2 electrons / 2 orbitals)   ■

■ **Example 1.1.2**
benzene (6 electrons / 6 orbitals)   ■

In the Hückel method electrons occupy molecular orbitals (MOs), $\psi_i(\mathbf{r})$, that are written as a linear combination of atomic orbitals (LCAO). The i-th molecular orbital $\psi_i(\mathbf{r})$ is written as

$$\psi_i(\mathbf{r}) = \sum_\mu^N \chi_\mu(\mathbf{r})C_{\mu i}, \qquad (1.1)$$

where:

- N is the number of atomic orbitals (AOs) = number of molecular orbitals (MOs) = number of atoms that share p_z orbitals

- the functions $\chi_\mu(\mathbf{r}) : \mathbb{R}^3 \to \mathbb{R}$ are atomic p_z orbitals (also called basis functions)

- $\mathbf{r} = (x, y, z)$ is the electron coordinate (we will neglect spin for now)

- the matrix $\mathbf{C}$ with elements $(\mathbf{C})_{\mu i} = C_{\mu i}$ gives the coefficient of the μ-th AO in the i-th MO. In other words, read the coefficient of ψ_i from the i-th column of the matrix $\mathbf{C}$.

■ **Example 1.1.3**
The MOs of ethylene are written as $\psi_i(r) = \chi_1(r)C_{1i} + \chi_2(r)C_{2i}$.   ■

Hückel theory postulates that the MOs satisfy the following Schrödinger equation:

$$\hat{h}(1)\psi_i(1) = \epsilon_i \psi_i(1), \qquad (1.2)$$

where

- $\hat{h}(1)$ is an effective one-electron Hamiltonian

- ϵ_i is energy of the i-th MO

- $(1) = (x_1, y_1, z_1)$ collects the space coordinate of an electron

The Hückel one-electron Hamiltonian is expressed as

$$\hat{h}(1) = \hat{T}(1) + \hat{V}(1), \tag{1.3}$$

where $\hat{T}(1)$ is the kinetic energy operator

$$\hat{T}(1) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right), \tag{1.4}$$

and $\hat{V}(1)$ is an "effective" potential energy for an electron. In Hückel we do not assume that $\hat{V}(1)$ is known. All the integrals that enter in the theory are parameters that are adjusted to match experiment.

It is convenient to introduce the following integrals in the AO basis:

$$h_{\mu\mu} = \langle \chi_\mu | \hat{h} | \chi_\mu \rangle = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r}) \hat{h}(\mathbf{r}) \chi_\mu(\mathbf{r}) \quad \text{(Coulomb integral of AO } \mu) \tag{1.5}$$

$$h_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r}) \hat{h} \chi_\nu(\mathbf{r}) \quad \text{(Resonance integral between AOs } \mu \text{ and } \nu) \tag{1.6}$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \quad \text{(Overlap integral between AOs } \mu \text{ and } \nu) \tag{1.7}$$

1.2 Determination of the MO coefficients

To determine the MO orbitals we insert the definition $|\psi_i\rangle = \sum_\mu^N |\chi_\mu\rangle C_{\mu i}$ into the Schrödinger equation [Eq. (1.2)]

$$\hat{h}(1) \sum_\mu^N |\chi_\mu\rangle C_{\mu i} = \epsilon_i \sum_\mu^N |\chi_\mu\rangle C_{\mu i}, \tag{1.8}$$

Multiply by $\langle \chi_\nu |$ from the left. The left hand side becomes:

$$\langle \chi_\nu | \hat{h}(1) \sum_\mu^N |\chi_\mu\rangle C_{\mu i} = \sum_\mu^N \langle \chi_\nu | \hat{h}(1) | \chi_\mu \rangle C_{\mu i} = \sum_\mu^N h_{\nu\mu} C_{\mu i} \tag{1.9}$$

The right hand side is:

$$\langle \chi_\nu | \epsilon_i \sum_\mu^N |\chi_\mu\rangle C_{\mu i} = \sum_\mu^N \langle \chi_\nu | \chi_\mu \rangle C_{\mu i} \epsilon_i = \sum_\mu^N S_{\nu\mu} C_{\mu i} \epsilon_i \tag{1.10}$$

Therefore we have:

$$\sum_\mu^N h_{\nu\mu} C_{\mu i} = \sum_\mu^N S_{\nu\mu} C_{\mu i} \epsilon_i, \tag{1.11}$$

which in matrix notation reads:

$$\begin{pmatrix} h_{11} & h_{12} & \dots & h_{1N} \\ h_{21} & h_{22} & \dots & h_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ h_{N1} & h_{N2} & \dots & h_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1N} \\ S_{21} & S_{22} & \dots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \dots & S_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} \epsilon_i, \tag{1.12}$$

or more compactly:

$$\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i\epsilon_i, \tag{1.13}$$

where $\mathbf{c}_i$ is the column matrix

$$\mathbf{c}_i = \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix}. \tag{1.14}$$

If we combine all the columns together into the matrix $\mathbf{C} = (\mathbf{c}_1, \mathbf{c}_2, \ldots, \mathbf{c}_N)$, we can write Eq. (1.13) as

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \tag{1.15}$$

where the matrix ϵ contains all the orbital energies in the diagonal elements

$$\epsilon = \begin{pmatrix} \epsilon_1 & 0 & \ldots & 0 \\ 0 & \epsilon_2 & \ldots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \ldots & \epsilon_N \end{pmatrix} \tag{1.16}$$

Problem 1.2.1 Convince yourself that Eq. 1.15 is correct.

The Hückel method for conjugated hydrocarbons further assumes:

- $h_{\mu\mu} = \alpha < 0$ (same for all carbon atoms), where α is the energy of an electron in AO $\chi_\mu \approx -I_\mu$ (ionization energy)

- $h_{\mu\nu} = \begin{cases} \beta < 0 & \text{if } \mu \text{ and } \nu \text{ are on adjacent atoms} \\ 0 & \text{otherwise} \end{cases}$

  $|\beta|$ measures the strength of interaction between AOs μ and ν

- That we neglect the overlap of atomic orbitals. This means that atomic orbitals are normalized ($\langle \chi_\mu | \chi_\mu \rangle = 1$) and orthogonal ($\langle \chi_\mu | \chi_\nu \rangle = 0$ if $\mu \neq \nu$). This implies that the overlap matrix $\mathbf{S}$ is the identity matrix, that is, $S_{\mu\nu} = \delta_{\mu\nu} = \begin{cases} 1 & \text{if } \mu = \nu \\ 0 & \text{if } \mu \neq \nu \end{cases}$.

1.3 The Hückel Method in Practice

■ Example 1.3.1 (Ethylene).

The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \tag{1.17}$$

The Schrödinger equation reads:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} \epsilon_i \tag{1.18}$$

Simplify and rearrange:

$$\begin{pmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = 0 \tag{1.19}$$

This equation has non-trivial solutions [1] only if the determinant of the secular matrix is equal to zero:

$$\begin{vmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{vmatrix} = 0 \Rightarrow \beta^2 \begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = 0 \tag{1.20}$$

[1] A trivial solution to a linear system $\mathbf{A}\mathbf{x} = \mathbf{0}$ is the solution $\mathbf{x} = \mathbf{0}$. In this example the trivial solution is $\begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

Introduce the reduced variable $\frac{\alpha - \epsilon_i}{\beta} = -\lambda$ and evaluate the secular determinant:

$$\begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = \begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = \lambda^2 - 1 = 0, \tag{1.21}$$

from this equation we obtain the eigenvalues:

$$\lambda^2 = \left(\frac{\alpha - \epsilon_i}{\beta} \right)^2 = 1 \Rightarrow \frac{\alpha - \epsilon_i}{\beta} = \pm 1 \Rightarrow \epsilon_i = \alpha \pm \beta \tag{1.22}$$

∎

■ **Example 1.3.2 (Benzene).**

The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & & \beta \\ \beta & \alpha & \beta & & & \\ & \beta & \alpha & \beta & & \\ & & \beta & \alpha & \beta & \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix} \tag{1.23}$$

∎

You only need the "connectivity" of a molecule to write down the Hückel Hamiltonian.

Problem 1.3.1 Write down the Hückel Hamiltonian for:

1. butadiene

2. naphthalene

3. azulene

In the Hückel method, the energy is given by the sum of the orbital energies (ϵ_i) of all the occupied orbitals

$$E = \sum_i \epsilon_i n_i, \tag{1.24}$$

where n_i is the occupation number of the orbital i. This quantity can be 0, 1, or 2

$$n_i \in \{0, 1, 2\}. \tag{1.25}$$

1.4   Heteroatoms

For hydrocarbons containing heteroatoms we introduce atom-specific and bond-specific matrix elements.

■ **Example 1.4.1 (Acrolein).**

In the case of acrolein we define modified Hückel parameters:

- $\alpha_O = \alpha + 2\beta$ (O is more electronegative than C)
- $\beta_{CO} = \sqrt{2}\beta$ (C = 0 π bond is shorter and stronger than C=C)
- $\alpha_{C'} = \alpha + 0.2\beta$ (C of CO is slightly more electronegative due to C→O charge transfer)

∎

Hamiltonian for acrolein

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & \\ \beta & \alpha & \beta & \\ & \beta & \alpha + 0.2\beta & \sqrt{2}\beta \\ & & \sqrt{2}\beta & \alpha + 2\beta \end{pmatrix}. \tag{1.26}$$

Table 1.1: Recommended values of the parameters for heteroatoms in the Hückel method

Diagonal elements			Off-diagonal elements		
Coulomb Integrals $\alpha_X = \alpha_C + l_X \beta_{CC}$			Resonance Integrals $\beta_{XY} = k_{XY}\beta_{CC}$		
atom X	# of π electrons	l_X	atom X-Y	# of π electrons	k_{XY}
= C –	(1)	0.0	C–C	(1-1)	1.0
= N –	(1)	0.5	C = N	(1-1)	1.1
- N:<	(2)	0.8	C ≡ N	(1-1)	1.3
- O -	(1)	1.1	C–N:	(1-2)	0.9
- O:	(2)	1.5	C = O	(1-1)	1.2
- F:	(2)	2.0	C–O:	(1-2)	0.7
- Cl:	(2)	1.7	C = S	(1-1)	1.0
- Br:	(2)	1.3	C–S:	(1-2)	0.5
- I:	(2)	1.15	C–F	(1-2)	0.95
= S	(1)	0.3	C–Cl	(1-2)	0.7
- S:	(2)	1.0	C–I	(1-2)	0.5
			N = N	(1-1)	1.2
			N–O	(2-1)	1.1

Hyperconjugated methyl group (CH_3)					
C	(1)	−0.1	C ≡ H_3	(1-1)	2.5
H_3	(1)	−0.5	C–CH_3	(1-1)	0.6

Larger l_X, more electronegative the atom X. Larger k_{XY}, stronger the bond XY.
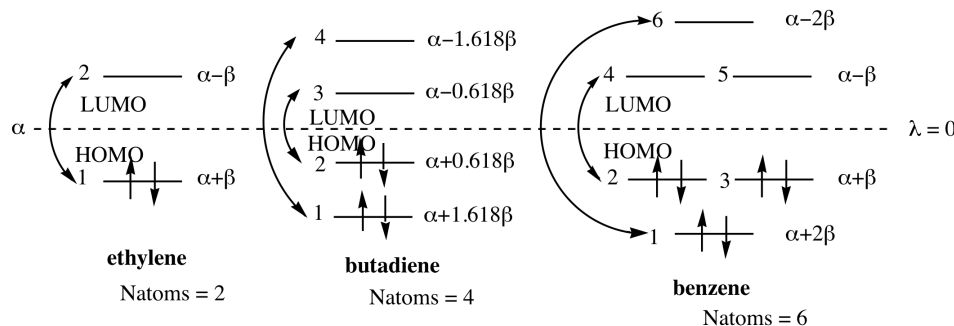
1.5 Pairing Theorem for Alternant Hydrocarbons (AHs)

For alternant hydrocarbons (hydrocarbons without odd-membered rings), MO energies are paired, which means that they are symmetric with respect to the energy α [2]

[2]Recall that $\frac{\alpha - \epsilon_i}{\beta} = -\lambda_i$.

$$\epsilon_i = \alpha + \lambda_i \beta, \tag{1.27}$$
$$\epsilon_{N-i+1} = \alpha - \lambda_i \beta. \tag{1.28}$$

■ **Example 1.5.1 (Pairing theorem for ethylene, butadiene, and benzene).**

ethylene
Natoms = 2

butadiene
Natoms = 4

benzene
Natoms = 6 ■

An interesting implication is that alternant hydrocarbons with an odd number of carbons have an orbital with $\lambda_i = 0$, that is $\epsilon_i = \alpha$. To see this consider the case $N = 2k + 1$ and consider the level $i = k + 1$. In this case the energy ϵ_{k+1} is equal to that of $\epsilon_{N-(k+1)+1}$, from which we obtain

$$\epsilon_{k+1} = \epsilon_{N-(k+1)+1} \Rightarrow \alpha + \lambda_i \beta = \alpha - \lambda_i \beta \Rightarrow \lambda_i = 0. \tag{1.29}$$

■ **Example 1.5.2 (Pairing theorem for the allyl and benzyl radicals (odd alternant)).**

allenyl (allyl radical)

Natoms = 3

benzyl radical

Natoms = 7
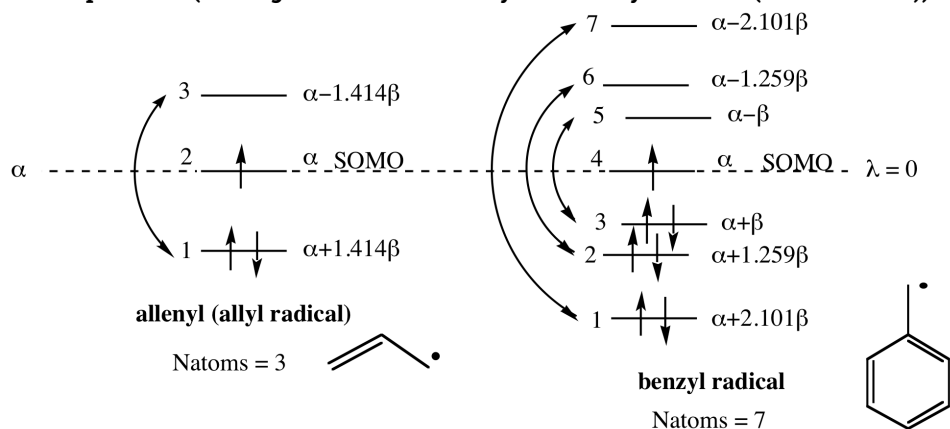
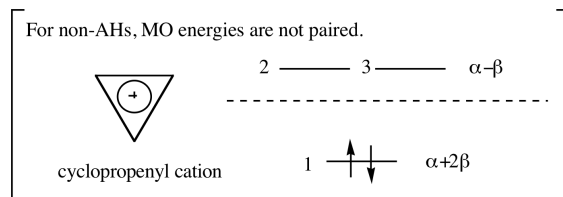In the allyl radical the second MO (ψ_2, $\epsilon_2 = \alpha$) is paired to itself. In the benzyl radical the fourth MO (ψ_4, $\epsilon_4 = \alpha$) is paired to itself.   ■

■ **Example 1.5.3 (Non alternant hydrocarbons).**
In this example, the energies of the cyclopropenyl cation are not paired

■

Another consequence of this theorem is that the coefficients of paired orbitals are also paired (MOs ψ_i and ψ_{N-i+1} are paired). This property is best expressed by labeling alternating carbon atoms with a star (*) and the relationship

$$C_{\mu,N-i+1} = \quad C_{\mu i} \quad \text{when } \mu = \text{starred atom} \qquad (1.30)$$
$$= -C_{\mu i} \quad \text{when } \mu = \text{unstarred atom.} \qquad (1.31)$$

• Method of putting * on <u>alternating</u> carbon atoms
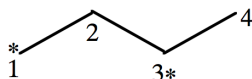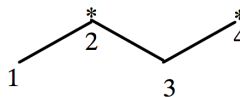
OR   Either is OK.

For odd AHs, the number of *'s must be greater than the number of non-* atoms.

For non-AH, one cannot do this:
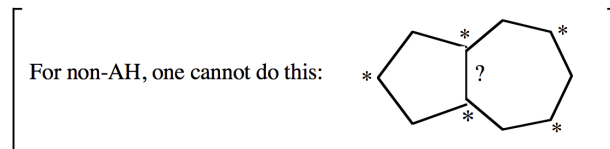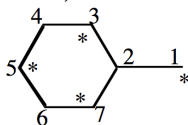
■ **Example 1.5.4 (Hückel computation on butadiene).**
The following shows the energy and coefficient matrix for butadiene.

```
Energies
```

```
        1        2(HOMO)  3(LUMO)   4
      1.618034   .618034 -.618034 -1.618034    MO energies


MO coefficients
     0    .371748  -.601501   .601501  -.371748    <- AO1
     1    .601501  -.371748  -.371748   .601501    <- AO2
     2    .601501   .371748  -.371748  -.601501    <- AO3
     3    .371748   .601501   .601501   .371748    <- AO4
         MO1        MO2       MO3       MO4
```

Note that the energies and coefficients of MOs 1 and 4 and MOs 2 and 3 are paired. Do not forget that the sign of MO as a whole is arbitrary. i.e. ψ_i or $-\psi_i$ are both OK.   ∎

■ **Example 1.5.5 (Hückel computation on allyl radical).**
The following shows the energy and coefficient matrix for the allyl radical.

```
 Energies
        1        2(SOMO)   3(LUMO)
      1.414214 .000000 -1.414214     MO energies


MO coefficients
     0   -.500000 -.707107   .500000    <- AO1
     1   -.707107  .000000  -.707107    <- AO2
     2   -.500000  .707107   .500000    <- AO3
        MO1        MO2        MO3


DENSITY AND BOND ORDER MATRIX
         1        2        3
     1   1.000000
     2    .707107 1.000000
     3    .000000  .707107  1.000000


DEGENERACIES: HOMO=0 LUMO = 0 TOTAL ENERGY = 3 ALPHA + 2.828427 BETA
```

Note that the energies and coefficients of MOs 1 and 3 are paired.   ∎

When MOs are degenerate (i.e., two MOs have same energy), their MO coefficients can not be uniquely determined. Any linear combination of degenerate MOs is also acceptable MO of the same energy. Appropriate transformation among degenerate MOs is needed to show pairing.

■ **Example 1.5.6 (Hückel computation on benzene).**
In this example, the MOs of the benzene molecule were transformed according to

$$\psi_2^{\text{new}} = + \cos\theta\psi_2 + \sin\theta\psi_3$$
$$\psi_3^{\text{new}} = - \sin\theta\psi_2 + \cos\theta\psi_3$$

and chosen either to be such that $|C_{12}|$ is maximized, which in this case is also equivalent to $C_{13} = 0$.

```
 Energies
        1        2        3        4        5        6
      2.000000  1.000000  1.000000 -1.000000 -1.000000 -2.000000


MO coefficients

     1   .408248   .455142   .355218   .567622  -.105541  -.408248
     2   .408248   .535198  -.216555  -.192409   .544345   .408248
     3   .408248   .080057  -.571773  -.375212  -.438804  -.408248
     4   .408248  -.455142  -.355218   .567622  -.105541   .408248
     5   .408248  -.535198   .216555  -.192409   .544345  -.408248
     6   .408248  -.080057   .571773  -.375212  -.438804   .408248
```

```
                    1          2          3          4          5          6

New Energies
        1          2          3          4          5          6
      2.000000   1.000000   1.000000  -1.000000  -1.000000  -2.000000


New MO coefficients
    1    .408248    .577350    .000000    .577350    .000000   -.408248
    2    .408248    .288675   -.500000   -.288675    .500000    .408248
    3    .408248   -.288675   -.500000   -.288675   -.500000   -.408248
    4    .408248   -.577350    .000000    .577350    .000000    .408248
    5    .408248   -.288675    .500000   -.288675    .500000   -.408248
    6    .408248    .288675    .500000   -.288675   -.500000    .408248
         1          2          3          4          5          6


DEGENERACIES:  HOMO=  2    LUMO=  2
```
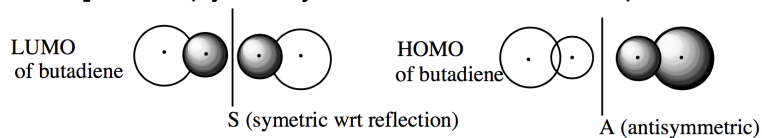
Shown above are two sets of orbitals for benzene. Note that orbitals 2 and 3 and 4 and 5 are degenerate. Therefore, we are allowed to separately mix them without changing the orbital energies. ∎

1.6   Symmetry of MOs
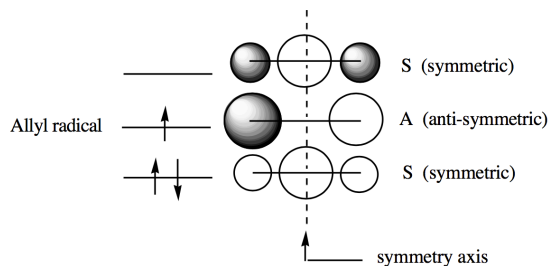
Each MO is symmetric or antisymmetric with respect to symmetry operations of the system.

■ **Example 1.6.1   (Symmetry of the orbitals in butadiene).**
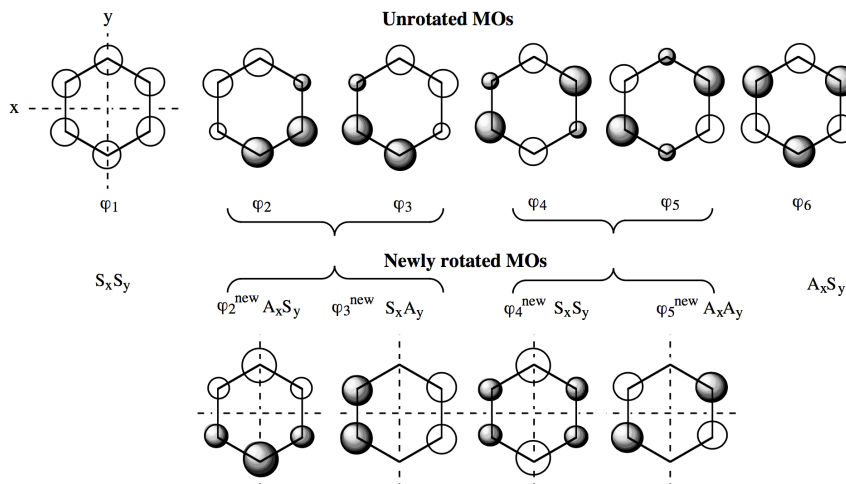

■ **Example 1.6.2   (Symmetry of the orbitals in the allyl radical).**

■ **Example 1.6.3   (Symmetry of the orbitals in benzene).**
This example shows that when MOs are degenerate, appropriate linear combinations of degenerate MOs

can be made to satisfy symmetry.

■

1.7   NBMO (Non-bonding MO) back-of-the-envelope calculation

Once a wise man said: "For odd alternant hydrocarbon radicals, the SOMO (Singly Occupied MO, $\lambda_i = 0$) can be calculated by hand".

This is a consequence of the pairing theorem for odd alternant hydrocarbon. Recall that the μ-th row of the secular equation for the SOMO and $\mu = $ a non-starred atom is given by:

$$C_{\sigma_1 i} - \lambda_i C_{\mu i} + C_{\sigma_2 i} + C_{\sigma_3 i} = 0, \qquad (1.32)$$

where σ_j stands for a surrounding starred atom. Since for the SOMO we have that $\lambda_i = 0$ then it follows that

$$\overset{\text{neighbors of non *atom}}{\underset{\sigma}{\sum}} C_{\sigma i} = 0. \qquad (1.33)$$

■ **Example 1.7.1 (Allyl radical).**

For the allyl radical we can easily compute the SOMO
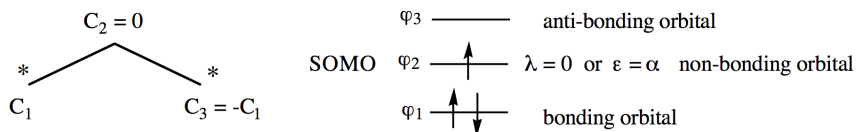
$C_2 = 0, \quad C_1 + C_3 = 0$

$C_1^2 + C_2^2 + C_3^2 = C_1^2 + C_1^2 = 1 \qquad \therefore \quad C_1 = -C_3 = 1/\sqrt{2}$

$$\varphi_{SOMO} = \frac{1}{\sqrt{2}} \chi_1 + 0 \chi_2 - \frac{1}{\sqrt{2}} \chi_3 = \frac{1}{\sqrt{2}} (\chi_1 - \chi_3)$$

■

■ **Example 1.7.2 (Benzyl radical).**

We can evaluate the reactivity

$$C_1 + C_3 = 0, \quad C_1 + C_5 = 0, \quad C_3 + C_5 + C_7 = 0$$
$$C_1^2 + C_2^2 + C_3^2 + C_4^2 + C_5^2 + C_6^2 + C_7^2 = C_1^2 + C_1^2 + C_1^2 + (2C_1)^2 = 1$$
$$\therefore \quad C_1 = 1/\sqrt{7}$$

■

What is this good for:

1. Showing off.

2. Predict the qualitative spin density distribution. (exp. measured by ESR)

3. Predict the qualitative reactivity of radicals.

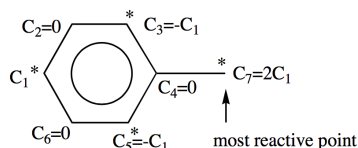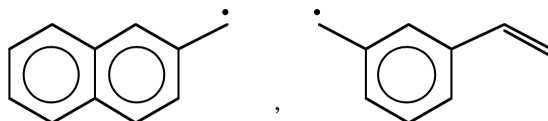■ **Example 1.7.3 (Further examples).**
Consider the following molecules:

■

1.8 MO electron density and bond order, total electron density and total bond order

Recall that i-th MO can be expanded in terms of the AOs (χ_μ = AO) and the coefficient matrix ($C_{\mu i}$) as:

$$\psi_i = \sum_\mu^N \chi_\mu C_{\mu i}. \tag{1.34}$$

[3]Recall that in quantum mechanics $|\Psi|^2 = \Psi^* \Psi$ is a probability density.

Since each MO is normalized we can write: [3]

$$1 = \langle \psi_i | \psi_i \rangle = \sum_{\mu\nu}^N C_{\mu i}^* \underbrace{\langle \chi_\mu | \chi_\nu \rangle}_{S_{\mu\nu}} C_{\nu i} = \sum_\mu^N C_{\mu i}^* C_{\mu i} S_{\mu\mu} + \sum_\mu^N \sum_{\nu \neq \mu}^N C_{\mu i}^* C_{\nu i} S_{\mu\nu}$$
$$= \sum_\mu |C_{\mu i}|^2 + \sum_{\mu \neq \nu} C_{\mu i}^* C_{\nu i} S_{\mu\nu}. \tag{1.35}$$

[4]To simplify the notation we will write $\sum_\mu \sum_{\nu \neq \mu}$ as $\sum_{\mu \neq \nu}$ and omit the superscript N.

[4] We can interpret the last two terms in the following way

- $q_\mu^i = |C_{\mu i}|^2$ is the probability of finding an electron in MO ψ_i on the atomic orbital χ_μ. Therefore, we call this the **electron density** on AO χ_μ due to the MO ψ_i.

- $p_{\mu\nu}^i = C_{\mu i}^* C_{\nu i}$ may be interpreted as the **bond order** for bond μ-ν in MO ψ_i (recall that the Hückel method assumes $S_{\mu\nu} = 0$ when $\mu \neq \nu$).

■ **Example 1.8.1 (Electron density for the first and second MOs of the allyl radical).**
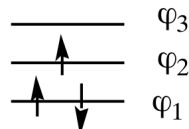
For ψ_1

AO	MO Coefficient ($C_{\mu i}$)	Electron density ($q_\mu^i = |C_{\mu i}|^2$)
1	$C_{11} = -0.5$	$q_1^1 = 0.25$
2	$C_{21} = -0.7071$	$q_2^1 = 0.5$
3	$C_{31} = -0.5$	$q_3^1 = 0.25$
Sum		$\sum_{\mu=1}^{N} q_\mu^1 = 1.0$

For ψ_2

AO	MO Coefficient ($C_{\mu i}$)	Electron density ($q_\mu^i = |C_{\mu i}|^2$)
1	$C_{12} = 0.7071$	$q_1^2 = 0.5$
2	$C_{22} = 0$	$q_2^2 = 0$
3	$C_{32} = -0.7071$	$q_3^2 = 0.5$
Sum		$\sum_{\mu=1}^{N} q_\mu^2 = 1.0$

∎

Using these quantities we define:

- **Total density on atom μ (q_μ):**

$$q_\mu = \sum_i^{\text{MO}} n_i |C_{\mu i}|^2 = \sum_i^{\text{MO}} n_i q_\mu^i \quad n_i = \text{occupation (2, 1, or 0)} \tag{1.36}$$

- **Total charge on atom μ (N_μ):**

$$N_\mu = (\text{number of } \pi \text{ electrons donated by atom } \mu) - q_\mu \tag{1.37}$$

- **Total bond order between atoms μ and ν ($p_{\mu\nu}$):**

$$p_{\mu\nu} = \sum_i^{\text{MO}} n_i C_{\mu i}^* C_{\nu i} = \sum_i^{\text{MO}} n_i p_{\mu\nu}^i \tag{1.38}$$

Note that the orbital energy may be rewritten using the orbital density ($q_\mu^i = |C_{\mu i}|^2$) and bond order ($p_{\mu\nu}^i = C_{\mu i}^* C_{\nu i}$)

$$\epsilon_i = \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_\mu q_\mu^i \alpha_\mu + 2 \sum_{\mu < \nu} p_{\mu\nu}^i \beta_{\mu\nu}. \tag{1.39}$$

and the total energy can be also expressed using the total density and bond order as

$$E = \sum_i^{\text{occ}} n_i \epsilon_i = \sum_\mu q_\mu \alpha_\mu + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu}. \tag{1.40}$$

■ **Example 1.8.2 (Hückel computation on allyl radical).**
The following shows the density and bond order matrix for the allyl radical.

```
Density and bond order matrix
         1         2         3
   1  1.000000  0.707107  0.000000
   2  0.707107  1.000000  0.707107
   3  0.000000  0.707107  1.000000
```
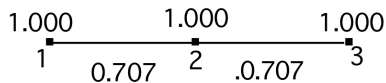
$$p_{12} = 2C_{11}C_{21} + C_{12}C_{22} = 2 \times 0.5 \times (-0.7071) + 0.7071 \times 0 = 0.7071. \qquad (1.41)$$

Note that for alternant hydrocarbons the pairing theorem always gives $q_\mu = 1$.   ■

■ **Example 1.8.3 (Hückel computation on butadiene).**
The following shows the density and bond order matrix for butadiene.

```
Density and bond order matrix
          1          2          3          4
   1   1.000000   0.894427   0.000000  -0.447214
   2   0.894427   1.000000   0.447214   0.000000
   3   0.000000   0.447214   1.000000   0.894427
   4  -0.447214   0.000000   0.894427   1.000000
```

Note that the 1-2 and 3-4 bonds ($p_{12} = p_{34} = 0.894427$) are stronger than the 2-3 bond ($p_{23} = 0.447214$). Also, ignore the negative values for non-nearneighbor atoms.   ■

■ **Example 1.8.4 (Hückel computation on pyridine).**
The following shows a full Hückel computation for pyridine.

```
NATOMS  NELECS  NINDEX   NLAB   NHOMO   NLUMO
   6       6       0       1       3       4

 Input Matrix
       1       2       3       4       5       6
   1    .5000
   2   1.1000    .0000
   3    .0000   1.0000    .0000
   4    .0000    .0000   1.0000    .0000
   5    .0000    .0000    .0000   1.0000    .0000
   6   1.1000    .0000    .0000    .0000   1.0000    .0000


 Energies
     1          2          3          4          5          6
  2.199322   1.206641   1.000000  -.916933  -1.000000  -1.989029


MO coefficients
   1    .558416    .525891    .000000    .528265    .000000   -.364069
   2    .431331    .168916    .500000   -.340234    .500000    .411900
   3    .334378   -.374659    .500000   -.269119   -.500000   -.418804
   4    .304074   -.620995    .000000    .586999    .000000    .421114
   5    .334378   -.374659   -.500000   -.269119    .500000   -.418804
   6    .431331    .168916   -.500000   -.340234   -.500000    .411900


Total energy = 6 ALPHA +  8.811924 BETA


Density and bond-order matrix
         1          2          3          4          5          6
   1  1.176780
   2  0.659388    0.929159
   3 -0.020615    0.661883   1.004356
   4 -0.313552    0.052521   0.668674   0.956191
   5 -0.020615   -0.338117   0.004356   0.668674   1.004356
   6  0.659388   -0.070841   -.338117   0.052521   0.661883   0.929159
```

```
 Total charges:
N1: 1 - 1.177= -0.177
C2: 1 - 0.929= +0.071
C3: 1 - 1.004= -0.104
C4: 1 - 0.956= +0.044
```

∎

∎ Example 1.8.5 (Hückel computation on pyrrole).

The following shows a full Hückel computation for pyrrole.

```
NATOMS   NELECS   NINDEX    NLAB    NHOMO    NLUMO
    5        6        0       1        3        4

 Input Matrix
        1       2       3       4       5
    1   .8000
    2   .9000    .0000
    3   .0000  1.0000    .0000
    4   .0000    .0000  1.0000    .0000
    5   .9000    .0000    .0000  1.0000    .0000

 Energies
          1         2         3         4         5
      2.120048   .920296    .618034 -1.240344 -1.618034

MO coefficients
    1  -.583903  -.643479   .000000   .494968   .000000
    2  -.428211  -.043004  -.601501  -.561058  -.371748
    3  -.382315   .539554  -.371748   .250434   .601501
    4  -.382315   .539554   .371748   .250434  -.601501
    5  -.428211  -.043004   .601501  -.561058   .371748

Total energy = 6 ALPHA +  7.316756 BETA

Density and bond-order matrix
          1         2         3         4         5
    1  1.510014
    2   .555412  1.094034
    3  -.247914   .728230  1.150959
    4  -.247914  -.166198   .598172  1.150959
    5   .555412  -.353179  -.166198   .728230  1.094034

Total charges:
   N1: 2 - 1.510= +0.490
   C2: 1 - 1.094= -0.094
   C3: 1 - 1.151= -0.151
```

∎

Chapter 2

Electronic wave functions

2.1 Spin

So far we have neglected to account for spin. To introduce spin, we consider a set of spin operators $\hat{s}_x$, $\hat{s}_y$, $\hat{s}_z$, analogous to angular momentum operators. [5] The spin operators satisfy the following commutation relationship

$$[\hat{s}_j, \hat{s}_k] = \hat{s}_j\hat{s}_k - \hat{s}_k\hat{s}_j = i\hbar\varepsilon_{jkl}\hat{s}_l \quad \text{with } j, k, l \in \{x, y, z\}, \tag{2.1}$$

where ε_{jkl} is the Levi-Civita symbol defined as

$$\varepsilon_{jkl} = \begin{cases} +1 & \text{if } (j, k, l) \text{ is an even permutation of } (x, y, z) \\ -1 & \text{if } (j, k, l) \text{ is an odd permutation of } (x, y, z) \\ 0 & \text{otherwise.} \end{cases} \tag{2.2}$$

The total spin operator $\hat{\vec{s}}$ is a vector operator with components

$$\hat{\vec{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z). \tag{2.3}$$

We also define the angular momentum squared operator $(\hat{s}^2)$ as

$$\hat{s}^2 = \hat{\vec{s}} \cdot \hat{\vec{s}} = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2. \tag{2.4}$$

Since the $\hat{s}^2$ commutes with all vector components of $\hat{\vec{s}}$

$$[\hat{s}^2, \hat{s}_j] = 0 \quad \text{with } j \in \{x, y, z\}, \tag{2.5}$$

we can pick one component, say the z axis and introduce a basis of spin functions $|s, m_s\rangle$ that are simultaneous eigenfunctions of $\hat{s}^2$ and $\hat{s}_z$. Note that for a given value of s, m_s can take values $s, s-1, s-2, \ldots, -s$. The spin eigenfunctions satisfy:

$$\hat{s}^2 |s, m_s\rangle = \hbar^2 s(s+1), \tag{2.6}$$

$$\hat{s}_z |s, m_s\rangle = \hbar m_s. \tag{2.7}$$

In the case of electrons we have that $s = \frac{1}{2}$, and so we label the two spin functions as α and β [6]

$$|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle, \tag{2.8}$$

$$|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle. \tag{2.9}$$

[5] We use lower case s for spin operators that act only on one particle. This notation will help us distinguish from the spin operators for a collection of electrons.

[6] Other notations are common. For example $|0\rangle$ and $|1\rangle$ is commonly used in quantum computing and $|\uparrow\rangle$ and $|\downarrow\rangle$ in physics.

These functions are normalized and orthogonal:

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1, \tag{2.10}$$

$$\langle\alpha|\beta\rangle = 0. \tag{2.11}$$

At times, we might write these functions as

$$\alpha(\omega) = \langle\omega|\alpha\rangle \tag{2.12}$$

$$\beta(\omega) = \langle\omega|\beta\rangle, \tag{2.13}$$

where ω is a fictitious spin variable. This allow us to treat $\alpha(\omega)$ and $\beta(\omega)$ as traditional wave functions. For example, the orthogonality condition [Eq. (2.11)] may be written as

$$\langle\alpha|\beta\rangle = \int d\omega\, \alpha^*(\omega)\beta(\omega) = 0. \tag{2.14}$$

When talking about spin it is also convenient to introduce the raising ($\hat{s}_+$) and lowering ($\hat{s}_-$) spin operators. These are defined as:

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \tag{2.15}$$

$$\hat{s}_- = \hat{s}_x - i\hat{s}_y \tag{2.16}$$

In the case of $s = \frac{1}{2}$ particles, the action of $\hat{s}_+$ and $\hat{s}_-$ on the spin eigenfunctions is

$$\hat{s}_+ |\alpha\rangle = 0, \tag{2.17}$$

$$\hat{s}_+ |\beta\rangle = |\alpha\rangle \quad (m_s: -\frac{1}{2} \to \frac{1}{2}), \tag{2.18}$$

$$\hat{s}_- |\alpha\rangle = |\beta\rangle \quad (m_s: \frac{1}{2} \to -\frac{1}{2}), \tag{2.19}$$

$$\hat{s}_- |\beta\rangle = 0. \tag{2.20}$$

These operator raise or lower the value of m_s or return zero if an eigenfunction with higher (lower) value of m_s does not exist. The $\hat{s}^2$ operator may be represented using the raising and lowering operators as

$$\hat{s}^2 = \hat{s}_+\hat{s}_- + \hat{s}_z^2 - \hat{s}_z. \tag{2.21}$$

It is also convenient to introduce many-electron generalizations of the spin operators. For a system of N electrons, we define total spin operators as the sum of operators action on each particle.

$$\hat{S}^2 = \sum_i^N \hat{s}^2(i), \tag{2.22}$$

$$\hat{S}_z = \sum_i^N \hat{s}_z(i), \tag{2.23}$$

$$\hat{S}_+ = \sum_i^N \hat{s}_+(i), \tag{2.24}$$

$$\hat{S}_- = \sum_i^N \hat{s}_-(i), \tag{2.25}$$

where $\hat{s}^2(i)$ means that an operator $\hat{s}^2$ acts only on electron i.

2.2 Spin orbitals

Let us introduce some important nomenclature. Functions that describe electrons in real space are called **spatial orbitals** and we will indicate them with the Greek symbol phi, $\phi_i(\vec{r})$. In general the set $\{\phi_i(\vec{r})\}$ is infinite, complete, and may be orthonormalized. [7] If the functions $\phi_i(\vec{r})$ are normalized then the quantity $|\phi_i(\vec{r})|^2 d\vec{r}$ is the probability of finding the electron in the volume element $d\vec{r}$. The completeness condition implies that we can expand any function $f(\vec{r})$ using the set $\{\phi_i(\vec{r})\}$

$$f(\vec{r}) = \sum_i^\infty a_i \phi_i(\vec{r}). \tag{2.26}$$

In practice, we use finite sets, so that $\dim\{\phi_i(\vec{r})\} = K < \infty$.

Spin orbitals are the product of a spatial orbital and a spin function: [8]

$$\psi_{i,\sigma}(x) = \psi_{i,\sigma}(\vec{r},\omega) = \phi_i(\vec{r})\sigma(\omega), \tag{2.27}$$

where $\sigma(\omega) \in \{\alpha(\omega), \beta(\omega)\}$ indicates a generic spin function. For a basis of spatial orbitals with dimension K we can collect the indices (i,σ) in one integer and define $2K$ spin orbitals:

$$\psi_{2i-1}(x) = \phi_i(\vec{r})\alpha(\omega), \tag{2.28}$$
$$\psi_{2i}(x) = \phi_i(\vec{r})\beta(\omega). \tag{2.29}$$

Note that if the spatial orbitals are orthonormal, then the spin orbital basis is also orthonormal:

$$\int d\vec{r}\, \psi_i^*(\vec{r})\psi_j(\vec{r}) = \delta_{ij}. \tag{2.30}$$

2.3 N-electron wave functions

How can we build a wave function for N electrons $\Phi(x_1, x_2, \ldots, x_N)$ from a basis of spin orbitals? Pauli's principle requires that Φ is antisymmetric with respect to odd permutations of the coordinates (spatial and spin) of any two electrons i and j:

$$\Phi(\ldots, x_i, \ldots, x_j, \ldots, x_N) = -\Phi(\ldots, x_j, \ldots, x_i, \ldots, x_N). \tag{2.31}$$

Particles whose wave functions satisfies this condition are called **fermions**.

■ **Example 2.3.1 (Wave function for two electrons).**
Consider a system of two electrons. The wave function is $\Phi(x_1, x_2)$ and the antisymmetry requirement is

$$\Phi(x_2, x_1) = -\Phi(x_1, x_2). \tag{2.32}$$

Now let us assume that we are given a complete spin orbital basis $\{\psi_i(x)\}$. We can think of $\Phi(x_1, x_2)$ with x_2 held constant as a function only of the variable x_1. Therefore, we may expand $\Phi(x_1, x_2)$ using the spin orbital basis as:

$$\Phi(x_1, x_2) = \sum_i^\infty a_i(x_2)\psi_i(x_1), \tag{2.33}$$

notice, however, that the expansions coefficients $a_i(x_2)$ will depend on the value of x_2, in other words, a_i is a function of x_2. We can now expand $a_i(x_2)$ using the same spin orbital basis:

$$a_i(x_2) = \sum_j^\infty a_{ij}\psi_j(x_2), \tag{2.34}$$

and introduced the quantity a_{ij}, which carries both the indices for the x_1 and x_2 expansions. Combining Eqs. (2.33)–(2.34) we obtain:

$$\Phi(x_1, x_2) = \sum_{ij}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2). \tag{2.35}$$

[7] A set of functions $\{\phi_i(\vec{r})\}$ is called **orthonormal** if any two functions satisfy $\int d\vec{r}\,\phi_i^*(\vec{r})\phi_j(\vec{r}) = \delta_{ij}$.

[8] We will abbreviate the spatial and spin coordinates with the symbol $x \equiv (\vec{r}, \omega)$.

This functions may satisfy the antisymmetry condition if:

$$\sum_{ij}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) = -\sum_{ij}^{\infty} a_{ij}\psi_i(x_2)\psi_j(x_1). \tag{2.36}$$

To find out the implication of this condition onto the coefficients a_{ij}, first perform the index interchange $i \leftrightarrow j$ on the left hand side:

$$\sum_{ij}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) = -\sum_{ij}^{\infty} a_{ji}\psi_j(x_2)\psi_i(x_1), \tag{2.37}$$

and the collect terms that multiply the factor $\psi_i(x_1)\psi_j(x_2)$ to obtain the condition:

$$\sum_{ij}^{\infty} (a_{ij} + a_{ji})\psi_i(x_1)\psi_j(x_2) = 0. \tag{2.38}$$

Equation (2.38) must hold for any value of $\psi_i(x_1)\psi_j(x_2)$, and this is possible only if

$$a_{ij} + a_{ji} = 0. \tag{2.39}$$

This conditions may also be written as

$$a_{ij} = -a_{ji}. \tag{2.40}$$

As a consequence, the diagonal elements of a_{ij}, a_{ii}, are zero. [9] Eq. (2.39) shows that the when we expand an antisymmetric wave function using a single-particle basis, the antisymmetry condition is reflected in the properties of the coefficients a_{ij}. [10]

Using Eq. (2.39) we may write the two-electron wave function as:

$$\begin{aligned}
\Phi(x_1, x_2) &= \sum_{i<j}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) + \sum_{i>j}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) \\
&= \sum_{i<j}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) + \sum_{j>i}^{\infty} a_{ji}\psi_j(x_1)\psi_i(x_2) \\
&= \sum_{i<j}^{\infty} a_{ij}\psi_i(x_1)\psi_j(x_2) - \sum_{i<j}^{\infty} a_{ij}\psi_i(x_2)\psi_j(x_1) \\
&= \sum_{i<j}^{\infty} a_{ij}[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)].
\end{aligned} \tag{2.41}$$

The quantity $\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)$ can also be expressed as the determinant of a matrix since:

$$\det\begin{bmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{bmatrix} \equiv \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix} = \psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1). \tag{2.42}$$

Hence we discover that $\Phi(x_1, x_2)$ must be a linear combination of determinants:

$$\Phi(x_1, x_2) = \sum_{i<j}^{\infty} a_{ij} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix}. \tag{2.43}$$

$\blacksquare$

A convenient way to represent antisymmetric wave functions for N electrons is to expand it into a basis of functions that is automatically antisymmetric with respect to particle permutations. Such functions are known as **Slater determinants** and are defined as

$$\Phi_{ijk...}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) & \cdots & \psi_i(x_N) \\ \psi_j(x_1) & \psi_j(x_2) & \cdots & \psi_j(x_N) \\ \psi_k(x_1) & \psi_k(x_2) & \cdots & \psi_k(x_N) \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix}. \tag{2.44}$$

[9]To see this set $j = i$. Then $a_{ii} + a_{ii} = 2a_{ii} = 0$, so that $a_{ii} = 0$.

[10]The quantity a_{ij} is a skew-symmetric or antisymmetric matrix. For N electrons, the expansion coefficient will be an antisymmetric **tensor** with N indices, that is $a_{i_1 i_2 i_3 \cdots i_N}$.

Slater determinants automatically satisfy the antisymmetry requirement of fermionic wave functions because the determinant of a matrix changes sign when two columns are swapped. This operation is equivalent to permuting particle indices. For convenience we will write a Slater determinant, **including its normalization factor**, with the compact notation

$$|\Phi_{ijk\ldots}\rangle = |\psi_i \psi_j \psi_k \cdots\rangle, \tag{2.45}$$

omitting the labels of the electrons. The basis of Slater determinants $\{|\psi_i \psi_j \psi_k \cdots\rangle\}$ with $i, j, k, \ldots \in \{0, 1, 2, \ldots\}$ is complete. [11] Therefore, we may expand any electronic wave function using the Slater determinant basis:

$$|\Psi\rangle = \sum_{i<j<k\cdots} C_{ijk\ldots} |\psi_i \psi_j \psi_k \cdots\rangle. \tag{2.46}$$

[11] This property is inherited from the fact that the one-electron spin orbital basis is complete.

This expansion is called a **full configuration interaction** (FCI) wave function. The FCI wave function can provide the exact solution to the electronic Schrödinger equation. In practice, we always work with a finite spin orbital basis. Then we say that the FCI wave function provides the exact solution of the Schrödinger equation **within a finite basis**. For a system with N electrons and a spin orbital basis of dimension $2K$, the number of determinants in the FCI expansion is given by the number of ways to choose a subset of N electrons, disregarding their order, from a set of $2K$ spin orbitals:

$$N_{\text{FCI}} = \binom{2K}{N}. \tag{2.47}$$

N_{FCI} grows very quickly with N and K and so the FCI wave function is impractical for more than 16–18 electrons.

■ **Example 2.3.2 (Hartree products vs. Slater determinants).**
Let us compare a wave function that is just a product of spin orbitals with a Slater determinant for a two-electrons system. A Hartree product is simply the product of orbitals:

$$\Phi^{\text{HP}}(x_1, x_2) = \psi_i(x_1)\psi_j(x_2). \tag{2.48}$$

The modulus square of $\Phi^{\text{HP}}(x_1, x_2)$ shows that the probability distribution of two electrons is just the product of individual orbital probabilities:

$$|\Phi^{\text{HP}}(x_1, x_2)|^2 = |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 = P_i(x_1)P_j(x_2). \tag{2.49}$$

A Hartree product represents a state with **no correlation**.
    A Slater determinant:

$$\Phi^{\text{SD}}(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)]. \tag{2.50}$$

has a probability distribution equal to:

$$\begin{aligned}
|\Phi^{\text{SD}}(x_1, x_2)|^2 = \frac{1}{2}[&P_i(x_1)P_j(x_2) + P_j(x_1)P_i(x_2) \\
&- \psi_i^*(x_1)\psi_j(x_1)\psi_j^*(x_2)\psi_i(x_2) \\
&- \psi_j^*(x_1)\psi_i(x_1)\psi_j(x_2)\psi_i^*(x_2)].
\end{aligned} \tag{2.51}$$

The first two terms are symmetrized probability distributions for individual orbitals $[P_i(x_1)P_j(x_2) + P_j(x_1)P_i(x_2)]$, while the third and fourth terms couple the position of electron 1 and 2. If we integrate $|\Phi^{\text{SD}}(x_1, x_2)|^2$ over the spin variables ω_1 and ω_2 we can derive a probability distribution that depends only on the positions of the electrons:

$$P(\mathbf{r}_1, \mathbf{r}_2) = \int d\omega_1 d\omega_2 |\Phi^{\text{SD}}(x_1, x_2)|^2. \tag{2.52}$$

We now distinguish two cases. If electrons have *different* spin then the probability distribution is symmetric but not correlated:

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2)]. \tag{2.53}$$

If instead the two electrons have different spin, then the cross terms $[\psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2)]$ survive and introduce correlation in the probability distribution

$$
\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[& P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2) \\
& - \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\
& - \phi_j^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_i^*(\mathbf{r}_2)].
\end{aligned}
\tag{2.54}
$$

We say that a Slater determinant accounts for **Fermi correlation**, a consequence of the antisymmetry of fermionic wave functions. This form of correlation prevents two electrons with same spin to be found at the same point in space. ∎

2.4 Full configuration interaction wave function for H_2

In this section we will do an extensive study of the wave function of H_2 in a minimal basis set. Consider two hydrogen atoms (H_A and H_B) separated by a distance R_{AB}. We will assume that each atom has one atomic basis function, $\chi_{1s}^A(\mathbf{r})$ and $\chi_{1s}^B(\mathbf{r})$. Note that these two orbitals are not necessarily orthogonal as their overlap (S) is in general not equal to zero

$$
S = \int d\mathbf{r}\chi_{1s}^A*(\mathbf{r})\chi_{1s}^B(\mathbf{r}) \neq 0.
\tag{2.55}
$$

From these atomic orbitals we can form two spatial orbitals:

$$
\phi_g(\mathbf{r}) = N_g[\chi_{1s}^A(\mathbf{r}) + \chi_{1s}^B(\mathbf{r})],
\tag{2.56}
$$

$$
\phi_u(\mathbf{r}) = N_u[\chi_{1s}^A(\mathbf{r}) - \chi_{1s}^B(\mathbf{r})].
\tag{2.57}
$$

> **Problem 2.4.1 — Normalization of the molecular orbitals of H_2.** Express the value of the normalization constants (N_g and N_u) for the wave function $\phi_g(\mathbf{r})$ and $\phi_u(\mathbf{r})$ in terms of the overlap integral S.

By combining the spatial orbitals with spin functions we obtain four spin orbitals:

$$
\psi_1(x) = \psi_g(x) = \phi_g(\mathbf{r})\alpha(\omega),
\tag{2.58}
$$

$$
\psi_2(x) = \psi_{\bar{g}}(x) = \phi_g(\mathbf{r})\beta(\omega),
\tag{2.59}
$$

$$
\psi_3(x) = \psi_u(x) = \phi_u(\mathbf{r})\alpha(\omega),
\tag{2.60}
$$

$$
\psi_4(x) = \psi_{\bar{u}}(x) = \phi_u(\mathbf{r})\beta(\omega).
\tag{2.61}
$$

From these spin orbitals we can form Slater determinants. We cannot pick any pair of spin orbitals. For example, the determinant:

$$
|\psi_g\psi_g\rangle = 0,
\tag{2.62}
$$

[12]Just to avoid confusion: a spatial orbital may accommodate two electrons (with opposite spin) a spin orbitals can accommodate only one one electron.

is zero because we have placed two electrons in the same spin orbital. [12] We may form six

unique determinants:

$$|\Phi_1\rangle = |\psi_g \psi_{\bar{g}}\rangle = \uparrow\downarrow \tag{2.63}$$

$$|\Phi_2\rangle = |\psi_g \psi_{\bar{u}}\rangle = \begin{matrix}\downarrow \\ \uparrow\end{matrix} \tag{2.64}$$

$$|\Phi_3\rangle = |\psi_u \psi_{\bar{g}}\rangle = \begin{matrix}\uparrow \\ \downarrow\end{matrix} \tag{2.65}$$

$$|\Phi_4\rangle = |\psi_u \psi_{\bar{u}}\rangle = \uparrow\downarrow \tag{2.66}$$

$$|\Phi_5\rangle = |\psi_g \psi_u\rangle = \begin{matrix}\uparrow \\ \uparrow\end{matrix} \tag{2.67}$$

$$|\Phi_6\rangle = |\psi_{\bar{g}} \psi_{\bar{u}}\rangle = \begin{matrix}\downarrow \\ \downarrow\end{matrix} \tag{2.68}$$

Symmetry greatly simplifies this problem. [13] The determinants $|\Phi_1\rangle$ and $|\Phi_4\rangle$ are gerade since the product $\psi_g \psi_{\bar{g}}$ has symmetry equal to g $\times$ g = g. [14] Determinants $|\Phi_2\rangle$, $|\Phi_3\rangle$, $|\Phi_5\rangle$, $|\Phi_6\rangle$ instead are ungerade. Spin (which is another symmetry) helps. Determinants 1–4 have all $M_S = 0$, while 5 and 6 have $M_S = +1$ and -1, respectively. Determinants with different symmetry and spin will not contribute to the same eigenfunction. As a consequence, the eigenfunctions for H_2 will be either a gerade state with $M_S = 0$ and wave function:

$$C_1 |\Phi_1\rangle + C_4 |\Phi_4\rangle , \tag{2.69}$$

or a ungerade state with $M_S = 0$ and wave function:

$$C_2 |\Phi_2\rangle + C_3 |\Phi_3\rangle , \tag{2.70}$$

or one of the two ungerade states with $M_S = \pm 1$ ($|\Phi_5\rangle$, $|\Phi_6\rangle$).

Let us now analyze these determinants in terms of the atomic basis functions. Consider Φ_1, the lowest energy determinant. If we plug in the definitions of the spin orbitals we obtain:

$$\begin{aligned}|\Phi_1\rangle = |\psi_g \psi_{\bar{g}}\rangle &= N_g^2 \,|(\chi_{1s}^A + \chi_{1s}^B)\alpha(\chi_{1s}^A + \chi_{1s}^B)\beta\rangle \\ &= N_g^2 [|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle].\end{aligned} \tag{2.71}$$

The first and last terms correspond to ionic configurations of electrons:

$$|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle \equiv \textcircled{\uparrow\downarrow} \;\; \textcircled{--} \tag{2.72}$$

and

$$|\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle \equiv \textcircled{--} \;\; \textcircled{\uparrow\downarrow} \tag{2.73}$$

since both electrons occupy the atomic orbitals on atom A or B. The remaining contributions describe covalent bonds in which each atomic orbital is occupied with one electrons. These are:

$$|\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle \equiv \textcircled{\uparrow} \;\; \textcircled{\downarrow} \tag{2.74}$$

and

$$|\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle \equiv \textcircled{\downarrow} \;\; \textcircled{\uparrow} \tag{2.75}$$

All these four determinants contribute equally, so the determinant Φ_1 represents a state that has mixture of 50% covalent and 50% ionic electronic configurations. The determinant Φ_4 is

[13] Recall that when an operator $\hat{O}$ commutes with the Hamiltonian, $[\hat{H}, \hat{O}] = 0$, then it is possible to find a set of states that simultaneously diagonalize $\hat{H}$ and $\hat{O}$. For a set of symmetry operations this result implies that the eigensolutions of $\hat{H}$ may be classified according to the irreducible representations.

[14] Recall that for molecules that possess a center of inversion the following rules apply: g $\times$ g = g, g $\times$ u = u $\times$ g = u, u $\times$ u = g.

also a 50/50 combination of covalent and ionic terms, but the sign of the covalent contributions is different:

$$
\begin{aligned}
|\Phi_4\rangle = |\psi_u \psi_{\bar{u}}\rangle &= N_u^2 \, |(\chi_{1s}^A - \chi_{1s}^B)\alpha(\chi_{1s}^A - \chi_{1s}^B)\beta\rangle \\
&= N_u^2 [|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle - |\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle - |\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle].
\end{aligned}
\tag{2.76}
$$

Any linear combination of Φ_1 and Φ_4 may be used to represent covalent or ionic states because by carefully choosing C_1 and C_4 it is possible to cancel the ionic or covalent contributions.

The determinant Φ_5 has $M_S = +1$ and is a component of a triplet state ($S = 1$). Expanding Φ_5 in terms of spin orbital we find:

$$
\begin{aligned}
|\Phi_5\rangle = |\psi_g \psi_u\rangle &= N_g N_u \, |(\chi_{1s}^A + \chi_{1s}^B)\alpha(\chi_{1s}^A - \chi_{1s}^B)\alpha\rangle \\
&= N_g N_u [\underbrace{|\chi_{1s}^A \alpha \chi_{1s}^A \alpha\rangle}_{=0} - |\chi_{1s}^A \alpha \chi_{1s}^B \alpha\rangle + |\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle - \underbrace{|\chi_{1s}^B \alpha \chi_{1s}^B \alpha\rangle}_{=0}] \\
&= 2 N_g N_u \, |\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle \, .
\end{aligned}
\tag{2.77}
$$

Where in the last step we used the antisymmetry property of Slater determinants and swapped the two spin orbitals

$$
|\chi_{1s}^A \alpha \chi_{1s}^B \alpha\rangle = -|\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle \, .
\tag{2.78}
$$

We also eliminated the Pauli-principle violating terms like this:

$$
|\chi_{1s}^A \alpha \chi_{1s}^A \alpha\rangle \equiv \left(\uparrow\uparrow\right) \quad \left(\,\text{---}\,\right)
\tag{2.79}
$$

In other words, this determinant accounts for Fermi correlation. The state Φ_5 corresponds to having each atomic orbital occupied by one alpha electron.

Finally, we will consider the spin of the determinants. Apply the operator $\hat{S}^2$ to determinant Φ_5:

$$
\hat{S}^2 |\Phi_5\rangle = \hat{S}^2 |\psi_g \psi_u\rangle = (\hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hat{S}_z) |\psi_g \psi_u\rangle \, .
\tag{2.80}
$$

Let us consider these terms in detail [15]

$$
\hat{S}_+ \hat{S}_- |\psi_g \psi_u\rangle = \hat{S}_+ (|\psi_{\bar{g}} \psi_u\rangle + |\psi_g \psi_{\bar{u}}\rangle) = 2 |\psi_g \psi_u\rangle \, .
\tag{2.81}
$$

$$
\hat{S}_z |\psi_g \psi_u\rangle = \left(\frac{1}{2} + \frac{1}{2}\right) |\psi_g \psi_u\rangle = |\psi_g \psi_u\rangle \, .
\tag{2.82}
$$

Putting all together we get

$$
\begin{aligned}
\hat{S}^2 |\Phi_5\rangle &= (\hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hat{S}_z) |\psi_g \psi_u\rangle \\
&= 2 |\psi_g \psi_u\rangle + |\psi_g \psi_u\rangle - |\psi_g \psi_u\rangle = 2 |\psi_g \psi_u\rangle \, .
\end{aligned}
\tag{2.83}
$$

This result shows that Φ_5 is an eigenfunction of $\hat{S}^2$ with eigenvalue equal to 2. In other words, $S(S+1) = 2$, which implies $S = 1$. Therefore, Φ_5 is the component of a triplet state with $M_S = +1$. Since triplets are triply degenerate, there must be two other components of the triplet. The $M_S = -1$ component is the determinant Φ_6.

What about the $M_S = 0$ component? It turns out that this component is contained in determinants Φ_2 and Φ_3. Let us compute $\hat{S}^2 |\Phi_2\rangle$. We will need the quantity:

$$
\hat{S}_+ \hat{S}_- |\Phi_2\rangle = \hat{S}_+ \hat{S}_- |\psi_g \psi_{\bar{u}}\rangle = \hat{S}_+ |\psi_{\bar{g}} \psi_{\bar{u}}\rangle = |\psi_g \psi_{\bar{u}}\rangle + |\psi_{\bar{g}} \psi_u\rangle,
\tag{2.84}
$$

and

$$
\hat{S}_z |\psi_g \psi_{\bar{u}}\rangle = \left(\frac{1}{2} - \frac{1}{2}\right) |\psi_g \psi_{\bar{u}}\rangle = 0 \, .
\tag{2.85}
$$

From these results we find that:

$$\hat{S}^2 \ket{\Phi_2} = \ket{\psi_g \psi_{\bar{u}}} + \ket{\psi_{\bar{g}} \psi_u} = \ket{\psi_g \psi_{\bar{u}}} - \ket{\psi_u \psi_{\bar{g}}} = \ket{\Phi_2} - \ket{\Phi_3}. \tag{2.86}$$

This means that Φ_2 is not an eigenfunction of $\hat{S}^2$. The fact that $\hat{S}^2 \ket{\Phi_2}$ gives back both Φ_2 and Φ_3 is a hint that a **linear combination** of these two determinants is an eigenfunction of spin. The following result:

$$\hat{S}^2 \ket{\Phi_3} = \ket{\Phi_2} + \ket{\Phi_3}. \tag{2.87}$$

suggests that we consider the plus and minus combination of Φ_2 and Φ_3:

$$\ket{\Phi_\pm} = \frac{1}{\sqrt{2}} \left(\ket{\Phi_2} \pm \ket{\Phi_3} \right). \tag{2.88}$$

These two states are such that

$$\hat{S}^2 \ket{\Phi_+} = 0, \tag{2.89}$$

and

$$\hat{S}^2 \ket{\Phi_-} = 2 \ket{\Phi_-}. \tag{2.90}$$

Therefore, Φ_- is a triplet state while Φ_+ is a singlet state.

Chapter 3

The full CI equations and Slater rules

3.1 The FCI equations and their solution

In this section we will derive the equations that determine the coefficients in the FCI wave function. For convenience, we will introduce a short-hand notation for a Slater determinant $\Phi_{ijk\cdots}(x_1, x_2, \ldots, x_N)$ where we condense all the orbital indices $ijk\cdots$ to a multi-index $I = \{i_1, i_2, i_3, \cdots\}$ with $i_1 < i_2 < i_3 < \ldots$, so that we can write determinants with only one label as Φ_I. [16] Then the FCI wave function can be written as

$$|\Psi_{\mathrm{FCI}}\rangle = \sum_I c_I |\Phi_I\rangle. \tag{3.1}$$

To derive the FCI equations we first have to establish the properties of the basis of Slater determinant. Recall that a determinant may be written as

$$\Phi_{i_1 i_2 \cdots i_N}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(x_1) & \psi_{i_1}(x_2) & \cdots & \psi_{i_1}(x_N) \\ \psi_{i_2}(x_1) & \psi_{i_2}(x_2) & \cdots & \psi_{i_2}(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_N}(x_1) & \psi_{i_N}(x_2) & \cdots & \psi_{i_N}(x_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} \sum_\pi^{N!} (-1)^{p_\pi} P_\pi \left[\psi_{i_1}(x_1)\psi_{i_2}(x_2)\cdots\psi_{i_N}(x_N) \right], \tag{3.2}$$

where π labels a permutation, $(-1)^{p_\pi}$ is the parity of the permutation π, and P_π is a permutation operator that acts on the electron coordinates. [17]

The overlap integral $\langle \Phi_I | \Phi_I \rangle$ for a generic determinant Φ_I may be written as

$$\langle \Phi_I | \Phi_I \rangle = \frac{1}{N!} \sum_\pi^{N!} \sum_{\pi'}^{N!} (-1)^{p_\pi + p_{\pi'}} \int dx_1 dx_2 \cdots dx_N$$

$$P_\pi \left[\psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \right] P_\pi \left[\psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right]. \tag{3.3}$$

Since the spin-orbital basis is assumed to be orthonormal, [18] the integrals for each separate variable must contain the square of the same spin orbital to get a non-zero result. This happens when the two permutations coincide, $\pi = \pi'$, in which case the integral simplifies to:

$$\int dx_1 dx_2 \cdots dx_N P_\pi \left[|\psi_{i_1}(x_1)|^2 |\psi_{i_2}(x_2)|^2 \cdots |\psi_{i_N}(x_N)|^2 \right] = 1. \tag{3.4}$$

Summing over all permutations we have

$$\langle \Phi_I | \Phi_I \rangle = \frac{1}{N!} \sum_\pi^{N!} 1 = \frac{N!}{N!} = 1. \tag{3.5}$$

[16] The index I is also called a *string* of indices $I = \{i_1, i_2, \ldots, i_N\}$ that indicate the occupied spin orbitals.

[17] For example, for two indices $\pi = [(1,2),(2,1)]$ and $p_\pi = [0,1]$.

[18] $\langle \psi_i | \psi_j \rangle = \delta_{ij}$.

Problem 3.1.1 — Orthogonality of Slater determinants. Show that two determinants Φ_I and Φ_J that differ by one or more spin orbital have zero overlap

$$\langle \Phi_I | \Phi_J \rangle = 0. \tag{3.6}$$

The orthonormality condition for the Slater determinants may be summarized as:

$$\langle \Phi_I | \Phi_J \rangle = \delta_{IJ}. \tag{3.7}$$

We can now proceed to derive the FCI equations. Plugging in the FCI wave function in the Schrödinger equation we obtain

$$\hat{H} \sum_I c_I | \Phi_I \rangle = E \sum_I c_I | \Phi_I \rangle . \tag{3.8}$$

Projecting onto the left with $\langle \Phi_J |$ and rearranging terms we get

$$\sum_I \langle \Phi_J | \hat{H} | \Phi_I \rangle c_I = E \sum_I \underbrace{\langle \Phi_J | \Phi_I \rangle}_{\delta_{IJ}} c_I, \tag{3.9}$$

which may be simplified to

$$\sum_I H_{IJ} c_I = E c_J, \tag{3.10}$$

with the matrix elements H_{IJ} defined as $H_{IJ} = \langle \Phi_J | \hat{H} | \Phi_I \rangle$. This is an eigenvalue problem that can be written compactly as

$$\mathbf{HC} = \mathbf{CE}, \tag{3.11}$$

where $\mathbf{H}$ is a matrix of dimension $N_{\text{FCI}} \times N_{\text{FCI}}$, where N_{FCI} is the number of FCI determinants. To solve this equation we have to derive equations for the matrix elements of the Hamiltonian operator $H_{IJ} = \langle \Phi_J | \hat{H} | \Phi_I \rangle$. The set of rules that determine the value of these matrix elements are called **Slater rules**.

3.2 Deriving the FCI equations using the Lagrangian approach

In this section we will derive the FCI equations using a different approach based on the formalism of Lagrange multipliers. In this approach we seek to minimize the Rayleigh–Ritz functional

$$E_{\mathbf{RR}}[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{3.12}$$

Note that the denominator $\langle \Psi | \Psi \rangle$ is necessary to guarantee that the functional is valid irrespective of the way we normalize the wave function Ψ. If the smallest eigenvalue of the Hamiltonian (E_0) is bound, that is, $E_0 > -\infty$, then minimization of $E_{\text{RR}}[\Psi]$ with respect to Ψ will give the lowest eigenvalue and eigenstate (Ψ_0) of the Hamiltonian

$$\min_{\Psi} E_{\mathbf{RR}}[\Psi] = E_0. \tag{3.13}$$

The minimum of $E_{\text{RR}}[\Psi]$ is obtained by solving the set of equations

$$\frac{\partial E_{\text{RR}}[\Psi]}{\partial c_I} = 0. \tag{3.14}$$

This approach is a bit clumsy because the expression that we want to minimize contains the quantity $\langle \Psi | \Psi \rangle$ in the denominator.

The Lagrangian approach offers a more direct way to find the FCI equations. To begin with, we write a Lagrangian, that is a function that contains the quantity that we want to minimize and the constraints that we need to satisfy.

■ **Example 3.2.1 (Minimization of a function of two variables with a constraint).**
Let us consider the problem of minimizing the function $f(x,y) = x^2 + 2y^2$ with the constraint that $x + y = 2$. We rewrite the constraint as a function $g(x,y) = x + y - 2$ and we will try to impose $g(x,y) = 0$. Consider the Lagrangian function of three independent variables (x, y, λ):

$$\mathcal{L}(x,y,\lambda) = f(x,y) - \lambda g(x,y) = x^2 + 2y^2 - \lambda(x + y - 2). \tag{3.15}$$

The stationary point of $\mathcal{L}(x, y, \lambda)$ with respect to the variables x, y, and λ corresponds to:

$$\frac{\partial \mathcal{L}(x,y,\lambda)}{\partial x} = 2x - \lambda = 0 \tag{3.16}$$

$$\frac{\partial \mathcal{L}(x,y,\lambda)}{\partial y} = 4y - \lambda = 0 \tag{3.17}$$

$$\frac{\partial \mathcal{L}(x,y,\lambda)}{\partial \lambda} = g(x,y) = 0. \tag{3.18}$$

From Eqs. (4.6) and (4.7) we obtain:

$$x = 2y, \tag{3.19}$$

which combined with Eq. (4.8) gives:

$$g(2y, y) = 2y + y - 2 = 0 \quad \Rightarrow \quad y = \frac{2}{3}, \tag{3.20}$$

and $x = \frac{4}{3}$. ■

The FCI Lagrangian is given by the energy minus the normalization constraint

$$\mathcal{L}[\Psi] = \underbrace{\langle \Psi | \hat{H} | \Psi \rangle}_{\text{energy}} - \underbrace{\lambda(\langle \Psi | \Psi \rangle - 1)}_{\text{normalization constraint}}$$
$$= \sum_{IJ} c_I^* H_{IJ} c_J - \lambda(\sum_I |c_I^2| - 1). \tag{3.21}$$

Taking the derivative of $\mathcal{L}[\Psi]$ with respect to c_I^* gives

$$\frac{\partial \mathcal{L}[\Psi]}{\partial c_I^*} = \sum_J H_{IJ} c_J - \lambda c_I, \tag{3.22}$$

from which we conclude that the FCI vector **c** must satisfy the eigenvalue equation

$$\sum_J H_{IJ} c_J = \lambda c_I. \tag{3.23}$$

3.3 Slater rules

In this section we look at how can we compute matrix elements of the Hamiltonian $\langle \Phi_I | \hat{H} | \Phi_J \rangle$, where Φ_I and Φ_J are two determinants built out of the same orthonormal spin orbital basis. [19] For convenience we will write the electronic Hamiltonians as

$$\hat{H} = V_{\text{NN}} + \hat{H}_1 + \hat{H}_2, \tag{3.24}$$

where

$$V_{NN} = \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}} \tag{3.25}$$

$$\hat{H}_1 = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{r_{iA}} = \sum_i \hat{h}(i) \tag{3.26}$$

$$\hat{H}_2 = \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} = \sum_i^N \sum_{j>i}^N \hat{v}(i,j). \tag{3.27}$$

[19] More general rules exist for nonorthonormal spin orbitals, and when Φ_I and Φ_J use different set of spin orbitals.

3.3.1   Matrix elements of the scalar term

The simplest matrix element is that of the scalar term (V_{NN}), which can be derived using only the orthonormality condition of the Slater determinant basis

$$\langle \Phi_I | V_{\text{NN}} | \Phi_J \rangle = V_{\text{NN}} \langle \Phi_I | \Phi_J \rangle = V_{\text{NN}} \delta_{IJ}. \tag{3.28}$$

3.3.2   Matrix elements of the Hamiltonian

Let us consider the matrix element of the one-body operator:

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi\pi'}^{N!} \sum_j (-1)^{p_\pi + p_{\pi'}} \int dx_1 dx_2 \cdots dx_N \tag{3.29}$$

$$P_\pi \left[\psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \right] \hat{h}(x_j) P_{\pi'} \left[\psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right].$$

In this case the only permutations that give nonzero contributions are those for which $\pi = \pi'$. Otherwise, there would be one or more mismatched spin orbitals, for example

$$\psi_{i_l}^*(x_k) \psi_{i_m}(x_k) \quad \text{with } i_l \neq i_m, \tag{3.30}$$

that when integrated over the same variable gives a factor of zero. Since for any permutation $P_\pi \sum_j \hat{h}(x_j) = \sum_j \hat{h}(x_j)$, we may combine the permutation operators into a single term

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_\pi^{N!} \int dx_1 dx_2 \cdots dx_N \tag{3.31}$$

$$P_\pi \left\{ \psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \left[\sum_j \hat{h}(x_j) \right] \psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right\}.$$

Each permutation of the integral will give a contribution equal to:

$$\sum_j^N \int dx \psi_{i_j}^*(x) \hat{h}(x) \psi_{i_j}(x) = \sum_j^N \langle \psi_{i_j} | \hat{h} | \psi_{i_j} \rangle = \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \psi_i \rangle, \tag{3.32}$$

and since there are $N!$ permutations, we find that

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_\pi^{N!} \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle. \tag{3.33}$$

In the last term we introduced the abbreviated notation $\langle i | \hat{h} | i \rangle \equiv \langle \psi_i | \hat{h} | \psi_i \rangle$. The derivation of the two-electron contribution is more involved, and it gives the following result:

$$\langle \Phi_I | \hat{H}_2 | \Phi_I \rangle = \sum_i \sum_{j<i} \left[\langle ij | ij \rangle - \langle ij | ji \rangle \right], \tag{3.34}$$

where the quantity $\langle ij | kl \rangle$ is a two-electron integral in **physicist notation**:

$$\langle ij | kl \rangle = \int dx_1 dx_2 \psi_i^*(x_1) \psi_j^*(x_2) \hat{v}(x_1, x_2) \psi_k(x_1) \psi_l(x_2). \tag{3.35}$$

If we introduce the antisymmetrized two-electron integral:

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle, \tag{3.36}$$

then it is possible to rewrite as an unconstrained double sum

$$\langle \Phi_I | \hat{H}_2 | \Phi_I \rangle = \sum_i \sum_{j<i} \langle ij || ij \rangle = \frac{1}{2} \sum_{ij} \langle ij || ij \rangle, \tag{3.37}$$

[20] This is simple to see: $\langle ii || ii \rangle =$ since the term that corresponds to $i = j$ is null [20] and $\langle ji || ji \rangle = \langle ij || ij \rangle$.
$\langle ii | ii \rangle - \langle ii | ii \rangle = 0.$ In summary we can express the diagonal element of the Hamiltonian matrix as

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = V_{\text{NN}} + \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij||ij \rangle, \tag{3.38}$$

where each sum is over the set of occupied molecular orbitals in Φ_I [denotes as $\text{occ}(\Phi_I)$].

■ **Example 3.3.1 (Energy of a single electron).**
Consider the determinant for a single electron:

$$|\psi_1\rangle. \tag{3.39}$$

The energy is then given by:

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = \langle 1 | \hat{h} | 1 \rangle + \frac{1}{2} \underbrace{\langle 11||11 \rangle}_{=0} = \langle 1 | \hat{h} | 1 \rangle. \tag{3.40}$$

■

■ **Example 3.3.2 (Energy of a pair of electrons in a closed-shell configuration).**
Let us consider the determinant:

$$|\Phi_I\rangle = |\psi_1 \psi_{\bar{1}}\rangle \tag{3.41}$$

The energy is given by:

$$\begin{aligned}
\langle \Psi_I | \hat{H} | \Psi_I \rangle &= \langle 1 | \hat{h} | 1 \rangle + \langle \bar{1} | \hat{h} | \bar{1} \rangle \\
&\quad + \frac{1}{2} [\langle 11|11 \rangle + \langle 1\bar{1}|1\bar{1} \rangle + \langle \bar{1}1|\bar{1}1 \rangle + + \langle \bar{1}\bar{1}|\bar{1}\bar{1} \rangle] \\
&= \langle 1 | \hat{h} | 1 \rangle + \langle \bar{1} | \hat{h} | \bar{1} \rangle + \langle 1\bar{1}|1\bar{1} \rangle,
\end{aligned} \tag{3.42}$$

where we have eliminated two-electron integrals that are zero due to a mismatch in the spin function. ■

To simplify this notation, sometimes we will use the **Coulomb integral** (J_{ij})

$$J_{ij} = \langle ij|ij \rangle = \int dx_1 dx_2 \frac{|\psi_i(x_1)|^2 |\psi_j(x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int dx_1 dx_2 \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{3.43}$$

which is just Coulomb's law for a two charges with density distribution $\rho_i(\mathbf{r}) = |\phi_i(\mathbf{r})|^2$ and $\rho_j(\mathbf{r}) = |\phi_j(\mathbf{r})|^2$. We can also define the **exchange** integral (K_{ij}) as

$$K_{ij} = \langle ij|ji \rangle = \int dx_1 dx_2 \frac{\psi_i^*(x_1) \psi_j^*(x_1) \psi_j(x_2) \psi_i(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{3.44}$$

Using these two quantities the energy of a determinant may be written as

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = V_{NN} + \sum_i^{\text{occ}(\Phi_I)} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}(\Phi_I)} (J_{ij} - K_{ij}). \tag{3.45}$$

3.4 Slater rules for off-diagonal terms

For matrix elements between two Slater determinants with different spin orbitals we have to consider different case.

3.4.1 Single replacement

First, we consider two determinants that differ in the occupation of one spin orbital. For example, consider the two determinants

$$|\Phi_I\rangle = |\psi_1 \cdots \psi_i \cdots \psi_N\rangle \tag{3.46}$$
$$|\Phi_J\rangle = |\psi_1 \cdots \psi_a \cdots \psi_N\rangle, \tag{3.47}$$

where the spin orbital ψ_i is replaced by ψ_a. In this case we say that the two determinant have been brought to have maximum coincidence in the order of the spin orbitals. The matrix elements between $|\Phi_I\rangle$ and $|\Phi_J\rangle$ is given by

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle = \langle i | \hat{h} | a \rangle + \sum_{k}^{\text{occ}(\Phi_I)} \langle ik || ak \rangle . \tag{3.48}$$

This expression contains contributions from both the one- and two-electron operator.

3.4.2 Double replacement

Next, we consider two determinants that when brought to have maximum coincidence still differ in the occupation of two spin orbitals, for example

$$|\Phi_I\rangle = |\psi_1 \cdots \psi_i \psi_j \cdots \psi_N\rangle \tag{3.49}$$

$$|\Phi_J\rangle = |\psi_1 \cdots \psi_a \psi_b \cdots \psi_N\rangle . \tag{3.50}$$

The matrix elements between $|\Phi_I\rangle$ and $|\Phi_J\rangle$ is given by a single element of the. two-electron integrals

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle = \langle ij || ab \rangle . \tag{3.51}$$

Equations (3.38), (3.48), and (3.51) are called Slater's rules and account for all nonzero matrix elements of a two-body Hamiltonian. When two determinants differ by more than two spin orbitals then a matrix element is automatically zero.

3.5   Structure of the FCI wave function and Hamiltonian

In many cases, the FCI wave function is well approximated by a single Slater determinant, say Φ_0, where

$$|\Phi_0\rangle = |\psi_1 \psi_2 \cdots \psi_N\rangle . \tag{3.52}$$

Then, we can think of all other determinants as being obtained by **exciting** electrons from orbitals that are occupied in Ψ_0 $(\psi_1 \psi_2 \cdots \psi_N)$ to those that are unoccupied $(\psi_{N+1} \psi_{N+2} \cdots \psi_{2K})$. Determinants that differ from Φ_0 by one spin orbital, for example, by replacing $\psi_N \to \psi_{N+1}$

$$|\psi_1 \psi_2 \cdots \psi_{N-1} \psi_{N+1}\rangle , \tag{3.53}$$

are called **singly excited**. We can similarly define determinants with two, three, etc. spin orbital replaced as doubly, triply, etc. excited determinants. This classification of determinants allows us to rearrange the FCI wave function as

$$|\Psi_{\text{FCI}}\rangle = c_0 |\Phi_0\rangle + \sum_{S} c_S |\Phi_S\rangle + \sum_{D} c_D |\Phi_D\rangle + \sum_{T} c_T |\Phi_T\rangle + \dots, \tag{3.54}$$

where summations over the indices S, D, and T, indicate singly, doubly, and triply excited determinants. For an N-electron system this series truncates when we reach at most N-tuply excited determinants.

Often, the FCI wave function may be expressed assuming **intermediate normalization**. This means that we scale the coefficients so that $c_0 = 1$

$$|\Psi_{\text{FCI}}\rangle = |\Phi_0\rangle + \sum_{S} c_S |\Phi_S\rangle + \sum_{D} c_D |\Phi_D\rangle + \sum_{T} c_T |\Phi_T\rangle + \dots . \tag{3.55}$$

Note that assuming this normalization of the wave function we have that

$$\langle \Psi_0 | \Phi_{\text{FCI}} \rangle = 1, \tag{3.56}$$

and the wave function is not normalized

$$\langle \Psi_{\text{FCI}} | \Phi_{\text{FCI}} \rangle \neq 1. \tag{3.57}$$

Note also that in intermediate normalization we have that

$$\langle \Phi_0 | \, \hat{H} \, | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | \, E \, | \Psi_{\text{FCI}} \rangle = E \langle \Phi_0 | \Psi_{\text{FCI}} \rangle = E. \tag{3.58}$$

Writing this expression as $E = \langle \Phi_0 | \, \hat{H} \, | \Psi_{\text{FCI}} \rangle$ and plugging in the definition of Ψ_{FCI} in intermediate normalization [Eq. (3.55)] we can express the energy in terms of only FCI coefficients for single and double excitations

$$E = \langle \Phi_0 | \, \hat{H} \, | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | \, \hat{H} \, | \Phi_0 \rangle + \sum_S c_S \langle \Phi_0 | \, \hat{H} \, | \Phi_S \rangle + \sum_D c_D \langle \Phi_0 | \, \hat{H} \, | \Phi_D \rangle . \tag{3.59}$$

Terms like $\langle \Phi_0 | \, \hat{H} \, | \Phi_T \rangle$ that arise in this expansion are zero due to Slater rules (Φ_T and Φ_0 differ by more than two spin orbitals!).

Applying a similar logic, we can map out the general structure of the FCI Hamiltonian matrix. In this case several blocks will be zero due to difference in more than two spin orbitals. For example the terms that couple the singly (Φ_S) and quadruply (Φ_Q) excited determinants

$$H_{SQ} = \langle \Phi_S | \, \hat{H} \, | \Phi_Q \rangle = 0, \tag{3.60}$$

because Φ_S and Φ_Q differ by more than two spin orbitals. The general structure of the Hamiltonian matrix is indicated below

$$\tag{3.61}$$

As you can see, only the diagonal blocks and determinant connected by two or less substitutions are nonzero. This means that the FCI matrix is very sparse. To be more precise, for each row of the matrix, there will be as many elements as the number of singly and doubly substituted determinants, which is of the order of (neglecting spin and spatial symmetry)

$$N(2K - N) + \frac{1}{4}N^2(2K - N)^2. \tag{3.62}$$

Since the number of rows contains of the order of $\binom{2K}{N}$ elements, we can see that the number of nonzero elements divided by the number of matrix elements is

$$\text{fraction of nonzero elements} = \frac{N(2K - N) + \frac{1}{4}N^2(2K - N)^2}{\binom{2K}{N}}. \tag{3.63}$$

This quantity becomes smaller as N and K increase showing that **H** is mostly empty.

3.6   Iterative solution of the FCI equations

In practical applications of FCI, it is impossible to store the full Hamiltonian matrix. Instead, one uses a **direct** diagonalization algorithm that requires storage of only several trial coefficient vectors. To see how direct algorithms work, suppose that we have a good initial guess to the FCI vector, $\tilde{\mathbf{c}}$, and that the exact eigenvector can be written as

$$\mathbf{c} = \tilde{\mathbf{c}} + \delta\mathbf{c}. \tag{3.64}$$

From this approximate eigenvector we can compute an approximate energy $\tilde{E}$

$$\tilde{E} = \frac{\tilde{\mathbf{c}}^T \mathbf{H} \tilde{\mathbf{c}}}{\tilde{\mathbf{c}}^T \tilde{\mathbf{c}}} \tag{3.65}$$

and write $E = \tilde{E} + \delta E$, where δE is the energy error with respect to the eigenvalue E. Substitute these quantity in the Schrödinger equation ($\mathbf{H}\mathbf{c} = E\mathbf{c}$) gives

$$\mathbf{H}(\tilde{\mathbf{c}} + \delta \mathbf{c}) = E(\tilde{\mathbf{c}} + \delta \mathbf{c}), \tag{3.66}$$

from which we get

$$(\mathbf{H} - \tilde{E} - \delta E)\delta \mathbf{c} = -(\mathbf{H} - \tilde{E} - \delta E)\tilde{\mathbf{c}} = -(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}} + \delta E \tilde{\mathbf{c}}. \tag{3.67}$$

Ignoring δE, we can write an equation for $\delta \mathbf{c}$ that reads as

$$\delta \mathbf{c} = -(\mathbf{H} - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \tag{3.68}$$

The inverse $(\mathbf{H} - \tilde{E})^{-1}$ can be simplified by retaining only the diagonal part of $\mathbf{H}$ ($\mathbf{H}_\mathrm{d}$) to get

$$\delta \mathbf{c} = -(\mathbf{H}_\mathrm{d} - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \tag{3.69}$$

This equation shows that if we want to improve the trial eigenvector, we just need to evaluate an expression in which only the product, $\mathbf{H}\tilde{\mathbf{c}}$, appears. This quantity is usually called the **sigma vector** and it is indicated with $\boldsymbol{\sigma} = \mathbf{H}\tilde{\mathbf{c}}$. Approaches based on direct diagonalization methods have extended the domain of FCI from several thousand determinants to several billions.

Chapter 4

Hartree–Fock theory

4.1 The Hartree–Fock wave function

The main assumption of Hartree–Fock theory is that the wave functions for N electrons may be approximated with a single Slater determinant built from a set of "optimal" spin orbitals $\{\psi_1, \psi_2, \ldots, \psi_N\}$:

$$|\Phi_0\rangle = |\psi_1, \psi_2, \ldots, \psi_N\rangle. \tag{4.1}$$

The goal is to find the best set of spin orbitals in the variational sense. Let us define the functional $E[\tilde{\Phi}]$ of a trial wave function $\tilde{\Phi}$:

$$E[\Phi] = \langle \Phi| \hat{H} |\Phi\rangle, \tag{4.2}$$

then the Hartree–Fock energy is given by:

$$E_0 = \min_{\Phi} E[\Phi] \quad \text{enforcing} \quad \langle\Phi|\Phi\rangle = 1, \tag{4.3}$$

where we assume that the determinant Φ is normalized.

In a spin orbital basis the Hartree–Fock energy is:

$$E_0[\{\psi_i\}] = \sum_i^{\text{occ}} \langle i| \hat{h} |i\rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij||ij\rangle. \tag{4.4}$$

4.1.1 Minimization of the Hartree–Fock energy functional

As we have seen in the previous section, if the spin orbitals are orthonormal then Φ is guaranteed to be normalized. How can we minimize the Hartree–Fock energy functional and at the same time impose the condition $\langle\psi_i|\psi_j\rangle = \delta_{ij}$? We will use the technique of Lagrange multipliers.

■ **Example 4.1.1 (Minimization of a function of two variables with a constraint).**
Let us consider the problem of minimizing the function $f(x, y) = x^2 + 2y^2$ with the constraint that $x + y = 2$. We rewrite the constraint as a function $g(x, y) = x + y - 2$ and we will try to impose $g(x, y) = 0$. Consider the Lagrangian function of three independent variables (x, y, λ):

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda g(x, y) = x^2 + 2y^2 - \lambda(x + y - 2). \tag{4.5}$$

The stationary point of $\mathcal{L}(x, y, \lambda)$ with respect to the variables x, y, and λ corresponds to:

$$\frac{\partial\mathcal{L}(x, y, \lambda)}{\partial x} = 2x - \lambda = 0 \tag{4.6}$$

$$\frac{\partial\mathcal{L}(x, y, \lambda)}{\partial y} = 4y - \lambda = 0 \tag{4.7}$$

$$\frac{\partial\mathcal{L}(x, y, \lambda)}{\partial\lambda} = g(x, y) = 0. \tag{4.8}$$

From Eqs. (4.6) and (4.7) we obtain:

$$x = 2y, \tag{4.9}$$

which combined with Eq. (4.8) gives:

$$g(2y, y) = 2y + y - 2 = 0 \quad \Rightarrow \quad y = \frac{2}{3}, \tag{4.10}$$

and $x = \frac{4}{3}$.   ∎

To enforce orthonormality of the spin orbitals we need to enforce the condition:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \forall i, j \in \text{occupied.} \tag{4.11}$$

To enforce this constraint we consider the following Lagrangian:

$$\mathcal{L}[\{\psi_i\}] = E_0[\{\psi_i\}] - \sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_i | \psi_j \rangle - \delta_{ij}), \tag{4.12}$$

[21] In writing the Lagrange multiplier we chose for convenience to put the index "q" before "p". This notation will be convenient later in the derivation.

[22] That is $\lambda_{ji} = \lambda_{ji}^*$.

[23] A complex Lagrangian cannot be minimized because there is no such a thing as the minimum of a complex function.

where λ_{ji} is a matrix of Lagrange multipliers. [21] Note that λ_{ji} must be a Hermitian matrix [22], which is a consequence of requiring the Lagrangian to be a real function. [23] To find the minimum of $\mathcal{L}[\{\psi_i\}]$ we require that the Lagrangian is stationary with respect to small variations of the spin orbitals $\{\delta\psi_i\}$. This mean that for any arbitrary variation of the spin orbitals $\{\delta\psi_i\}$ the Lagrangian must satisfy:

$$\mathcal{L}[\{\psi_i + \delta\psi_i\}] = \mathcal{L}[\{\psi_i\}], \tag{4.13}$$

up to first order in $\{\delta\psi_i\}$. Let us first evaluate the variation of the energy:

$$
\begin{aligned}
E_0[\{\psi_i + \delta\psi_i\}] =& \sum_i^{\text{occ}} \langle \psi_i + \delta\psi_i | \hat{h} | \psi_i + \delta\psi_i \rangle \\
&+ \frac{1}{2} \sum_{ij}^{\text{occ}} \langle (\psi_i + \delta\psi_i)(\psi_j + \delta\psi_j) || (\psi_i + \delta\psi_i)(j + \delta\psi_j) \rangle \\
=& E_0[\{\psi_i\}] + \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \delta\psi_i \rangle + \sum_i^{\text{occ}} \langle \delta\psi_i | \hat{h} | \psi_i \rangle \\
&+ \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \delta\psi_i \psi_j || \psi_i \psi_j \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \delta\psi_j || \psi_i \psi_j \rangle \\
&+ \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \psi_j || \delta\psi_i \psi_j \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \psi_j || \psi_i \delta\psi_j \rangle \\
&+ \text{(higher order)} \\
=& E_0[\{\psi_i\}] + \sum_i^{\text{occ}} \left[\langle \delta\psi_i | \hat{h} | \psi_i \rangle + \sum_j^{\text{occ}} \langle \delta\psi_i \psi_j || \psi_i \psi_j \rangle \right] \\
&+ \text{h.c.} + \text{(higher order)},
\end{aligned}
\tag{4.14}
$$

where "h.c." stands for Hermitian conjugate.

The variation of the constraint $-\sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_p \rangle \psi_q - \delta_{pq})$ is equal to:

$$
\begin{aligned}
-\sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_i + \delta\psi_i \rangle \psi_j + \delta\psi_j - \delta_{ij}) =& -\sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_i \rangle \psi_j - \delta_{ij}) \\
&- \sum_{ij}^{\text{occ}} \lambda_{ji} \langle \delta\psi_i \rangle \psi_j - \sum_{ij}^{\text{occ}} \lambda_{ji} \langle \psi_i \rangle \delta\psi_j \\
&+ \text{(higher order)}.
\end{aligned}
\tag{4.15}
$$

Let us identify the change in the Lagrangian up to linear terms, that is:

$$\delta\mathcal{L} = \mathcal{L}[\{\psi_i + \delta\psi_i\}] - \mathcal{L}[\{\psi_i\}] \tag{4.16}$$

$$\delta\mathcal{L} = \sum_i^{occ} \left[\langle \delta\psi_i | \hat{h} | \psi_i \rangle + \sum_j^{occ} \langle \delta\psi_i\psi_j || \psi_i\psi_j \rangle - \sum_{ij}^{occ} \lambda_{ji} \langle \delta\psi_p \rangle \psi_q \right] + \text{h.c.} \tag{4.17}$$

We now rewrite this expression in terms of integrals:

$$\delta\mathcal{L} = \sum_i^{occ} \int dx_1 \delta\psi_i^*(x_1) \times$$

$$\times \left[\hat{h}\psi_i(x_1) + \sum_j^{occ} \int dx_2 \frac{|\psi_j(x_2)|^2 \psi_i(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{occ} \int dx_2 \frac{\psi_j^*(x_2)\psi_i(x_2)\psi_j(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{occ} \lambda_{ji}\psi_j(x_1) \right].$$
$$\tag{4.18}$$

If we require $\delta\mathcal{L}$ to be null for any variation of the orbitals then the quantity inside the square bracket must be identically null. We can write this condition in the following way, which is suggestive of a eigenvalue problem:

$$\hat{h}\psi_i(x_1) + \sum_j^{occ} \int dx_2 \frac{|\psi_j(x_2)|^2 \psi_i(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{occ} \int dx_2 \frac{\psi_j(x_2)^*\psi_i(x_2)\psi_j(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_j^{occ} \lambda_{ji}\psi_j(x_1). \tag{4.19}$$

If we introduce the Coulomb ($\hat{J}_j$) and exchange ($\hat{K}_j$) operators:

$$\hat{J}_j(x_1)\psi_i(x_1) = \int dx_2 \frac{|\psi_j(x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_i(x_1) \tag{4.20}$$

$$\hat{K}_j(x_1)\psi_i(x_1) = \int dx_2 \frac{\psi_j^*(x_2)\psi_i(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j(x_1), \tag{4.21}$$

we may rewrite the stationary conditions as:

$$\left[\hat{h}(x_1) + \sum_j^{occ} \hat{J}_j(x_1) - \hat{K}_j(x_1) \right] \psi_i(x_1) = \sum_j^{occ} \lambda_{ji}\psi_j(x_1), \tag{4.22}$$

or

$$\hat{f}(x_1)\psi_i(x_1) = \sum_j^{occ} \lambda_{ji}\psi_j(x_1). \tag{4.23}$$

Eq. (4.23) is called the **Hartree–Fock equation in noncanonical form** and the operator $\hat{f}(x_1) = \hat{h}(x_1) + \sum_j^{occ} \hat{J}_j(x_1) - \hat{K}_j(x_1)$ is called the Fock operator. Note, that this is not an eigenvalue problem because on the r.h.s. we have a sum of functions. Essentially this equations says that when we apply the Fock operator to any occupied orbital, we get back a linear combination of occupied orbitals. This implies that if we apply the Fock operator to a unoccupied (virtual) orbital, then we get back a linear combination of virtual orbitals.

4.1.2 Hartree–Fock equations in the canonical form

Consider a unitary transformation of the occupied orbitals:

$$|\psi_i'\rangle = \sum_j^{occ} |\psi_j\rangle U_{ji}, \tag{4.24}$$

[24] $\mathbf{U}^{-1} = \mathbf{U}^\dagger$

where the matrix $\mathbf{U}$ is unitary. [24] It is possible to prove that a determinant built from the spin orbitals ψ_i' is related to the determinant in the original basis by a complex phase factor:

$$|\Phi'\rangle = |\psi_1'\psi_2'\cdots\psi_N'\rangle = e^{i\theta}|\Phi\rangle. \tag{4.25}$$

From this it can be seen that any property that is given by expectation value is invariant:

$$\langle\Phi'|\hat{A}|\Phi'\rangle = \langle\Phi|\hat{A}|\Phi\rangle\, e^{-i\theta}e^{i\theta} = \langle\Phi|\hat{A}|\Phi\rangle. \tag{4.26}$$

It is possible to prove that the Coulomb and exchange operators are invariant:

$$\sum_j \hat{J}_j'(x_1) = \sum_j \hat{J}_j(x_1), \tag{4.27}$$

$$\sum_j \hat{K}_j'(x_1) = \sum_j \hat{K}_j(x_1) \tag{4.28}$$

and consequently the Fock operator is invariant with respect to this orbital rotation, that is, $\hat{f}' = \hat{f}$. From Eq. (4.23) it is easy to show that:

$$\langle\psi_j|\hat{f}|\psi_i\rangle = \lambda_{ji}. \tag{4.29}$$

In the unitarily-transformed basis this condition reads:

$$\langle\psi_j'|\hat{f}'|\psi_i'\rangle = \lambda_{ji}' = \sum_{kl} U_{lj}^*\langle\psi_l|\hat{f}'|\psi_k\rangle U_{ki} = \sum_{kl} U_{lj}^*\lambda_{lk}U_{ki}, \tag{4.30}$$

which may be written in the equivalent form:

$$\boldsymbol{\lambda}' = \mathbf{U}^\dagger\boldsymbol{\lambda}\mathbf{U}. \tag{4.31}$$

This result tells us that the Lagrange multipliers in the transformed basis are a unitary transformation of the original Lagrange multipliers. If we choose the unitary transformation in such a way that $\boldsymbol{\lambda}'$ is diagonal, then we can rewrite the Hartree–Fock equation as:

$$\hat{f}'(x_1)\psi_i'(x_1) = \lambda_{ii}'\psi_i'(x_1). \tag{4.32}$$

Eq. (4.33) is the **Hartree–Fock equation in canonical form**. The orbitals that satisfy this equation are called canonical Hartree–Fock MOs. In writing this equation we may assume that we are using the set of canonical orbitals so we can drop the prime and replace λ_{ii}' with ϵ_i:

$$\hat{f}(x_1)\psi_i(x_1) = \epsilon_i\psi_i(x_1). \tag{4.33}$$

The quantity ϵ_i is called the canonical orbital energy.

4.1.3   Meaning of the Hartree–Fock orbital energies. Koopman's theorem

From the canonical Hartree–Fock equation [Eq. (4.33)] we can derive an expression for the energy of an orbital:

$$\epsilon_i = \langle\psi_i|\hat{f}|\psi_i\rangle = \langle i|\hat{h}|i\rangle + \sum_k^{occ}\langle ik||ik\rangle. \tag{4.34}$$

By manipulation of the energy of a determinant we can relate it to the orbital energies:

$$\begin{aligned}
E_0[\{\psi_i\}] &= \sum_i^{occ}\langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^{occ}\langle ij||ij\rangle \\
&= \sum_i^{occ}\langle i|\hat{h}|i\rangle + \sum_{ij}^{occ}\langle ij||ij\rangle - \frac{1}{2}\sum_{ij}^{occ}\langle ij||ij\rangle \\
&= \sum_i\epsilon_i - \frac{1}{2}\sum_{ij}^{occ}\langle ij||ij\rangle.
\end{aligned} \tag{4.35}$$

It is important to note that the HF energy is not the sum of orbital energies.

Now consider a Slater determinant built from the Hartree–Fock orbitals in which one of the spin orbitals, in this case the last one, has been removed:

$$|\Phi_0^{N-1}\rangle = |\psi_1, \psi_2, \ldots, \psi_{N-1}\rangle. \tag{4.36}$$

The energy of Φ_0^{N-1} is:

$$E_0^{N-1}[\{\psi_i\}] = \sum_i^{N-1} \langle i| \hat{h} |i\rangle + \frac{1}{2} \sum_{ij}^{N-1} \langle ij||ij\rangle. \tag{4.37}$$

and the difference $E_0 - E_0^{N-1}$ is given by: [25]

$$E_0 - E_0^{N-1} = \langle N| \hat{h} |N\rangle + \frac{1}{2} \sum_i^{N-1} \langle iN||iN\rangle + \frac{1}{2} \sum_j^{N-1} \langle Nj||Nj\rangle$$

$$+ \langle NN||NN\rangle \tag{4.38}$$

$$= \langle N| \hat{h} |N\rangle + \sum_i^{N-1} \langle iN||iN\rangle = \epsilon_N.$$

> [25] Note that the difference between $\sum_{ij}^N A_{ij} - \sum_{ij}^{N-1} A_{ij}$ is equal to $A_{NN} + \sum_i^{N-1} A_{iN} + \sum_j^{N-1} A_{Nj}$.

This result shows that the energy of the last occupied orbital is the energy necessary to remove one electron (ionize) from the system. This result may be generalized to any occupied orbital. In general we find that for a general occupied spin orbital (ψ_i):

$$\text{Ionization potential} = \text{IP} = E_0^{N-1} - E_0^N = -\epsilon_i. \tag{4.39}$$

By a similar procedure it is possible to show that for a generic unoccupied orbital (ψ_a):

$$\text{Electron affinity} = \text{EA} = E_0^N - E_0^{N+1} = -\epsilon_a. \tag{4.40}$$

These results are called Koopman's theorem. Note that orbitals are assumed to be frozen, which means that we are ignoring relaxation effects to the addition or removal of electrons. Koopman's theorem also ignores electron correlation, so the IP and EA will deviate from experiment.

We can also investigate the energy of an electronically excited determinant. Consider for example the orbital substitution $\psi_i \to \psi_a$ to give the determinant Φ_i^a. The energy of this excited determinant is:

$$\langle \Phi_i^a| \hat{H} |\Phi_i^a\rangle = \sum_j^N \langle j| \hat{h} |j\rangle + \langle a| \hat{h} |a\rangle - \langle i| \hat{h} |i\rangle$$

$$+ \frac{1}{2} \sum_{ij}^N \langle ij||ij\rangle + \sum_j^N \langle aj||aj\rangle - \sum_j^N \langle ij||ij\rangle \tag{4.41}$$

$$- \langle ia||ia\rangle,$$

where we subtract $\langle ia||ia\rangle$ to avoid counting the interaction of an electron in ψ_a with ψ_i. If we collect terms that contribute to E_0, ϵ_a, and ϵ_i, we may rewrite the energy of an excited state as:

$$\langle \Phi_i^a| \hat{H} |\Phi_i^a\rangle = E_0 + \epsilon_a - \epsilon_i - \underbrace{\langle ia||ia\rangle}_{\text{hole/electron interaction}}. \tag{4.42}$$

This expression shows that the excitation energy is the difference between orbital energies minus a term that represents the Coulomb/exchange interaction of the hole created by removing an electron from ψ_i and the electron in ψ_a.

4.1.4   Generalized, unrestricted, and restricted Hartree–Fock theory

So far we have not imposed any restriction on the spin orbital basis. Within HF theory one may form a hierarchy of increasingly more constrained theory. The most general case is *generalized* Hartree–Fock (GHF). In this formalism spin orbitals are a linear combination of a alpha plus beta component:

$$\psi_p^{\mathrm{GHF}}(\mathbf{r}, \omega) = \phi_{p,\alpha}(\mathbf{r})\alpha(\omega) + \phi_{p,\beta}(\mathbf{r})\beta(\omega). \tag{4.43}$$

In GHF electrons is also called a non-collinear HF because electron spins are not constrained to be eigenfunctions of $\hat{S}_z$.

   Unrestricted Hartree–Fock (UHF) restricts spin orbitals to be alpha or beta. If we arrange spin orbitals in such a way that alpha and beta spin alternate we can write the unrestricted spin orbitals as:

$$\begin{aligned}
\psi_{2p-1}^{\mathrm{UHF}}(\mathbf{r}, \omega) &= \phi_{2p-1}(\mathbf{r})\alpha(\omega), \\
\psi_{2p}^{\mathrm{UHF}}(\mathbf{r}, \omega) &= \phi_{2p}(\mathbf{r})\beta(\omega),
\end{aligned} \tag{4.44}$$

with $p = 1, \ldots, K$, where K is the size of the spatial orbital basis. We are free to arrange these functions and later we will use an indexing that puts alpha spin orbitals before beta spin orbitals:

$$\psi_p^{\mathrm{UHF}}(\mathbf{r}, \omega) = \phi_p(\mathbf{r})\begin{cases}\alpha(\omega) & \text{if } p < K \\ \beta(\omega) & \text{if } p \geq K\end{cases}, \tag{4.45}$$

with $p = 1, \ldots, 2K$.

   Restricted Hartree–Fock (RHF) theory constrains spin orbitals to have alpha or beta spin. Spin orbitals come in pairs with identical spatial components:

$$\begin{aligned}
\psi_{2p-1}^{\mathrm{RHF}}(\mathbf{r}, \omega) &= \phi_p(\mathbf{r})\alpha(\omega), \\
\psi_{2p}^{\mathrm{RHF}}(\mathbf{r}, \omega) &= \phi_p(\mathbf{r})\beta(\omega),
\end{aligned} \tag{4.46}$$

with $p = 1, \ldots, K$. If the spin orbitals are arranged so that the alpha spin orbitals come before the beta spin orbitals then:

$$\psi_p^{\mathrm{RHF}}(\mathbf{r}, \omega) = \begin{cases}\phi_p(\mathbf{r})\alpha(\omega) & \text{if } p < K \\ \phi_{p-K}(\mathbf{r})\beta(\omega) & \text{if } p \geq K\end{cases}, \tag{4.47}$$

with $p = 1, \ldots, 2K$.

4.1.5   Closed-shell restricted Hartree–Fock theory

The Hartree–Fock equations can be further simplified in the case of closed-shell species with equal number of alpha and beta electrons. In this case, we assume electrons with alpha and beta spin are paired in orbitals with identical spatial component and the wave function is approximated with the following Slater determinant:

$$\left|\Phi_0^{\mathrm{RHF}}\right\rangle = \left|\phi_1\alpha, \ldots, \phi_{N/2}\alpha, \phi_1\beta, \ldots, \phi_{N/2}\beta\right\rangle. \tag{4.48}$$

Expressions for the energy and Fock matrix in terms of spatial orbitals can be derived by expressing a sum over spin orbitals in terms of sums over spatial orbitals:

$$\sum_i^N \psi_i = \sum_i^{N/2} \phi_i\alpha + \sum_i^{N/2} \phi_i\beta. \tag{4.49}$$

In this case the energy expression then takes the simplified form:

$$E_0 = \sum_{i=1}^{N/2} \langle i| \hat{h} |i\rangle + \sum_{i=1}^{N/2} \langle \bar{i}| \hat{h} |\bar{i}\rangle$$
$$\frac{1}{2}\sum_{ij}^{N/2} \langle ij||ij\rangle + \frac{1}{2}\sum_{i\bar{j}}^{N/2} \langle i\bar{j}||i\bar{j}\rangle + \frac{1}{2}\sum_{\bar{i}j}^{N/2} \langle \bar{i}j||\bar{i}j\rangle + \frac{1}{2}\sum_{\bar{i}\bar{j}}^{N/2} \langle \bar{i}\bar{j}||\bar{i}\bar{j}\rangle. \tag{4.50}$$

We can use the fact that in the restricted closed-shell case:

$$\langle i| \hat{h} |i\rangle = \langle \bar{i}| \hat{h} |\bar{i}\rangle, \tag{4.51}$$

while for the two-electron integrals:

$$\langle ij||ij\rangle = \langle \bar{i}\bar{j}||\bar{i}\bar{j}\rangle = \langle ij \rangle\, ij - \langle ij \rangle\, ji, \tag{4.52}$$

and

$$\langle i\bar{j}||i\bar{j}\rangle = \langle \bar{i}j||\bar{i}j\rangle = \langle ij \rangle\, ij, \tag{4.53}$$

to write the energy expression as:

$$E_0 = 2\sum_{i=1}^{N/2} \langle i| \hat{h} |i\rangle + \sum_{ij}^{N/2}[2 \langle ij \rangle\, ij - \langle ij \rangle\, ji]. \tag{4.54}$$

Similarly, we can express the Fock matrix as:

$$\langle i| \hat{f} |j\rangle = \langle i| \hat{h} |j\rangle + \sum_{k}^{N/2}[2 \langle ik \rangle\, jk - \langle ik \rangle\, kj]. \tag{4.55}$$

4.1.6 The Roothan equations

In this section we will derive the Roothan equations. These equations correspond to the Hartree–Fock equations expressed in a finite computational basis $\{\chi_\mu\}$. The main idea is to express the spatial molecular orbitals $\phi_i(\mathbf{r})$ as a linear combination of the computational basis:

$$\phi_i(\mathbf{r}) = \sum_\mu \chi_\mu(\mathbf{r})C_{\mu i}. \tag{4.56}$$

Let us consider the Hartree–Fock equation:

$$\hat{f} |\psi_i\rangle = |\psi_i\rangle\, \epsilon_i, \tag{4.57}$$

next, insert the expansion on the computational basis and project on the left with $\langle \chi_\nu \alpha|$ to get:

$$\sum_\mu \langle \chi_\nu| \hat{f} |\chi_\mu\rangle C_{\mu i} = \sum_\mu \langle \chi_\nu \rangle \chi_\mu C_{\mu i}\epsilon_i. \tag{4.58}$$

In general, the computational basis may not be orthonormal. Therefore, we write $\langle \chi_\nu \rangle \chi_\mu = S_{\nu\mu}$, where $S_{\nu\mu}$ is the *overlap matrix*. If we denote the matrix elements of the Fock operator as $F_{\nu\mu} = \langle \chi_\nu| \hat{f} |\chi_\mu\rangle$, we may write:

$$\sum_\mu F_{\nu\mu}C_{\mu i} = \sum_\mu S_{\nu\mu}C_{\mu i}\epsilon_i, \tag{4.59}$$

or in matrix notation

$$\mathbf{FC} = \mathbf{SC}\epsilon, \tag{4.60}$$

where ϵ is a diagonal matrix. This is Roothan's form of the Hartree–Fock equations. Note that due to the presence of **S**, this is a generalized eigenvalue problem.

The matrix **F** is the Fock operator expressed in the computational basis and is given by:

$$(\mathbf{F})_{\mu\nu} = f_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle + \sum_k^{N/2} [2 \langle \chi_\mu \phi_k \rangle \chi_\nu \phi_k - \langle \chi_\mu \phi_k \rangle \phi_k \chi_\nu]$$

$$= h_{\mu\nu} + \sum_k^{N/2} [2 \langle \chi_\mu \chi_\rho \rangle \chi_\nu \chi_\sigma - \langle \chi_\mu \chi_\rho \rangle \chi_\sigma \chi_\nu] C_{\rho k}^* C_{\sigma k}. \tag{4.61}$$

If we introduce the density matrix:

$$P_{\rho\sigma} = \sum_k^{N/2} C_{\rho k}^* C_{\sigma k}, \tag{4.62}$$

the Fock matrix may be expressed as a function of $P_{\rho\sigma}$:

$$f_{\mu\nu}(\mathbf{P}) = h_{\mu\nu} + \underbrace{\sum_k^{N/2} [2 \langle \chi_\mu \chi_\rho \rangle \chi_\nu \chi_\sigma - \langle \chi_\mu \chi_\rho \rangle \chi_\sigma \chi_\nu] P_{\rho\sigma}}_{G_{\mu\nu}}. \tag{4.63}$$

Since the Fock matrix depends on **P** and ultimately on **C**, the Hartree–Fock equations are nonlinear and require an interative solution:

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \tag{4.64}$$

How can we reduce this generalized eigenvalue problem to a normal eigenvalue problem? Consider a transformation of the computational basis:

$$\chi_\mu \to \chi_\mu' = \sum_\nu \chi_\nu X_{\nu\mu}. \tag{4.65}$$

The molecular orbital represented in the $\{\chi_\mu\}$ and $\{\chi_\mu'\}$ basis are related via:

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} = \sum_\mu \chi_\mu' C_{\mu i}' = \sum_{\mu\nu} \chi_\nu X_{\nu\mu} C_{\mu i}', \tag{4.66}$$

from which we get

$$\mathbf{C} = \mathbf{X}\mathbf{C}'. \tag{4.67}$$

Suppose we choose **X** to satisfy the condition:

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}, \tag{4.68}$$

then we can take Roothan's equation, multiply on the left with $\mathbf{X}^\dagger$, and substitute $\mathbf{C} = \mathbf{X}\mathbf{C}'$ to get:

$$\underbrace{\mathbf{X}^\dagger \mathbf{F} \mathbf{X}}_{\mathbf{F}'} \mathbf{C}' = \underbrace{\mathbf{X}^\dagger \mathbf{S} \mathbf{X}}_{\mathbf{1}} \mathbf{C}' \epsilon$$

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\epsilon. \tag{4.69}$$

Thanks to this transformation we were able to transform Roothan's equation (a generalized eigenvalue problem) to a normal eigenvalue problem. Note that the definition of the Fock matrix and eigenvector have changed, but the eigenvalues of this equation are identical to those of the generalized eigenvalue problem. To solve Roothan's equation in the orthonormal

basis we first compute $\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}$, then solve the eigenvalue equation, $\mathbf{F}'\mathbf{C}' = \mathbf{C}'\epsilon$, and then obtain the eigenvector from $\mathbf{C} = \mathbf{X}\mathbf{C}'$.

How can we pick a transformation $\mathbf{X}$ such that $\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}$? It is easy to see that there are several ways to choose $\mathbf{X}$. In the symmetric orthogonalization procedure $\mathbf{X}$ is choosen to be the (matrix) square root of $\mathbf{S}$:

$$\mathbf{X} = \mathbf{S}^{-\frac{1}{2}}. \tag{4.70}$$

This form of $\mathbf{X}$ fits the role since:

$$\mathbf{S}^{-\frac{1}{2}}\mathbf{S}\mathbf{S}^{-\frac{1}{2}} = \mathbf{S}^{-\frac{1}{2}}\mathbf{S}^{\frac{1}{2}} = \mathbf{1}. \tag{4.71}$$

The matrix $\mathbf{S}^{-\frac{1}{2}}$ may be built by first diagonalizing $\mathbf{S}$ with the unitary matrix $\mathbf{U}$:

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s}, \tag{4.72}$$

and then building

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{U}\mathbf{s}^{-\frac{1}{2}}\mathbf{U}^\dagger. \tag{4.73}$$

Alternatively, in the canonical orthogonalization procedure, $\mathbf{X}$ is be defined as:

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-\frac{1}{2}}. \tag{4.74}$$

This form of $\mathbf{X}$ also does the job:

$$\mathbf{s}^{-\frac{1}{2}}\mathbf{U}^\dagger \mathbf{S}\mathbf{U}\mathbf{s}^{-\frac{1}{2}} = \mathbf{s}^{-\frac{1}{2}}\mathbf{s}\mathbf{s}^{-\frac{1}{2}} = \mathbf{1}. \tag{4.75}$$

4.1.7 Outline of the Hartree–Fock–Roothan procedure

In this section we will discuss the computational steps required to solve the Hartree–Fock equations projected onto a finite computational basis. For now we will assume that this computational basis is an atomic basis but we will neglect the details of how it is constructed and what type of functions are used. Note that the computational basis might also be a set of delocalized functions that does not have a well defined atomic character.

The input to a HF computation is the molecule, which is specified by the coordinates ($\{\mathbf{R}_A\}$) and charges ($\{\mathbf{Z}_A\}$) of the nuclei, the number of electrons (N), and the projection of spin onto the z axis (M_S). We also have to provide a computation basis $\{\chi_\mu\}$.

The major steps in the Hartree–Fock procedure are:

1. **Evaluation of the integrals over basis functions**. The following integrals are needed:

$$S_{\mu\nu} = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r})\chi_\nu(\mathbf{r}), \tag{4.76}$$

$$V_{\mu\nu} = \int d\mathbf{r}\, \chi_\mu^*(\mathbf{r})[-\frac{1}{2}\nabla^2 + V_{eN}(\mathbf{r})]\chi_\nu(\mathbf{r}), \tag{4.77}$$

and the two-electron integrals $\langle \mu\nu \rangle \rho\sigma = \langle \chi_\mu\chi_\nu \rangle \chi_\rho\chi_\sigma$.

2. **Diagonalization of the overlap matrix**. From $\mathbf{S}$ we solve the eigenvalue problem:

$$\mathbf{S}\mathbf{U} = \mathbf{U}\mathbf{s}. \tag{4.78}$$

3. **Formation of the matrix $\mathbf{X}$**. The matrix $\mathbf{X}$ is built as

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-\frac{1}{2}}. \tag{4.79}$$

4. **Initialization of the density matrix**. The density matrix $\mathbf{P}$ is initialized to zero:

$$\mathbf{P}^{(0)} = \mathbf{0}. \tag{4.80}$$

5. **Computation of the two-electron contribution to the Fock matrix**. The two matrix $\mathbf{G}$ is built from the current density matrix ($\mathbf{P}^{(k)}$) and the two-electron integrals:

$$\mathbf{G} = \mathbf{G}[\mathbf{P}^{(k)}, \langle \mu\nu \rangle \rho\sigma]. \tag{4.81}$$

6. **Formation the Fock matrix**.
$$\mathbf{F} = \mathbf{H} + \mathbf{G}. \tag{4.82}$$

7. **Transformation the atomic orthonormal basis**.

$$\mathbf{F}' = \mathbf{X}^{\dagger} \mathbf{F} \mathbf{X}. \tag{4.83}$$

8. **Diagonalization of $\mathbf{F}'$**. We solve the eigenvalue problem:

$$\mathbf{F}'\mathbf{C}' = \mathbf{F}'\epsilon. \tag{4.84}$$

9. **Backtransformation to the nonorthogonal basis**.

$$\mathbf{C} = \mathbf{X}\mathbf{C}'. \tag{4.85}$$

10. **Update of the density matrix and energy**. Using the updated MO coefficient ($\mathbf{C}$) we compute an updated density matrix

$$P_{\mu\nu}^{(k+1)} = \sum_{i}^{N} C_{\mu i}^{*} C_{\nu i}. \tag{4.86}$$

Using the updated density matrix we recompute the energy. The change in energy:

$$\Delta E^{(k+1)} = E^{(k+1)} - E^{(k)}, \tag{4.87}$$

and the change in the density matrix:

$$\Delta \mathbf{P}^{(k+1)} = \mathbf{P}^{(k+1)} - \mathbf{P}^{(k)}, \tag{4.88}$$

are used to determine if the Hartree–Fock equation have converged. If $|\Delta E^{(k+1)}| \leq \eta_E$ and $\|\Delta \mathbf{P}^{(k+1)}\| \leq \eta_{\mathbf{P}}$, where η_E and $\eta_{\mathbf{P}}$ are user-provided convergence thresholds, then the HF procedure is terminated. Otherwise, we go back to step 5 and build the matrix $\mathbf{G}$ using the updated density matrix. This procedure is iterated until convergence.