

# Notes on Electronic Structure Theory

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## CHAPTER 1

# The molecular Hamiltonian and the Born–Oppenheimer approximation

## 1.1 Atomic Units

When we study atoms and molecules, it is convenient to express positions, masses, and other properties in units that are close to one, so we can avoid carrying very large or small powers of 10. The most common units used in quantum chemistry are **atomic units** (abbreviated a.u.). Atomic units are defined by the following conditions:

$$\text{electron mass} = m_e = 1 \quad (1.1)$$

$$\text{electron charge} = e = 1 \quad (1.2)$$

$$\text{action} = \hbar = \frac{h}{2\pi} = 1 \quad (1.3)$$

$$\text{Coulomb's constant} = k_e = \frac{1}{4\pi\epsilon_0} = 1 \quad (1.4)$$

The following table report conversion factors between atomic units and other units

Dimension	Symbol (Name)	Value in Other Units
Length	$a_0$ (bohr)	$0.52918 \text{ \AA} = 0.52918 \cdot 10^{-10} \text{ m}$
Mass	$m_e$	$9.1095 \times 10^{-31} \text{ Kg}$
Charge	$e$	$1.6022 \times 10^{-19} \text{ C}$
Action	$\hbar$	$1.05457 \times 10^{-34} \text{ J} \cdot \text{s}$
Energy	$E_h$ (Hartree)	$627.51 \text{ kcal/mol}$
		$27.211 \text{ eV}$
		$219474.63 \text{ cm}^{-1}$
		$4.3598 \times 10^{-18} \text{ J}$
Time		$2.41889 \times 10^{-17} \text{ s} \approx 1/41.3 \text{ fs}$

The speed of light in atomic units is  $\alpha^{-1} \approx 137 \text{ a.u.}^1$

<sup>1</sup> $\alpha$  is the fine-structure constant.

## 1.2 The molecular Hamiltonian

Consider a molecule containing  $N$  electrons and  $M$  nuclei. We will indicate the position of the nuclei with  $\vec{R}_A = \mathbf{R}_A = (x_A, y_A, z_A)$  and that of electrons with  $\vec{r}_i = \mathbf{r}_i = (x_i, y_i, z_i)$ . In the absence of external potentials or fields, the total Hamiltonian is given by

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}, \quad (1.5)$$

where

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_i^N \nabla_i^2, \quad (1.6)$$

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_A^M \frac{1}{M_A} \nabla_A^2, \quad (1.7)$$

$$\hat{V}_{ee} = + \sum_i^N \sum_{j>i}^N \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}}, \quad (1.8)$$

$$\hat{V}_{eN} = - \sum_i^N \sum_A^M \frac{1}{4\pi\epsilon_0} \frac{e^2 Z_A}{r_{iA}}, \quad (1.9)$$

$$\hat{V}_{NN} = + \sum_A^M \sum_{B>A}^M \frac{1}{4\pi\epsilon_0} \frac{e^2 Z_A Z_B}{r_{AB}}, \quad (1.10)$$

and the quantity  $r_{ij}$  is the distance between electrons labeled with indices  $i$  and  $j$

$$r_{ij} = |\vec{r}_i - \vec{r}_j| = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}, \quad (1.11)$$

and  $r_{iA} = |\vec{r}_i - \vec{R}_A|$  and  $r_{AB} = |\vec{R}_A - \vec{R}_B|$  are defined similarly.

In atomic units the Hamiltonian is more compact:

$$\hat{H} = -\frac{1}{2} \sum_i^N \nabla_i^2 - \frac{1}{2} \sum_A^M \frac{1}{M_A} \nabla_A^2 + \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_i^N \sum_A^M \frac{Z_A}{r_{iA}} + \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}, \quad (1.12)$$

where  $M_A$  is understood to be the mass of nucleus  $A$  in atomic units.

If we define the collective electronic ( $\mathbf{r} = \{\vec{r}_i\}$ ) and nuclear ( $\mathbf{R} = \{\vec{R}_A\}$ ) degrees of freedom, we may write the Schrödinger equation compactly as:

$$\hat{H} \Psi_k(\mathbf{r}, \mathbf{R}) = E_k \Psi_k(\mathbf{r}, \mathbf{R}). \quad (1.13)$$

Note that  $\Psi_k(\mathbf{r}, \mathbf{R})$  is a complicated function of  $3(N + M)$  variables (excluding spin) because it depends both on the coordinate of the electrons and nuclei. For a free molecule it includes translational, rotational, vibrational, and electronic degrees of freedom. The terms that make this Hamiltonian difficult to solve are those that couple electrons and nuclei, that is,  $\hat{V}_{NN}$ ,  $\hat{V}_{eN}$ , and  $\hat{V}_{eN}$  is problematic because it couples electrons and nuclei.

**Problem 1.2.1** What does the spectrum of  $\hat{H}$  look like for a diatomic molecule?

### 1.3 The Born–Oppenheimer approximation

One way to simplify the molecular Hamiltonian is to recognize that since electrons and nuclei have very different masses (the smallest value that  $M_A$  can have is  $1837 m_e$ , for the hydrogen atom) and treat the electronic and nuclear degrees of freedom separately. More precisely, we are going to assume that we can break down the wave function into a product of an electronic wave function  $[\Phi_{el}(\mathbf{r}; \mathbf{R})]$  and a nuclear wave function  $[\chi_{nuc}(\mathbf{R})]$

$$\Psi(\mathbf{r}, \mathbf{R}) \approx \Phi_{el}(\mathbf{r}; \mathbf{R}) \chi_{nuc}(\mathbf{R}). \quad (1.14)$$

Note that the nuclear coordinates  $\mathbf{R}$  enter in the electronic wave functions as a parameter, hence we use the symbol “;” to separate it from the electron coordinates  $\mathbf{r}$ . The nuclear wave

function is instead independent of the electron coordinates; however, this does not mean that it will be independent from the electronic wave function (see later).

If we plug this trial state in the Schrödinger equation, we get the following equation

$$(\hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN})\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R}) = E\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R}) \quad (1.15)$$

These five operators act on the wave function in different ways. The kinetic energy operators take derivatives with respect to coordinates, while the potential operators just multiply the wave function by a number. The kinetic energy operator for the electrons acts only on the electronic coordinates and so we can write

$$\hat{T}_e\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R}) = \chi_{nuc}(\mathbf{R})\hat{T}_e\Phi_{el}(\mathbf{r}; \mathbf{R}). \quad (1.16)$$

The nuclear kinetic energy operator complicates things a bit, because when we apply it to the wave function we get three terms

$$\begin{aligned} \hat{T}_N\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R}) &= -\frac{1}{2} \sum_A^M \frac{1}{M_A} \nabla_A^2 [\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R})] \\ &= -\frac{1}{2} \sum_A^M \frac{1}{M_A} \chi_{nuc}(\mathbf{R}) \nabla_A^2 \Phi_{el}(\mathbf{r}; \mathbf{R}) \\ &\quad - \sum_A^M \frac{1}{M_A} \nabla_A \chi_{nuc}(\mathbf{R}) \cdot \nabla_A \Phi_{el}(\mathbf{r}; \mathbf{R}) \\ &\quad - \frac{1}{2} \sum_A^M \frac{1}{M_A} \Phi_{el}(\mathbf{r}; \mathbf{R}) \nabla_A^2 \chi_{nuc}(\mathbf{R}). \end{aligned} \quad (1.17)$$

The first and second terms on the right hand side of this equation couple the electronic and nuclear degrees of freedom. If we neglect them and keep only the last term, we can rewrite the Schrödinger equation as

$$\Phi_{el}(\mathbf{r}; \mathbf{R})\hat{T}_N\chi_{nuc}(\mathbf{R}) + \chi_{nuc}(\mathbf{R})(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN})\Phi_{el}(\mathbf{r}; \mathbf{R}) = E\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R}) \quad (1.18)$$

To get this expression we collected all the wave functions not affected by operators to the left side of each term. Next we collect all the terms in the following way

$$\chi_{nuc}(\mathbf{R})(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN})\Phi_{el}(\mathbf{r}; \mathbf{R}) = \Phi_{el}(\mathbf{r}; \mathbf{R})(E - \hat{T}_N)\chi_{nuc}(\mathbf{R}), \quad (1.19)$$

and finally divide each side by  $\Phi_{el}(\mathbf{r}; \mathbf{R})\chi_{nuc}(\mathbf{R})$  to get

$$\frac{1}{\Phi_{el}(\mathbf{r}; \mathbf{R})}(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN})\Phi_{el}(\mathbf{r}; \mathbf{R}) = \frac{1}{\chi_{nuc}(\mathbf{R})}(E - \hat{T}_N)\chi_{nuc}(\mathbf{R}) \quad (1.20)$$

The left and right sides of this equation must be equal for any values of  $\mathbf{r}$  and  $\mathbf{R}$ , but since the right side does not depend on  $\mathbf{r}$ , both sides must depend only the variable  $\mathbf{R}$ . Let us call this quantity  $V(\mathbf{R})$ . Then Eq. (1.20) corresponds to two set of conditions

$$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN})\Phi_{el}(\mathbf{r}; \mathbf{R}) = V(\mathbf{R})\Phi_{el}(\mathbf{r}; \mathbf{R}), \quad (1.21)$$

and

$$[\hat{T}_N + V(\mathbf{R})]\chi_{nuc}(\mathbf{R}) = E\chi_{nuc}(\mathbf{R}). \quad (1.22)$$

Eqs. (1.21) and (1.22) are coupled equations. We can find their solution by first solving the Schrödinger equation for the electrons assuming that the nuclei are fixed in space ( $\mathbf{R}$  is a constant). Eq. (1.21) is equivalent to the following **electronic** Schrödinger equation

$$(\hat{H}_{el} + \hat{V}_{NN})\Phi_{el,k}(\mathbf{r}; \mathbf{R}) = V_k(\mathbf{R})\Phi_{el,k}(\mathbf{r}; \mathbf{R}). \quad (1.23)$$

where the **electronic** Hamiltonian ( $\hat{H}_{\text{el}}$ ) is defined as:

$$\hat{H}_{\text{el}} = \hat{T}_{\text{e}} + \hat{V}_{\text{eN}} + \hat{V}_{\text{ee}}. \quad (1.24)$$

Note that there are multiple solutions of the electronic Schrödinger equation, so different pairs of eigenvalues/eigenfunctions are labeled by the state index  $k$ , which can take the values 0, 1, .... The state with  $k = 0$  is called the **ground electronic state**, while states with  $k > 0$  are **excited electronic states**. The function  $V_k(\mathbf{R})$  is commonly known as the **potential energy surface** (abbreviates as PES). Note that  $V_k(\mathbf{R})$  gives us the potential energy at a given molecular geometry  $\mathbf{R}$  and therefore it describes a set of surfaces in  $3M + 1$  dimensions (nuclear coordinates plus energy).

Note that since for a fixed geometry  $\hat{V}_{\text{NN}}$  is a constant (it depends only on the relative positions of the nuclei), we can in practice solve the following eigenvalue problem

$$\hat{H}_{\text{el}} \Phi_{\text{el},k}(\mathbf{r}; \mathbf{R}) = E_{\text{el},k}(\mathbf{R}) \Phi_{\text{el},k}(\mathbf{r}; \mathbf{R}). \quad (1.25)$$

which has the same eigenfunctions  $[\Phi_{\text{el},k}(\mathbf{r}; \mathbf{R})]$  but different eigenvalues  $[E_{\text{el},k}(\mathbf{R})]$ . The quantity  $E_{\text{el},k}(\mathbf{R})$  is also called the **electronic energy** and it is related to  $V_k(\mathbf{R})$  via the equation

$$V_k(\mathbf{R}) = E_{\text{el},k}(\mathbf{R}) + \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}}. \quad (1.26)$$

The concept of the potential energy surface is at the basis of many concepts used to describe molecules like, the molecular geometry, transition states, etc. The equilibrium geometry of a molecule in a given electronic state  $k$ ,  $\mathbf{R}_{\text{eq}}$ , is defined as the minimum of  $V_k(\mathbf{R})$ , that is, the gradient of  $V_k(\mathbf{R})$  at this geometry is zero

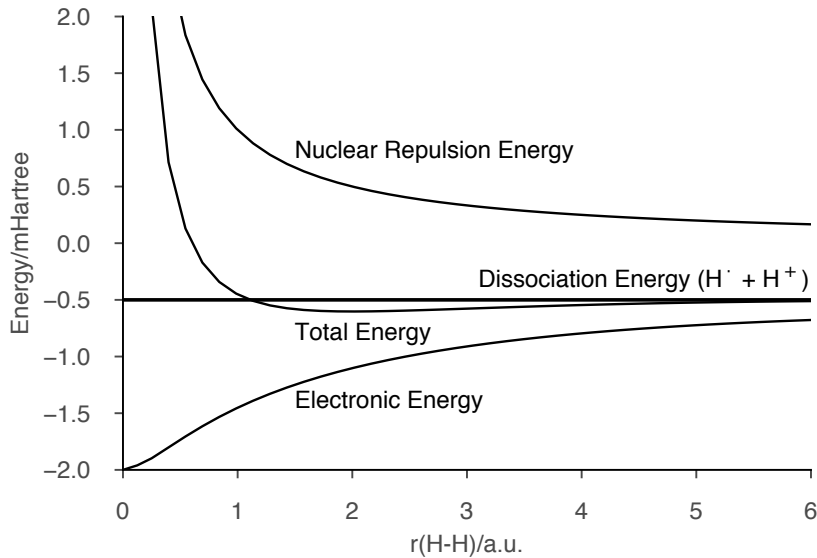
$$\left. \frac{\partial V_k(\mathbf{R})}{\partial \mathbf{R}} \right|_{\mathbf{R}=\mathbf{R}_{\text{eq}}} = 0, \quad (1.27)$$

and the curvature of  $V_k(\mathbf{R})$  at  $\mathbf{R}_{\text{eq}}$  is positive (the eigenvalues of the second derivative matrix or Hessian are all positive). Note that for a given electronic state the equilibrium geometry may be unique or there might be several minima with the same energy. In certain cases, the ground state might not be a bound molecular state (e.g., for dications like  $\text{Li}_2^{2+}$  the energy minimum corresponds to the molecule dissociated into two  $\text{Li}^+$  atoms).

### ■ Example 1.3.1 | Potential energy surface of $\text{H}_2^+$ .

The following plot shows the contributions of the electronic energy ( $E_{\text{el}}$ ) and the nuclear repulsion energy ( $V_{\text{NN}}$ ) to the potential energy of the ground state of  $\text{H}_2^+$ .





Although there are  $3M$  nuclear degrees of freedom (DOF), in absence of an external potential translations and rotations of a molecule do not change the value of  $V_k(\mathbf{R})$ . Therefore, the number of internal degrees of freedom that change the value of  $V_k(\mathbf{R})$  is less than  $3M$ . For a non-linear molecule we have that

$$\text{internal DOF} = \underbrace{3M}_{\text{total DOF}} - \underbrace{3}_{\text{rotations}} - \underbrace{3}_{\text{translations}} = 3M - 6, \quad (1.28)$$

while for a linear molecule

$$\text{internal DOF} = \underbrace{3M}_{\text{total DOF}} - \underbrace{2}_{\text{rotations}} - \underbrace{3}_{\text{translations}} = 3M - 5. \quad (1.29)$$

### ■ Example 1.3.2 | Diatomic molecule.

For a diatomic molecule there is  $2 \cdot 3 - 5 = 1$  degrees of freedom. In this case  $V_k(\mathbf{R})$  may be expressed in terms of the bond distance  $R$  as  $V_k(R)$ . In this case we call these quantities **potential energy curves**.

## 1.4 Avoided crossings

In this section we discuss some properties of potential energy surfaces. We are particularly interested in understanding when two surfaces become degenerate, because in this case the Born–Oppenheimer approximation is no longer qualitatively correct. Consider two electronic states  $\tilde{\Phi}_1(\mathbf{R})$  and  $\tilde{\Phi}_2(\mathbf{R})$  that are not eigenfunctions of the electronic Hamiltonian. When do the potential energy surfaces obtained by diagonalizing the Hamiltonian in this basis become degenerate?

Let us write the electronic Hamiltonian in the general<sup>2</sup> basis  $\{\tilde{\Phi}_1(\mathbf{R}), \tilde{\Phi}_2(\mathbf{R})\}$  omitting the dependence on the coordinate  $\mathbf{R}$

$$\mathbf{H}_{\text{el}} = \begin{pmatrix} \langle \tilde{\Phi}_1 | \hat{H}_{\text{el}} | \tilde{\Phi}_1 \rangle & \langle \tilde{\Phi}_1 | \hat{H}_{\text{el}} | \tilde{\Phi}_2 \rangle \\ \langle \tilde{\Phi}_2 | \hat{H}_{\text{el}} | \tilde{\Phi}_1 \rangle & \langle \tilde{\Phi}_2 | \hat{H}_{\text{el}} | \tilde{\Phi}_2 \rangle \end{pmatrix} = \begin{pmatrix} \tilde{E}_1 & V \\ V^* & \tilde{E}_2 \end{pmatrix}, \quad (1.30)$$

where we used the fact that the Hamiltonian is Hermitian.<sup>3</sup>

<sup>2</sup>Here we do not assume that  $\tilde{\Phi}_1$  and  $\tilde{\Phi}_2$  are eigenfunctions of the Hamiltonian.

<sup>3</sup>Because the Hamiltonian is Hermitian we have that  $\langle \tilde{\Phi}_2 | \hat{H} | \tilde{\Phi}_1 \rangle = \langle \tilde{\Phi}_1 | \hat{H} | \tilde{\Phi}_2 \rangle^* = V^*$ .

The difference between the eigenvalues  $E_1$  and  $E_2$  of  $\mathbf{H}$  is

$$E_2 - E_1 = \sqrt{(\tilde{E}_1 - \tilde{E}_2)^2 + 4|V|^2}. \quad (1.31)$$

From this equation we deduce that for  $E_1$  and  $E_2$  to be degenerate, the following conditions must be satisfied **simultaneously**:

$$\tilde{E}_1(\mathbf{R}) = \tilde{E}_2(\mathbf{R}), \quad (1.32)$$

$$|V(\mathbf{R})| = 0, \quad (1.33)$$

that is, the states that form our basis must be degenerate and there should be no coupling.

In general, these two conditions are independent. So suppose we find a point  $\mathbf{R}^*$  for which Eqs.(1.32)-(1.33) are satisfied, then we can ask what is the dimensionality of the space in which these two states are degenerate? If we consider a system with  $M$  atoms and assume that  $|V|$  is not zero for all molecular geometries,<sup>4</sup> then the subset of molecular geometries for which two potential energy surfaces intersect has dimension  $3M - 6 - 2 = 3M - 8$  for non-linear molecules and  $3M - 5 - 2 = 3M - 7$  for linear molecules. Here we subtract 2 from the number of degrees of freedom to account for the two constraints that must be satisfied for the levels to be degenerate. This result tells us when a crossing can happen, and if a crossing can happen, it tells us what is the dimension of the space of degenerate electronic energies.

<sup>4</sup>In other words,  $|V|$  is only **accidentally zero**.

#### ■ Example 1.4.1 | Diatomic molecules.

For a diatomic molecule degenerate electronic states live in a  $3 \cdot 2 - 7 = -1$  dimensional space. That is, in general two curves do not cross. However, if for some reason the coupling  $|V| = 0$  for all bond lengths then only one of the two constraints applies. In this case, degenerate electronic states live in a space of dimension  $3 \cdot 2 - 6 = 0$ , that is, there may be a finite set of points for which  $E_2 = E_1$ . Typical examples of situations when  $|V| = 0$  include states with different spin or spatial symmetry. For example, the singlet and triplet states of  $\text{H}_2$  are allowed to cross. Crossings may also occur when two electronic states have different number of electrons. ■

## 1.5 The nuclear Schrödinger equation

Given the eigenvalues and eigenfunctions of the electronic Hamiltonian, it is possible to obtain wave functions for the nuclei by solving the nuclear Schrödinger equation:

$$\hat{H}_{\text{nuc},k} \chi_{v,k}(\mathbf{R}) = E_{v,k} \chi_{v,k}(\mathbf{R}), \quad (1.34)$$

where  $\hat{H}_{\text{nuc},k}$  is the nuclear Hamiltonian for electronic state  $k$ :

$$\hat{H}_{\text{nuc},k} = \hat{T}_N + V_k(\mathbf{R}). \quad (1.35)$$

In this approximation the nuclei experience a potential generated by the electrons plus the nuclear-nuclear repulsion:

$$V_k(\mathbf{R}) = \int d\mathbf{r} \Phi_{\text{el},k}^*(\mathbf{r}; \mathbf{R}) \hat{H}_{\text{el}}(\mathbf{r}; \mathbf{R}) \Phi_{\text{el},k}(\mathbf{r}; \mathbf{R}) + V_{\text{NN}}(\mathbf{R}). \quad (1.36)$$

This expression is an equivalent way to rewrite  $V_k(\mathbf{R})$ , and it emphasizes the fact that the potential energy surface is the potential experienced by the nuclei after averaging the interaction with the electrons in the state  $\Phi_{\text{el},k}(\mathbf{r}; \mathbf{R})$ .

Note that the solutions of the nuclear Schrödinger equation are **vibrational levels** of the electronic state  $k$ . Since each electronic state has a different shape, the vibrational levels for two electronic states are, in general, different. In this picture, the electrons react instantaneously to the motion of the nuclei, so the nuclei always see the electrons in a fully relaxed state (adiabatic approximation). The BO approximation is thus valid when nuclear and electronic motion occur on different time (energy) scales. In practice, the BO approximation is

accurate when electronic states are well separated from one another, and, conversely, it fails when two or more electronic states become near-degenerate. The first corrections to the BO approximation enter at order  $\lambda^6 = \left(\frac{m_e}{M}\right)^{3/2}$ , which for the hydrogen atom are of the order of  $1.3 \cdot 10^{-5} E_h$ .

### ■ Advanced topic

In deriving the nuclear Schrödinger equation we have neglected two terms that arise from the kinetic energy operator for the nuclei. So what happens if we introduce these terms back but still assume the BO factorized wave function for the electrons + nuclei? Let us go back to the Schrödinger equation for the electrons and nuclei where we plugged in the factorized form of the wave function [see Eq. (1.15)] and left project with the state  $\Phi_{el}^*(\mathbf{r}; \mathbf{R})$  and integrate over  $\mathbf{r}$  (we momentarily omit the electronic state index  $k$  in the next few equations). This gives us

$$\langle \Phi_{el}(\mathbf{r}; \mathbf{R}) | (\hat{T}_e + \hat{T}_N + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN}) | \Phi_{el}(\mathbf{r}; \mathbf{R}) \rangle \chi_{nuc}(\mathbf{R}) = E \chi_{nuc}(\mathbf{R}). \quad (1.37)$$

Using the fact that  $(\hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN}) \Phi_{el}(\mathbf{r}; \mathbf{R}) = V(\mathbf{R}) \Phi_{el}(\mathbf{r}; \mathbf{R})$ , we can simplify this equation to

$$\langle \Phi_{el}(\mathbf{r}; \mathbf{R}) | (\hat{T}_N + V(\mathbf{R})) | \Phi_{el}(\mathbf{r}; \mathbf{R}) \rangle \chi_{nuc}(\mathbf{R}) = E \chi_{nuc}(\mathbf{R}). \quad (1.38)$$

The left-hand-side of this equation can be written as the sum of three terms:

$$\begin{aligned} & [\hat{T}_N + V(\mathbf{R})] \chi_{nuc}(\mathbf{R}) \\ & - \frac{1}{2} \sum_A^M \frac{1}{M_A} \underbrace{\langle \Phi_{el}(\mathbf{r}; \mathbf{R}) | \nabla_A \Phi_{el}(\mathbf{r}; \mathbf{R}) \rangle \cdot \nabla_A}_{\text{First-order derivative coupling}} \chi_{nuc}(\mathbf{R}) \\ & - \frac{1}{2} \chi_{nuc}(\mathbf{R}) \sum_A^M \frac{1}{M_A} \underbrace{\langle \Phi_{el}(\mathbf{r}; \mathbf{R}) | \nabla_A^2 \Phi_{el}(\mathbf{r}; \mathbf{R}) \rangle}_{\text{Second-order derivative coupling}}. \end{aligned} \quad (1.39)$$

The first term appears in the nuclear Schrödinger equation that we have seen before, but the terms in the second and third lines are new. These are the so-called **diagonal corrections to the BO approximation** since they involve derivative couplings between the same electronic state. These terms can be included in the nuclear Schrödinger equation [Eq. (1.38)] to estimate corrections to the BO approximation. For heavy nuclei these corrections are somewhat small and so are typically neglected. However, diagonal corrections are sometime included in highly-accurate computations.

To go beyond diagonal BO corrections one has to consider solutions to the molecular Hamiltonian that mix various electronic states. Since at each value of  $\mathbf{R}$  the eigenfunctions of the electronic Hamiltonian form a complete basis for the electrons, we can expand the full wave function (electrons plus nuclei) as

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{k=0}^{\infty} \Phi_{el,k}(\mathbf{r}; \mathbf{R}) \chi_{nuc,k}(\mathbf{R}). \quad (1.40)$$

When this equation is substituted in the Schrödinger equation it leads to a set of coupled Schrödinger equations that determine the nuclear wave functions  $\chi_{nuc,k}(\mathbf{R})$ . Note, however, that these nuclear wave functions are different from the ones we have encountered before.

Eq. (1.40) is the most general solution that we can write for a wave function of electrons and nuclei, and it is required when the assumptions made in the Born–Oppenheimer approximation are not valid. A large number of interesting and important phenomena are associated with the break down of the adiabatic assumption and require a significantly more refined treatment than the one discussed here. ■

We will come back to the nuclear Schrödinger equation after learning how to compute potential energy surfaces.

## Study Questions

1. What are atomic units?
2. What is the unit of energy in atomic units?
3. What are the five terms in the molecular Hamiltonian?
4. What how many dimensions does the wave function for the molecular Hamiltonian have?
5. What is the basis for the Born–Oppenheimer approximation?
6. What terms in the expression  $\hat{T}_N \Phi_{\text{el}}(\mathbf{r}; \mathbf{R})$  are neglected when deriving the Born–Oppenheimer approximation?
7. What is the electronic Schrödinger equation?
8. What is the electronic Hamiltonian and what operators enter it?
9. What is the difference between the potential energy surface and the electronic energy?
10. Why do Eqs. (1.23) and (1.25) share the same eigenfunction?
11. How many internal degrees of freedom are there for a linear and a nonlinear molecule?
12. Can two electronic state of the same symmetry cross in a diatomic molecule? What happens if the have the same symmetry?
13. What is the nuclear Schrödinger equation?
14. Why do the solutions of the nuclear Schrödinger equation depend on the electronic state?
15. What are the diagonal corrections to the BO approximation?

## CHAPTER 2

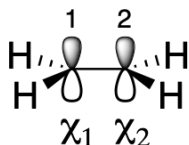
# Hückel Theory

### 2.1 Foundation of the Hückel MO Method

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

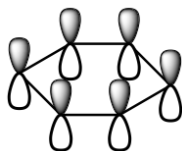
■ **Example 2.1.1 | ethylene, 2 electrons / 2 orbitals.**

The simplest problem that can be solved with the Hückel method is the ethylene molecule. For each carbon we describe the electrons in the C  $2p_z$  using one basis function ( $\chi_1$  and  $\chi_2$ )



■ **Example 2.1.2 | benzene, 6 electrons / 6 orbitals.**

In the case of benzene, the Hückel method only describes electrons in the C  $2p_z$  responsible for  $\pi$  bonding



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

$$\psi_i(\mathbf{r}) = \sum_{\mu}^N \chi_{\mu}(\mathbf{r}) C_{\mu i}, \quad (2.1)$$

where:

- $N$  is the number of atomic orbitals (AOs) = number of molecular orbitals (MOs) = number of atoms that share  $p_z$  orbitals
- the functions  $\chi_{\mu}(\mathbf{r}) : \mathbb{R}^3 \rightarrow \mathbb{R}$  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  $\mu$ -th AO in the  $i$ -th MO. In other words, read the coefficient of  $\psi_i$  from the  $i$ -th column of the matrix  $\mathbf{C}$ .

### ■ Example 2.1.3

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:

$$\hat{h}(1)\psi_i(1) = \epsilon_i\psi_i(1), \quad (2.2)$$

where

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

$$\hat{h}(1) = \hat{T}(1) + \hat{V}(1), \quad (2.3)$$

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

$$\hat{T}(1) = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right), \quad (2.4)$$

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:

$$h_{\mu\mu} = \langle \chi_\mu | \hat{h} | \chi_\mu \rangle = \int d\mathbf{r} \chi_\mu^* \hat{h}(\mathbf{r}) \chi_\mu(\mathbf{r}) \quad (\text{Coulomb integral of AO } \mu) \quad (2.5)$$

$$h_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle = \int d\mathbf{r} \chi_\mu^* \hat{h}(\mathbf{r}) \chi_\nu(\mathbf{r}) \quad (\text{Resonance integral between AOs } \mu \text{ and } \nu) \quad (2.6)$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle = \int d\mathbf{r} \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \quad (\text{Overlap integral between AOs } \mu \text{ and } \nu) \quad (2.7)$$

## 2.2 Determination of the MO coefficients

To determine the MO orbitals we insert the definition  $|\psi_i\rangle = \sum_\mu |\chi_\mu\rangle C_{\mu i}$  into the Schrödinger equation [Eq. (2.2)]

$$\hat{h}(1) \sum_\mu |\chi_\mu\rangle C_{\mu i} = \epsilon_i \sum_\mu |\chi_\mu\rangle C_{\mu i}, \quad (2.8)$$

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

$$\langle \chi_\nu | \hat{h}(1) \sum_\mu |\chi_\mu\rangle C_{\mu i} = \sum_\mu \langle \chi_\nu | \hat{h}(1) | \chi_\mu \rangle C_{\mu i} = \sum_\mu h_{\nu\mu} C_{\mu i} \quad (2.9)$$

The right hand side is:

$$\langle \chi_\nu | \epsilon_i \sum_{\mu} |\chi_\mu\rangle C_{\mu i} = \sum_{\mu} \langle \chi_\nu | \chi_\mu \rangle C_{\mu i} \epsilon_i = \sum_{\mu} S_{\nu\mu} C_{\mu i} \epsilon_i \quad (2.10)$$

Therefore we have:

$$\sum_{\mu} h_{\nu\mu} C_{\mu i} = \sum_{\mu} S_{\nu\mu} C_{\mu i} \epsilon_i, \quad (2.11)$$

which in matrix notation reads:

$$\begin{pmatrix} h_{11} & h_{12} & \dots & h_{1N} \\ h_{21} & h_{22} & \dots & h_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ h_{N1} & h_{N2} & \dots & h_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} & \dots & S_{1N} \\ S_{21} & S_{22} & \dots & S_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N1} & S_{N2} & \dots & S_{NN} \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix} \epsilon_i, \quad (2.12)$$

or more compactly:

$$\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_i\epsilon_i, \quad (2.13)$$

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

$$\mathbf{c}_i = \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{Ni} \end{pmatrix}. \quad (2.14)$$

If we combine all the columns together into the matrix  $\mathbf{C} = (\mathbf{c}_1, \mathbf{c}_2, \dots, \mathbf{c}_N)$ , we can write Eq. (2.13) as

$$\mathbf{H}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \quad (2.15)$$

where the matrix  $\epsilon$  contains all the orbital energies in the diagonal elements

$$\epsilon = \begin{pmatrix} \epsilon_1 & 0 & \dots & 0 \\ 0 & \epsilon_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon_N \end{pmatrix} \quad (2.16)$$

**Problem 2.2.1** Convince yourself that Eq. 2.15 is correct.

The Hückel method for conjugated hydrocarbons further **assumes**:

- $h_{\mu\mu} = \alpha < 0$  (same for all carbon atoms), where  $\alpha$  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  $\mu$  and  $\nu$  and it is a negative quantity.

- 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,  $S_{\mu\nu} = \delta_{\mu\nu} = \begin{cases} 1 & \text{if } \mu = \nu \\ 0 & \text{if } \mu \neq \nu \end{cases}$ .

## 2.3 The Hückel Method in Practice

### ■ Example 2.3.1 | Ethylene.

The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \quad (2.17)$$

The Schrödinger equation reads:

$$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} \epsilon_i \quad (2.18)$$

Simplify and rearrange:

$$\begin{pmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{pmatrix} \begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = 0 \quad (2.19)$$

This equation has non-trivial solutions. A trivial solution to a linear system  $\mathbf{Ax} = \mathbf{0}$  is the solution  $\mathbf{x} = \mathbf{0}$ . In this example the trivial solution is  $\begin{pmatrix} C_{1i} \\ C_{2i} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$  only if the determinant of the secular matrix is equal to zero:

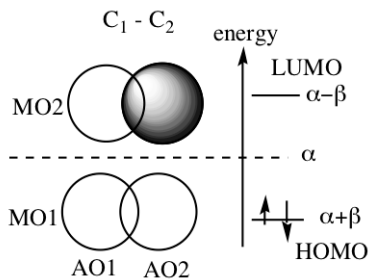
$$\begin{vmatrix} \alpha - \epsilon_i & \beta \\ \beta & \alpha - \epsilon_i \end{vmatrix} = 0 \Rightarrow \beta^2 \begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = 0 \quad (2.20)$$

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

$$\begin{vmatrix} \frac{\alpha - \epsilon_i}{\beta} & 1 \\ 1 & \frac{\alpha - \epsilon_i}{\beta} \end{vmatrix} = \begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = \lambda^2 - 1 = 0, \quad (2.21)$$

from this equation we obtain the eigenvalues:

$$\lambda^2 = \left( \frac{\alpha - \epsilon_i}{\beta} \right)^2 = 1 \Rightarrow \frac{\alpha - \epsilon_i}{\beta} = \pm 1 \Rightarrow \epsilon_i = \alpha \pm \beta \quad (2.22)$$

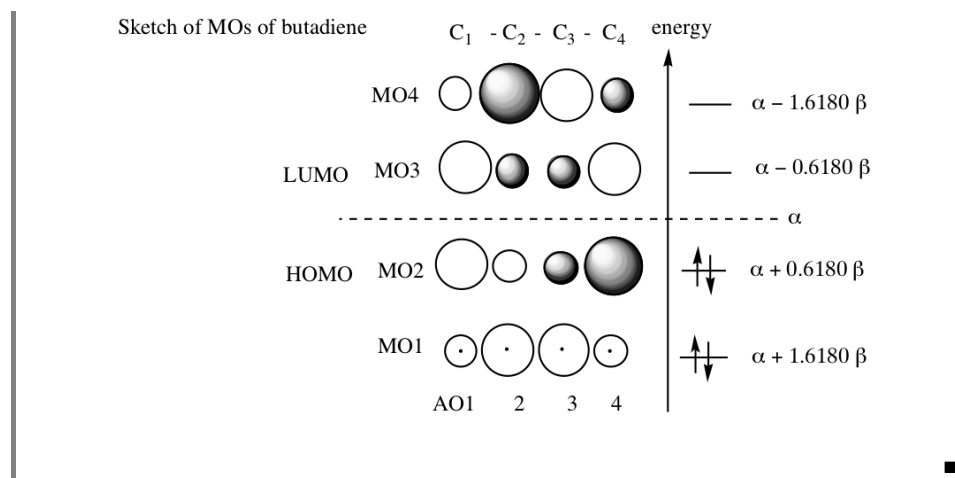


■

### ■ Example 2.3.2 | Butadiene.

Note that cis-butadiene and trans-butadiene are the same in Hückel MOs.





### ■ Example 2.3.3 | Benzene.

The Hamiltonian in the Hückel approximation is:

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & & \beta \\ \beta & \alpha & \beta & & \\ & \beta & \alpha & \beta & \\ & & \beta & \alpha & \beta \\ \beta & & & \beta & \alpha \end{pmatrix} \quad (2.23)$$

■

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

**Problem 2.3.1** 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 ( $\epsilon_i$ ) of all the occupied orbitals

$$E = \sum_i \epsilon_i n_i, \quad (2.24)$$

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

$$n_i \in \{0, 1, 2\}. \quad (2.25)$$

Note that some times the eigenvalues are also expressed in the following form

$$\epsilon_i = \alpha + \lambda_i \beta, \quad (2.26)$$

in terms of the reduced variable  $\lambda_i$ .

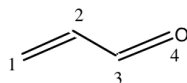
## 2.4 Heteroatoms

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

### ■ Example 2.4.1 | 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=O  $\pi$  bond is shorter and stronger than C=C)
- $\alpha_{C'} = \alpha + 0.2\beta$  (C of CO is slightly more electronegative due to C $\rightarrow$ O charge transfer)



The Hückel Hamiltonian for acrolein is

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & & \\ \beta & \alpha & \beta & \\ & \beta & \alpha + 0.2\beta & \sqrt{2}\beta \\ & & \sqrt{2}\beta & \alpha + 2\beta \end{pmatrix}. \quad (2.27)$$

■

Table 2.1: Recommended values of the parameters for heteroatoms in the Hückel method

Diagonal elements			Off-diagonal elements		
Coulomb Integrals			Resonance Integrals		
$\alpha_X = \alpha_C + l_X\beta_{CC}$			$\beta_{XY} = k_{XY}\beta_{CC}$		
atom X	# of $\pi$ electrons	$l_X$	atom X-Y	# of $\pi$ 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 $\equiv$ 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 <sub>3</sub> )					
C	(1)	-0.1	C $\equiv$ H <sub>3</sub>	(1-1)	2.5
H <sub>3</sub>	(1)	-0.5	C-CH <sub>3</sub>	(1-1)	0.6

Larger  $l_X$ , more electronegative the atom X. Larger  $k_{XY}$ , stronger the bond XY.

## 2.5 Pairing Theorem for Alternant Hydrocarbons (AHs)

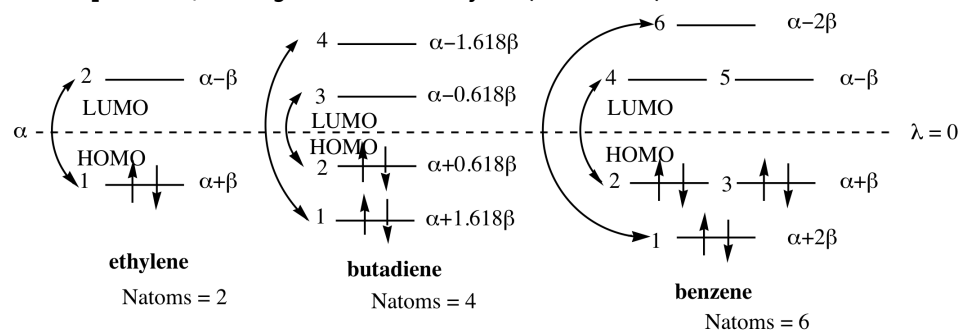
For alternant hydrocarbons (hydrocarbons without odd-membered rings), MO energies are paired, which means that they are symmetric with respect to the energy  $\alpha$ <sup>5</sup>

<sup>5</sup>Recall that  $\frac{\alpha - \epsilon_i}{\beta} = -\lambda_i$ .

$$\epsilon_i = \alpha + \lambda_i\beta, \quad (2.28)$$

$$\epsilon_{N-i+1} = \alpha - \lambda_i\beta. \quad (2.29)$$

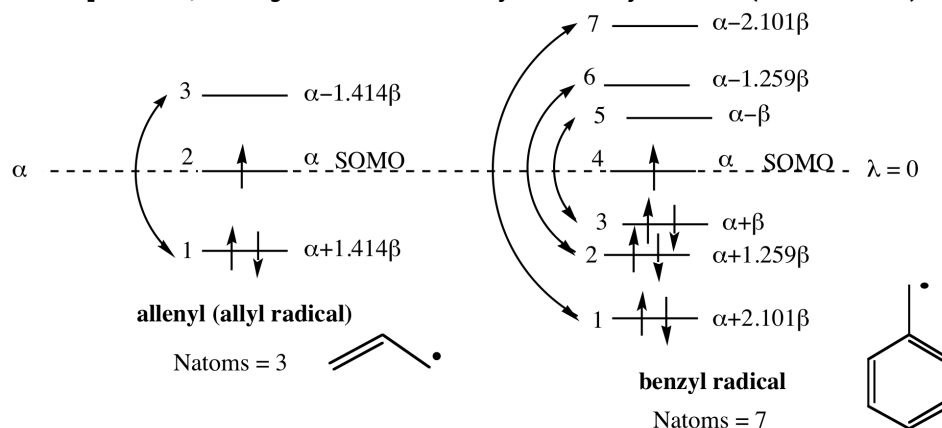
■ **Example 2.5.1 | Pairing theorem for ethylene, butadiene, and benzene.**



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  $\epsilon_{k+1}$  is equal to that of  $\epsilon_{N-(k+1)+1}$ , from which we obtain

$$\epsilon_{k+1} = \epsilon_{N-(k+1)+1} \Rightarrow \alpha + \lambda_i \beta = \alpha - \lambda_i \beta \Rightarrow \lambda_i = 0. \quad (2.30)$$

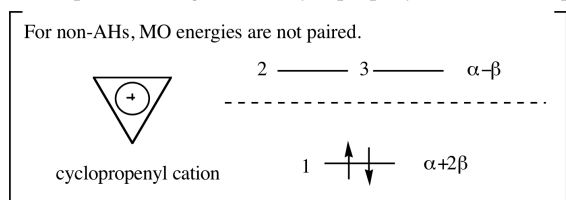
■ **Example 2.5.2 | Pairing theorem for the allyl and benzyl radicals (odd alternant).**



In the allyl radical the second MO ( $\psi_2, \epsilon_2 = \alpha$ ) is paired to itself. In the benzyl radical the fourth MO ( $\psi_4, \epsilon_4 = \alpha$ ) is paired to itself.

■ **Example 2.5.3 | Non alternant hydrocarbons.**

In this example, the energies of the cyclopropenyl cation are not paired

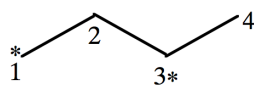


Another consequence of this theorem is that the coefficients of paired orbitals are also paired (MOs  $\psi_i$  and  $\psi_{N-i+1}$  are paired). This property is best expressed by labeling alternanting carbon atoms with a star (\*) and the relationship

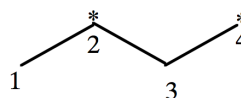
$$C_{\mu, N-i+1} = C_{\mu i} \quad \text{when } \mu = \text{starred atom} \quad (2.31)$$

$$= -C_{\mu i} \quad \text{when } \mu = \text{unstarred atom.} \quad (2.32)$$

- Method of putting \* on alternating carbon atoms

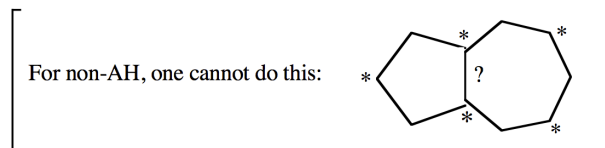
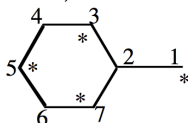


OR



Either is OK.

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



### ■ Example 2.5.4 | 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	<- A01
1	.601501	-.371748	-.371748	.601501	<- A02
2	.601501	.371748	-.371748	-.601501	<- A03
3	.371748	.601501	.601501	.371748	<- A04
	M01	M02	M03	M04	

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.  $\psi_i$  or  $-\psi_i$  are both OK. ■

### ■ Example 2.5.5 | 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	<- A01
1	-.707107	.000000	-.707107	<- A02
2	-.500000	.707107	.500000	<- A03
	M01	M02	M03	

#### 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

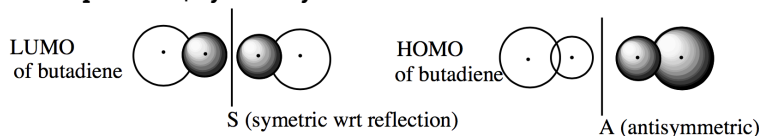
Note that the energies and coefficients of MOs 1 and 3 are paired. ■

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.

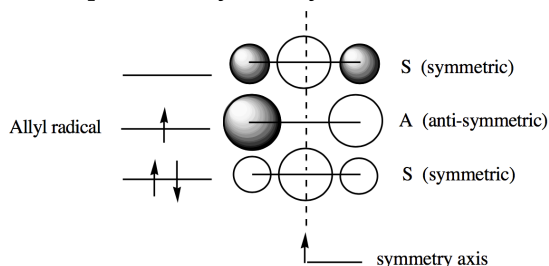
## 2.6 Symmetry of MOs

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

### ■ Example 2.6.1 | Symmetry of the orbitals in butadiene.

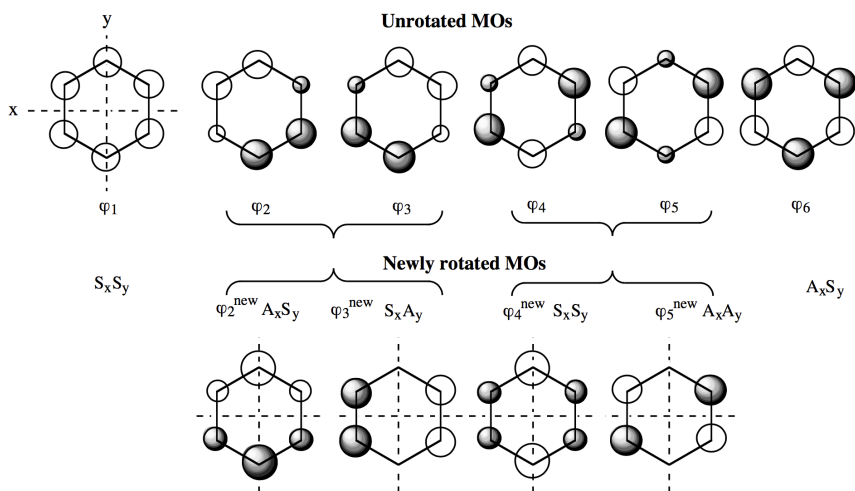


### ■ Example 2.6.2 | Symmetry of the orbitals in the allyl radical.



### ■ Example 2.6.3 | 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.



In this example, the MOs of the benzene molecule were transformed according to

$$\begin{aligned}\psi_2^{\text{new}} &= +\cos\theta\psi_2 + \sin\theta\psi_3 \\ \psi_3^{\text{new}} &= -\sin\theta\psi_2 + \cos\theta\psi_3\end{aligned}$$

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.

■

## 2.7 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 ( $\chi_\mu$  = AO) and the coefficient matrix ( $C_{\mu i}$ ) as:

$$\psi_i = \sum_{\mu}^N \chi_{\mu} C_{\mu i}. \quad (2.33)$$

<sup>6</sup>Recall that in quantum mechanics  $|\Psi|^2 = \Psi^* \Psi$  is a probability density.

Since each MO is normalized we can write:<sup>6</sup>

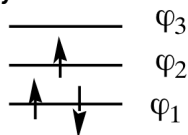
$$\begin{aligned} 1 = \langle \psi_i | \psi_i \rangle &= \sum_{\mu\nu} C_{\mu i}^* \underbrace{\langle \chi_{\mu} | \chi_{\nu} \rangle}_{S_{\mu\nu}} C_{\nu i} = \sum_{\mu} C_{\mu i}^* C_{\mu i} S_{\mu\mu} + \sum_{\mu} \sum_{\substack{\nu \\ \nu \neq \mu}}^N C_{\mu i}^* C_{\nu i} S_{\mu\nu} \\ &= \sum_{\mu} |C_{\mu i}|^2 + \sum_{\mu \neq \nu} C_{\mu i}^* C_{\nu i} S_{\mu\nu}. \end{aligned} \quad (2.34)$$

<sup>7</sup>To simplify the notation we will write  $\sum_{\mu} \sum_{\substack{\nu \\ \nu \neq \mu}}$  as  $\sum_{\mu \neq \nu}$  and omit the superscript  $N$ .

<sup>7</sup> 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  $\psi_i$  on the atomic orbital  $\chi_{\mu}$ . Therefore, we call this the **electron density** on AO  $\chi_{\mu}$  due to the MO  $\psi_i$ .
- $p_{\mu\nu}^i = C_{\mu i}^* C_{\nu i}$  may be interpreted as the **bond order** for bond  $\mu$ - $\nu$  in MO  $\psi_i$  (recall that the Hückel method assumes  $S_{\mu\nu} = 0$  when  $\mu \neq \nu$ ).

■ **Example 2.7.1 | Electron density for the first and second MOs of the allyl radical.**



For  $\psi_1$

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  $\psi_2$

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  $\mu$  ( $q_{\mu}$ ):**

$$q_{\mu} = \sum_i^{\text{MO}} n_i |C_{\mu i}|^2 = \sum_i^{\text{MO}} n_i q_{\mu}^i \quad n_i = \text{occupation (2, 1, or 0)} \quad (2.35)$$

- **Total charge on atom  $\mu$  ( $N_{\mu}$ ):**

$$N_{\mu} = (\text{number of } \pi \text{ electrons donated by atom } \mu) - q_{\mu} \quad (2.36)$$

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

$$p_{\mu\nu} = \sum_i^{\text{MO}} n_i C_{\mu i}^* C_{\nu i} = \sum_i^{\text{MO}} n_i p_{\mu\nu}^i \quad (2.37)$$

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

$$\epsilon_i = \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_{\mu} q_{\mu}^i \alpha_{\mu} + 2 \sum_{\mu < \nu} p_{\mu\nu}^i \beta_{\mu\nu}. \quad (2.38)$$

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

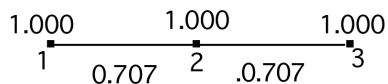
$$E = \sum_i^{\text{occ}} n_i \epsilon_i = \sum_{\mu} q_{\mu} \alpha_{\mu} + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta_{\mu\nu}. \quad (2.39)$$

### ■ Example 2.7.2 | 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



$$p_{12} = 2C_{11}C_{21} + C_{12}C_{22} = 2 \times 0.5 \times (-0.7071) + 0.7071 \times 0 = 0.7071. \quad (2.40)$$

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

### ■ Example 2.7.3 | 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 2.7.4 | 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	2	3	4	5	6
.558416	.525891	.000000	.528265	.000000	-.364069
.431331	.168916	.500000	-.340234	.500000	.411900
.334378	-.374659	.500000	-.269119	-.500000	-.418804
.304074	-.620995	.000000	.586999	.000000	.421114
.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 -0.338117  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 2.7.5 | 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

```

$$\begin{aligned} \text{C2: } 1 - 1.094 &= -0.094 \\ \text{C3: } 1 - 1.151 &= -0.151 \end{aligned}$$

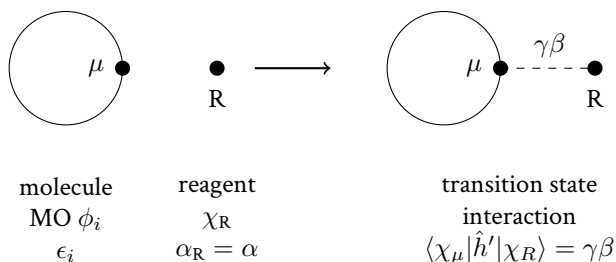
■

## 2.8 Orbital Interactions and Symmetry

Hückel theory can be used to qualitatively understand how the interaction of orbitals leads to the stabilization or destabilization intermediate species formed during a chemical reaction. To estimate the interaction of a molecule with a reagent (R) use second order perturbation theory. Consider the case of an electrophile reagent (R) that interacts with atom  $\mu$  of a given molecule. In Hückel theory the matrix element corresponding to this interaction can be represented with a scaled version of the resonance integral  $\beta$

$$\langle \chi_\mu | \hat{h}' | \chi_R \rangle = \gamma\beta, \quad (2.41)$$

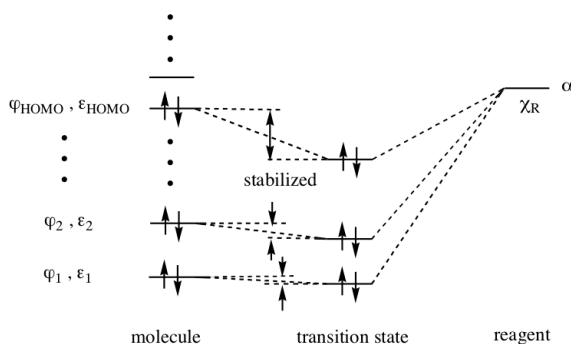
where  $0 \leq \gamma < 1$  is a parameter that describes the strength of this interaction.



Each molecular orbital  $\psi_i$  from Hückel theory gets stabilized by an energy amount given by

$$\Delta E_i^{(2)} = \frac{|\langle \psi_i | \hat{h}' | \chi_R \rangle|^2}{\epsilon_i - \epsilon_R}. \quad (2.42)$$

Note that there is no summation here because there is only one perturbing state (the empty orbital of the reagent). Here is a molecular orbital scheme that shows how the interaction of the reagent empty orbital stabilizes the orbitals in the transition state



The numerator of the expression for  $\Delta E_i^{(2)}$  may be easily computed as

$$\langle \psi_i | \hat{h}' | \chi_R \rangle = \sum_\nu C_{\mu i} \langle \chi_\nu | \hat{h}' | \chi_R \rangle = C_{\mu i} \langle \chi_\mu | \hat{h}' | \chi_R \rangle = \gamma\beta C_{\mu i}. \quad (2.43)$$

because  $\psi_i = \sum_\mu \chi_\mu C_{\mu i}$  and only the matrix element  $\langle \chi_\mu | \hat{h}' | \chi_R \rangle$  is nonzero. The denominator is instead given by

$$\epsilon_i - \epsilon_R = \alpha + \lambda_i \beta - \alpha = \lambda_i \beta, \quad (2.44)$$

where we assumed that the electrophile is a carbon atom ( $\epsilon_R = \alpha$ ). Putting everything together we get

$$\Delta E_i^{(2)} = \frac{(\gamma\beta C_{\mu i})^2}{\lambda_i \beta} = \frac{C_{\mu i}^2}{\lambda_i} \gamma^2 \beta. \quad (2.45)$$

If we sum this contribution over all the doubly occupied orbitals we get a total energy stabilization equal to

$$2 \sum_i^{\text{occ}} \Delta E_i^{(2)} = 2 \sum_i^{\text{occ}} \frac{C_{\mu i}^2}{\lambda_i} \gamma^2 \beta = S_R^E \gamma^2 \beta. \quad (2.46)$$

This equation partitions the interaction energy into a molecule specific part  $S_R^E$ , called the *superdelocalizability* and  $\gamma^2 \beta$ , a term that depends on the strength of the interaction.

The largest contribution to  $S_R^E$  comes from the MO with the smallest  $|\lambda_i|$ , which is called highest occupied molecular orbital (HOMO) and is given by the single term

$$2 \frac{C_{\mu, \text{HOMO}}^2}{\lambda_{\text{HOMO}}} \quad (2.47)$$

If we ignore the denominator we can consider a simplified reactivity index, the *frontier electron density*, given by

$$f_{\mu}^{\text{El}} = 2C_{\mu, \text{HOMO}}^2. \quad (2.48)$$

The most reactive atom towards an electrophile is the one with the largest value of  $f_{\mu}^{\text{El}}$ , among all possible values of  $\mu$ . This means that the atom with the largest absolute coefficient in the HOMO is the most reactive. One can repeat the same analysis for nucleophilic reactions, in which case the reactivity can be connected to a corresponding frontier electron density

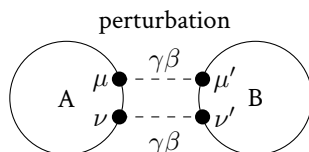
$$f_{\mu}^{\text{Nuc}} = 2C_{\mu, \text{LUMO}}^2, \quad (2.49)$$

where LUMO indicates the lowest unoccupied MO. These two indices allow to identify the atoms (labeled with  $\mu$ ) with the highest reactivity towards electrophiles and nucleophiles by just looking at the HOMO and LUMO of a molecule. For radical reactions, one considers instead the average of  $f_{\mu}^{\text{El}}$  and  $f_{\mu}^{\text{Nuc}}$

$$f_{\mu}^{\text{Rad}} = \frac{1}{2}(f_{\mu}^{\text{El}} + f_{\mu}^{\text{Nuc}}). \quad (2.50)$$

## 2.9 Two-center interactions

Another important application of Hückel theory is in reactions that involve two centers, like cyclization of unsaturated hydrocarbons. If we now consider two molecules, A and B, with centers  $\mu$  and  $\nu$  on A interacting with centers  $\mu'$  and  $\nu'$  on B, we can ask how much is the energy of the complex A + B stabilized by the interaction of the frontier orbitals (HOMO/LUMO) on each fragment.



Assuming again that each pair of orbitals interacts with a term equal to  $\gamma\beta$ , we can write

$$\begin{aligned} \langle \chi_{\mu} | \hat{h}' | \chi_{\mu'} \rangle &= \gamma\beta, \\ \langle \chi_{\nu} | \hat{h}' | \chi_{\nu'} \rangle &= \gamma\beta. \end{aligned} \quad (2.51)$$

Each orbital  $\psi_i^A$  on A will be stabilized by the interaction with the unoccupied orbitals on B

$$\Delta E_i^{A,(2)} = \sum_{k \neq i}^{\text{virtual B}} \frac{|\langle \psi_i^A | \hat{h}' | \psi_k^B \rangle|^2}{\epsilon_i^A - \epsilon_k^B}. \quad (2.52)$$

Similarly, an orbital  $\psi_i^B$  on B will be stabilized by the interaction with the unoccupied orbitals on A by an amount

$$\Delta E_i^{B,(2)} = \sum_{k \neq i}^{\text{virtual B}} \frac{|\langle \psi_i^B | \hat{h}' | \psi_k^A \rangle|^2}{\epsilon_i^B - \epsilon_k^A}. \quad (2.53)$$

Now let us suppose that the most important contribution comes from the interaction of the HOMO on A with the LUMO on B. The numerator for this contribution is given by

$$\Delta E_{\text{HOMO}}^{A,(2)} = \frac{|\langle \psi_{\text{HOMO}}^A | \hat{h}' | \psi_{\text{LUMO}}^B \rangle|^2}{\epsilon_{\text{HOMO}}^A - \epsilon_{\text{LUMO}}^B}. \quad (2.54)$$

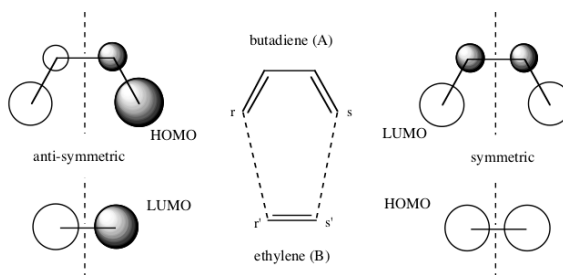
If we plug in the definition of these two orbitals we get for the numerator

$$\begin{aligned} \langle \psi_{\text{HOMO}}^A | \hat{h}' | \psi_{\text{LUMO}}^B \rangle &= \sum_{\rho\sigma} \langle \chi_\rho | \hat{h}' | \chi_\sigma \rangle C_{\rho,\text{HOMO}}^A C_{\sigma,\text{LUMO}}^B \\ &= \langle \chi_\mu | \hat{h}' | \chi_{\mu'} \rangle C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + \langle \chi_\nu | \hat{h}' | \chi_{\nu'} \rangle C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B \\ &= \gamma\beta \underbrace{(C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B)}_{\delta} = \gamma\beta\delta \end{aligned} \quad (2.55)$$

We can now use this result to analyze the cyclization reaction between two molecules.

## 2.10 Cyclization Reaction Between Two Molecules

Consider the case of the HOMO of butadiene interacting with the LUMO of ethylene. In this case we can use simple symmetry considerations to learn something about the interaction of these two molecules in a cyclization reaction. The following plot show the HOMO and LUMO of butadiene and ethylene



For butadiene (A) the HOMO is antisymmetric, that is, it takes values with opposite signs on the two interacting atoms

$$C_{\mu,\text{HOMO}}^A = -C_{\nu,\text{HOMO}}^A \quad (2.56)$$

and this is also true for the LUMO of ethylene (B)

$$C_{\mu',\text{LUMO}}^B = -C_{\nu',\text{LUMO}}^B. \quad (2.57)$$

Taking these results into considerations we obtain

$$\delta = C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B + C_{\nu,\text{HOMO}}^A C_{\nu',\text{LUMO}}^B = 2C_{\mu,\text{HOMO}}^A C_{\mu',\text{LUMO}}^B \quad (2.58)$$

This interaction leads to a lowering in energy since  $\epsilon_{\text{HOMO}}^{\text{A}} - \epsilon_{\text{LUMO}}^{\text{B}} < 0$ , therefore, we say that this interaction is **allowed**. In general, the interaction of orbitals with the same symmetry is allowed. For example, the interaction of the butadiene LUMO with the ethylene HOMO (the opposite of what we considered above) is a case where both orbitals are symmetric since

$$C_{\mu,\text{LUMO}}^{\text{A}} = C_{\nu,\text{LUMO}}^{\text{A}}, \quad (2.59)$$

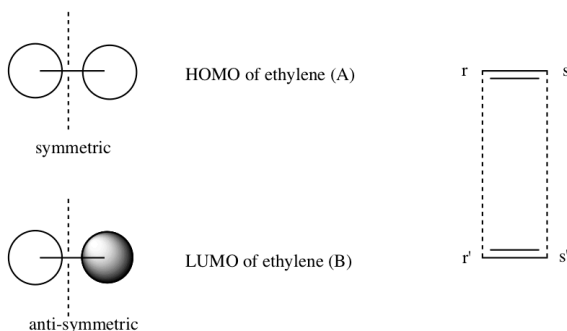
and

$$C_{\mu',\text{HOMO}}^{\text{B}} = C_{\nu',\text{HOMO}}^{\text{B}}. \quad (2.60)$$

For this case the quantity  $\delta$  is also nonzero

$$\delta = 2C_{\mu,\text{LUMO}}^{\text{A}}C_{\mu',\text{HOMO}}^{\text{B}} \quad (2.61)$$

The interaction of two ethylene molecules is an example where the HOMO and LUMO have different symmetry



In this case since

$$C_{\mu,\text{HOMO}}^{\text{A}} = C_{\nu,\text{HOMO}}^{\text{A}}, \quad (2.62)$$

and

$$C_{\mu',\text{LUMO}}^{\text{B}} = -C_{\nu',\text{LUMO}}^{\text{B}}. \quad (2.63)$$

we find that  $\delta = 0$ . This means that the interaction between orbitals of different symmetry is **forbidden**. For general polyenes one has the following result:

$$(4n + 2) + (4n') \rightarrow 4n'' + 2 \quad \text{symmetry allowed}, \quad (2.64)$$

while

$$\begin{aligned} (4n + 2) + (4n' + 2) &\rightarrow 4n'' + 4 \quad \text{forbidden}, \\ (4n) + (4n') &\rightarrow 4n'' \quad \text{forbidden}. \end{aligned} \quad (2.65)$$

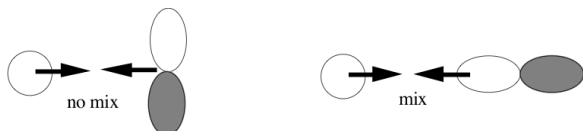
## 2.11 Orbital mixing rules

Let's consider two atomic orbitals  $\psi_i$  and  $\psi_j$  and let them interact by, for example, bringing them together. The interacting orbitals may be described by a two by two matrix of the form

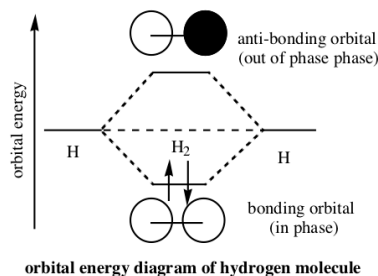
$$\mathbf{h} = \begin{pmatrix} \langle \psi_i | \hat{h} | \psi_i \rangle & \langle \psi_i | \hat{h} | \psi_j \rangle \\ \langle \psi_j | \hat{h} | \psi_i \rangle & \langle \psi_j | \hat{h} | \psi_j \rangle \end{pmatrix} = \begin{pmatrix} \epsilon_i & v \\ v & \epsilon_j \end{pmatrix}. \quad (2.66)$$

By examining the properties of the eigenvalues/eigenvectors of this matrix we can deduce some useful rules that can help us predict how orbitals mix.

- **Rule 1.** A pair of orbitals with zero overlap (orthogonal) do not mix. This is the case  $v = 0$ , which basically means that the two orbitals do not interact due to symmetry.



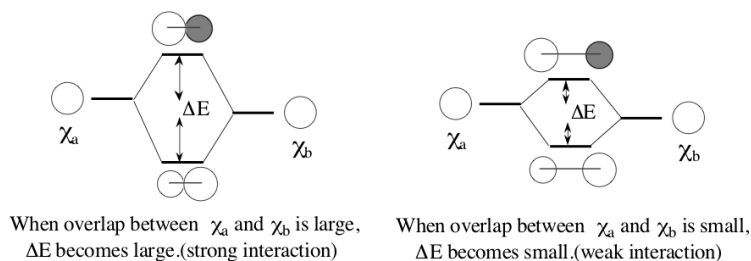
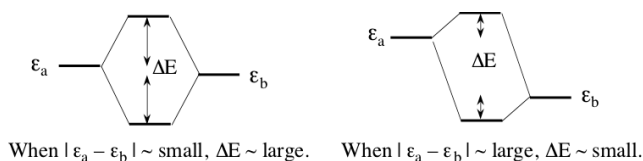
- **Rule 2.** When a pair of orbitals interact, they form a bonding (in-phase) orbital and an anti-bonding (out-of-phase) orbital. The bonding orbital is lower in energy than the antibonding orbital.



This rule follows from the equation for the eigenvalues of  $\mathbf{h}$

$$\lambda_{\pm} = \frac{1}{2}(\epsilon_i + \epsilon_j) \pm \frac{1}{2}\sqrt{(\epsilon_i - \epsilon_j)^2 + 4v^2}. \quad (2.67)$$

- **Rule 3.** When the energy difference between a pair of orbitals before mixing is small and/or the overlap between a pair of orbitals is large, the energy separation becomes large after mixing.



- **Rule 4.** When a pair of orbitals with different energies interact, the newly formed MO has large contribution of the original orbital whose energy is closest to the newly formed MO.

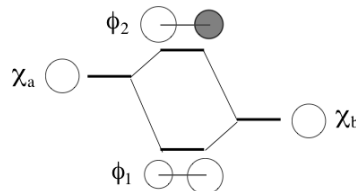
In the case of  $\epsilon_a > \epsilon_b$ ,

bonding orbital is

$$\phi_1 = C_{1a}\chi_a + C_{1b}\chi_b, \quad C_{1a} < C_{1b}$$

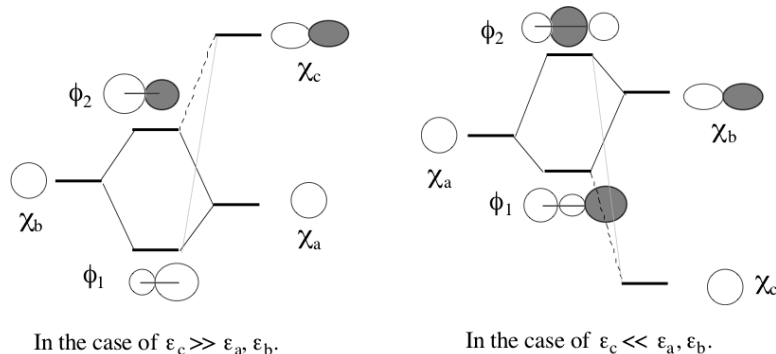
anti-bonding orbital is

$$\phi_2 = C_{2a}\chi_a + C_{2b}\chi_b, \quad C_{2a} > -C_{2b}$$



- **Rule 5.** The same number of new MOs are created from the original orbitals before mixing ( $N$  MOs from  $N$  AOs).
- **Rule 6.** Suppose another orbital  $\chi_c$  affects the two orbitals  $\phi_1$  and  $\phi_2$ , which were formed mainly by interacting two orbitals  $\chi_a$  and  $\chi_b$ . The perturbation caused by the third orbital  $\chi_c$  causes a small change of the orbital shape of  $\phi_1$  and  $\phi_2$ . When the energy of  $\chi_c$  is higher than the energies of  $\phi_1$  and  $\phi_2$ , the mixing of  $\chi_c$  with  $\phi_1$  and  $\phi_2$  is in-phase. When the energy of  $\chi_c$  is lower than the energies of  $\phi_1$  and  $\phi_2$ , the mixing

of  $\chi_c$  into  $\phi_1$  and  $\phi_2$  is out-of-phase. When three orbitals are interacting, the newly formed three MO's can be expressed with a linear combination of the original three orbitals. The mixing coefficients depend on the energies of the original three orbitals.

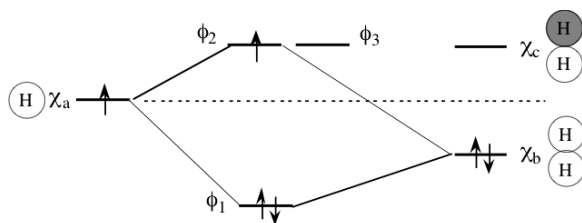


## 2.12 Examples and Problems

### 2.12.1 Molecular orbitals of $H_3$

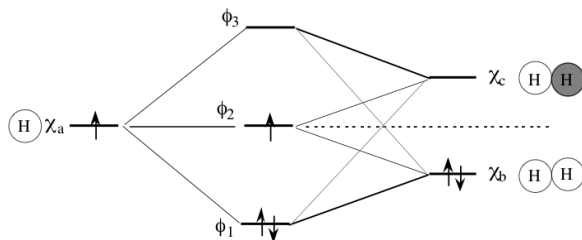
Let us construct the molecular orbitals for the triangular and linear  $H_3$  species from the hydrogen atom and the molecular orbital of the  $H_2$  molecule.

#### Triangular $H_3$



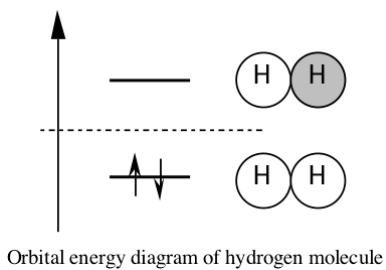
In the case of triangular  $H_3$ , let us assume that atomic hydrogen approaches on the bisecting axis of the hydrogen molecule. Note that  $\chi_a$  interacts only with  $\chi_b$  since the symmetry of  $\chi_c$  is such that no mixing happens. The newly formed molecular orbital  $\psi_1$  is the bonding combination between  $\chi_a$  and  $\chi_b$ , and the molecular orbital  $\psi_2$  is the corresponding anti-bonding combination.  $\psi_3$  is the original  $\chi_c$ .

#### Linear $H_3$ ( $H \cdots H-H$ )

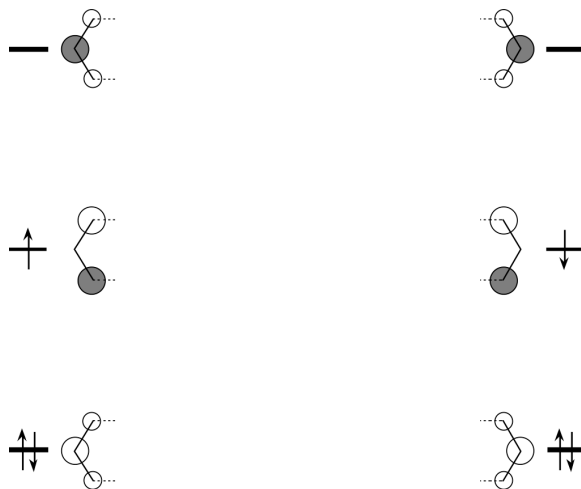


In the linear form of  $H_3$ , an hydrogen atom approaches the molecular axis of the hydrogen molecule. The situation becomes different from the triangular  $H_3$  case, because all orbitals  $\chi_a$ ,  $\chi_b$ , and  $\chi_c$  interact with each other. Comparing these two cases, we predict that the hydrogen exchange reaction  $H_2 + H$  prefers the linear transition-state structure since orbital interactions lead to an overall stabilization of the energy.

**Problem 2.12.1 – Molecular orbitals of  $H_4$ .** Construct the molecular orbitals for square  $H_4$  and linear  $H_4$  species from the two sets of molecular orbitals of the  $H_2$  molecule. Draw the orbital energy diagrams and discuss which structure is more stable.



**Problem 2.12.2 –  $\pi$  MOs of benzene.** Create the six  $\pi$ -molecular orbitals of benzene by combining the two sets of  $\pi$ -orbitals of the allyl radical. The picture shows only one side of  $\pi$ -plane (top view).





## CHAPTER 3

# Many-electron wave functions and Full Configuration Interaction

### 3.1 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.<sup>8</sup> The spin operators satisfy the following commutation relationship

$$[\hat{s}_j, \hat{s}_k] = \hat{s}_j \hat{s}_k - \hat{s}_k \hat{s}_j = i\hbar \varepsilon_{jkl} \hat{s}_l \quad \text{with } j, k, l \in \{x, y, z\}, \quad (3.1)$$

where  $\varepsilon_{jkl}$  is the Levi-Civita symbol defined as

$$\varepsilon_{jkl} = \begin{cases} +1 & \text{if } (j, k, l) \text{ is an even permutation of } (x, y, z) \\ -1 & \text{if } (j, k, l) \text{ is an odd permutation of } (x, y, z) \\ 0 & \text{otherwise.} \end{cases} \quad (3.2)$$

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

$$\hat{\vec{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z). \quad (3.3)$$

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

$$\hat{s}^2 = \hat{\vec{s}} \cdot \hat{\vec{s}} = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2. \quad (3.4)$$

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

$$[\hat{s}^2, \hat{s}_j] = 0 \quad \text{with } j \in \{x, y, z\}, \quad (3.5)$$

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  $s, s-1, s-2, \dots, -s$ . The spin eigenfunctions satisfy:

$$\hat{s}^2 |s, m_s\rangle = \hbar^2 s(s+1) |s, m_s\rangle, \quad (3.6)$$

$$\hat{s}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle. \quad (3.7)$$

In the case of electrons we have that  $s = \frac{1}{2}$ , and so we label the two spin functions as  $\alpha$  and  $\beta$ <sup>9</sup>

$$|\alpha\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle, \quad (3.8)$$

$$|\beta\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle. \quad (3.9)$$

<sup>8</sup>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.

<sup>9</sup>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:

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1, \quad (3.10)$$

$$\langle \alpha | \beta \rangle = 0. \quad (3.11)$$

At times, we might write these functions as

$$\alpha(\omega) = \langle \omega | \alpha \rangle \quad (3.12)$$

$$\beta(\omega) = \langle \omega | \beta \rangle, \quad (3.13)$$

where  $\omega$  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. (3.11)] may be written as

$$\langle \alpha | \beta \rangle = \int d\omega \alpha^*(\omega) \beta(\omega) = 0. \quad (3.14)$$

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

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \quad (3.15)$$

$$\hat{s}_- = \hat{s}_x - i\hat{s}_y \quad (3.16)$$

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

$$\hat{s}_+ |\alpha\rangle = 0, \quad (3.17)$$

$$\hat{s}_+ |\beta\rangle = |\alpha\rangle \quad (m_s : -\frac{1}{2} \rightarrow \frac{1}{2}), \quad (3.18)$$

$$\hat{s}_- |\alpha\rangle = |\beta\rangle \quad (m_s : \frac{1}{2} \rightarrow -\frac{1}{2}), \quad (3.19)$$

$$\hat{s}_- |\beta\rangle = 0. \quad (3.20)$$

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

$$\hat{s}^2 = \hat{s}_+ \hat{s}_- + \hat{s}_z^2 - \hat{s}_z. \quad (3.21)$$

It is also convenient to introduce many-electron generalizations of the spin operators. For a system of  $N$  electrons, we can generalize the six spin operators that we introduced above by taking the sum of operators acting on each particle

$$\begin{aligned} \hat{S}_x &= \sum_i^N \hat{s}_x(i), & \hat{S}_y &= \sum_i^N \hat{s}_y(i), & \hat{S}_z &= \sum_i^N \hat{s}_z(i), \\ \hat{S}^2 &= \sum_i^N \hat{s}^2(i), & \hat{S}_+ &= \sum_i^N \hat{s}_+(i), & \hat{S}_- &= \sum_i^N \hat{s}_-(i), \end{aligned}$$

where, for example,  $\hat{s}^2(i)$  means that an operator  $\hat{s}^2$  acts only on electron  $i$ . These operators satisfy the same commutation relationships of their one-electron versions (the lowercase operators). This implies that for  $N$  electron systems we can still find eigenstates of both  $\hat{S}^2$  and  $\hat{S}_z$ . Then the corresponding spin eigenfunctions will be of the form  $|S, M_S\rangle$ , and these will satisfy

$$\hat{S}^2 |S, M_S\rangle = S(S+1) |S, M_S\rangle, \quad (3.22)$$

$$\hat{S}_z |S, M_S\rangle = M_S |S, M_S\rangle, \quad M_S = -S, -S+1, \dots, S-1, S. \quad (3.23)$$

When describing a spin state with quantum number  $S$ , it is more common to refer to its multiplicity, which is given by

$$\text{multiplicity} = 2S + 1 \quad (3.24)$$

States with multiplicity = 1 ( $S = 0$ ) are called singlets, multiplicity = 2 ( $S = 1/2$ ) are called doublets, and so on.

## 3.2 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.<sup>10</sup> 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  $\{\phi_i(\vec{r})\}$

<sup>10</sup>A set of functions  $\{\phi_i(\vec{r})\}$  is called **orthonormal** if any two functions satisfy  $\int d\vec{r} \phi_i^*(\vec{r}) \phi_j(\vec{r}) = \delta_{ij}$ .

$$f(\vec{r}) = \sum_i a_i \phi_i(\vec{r}). \quad (3.25)$$

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:<sup>11</sup>

$$\psi_{i,\sigma}(x) = \psi_{i,\sigma}(\vec{r}, \omega) = \phi_i(\vec{r})\sigma(\omega), \quad (3.26)$$

<sup>11</sup>We will abbreviate the spatial and spin coordinates with the symbol  $x \equiv (\vec{r}, \omega)$ .

where  $\sigma(\omega) \in \{\alpha(\omega), \beta(\omega)\}$  indicates a generic spin function. Note that if the spatial orbitals are orthonormal, then the spin orbital basis is also orthonormal in the following sense

$$\begin{aligned} \langle \psi_{i,\sigma} | \psi_{j,\sigma'} \rangle &= \int d\vec{r} d\omega \psi_{i,\sigma}^*(\vec{r}, \omega) \psi_{j,\sigma'}(\vec{r}, \omega) \\ &= \int d\vec{r} \phi_i^*(\vec{r}) \phi_j(\vec{r}) \int d\omega \sigma^*(\omega) \sigma'(\omega) \\ &= \delta_{ij} \delta_{\sigma\sigma'}. \end{aligned} \quad (3.27)$$

Note that even if the spatial part of a spin orbital is the same ( $\psi_i = \psi_j$ ) the overlap integral can still be zero if the spin functions  $\sigma$  and  $\sigma'$  are different.

To avoid having to write the two subscripts  $i$  and  $\sigma$  every time we indicated a spin orbital, we will often collect the indices  $(i, \sigma)$  into one index  $k$  and specify an ordering of the spin orbitals. For example, for basis of  $K$  spatial orbitals we can define  $2K$  spin orbitals as:

$$\psi_{2i-1}(x) = \phi_i(\vec{r})\alpha(\omega), \quad (3.28)$$

$$\psi_{2i}(x) = \phi_i(\vec{r})\beta(\omega), \quad (3.29)$$

which is equivalent to ordering the spin orbitals in the following way

$$(\psi_1, \psi_2, \psi_3, \psi_4, \dots) = (\phi_1\alpha, \phi_1\beta, \phi_2\alpha, \phi_2\beta, \dots). \quad (3.30)$$

## 3.3 $N$ -electron wave functions

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

$$\Phi(\dots, x_i, \dots, x_j, \dots, x_N) = -\Phi(\dots, x_j, \dots, x_i, \dots, x_N). \quad (3.31)$$

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

■ **Example 3.3.1 | 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

$$\Phi(x_2, x_1) = -\Phi(x_1, x_2). \quad (3.32)$$

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:

$$\Phi(x_1, x_2) = \sum_i a_i(x_2) \psi_i(x_1), \quad (3.33)$$

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:

$$a_i(x_2) = \sum_j a_{ij} \psi_j(x_2), \quad (3.34)$$

and introduced the quantity  $a_{ij}$ , which carries both the indices for the  $x_1$  and  $x_2$  expansions. Combining Eqs. (3.33)–(3.34) we obtain:

$$\Phi(x_1, x_2) = \sum_{ij} a_{ij} \psi_i(x_1) \psi_j(x_2). \quad (3.35)$$

This functions may satisfy the antisymmetry condition if:

$$\sum_{ij} a_{ij} \psi_i(x_1) \psi_j(x_2) = - \sum_{ij} a_{ij} \psi_i(x_2) \psi_j(x_1). \quad (3.36)$$

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:

$$\sum_{ij} a_{ij} \psi_i(x_1) \psi_j(x_2) = - \sum_{ij} a_{ji} \psi_j(x_2) \psi_i(x_1), \quad (3.37)$$

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

$$\sum_{ij} (a_{ij} + a_{ji}) \psi_i(x_1) \psi_j(x_2) = 0. \quad (3.38)$$

Equation (3.38) must hold for any value of  $\psi_i(x_1) \psi_j(x_2)$ , and this is possible only if

$$a_{ij} + a_{ji} = 0. \quad (3.39)$$

This conditions may also be written as

$$a_{ij} = -a_{ji}. \quad (3.40)$$

As a consequence, the diagonal elements of  $a_{ij}$ ,  $a_{ii}$ , are zero. To see this set  $j = i$ . Then  $a_{ii} + a_{ii} = 2a_{ii} = 0$ , so that  $a_{ii} = 0$ . Eq. (3.39) 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  $a_{ij}$ . 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  $a_{i_1 i_2 i_3 \dots i_N}$ .

Using Eq. (3.39) we may write the two-electron wave function as:

$$\begin{aligned}
 \Phi(x_1, x_2) &= \sum_{i < j}^{\infty} a_{ij} \psi_i(x_1) \psi_j(x_2) + \sum_{i > j}^{\infty} a_{ij} \psi_i(x_1) \psi_j(x_2) \\
 &= \sum_{i < j}^{\infty} a_{ij} \psi_i(x_1) \psi_j(x_2) + \sum_{j > i}^{\infty} a_{ji} \psi_j(x_1) \psi_i(x_2) \\
 &= \sum_{i < j}^{\infty} a_{ij} \psi_i(x_1) \psi_j(x_2) - \sum_{i < j}^{\infty} a_{ij} \psi_i(x_2) \psi_j(x_1) \\
 &= \sum_{i < j}^{\infty} a_{ij} [\psi_i(x_1) \psi_j(x_2) - \psi_i(x_2) \psi_j(x_1)].
 \end{aligned} \tag{3.41}$$

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:

$$\det \begin{bmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{bmatrix} \equiv \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix} = \psi_i(x_1) \psi_j(x_2) - \psi_i(x_2) \psi_j(x_1). \tag{3.42}$$

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

$$\Phi(x_1, x_2) = \sum_{i < j}^{\infty} a_{ij} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix}. \tag{3.43}$$

■

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

$$\Phi_{ijk\dots}(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) & \cdots & \psi_i(x_N) \\ \psi_j(x_1) & \psi_j(x_2) & \cdots & \psi_j(x_N) \\ \psi_k(x_1) & \psi_k(x_2) & \cdots & \psi_k(x_N) \\ \vdots & \vdots & \ddots & \vdots \end{vmatrix}. \tag{3.44}$$

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

$$|\Phi_{ijk\dots}\rangle = |\psi_i \psi_j \psi_k \cdots\rangle, \tag{3.45}$$

omitting the labels of the electrons. The basis of Slater determinants  $\{|\psi_i \psi_j \psi_k \cdots\rangle\}$  with  $i, j, k, \dots \in \{0, 1, 2, \dots\}$  is complete.<sup>12</sup> Therefore, we may expand any electronic wave function  $\Psi$  using the Slater determinant basis:

<sup>12</sup>This property is inherited from the fact that the one-electron spin orbital basis is complete.

$$|\Psi\rangle = \sum_{i < j < k \dots}^{\infty} C_{ijk\dots} |\psi_i \psi_j \psi_k \cdots\rangle. \tag{3.46}$$

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:

$$N_{\text{FCI}} = \binom{2K}{N}. \tag{3.47}$$

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

■ **Example 3.3.2 | 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:

$$\Phi^{\text{HP}}(x_1, x_2) = \psi_i(x_1)\psi_j(x_2). \quad (3.48)$$

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:

$$|\Phi^{\text{HP}}(x_1, x_2)|^2 = |\psi_i(x_1)|^2 |\psi_j(x_2)|^2 = P_i(x_1)P_j(x_2). \quad (3.49)$$

A Hartree product represents a state with **no correlation**.

A Slater determinant:

$$\Phi^{\text{SD}}(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)]. \quad (3.50)$$

has a probability distribution equal to:

$$\begin{aligned} |\Phi^{\text{SD}}(x_1, x_2)|^2 = \frac{1}{2} [ & P_i(x_1)P_j(x_2) + P_j(x_1)P_i(x_2) \\ & - \psi_i^*(x_1)\psi_j(x_1)\psi_j^*(x_2)\psi_i(x_2) \\ & - \psi_j^*(x_1)\psi_i(x_1)\psi_j(x_2)\psi_i^*(x_2) ]. \end{aligned} \quad (3.51)$$

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  $\omega_1$  and  $\omega_2$  we can derive a probability distribution that depends only on the positions of the electrons:

$$P(\mathbf{r}_1, \mathbf{r}_2) = \int d\omega_1 d\omega_2 |\Phi^{\text{SD}}(x_1, x_2)|^2. \quad (3.52)$$

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

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2)]. \quad (3.53)$$

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

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} [ & P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2) \\ & - \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\ & - \phi_j^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_i^*(\mathbf{r}_2) ]. \end{aligned} \quad (3.54)$$

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. ■

### 3.4 Full configuration interaction wave function for $\text{H}_2$

In this section we will do an extensive study of the wave function of  $\text{H}_2$  in a minimal basis set. Consider two hydrogen atoms ( $\text{H}_\text{A}$  and  $\text{H}_\text{B}$ ) separated by a distance  $R_{\text{AB}}$ . We will assume that each atom has one atomic basis function,  $\chi_{1s}^{\text{A}}(\mathbf{r})$  and  $\chi_{1s}^{\text{B}}(\mathbf{r})$ . Note that these two orbitals are not necessarily orthogonal as their overlap ( $S$ ) is in general not equal to zero

$$S = \int d\mathbf{r} \chi_{1s}^{\text{A}}(\mathbf{r}) \chi_{1s}^{\text{B}}(\mathbf{r}) \neq 0. \quad (3.55)$$

From these atomic orbitals we can form two spatial orbitals:

$$\phi_g(\mathbf{r}) = N_g[\chi_{1s}^A(\mathbf{r}) + \chi_{1s}^B(\mathbf{r})], \quad (3.56)$$

$$\phi_u(\mathbf{r}) = N_u[\chi_{1s}^A(\mathbf{r}) - \chi_{1s}^B(\mathbf{r})]. \quad (3.57)$$

**Problem 3.4.1 — 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:

$$\psi_1(x) = \psi_g(x) = \phi_g(\mathbf{r})\alpha(\omega), \quad (3.58)$$

$$\psi_2(x) = \psi_{\bar{g}}(x) = \phi_g(\mathbf{r})\beta(\omega), \quad (3.59)$$

$$\psi_3(x) = \psi_u(x) = \phi_u(\mathbf{r})\alpha(\omega), \quad (3.60)$$

$$\psi_4(x) = \psi_{\bar{u}}(x) = \phi_u(\mathbf{r})\beta(\omega). \quad (3.61)$$

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

$$|\psi_g\psi_g\rangle = 0, \quad (3.62)$$

is zero because we have placed two electrons in the same spin orbital.<sup>13</sup> We may form six unique determinants:

$$|\Phi_1\rangle = |\psi_g\psi_{\bar{g}}\rangle = \begin{array}{c} \text{---} \\ \uparrow\downarrow \end{array} \quad (3.63)$$

$$|\Phi_2\rangle = |\psi_g\psi_{\bar{u}}\rangle = \begin{array}{c} \text{---} \\ \downarrow \\ \uparrow \end{array} \quad (3.64)$$

$$|\Phi_3\rangle = |\psi_u\psi_{\bar{g}}\rangle = \begin{array}{c} \uparrow \\ \text{---} \\ \downarrow \end{array} \quad (3.65)$$

$$|\Phi_4\rangle = |\psi_u\psi_{\bar{u}}\rangle = \begin{array}{c} \uparrow\downarrow \\ \text{---} \end{array} \quad (3.66)$$

$$|\Phi_5\rangle = |\psi_g\psi_u\rangle = \begin{array}{c} \uparrow \\ \text{---} \\ \uparrow \end{array} \quad (3.67)$$

$$|\Phi_6\rangle = |\psi_{\bar{g}}\psi_{\bar{u}}\rangle = \begin{array}{c} \text{---} \\ \downarrow \\ \text{---} \\ \downarrow \end{array} \quad (3.68)$$

Symmetry greatly simplifies this problem.<sup>14</sup> The determinants  $|\Phi_1\rangle$  and  $|\Phi_4\rangle$  are gerade since the product  $\psi_g\psi_{\bar{g}}$  has symmetry equal to  $g \times g = g$ .<sup>15</sup> Determinants  $|\Phi_2\rangle$ ,  $|\Phi_3\rangle$ ,  $|\Phi_5\rangle$ ,  $|\Phi_6\rangle$  instead are ungerade. Spin (which is another symmetry) also helps to classify the determinants. As shown in the table below, determinants 1–4 have  $M_S = 0$ , while 5 and 6 have  $M_S = +1$  and  $-1$ , respectively.

Determinant	Occupied spin orbitals	Symmetry	$M_S$
$\Phi_1$	$\psi_g\psi_{\bar{g}}$	$g$	0
$\Phi_2$	$\psi_g\psi_{\bar{u}}$	$u$	0
$\Phi_3$	$\psi_u\psi_{\bar{g}}$	$u$	0
$\Phi_4$	$\psi_u\psi_{\bar{u}}$	$g$	0
$\Phi_5$	$\psi_g\psi_u$	$u$	1
$\Phi_6$	$\psi_{\bar{g}}\psi_{\bar{u}}$	$u$	-1

<sup>13</sup>Just to avoid confusion: a spatial orbital may accommodate two electrons (with opposite spin) a spin orbitals can accommodate only one electron.

<sup>14</sup>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.

<sup>15</sup>Recall that for molecules that possess a center of inversion the following rules apply:  $g \times g = g$ ,  $g \times u = u \times g = u$ ,  $u \times u = g$ .

Why is this classification helpful? Because determinants with different symmetry and spin will not contribute to the same eigenfunction. We can immediately notice that there are only two determinants ( $\Phi_1$  and  $\Phi_4$ ) of gerade symmetry, and both have  $M_S = 0$ . Out of these two determinants one can form eigenfunctions of the form

$$C_1 |\Phi_1\rangle + C_4 |\Phi_4\rangle, \quad (3.70)$$

which will continue to have gerade symmetry and  $M_S = 0$ . What is spin state (singlet, double, triplets, etc.) corresponding to these solutions? Remember that for a system with total spin quantum number  $S$  the allowed values of  $M_S$  are  $-S, -S+1, \dots, S-1, S$ , in total  $2S+1$ . The only value of  $S$  that is compatible with the states that we found (g,  $M_S = 0$ ) is  $S = 0$ , since then  $M_S = 0$ . Therefore, the states of the form  $C_1 |\Phi_1\rangle + C_4 |\Phi_4\rangle$  are singlet states.

From the ungerade determinants with  $M_S = 0$  we can form wave functions that look like:

$$C_2 |\Phi_2\rangle + C_3 |\Phi_3\rangle, \quad (3.71)$$

plus we have two ungerade states with  $M_S = \pm 1$  ( $|\Phi_5\rangle, |\Phi_6\rangle$ ) that will not mix with any other determinants because their symmetry is distinct from that of all other determinants.

### 3.5 Electronic states of $H_2$

Let us now analyze these determinants in terms of the atomic basis functions. Consider  $\Phi_1$ , the lowest energy determinant. If we plug in the definitions of the spin orbitals we obtain:

$$\begin{aligned} |\Phi_1\rangle &= |\psi_g \psi_{\bar{g}}\rangle = N_g^2 |(\chi_{1s}^A + \chi_{1s}^B)\alpha(\chi_{1s}^A + \chi_{1s}^B)\beta\rangle \\ &= N_g^2 [|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle]. \end{aligned} \quad (3.72)$$

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

$$|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle \equiv \begin{pmatrix} \uparrow\downarrow \\ \text{---} \end{pmatrix} \quad (3.73)$$

and

$$|\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle \equiv \begin{pmatrix} \text{---} \\ \uparrow\downarrow \end{pmatrix} \quad (3.74)$$

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:

$$|\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle \equiv \begin{pmatrix} \uparrow \\ \text{---} \end{pmatrix} \quad \begin{pmatrix} \text{---} \\ \downarrow \end{pmatrix} \quad (3.75)$$

and

$$|\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle \equiv \begin{pmatrix} \text{---} \\ \downarrow \end{pmatrix} \quad \begin{pmatrix} \uparrow \\ \text{---} \end{pmatrix} \quad (3.76)$$

All these four determinants contribute equally, so the determinant  $\Phi_1$  represents a state that has mixture of 50% covalent and 50% ionic electronic configurations. The determinant  $\Phi_4$  is also a 50/50 combination of covalent and ionic terms, but the sign of the covalent contributions is different:

$$\begin{aligned} |\Phi_4\rangle &= |\psi_u \psi_{\bar{u}}\rangle = N_u^2 |(\chi_{1s}^A - \chi_{1s}^B)\alpha(\chi_{1s}^A - \chi_{1s}^B)\beta\rangle \\ &= N_u^2 [|\chi_{1s}^A \alpha \chi_{1s}^A \beta\rangle - |\chi_{1s}^A \alpha \chi_{1s}^B \beta\rangle - |\chi_{1s}^B \alpha \chi_{1s}^A \beta\rangle + |\chi_{1s}^B \alpha \chi_{1s}^B \beta\rangle]. \end{aligned} \quad (3.77)$$

Any linear combination of  $\Phi_1$  and  $\Phi_4$  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  $\Phi_5$  has  $M_S = +1$  and is a component of a triplet state ( $S = 1$ ). Expanding  $\Phi_5$  in terms of spin orbital we find:

$$\begin{aligned} |\Phi_5\rangle &= |\psi_g \psi_u\rangle = N_g N_u |(\chi_{1s}^A + \chi_{1s}^B)\alpha(\chi_{1s}^A - \chi_{1s}^B)\alpha\rangle \\ &= N_g N_u [\underbrace{|\chi_{1s}^A \alpha \chi_{1s}^A \alpha\rangle}_{=0} - |\chi_{1s}^A \alpha \chi_{1s}^B \alpha\rangle + |\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle - \underbrace{|\chi_{1s}^B \alpha \chi_{1s}^B \alpha\rangle}_{=0}] \\ &= 2N_g N_u |\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle. \end{aligned} \quad (3.78)$$

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

$$|\chi_{1s}^A \alpha \chi_{1s}^B \alpha\rangle = -|\chi_{1s}^B \alpha \chi_{1s}^A \alpha\rangle. \quad (3.79)$$

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

$$|\chi_{1s}^A \alpha \chi_{1s}^A \alpha\rangle \equiv \begin{pmatrix} \uparrow \uparrow \end{pmatrix} \quad \begin{pmatrix} \text{---} \end{pmatrix} \quad (3.80)$$

In other words, this determinant includes a form of correlation that is a consequence of the antisymmetry of the wave function of electrons, the so-called **Fermi correlation**. The state  $\Phi_5$  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  $\Phi_5$ :

$$\hat{S}^2 |\Phi_5\rangle = \hat{S}^2 |\psi_g \psi_u\rangle = (\hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hat{S}_z) |\psi_g \psi_u\rangle. \quad (3.81)$$

Let us consider these terms in detail<sup>16</sup>

$$^{16} \hat{S}_- = \hat{s}_-(1) + \hat{s}_-(2).$$

$$\hat{S}_+ \hat{S}_- |\psi_g \psi_u\rangle = \hat{S}_+ (|\psi_g \psi_u\rangle + |\psi_g \psi_{\bar{u}}\rangle) = 2 |\psi_g \psi_u\rangle. \quad (3.82)$$

$$\hat{S}_z |\psi_g \psi_u\rangle = \left(\frac{1}{2} + \frac{1}{2}\right) |\psi_g \psi_u\rangle = |\psi_g \psi_u\rangle. \quad (3.83)$$

Putting all together we get

$$\begin{aligned} \hat{S}^2 |\Phi_5\rangle &= (\hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hat{S}_z) |\psi_g \psi_u\rangle \\ &= 2 |\psi_g \psi_u\rangle + |\psi_g \psi_u\rangle - |\psi_g \psi_u\rangle = 2 |\psi_g \psi_u\rangle. \end{aligned} \quad (3.84)$$

This result shows that  $\Phi_5$  is an eigenfunction of  $\hat{S}^2$  with eigenvalue equal to 2. In other words,  $S(S+1) = 2$ , which implies  $S = 1$ . Therefore,  $\Phi_5$  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  $\Phi_6$ .

What about the  $M_S = 0$  component? It turns out that this component is contained in the determinants  $\Phi_2$  and  $\Phi_3$ . Let us compute  $\hat{S}^2 |\Phi_2\rangle$ . We will need the quantity:

$$\hat{S}_+ \hat{S}_- |\Phi_2\rangle = \hat{S}_+ \hat{S}_- |\psi_g \psi_{\bar{u}}\rangle = \hat{S}_+ |\psi_g \psi_{\bar{u}}\rangle = |\psi_g \psi_{\bar{u}}\rangle + |\psi_{\bar{g}} \psi_u\rangle, \quad (3.85)$$

and

$$\hat{S}_z |\psi_g \psi_{\bar{u}}\rangle = \left(\frac{1}{2} - \frac{1}{2}\right) |\psi_g \psi_{\bar{u}}\rangle = 0. \quad (3.86)$$

From these results we find that:

$$\hat{S}^2 |\Phi_2\rangle = |\psi_g \psi_{\bar{u}}\rangle + |\psi_{\bar{g}} \psi_u\rangle = |\psi_g \psi_{\bar{u}}\rangle - |\psi_u \psi_{\bar{g}}\rangle = |\Phi_2\rangle - |\Phi_3\rangle. \quad (3.87)$$

This means that  $\Phi_2$  is not an eigenfunction of  $\hat{S}^2$ . The fact that  $\hat{S}^2 |\Phi_2\rangle$  gives back both  $\Phi_2$  and  $\Phi_3$  is a hint that a **linear combination** of these two determinants is an eigenfunction of spin. The following result:

$$\hat{S}^2 |\Phi_3\rangle = |\Phi_3\rangle - |\Phi_2\rangle. \quad (3.88)$$

suggests that we consider the plus and minus combination of  $\Phi_2$  and  $\Phi_3$ :

$$|\Phi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|\Phi_2\rangle \pm |\Phi_3\rangle). \quad (3.89)$$

These two states are such that

$$\hat{S}^2 |\Phi_+\rangle = 0, \quad (3.90)$$

and

$$\hat{S}^2 |\Phi_-\rangle = 2 |\Phi_-\rangle. \quad (3.91)$$

Therefore,  $\Phi_-$  is a triplet state while  $\Phi_+$  is a singlet state.

Putting everything together we can summarize the our results as

Wave function	Symmetry	$S$	$M_S$	Note
$C'_1  \Phi_1\rangle + C'_4  \Phi_4\rangle$	g	0	0	Ground singlet state
$C'_1  \Phi_1\rangle + C'_4  \Phi_4\rangle$	g	0	0	Excited singlet state
$\frac{1}{\sqrt{2}} ( \Phi_2\rangle +  \Phi_3\rangle)$	u	0	0	Excited singlet state
$ \Phi_5\rangle$	u	1	1	Triplet state (degenerate)
$\frac{1}{\sqrt{2}} ( \Phi_2\rangle -  \Phi_3\rangle)$	u	1	0	
$ \Phi_6\rangle$	u	1	-1	

### ■ Example 3.5.1 | Electronic states of the $(2p)^2$ configuration of carbon.

When classifying the states of atoms we can use the quantum numbers corresponding to the operators  $\hat{L}^2$  (total angular momentum squared),  $\hat{L}_z$  (projection of angular momentum on the z axis),  $\hat{S}^2$  (total spin squared),  $\hat{S}_z$  (projection of spin on the z axis). This is a consequence of the fact that the Hamiltonian commutes with all of these operators, and therefore, we are guaranteed that we can find eigenfunctions of  $\hat{H}$  that are also eigenfunctions of  $\hat{L}^2$ ,  $\hat{L}_z$ ,  $\hat{S}^2$ , and  $\hat{S}_z$ .

The ground-state electronic configuration of carbon is  $(1s)^2 (2s)^2 (2p)^2$ . To classify the electronic states that arise from this configuration we can ignore the 1s and 2s shells since they are fully occupied and turn our attention to the 2p shell. The 2p shell consists of three orbitals with angular momentum quantum number  $l = 1$  and  $m_l = -1, 0, 1$ .

$$2p_{-1}, 2p_0, 2p_1 \quad (3.92)$$

Note that these are not the Cartesian orbitals  $2p_x$ ,  $2p_y$ , and  $2p_z$ , but they are related to them via

$$\begin{aligned} 2p_{-1} &= 2p_x - i2p_y \\ 2p_0 &= 2p_z \\ 2p_{+1} &= 2p_x + i2p_y \end{aligned} \quad (3.93)$$

From these three orbitals we can form six spin orbitals, and construct a total of 15 determinants:

Number	Determinant	$M_L$	$M_S$
1	$ (2p_{-1}\alpha)(2p_0\alpha)\rangle$	-1	1
2	$ (2p_{-1}\alpha)(2p_1\alpha)\rangle$	0	1
3	$ (2p_0\alpha)(2p_1\alpha)\rangle$	1	1
4	$ (2p_{-1}\alpha)(2p_{-1}\beta)\rangle$	-2	0
5	$ (2p_{-1}\alpha)(2p_0\beta)\rangle$	-1	0
6	$ (2p_{-1}\alpha)(2p_1\beta)\rangle$	0	0
7	$ (2p_0\alpha)(2p_{-1}\beta)\rangle$	-1	0
8	$ (2p_0\alpha)(2p_0\beta)\rangle$	0	0
9	$ (2p_0\alpha)(2p_1\beta)\rangle$	1	0
10	$ (2p_1\alpha)(2p_{-1}\beta)\rangle$	0	0
11	$ (2p_1\alpha)(2p_0\beta)\rangle$	1	0
12	$ (2p_1\alpha)(2p_1\beta)\rangle$	2	0
13	$ (2p_{-1}\beta)(2p_0\beta)\rangle$	-1	-1
14	$ (2p_{-1}\beta)(2p_1\beta)\rangle$	0	-1
15	$ (2p_0\beta)(2p_1\beta)\rangle$	1	-1

(3.94)

We can now represent these determinants in a grid of  $M_L$  and  $M_S$  values like indicated below

$M_L \backslash M_S$	-1	0	1
-2		•	
-1	•	••	•
0	•	•••	•
1	•	••	•
2		•	

(3.95)

To identify the spin and symmetry of the state that originate from the 15 determinants we look for a state with the highest possible value of  $L$  or  $S$ . Consider determinant 12, with  $M_L = 2$  and  $M_S = 0$ . This determinant arises from a state with  $L = 2$  and  $S = 0$ . Why? Because there are no other values of  $L$  and  $S$  that could generate a set of determinants consistent with the ones we found. For example, if this determinant belonged to a state with  $L = 2$  and  $S = 1$ , we would have expected to see determinants with  $M_L = 2$  and  $M_S = -1, 0, 1$  (which is not the case). The state  $L = 2$  and  $S = 0$  contains five levels with  $M_L = -2, -1, 0, 1, 2$ , which we can identify with the five determinants in the middle column. These are indicated in red in the left figure below. Once these are removed there are only 10 states left, as shown in the right figure below

$M_L \backslash M_S$	-1	0	1
-2		•	
-1	•	••	•
0	•	•••	•
1	•	••	•
2		•	

→

$M_L \backslash M_S$	-1	0	1
-2			
-1	•	•	•
0	•	••	•
1	•	•	•
2			

Of the states left, we then move to consider the one with  $M_L = 1$  and  $M_S = 1$ . This state must originate from a  $L = 1$  and  $S = 1$  state, to which correspond all the possible combinations of  $M_L = -1, 0, 1$  and  $M_S = -1, 0, 1$ . These nine combinations are indicated in the left figure below in red.

$M_L \backslash M_S$	-1	0	1
-2			
-1	•	•	•
0	•	••	•
1	•	•	•
2			

→

$M_L \backslash M_S$	-1	0	1
-2			
-1			
0		•	
1			
2			

After eliminating the nine states, we are left with one state with  $M_L = 0$  and  $M_S = 0$ . This state corresponds to the total quantum numbers  $L = 0$  and  $S = 0$ . To summarize, we found three groups of states: 1) a five-fold degenerate state with  $L = 2$ ,  $S = 0$ , 2) a nine-fold degenerate state with  $L = 1$ ,  $S = 1$ , and a nondegenerate state with  $L = 0$ ,  $S = 0$ . Atomic states are given labels

that depend on the value of  $L$  and  $S$ . The spin state is specified by its multiplicity  $(2S + 1)$  and is written as a superscript. This is followed by a capital letter that corresponds to the value of  $L$ . These correspond to the symbols used to label atomic orbitals: S ( $L = 0$ ), P ( $L = 1$ ), D ( $L = 2$ ), F ( $L = 3$ ), G ( $L = 4$ ), .... Using this convention the three states that we found are labeled as follows

State	$L$	$S$	Degeneracy	Symbol
1	2	1	5	$^1D$
2	1	1	9	$^3P$
3	0	0	1	$^1S$

■

### ■ Example 3.5.2 | Electronic states of the oxygen dimer.

Diatomic molecules have lower symmetry than atoms, and so their electronic states can be characterized only in terms of the  $\hat{L}_z$  and  $\hat{S}_z$  operators. In this case we classify electronic states according to the absolute value of the projection of angular momentum on the  $z$  axis ( $|M_L|$ ) and the spin quantum number  $S$ .

To classify the states of the oxygen dimer we will start by considering the molecular orbitals that arise from the interaction of two oxygen atoms. A single oxygen atom has an electronic configuration  $(1s)^2(2s)^2(2p)^4$ . When we bring together two oxygen atoms we can form sets of molecular orbitals obtained by combining atomic orbitals that belong to the same shell (we will ignore the fact that symmetry allows some orbitals of different shells to mix). The  $1s$  orbitals yield a pair of bonding and antibonding orbitals obtained from the plus and minus combinations:

$$\begin{aligned} 1\sigma_g &\propto 1s_A + 1s_B \\ 1\sigma_u &\propto 1s_A - 1s_B \end{aligned} \quad (3.96)$$

These orbitals have been labeled “ $\sigma$ ” because they are linear combinations of atomic orbitals with  $m_l = 0$ . The  $1\sigma_g$  orbital has no nodes, while  $1\sigma_u$  has one node, and so of the two it is highest in energy. Similarly, the  $2s$  orbitals yield the molecular orbitals

$$\begin{aligned} 2\sigma_g &\propto 2s + 2s \\ 2\sigma_u &\propto 2s - 2s \end{aligned} \quad (3.97)$$

The combination of the two  $2p_0$  orbitals also gives sigma orbitals

$$\begin{aligned} 3\sigma_u &\propto 2p_0 - 2p_0 \\ 3\sigma_g &\propto 2p_0 + 2p_0 \end{aligned} \quad (3.98)$$

In this case, the  $3\sigma_u$  is lower in energy since it has one less node than the  $3\sigma_g$  orbital. The combination of  $2p_{\pm 1}$  atomic orbitals gives two sets of  $\pi$  orbitals (named so because  $|m_l| = 1$ ).

$$\begin{aligned} 1\pi_{u_1} &\propto 2p_1 + 2p_1, & 1\pi_{u_{-1}} &\propto 2p_{-1} + 2p_{-1} \\ 1\pi_{g_1} &\propto 2p_1 - 2p_1, & 1\pi_{g_{-1}} &\propto 2p_{-1} - 2p_{-1} \end{aligned} \quad (3.99)$$

The energetic order of these orbitals is

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_u < 1\pi_u < 1\pi_g < 3\sigma_g \quad (3.100)$$

If we fill up these orbitals with the 16 electrons of  $O_2$  we get the configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^2 \quad (3.101)$$

All the molecular orbital shells are filled except for the  $1\pi_g$ , so we can focus on studying the angular momentum/spin states that originate from the  $(1\pi_g)^2$  configuration.

From these three orbitals we can form eight spin orbitals, and construct a total of 6 determinants, which we classify according to the values of  $M_L$ ,  $M_S$ , and their symmetry

Number	Determinant	$M_L$	$M_S$	symmetry
1	$ (1\pi_{g-1}\alpha)(1\pi_{g1}\alpha)\rangle$	0	1	$g$
2	$ (1\pi_{g-1}\alpha)(1\pi_{g-1}\beta)\rangle$	-2	0	$g$
3	$ (1\pi_{g-1}\alpha)(1\pi_{g1}\beta)\rangle$	0	0	$g$
4	$ (1\pi_{g1}\alpha)(1\pi_{g-1}\beta)\rangle$	0	0	$g$
5	$ (1\pi_{g1}\alpha)(1\pi_{g1}\beta)\rangle$	2	0	$g$
6	$ (1\pi_{g-1}\beta)(1\pi_{g1}\beta)\rangle$	0	-1	$g$

(3.102)

If we organize these determinants in a table of  $M_L$  and  $M_S$  values we can start to identify one state with  $|M_L| = 2$  and  $M_S = 0$ .

$M_L \backslash M_S$	-1	0	1		$M_L \backslash M_S$	-1	0	1
-2		•			-2			
-1					-1			
0	•	•	•	→	0	•	•	•
1					1			
2		•			2			

After we eliminate the first state, we are left with four determinants. This case is similar to that of the  $H_2$  molecule, where we found a triplet state and a singlet. In this case the triplet state has  $|M_L| = 0$  and  $S = 1$ , and the remaining last state is a singlet with  $|M_L| = 0$  and  $S = 0$ .

To label the final states, we use the  $|M_L|$  and  $S$  values like in the case of atomic state; however, we use the symbols:  $\Sigma$  ( $|M_L| = 0$ ),  $\Pi$  ( $|M_L| = 1$ ),  $\Delta$  ( $|M_L| = 2$ ),  $\Phi$  ( $|M_L| = 3$ ), etc. Using this convention, the three states that we found are labeled as follows

State	$ M_L $	$S$	Symmetry	Degeneracy	Symbol
1	2	0	$g$	2	$^1\Delta_g$
2	0	1	$g$	3	$^3\Sigma_g^-$
3	0	0	$g$	1	$^1\Sigma_g^+$

Note that in labeling these states, we have also indicated how the sigma states behave when we apply a reflection through a plane containing the internuclear axis. This symmetry is considered only for  $\Sigma$  states since states with higher values of  $M_L$  always have both values. To determine the “+/-” symmetry of the sigma states we first consider how the orbitals behave upon reflection of a plane perpendicular to a plane orthogonal to the x axis. We chose this plane because it only flips the y component of the  $\pi$  orbitals. One can show that the corresponding symmetry operator ( $\hat{\sigma}_v$ ) switches the two  $1\pi_g$  orbitals

$$\hat{\sigma}_v(1\pi_{g1}) \propto \hat{\sigma}_v(2p_1^A - 2p_1^B) = 2p_{-1}^A - 2p_{-1}^B = 1\pi_{g-1} \quad (3.103)$$

and similarly  $\hat{\sigma}_v(1\pi_{g-1}) = 1\pi_{g1}$ . To understand how the  $^3\Sigma_g$  and  $^1\Sigma_g$  states behave under this symmetry let us consider the the  $M_S = 1$  component of the triplet, given by the determinant  $|(1\pi_{g-1}\alpha)(1\pi_{g1}\alpha)\rangle$ . When we apply the  $\hat{\sigma}_v$  operation to this determinant, we distribute this operator to all of its orbitals

$$\hat{\sigma}_v |(1\pi_{g-1}\alpha)(1\pi_{g1}\alpha)\rangle = |\hat{\sigma}_v(1\pi_{g-1}\alpha)\hat{\sigma}_v(1\pi_{g1}\alpha)\rangle = |(1\pi_{g1}\alpha)(1\pi_{g-1}\alpha)\rangle = -|(1\pi_{g-1}\alpha)(1\pi_{g1}\alpha)\rangle \quad (3.104)$$

Here we get a minus sign because after the  $\hat{\sigma}_v$  operator switches the two spin orbitals, we swap the two columns of the Slater determinant to get back to the original ordering. Since the triplet state has changed sign when we applied the  $\hat{\sigma}_v$  operator, the state is “-” and the full symbol for the triplet state is  $^3\Sigma_g^-$ . In the case of the singlet state,

$$\frac{1}{\sqrt{2}} [|(1\pi_{g-1}\alpha)(1\pi_{g1}\beta)\rangle + |(1\pi_{g1}\alpha)(1\pi_{g-1}\beta)\rangle] \quad (3.105)$$

we find that the state does not change when we apply the  $\hat{\sigma}_v$  operator,

$$\begin{aligned}
 & \hat{\sigma}_v \frac{1}{\sqrt{2}} [|(1\pi_{g-1}\alpha)(1\pi_{g1}\beta)\rangle + |(1\pi_{g1}\alpha)(1\pi_{g-1}\beta)\rangle] \\
 &= \frac{1}{\sqrt{2}} [|(1\pi_{g1}\alpha)(1\pi_{g-1}\beta)\rangle + |(1\pi_{g-1}\alpha)(1\pi_{g1}\beta)\rangle] \\
 &= \frac{1}{\sqrt{2}} [|(1\pi_{g-1}\alpha)(1\pi_{g1}\beta)\rangle + |(1\pi_{g1}\alpha)(1\pi_{g-1}\beta)\rangle]
 \end{aligned} \tag{3.106}$$

Therefore, the singlet state is of type “+” and its symbol is  $^1\Sigma_g^+$ . ■

## Study Questions

1. What is spin?
2. What is the commutation relationship for the three components of the spin operator?
3. What are the allowed  $s$  and  $m_s$  values for one electron?
4. What are spin raising and lowering operators?
5. How do spin operator generalize to  $N$  particle systems?
6. What is the multiplicity of a spin state?
7. What is a spin orbital?
8. What does it mean to expand a function in a complete basis set?
9. What is special about wave functions for fermions?
10. What is a Slater determinant?
11. What is the full configuration interaction wave function?
12. How do Hartree products and Slater determinant differ?
13. What is Fermi correlation?
14. How many orbitals are there for  $H_2$  in a minimal basis set?
15. What are the electronic states of  $H_2$  in a minimal basis set?
16. Can you find the electronic states of the  $p^1$  and  $p^3$  configurations?
17. Can you find the electronic states of the  $d^2$  configuration?

## CHAPTER 4

# The full CI equations and Slater rules

### 4.1 The FCI equations and their solution

In this section we will derive the equations that determine the coefficients in the FCI wave function. In this chapter, **we always assume that the spin orbital basis is orthonormal**, that is  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ , and that there are  $2K$  spin orbitals formed from a set of  $K$  spatial orbitals  $\{\phi_j\}$ . For convenience, we will introduce a short-hand notation for a Slater determinant  $\Phi_{ijk\dots}(x_1, x_2, \dots, x_N)$  where we condense all the orbital indices  $ijk\dots$  to a multi-index  $I = \{i_1, i_2, i_3, \dots\}$  with  $i_1 < i_2 < i_3 < \dots$ , so that we can write determinants with only one label as  $\Phi_I$ .<sup>17</sup> Then the FCI wave function can be written as

$$|\Psi_{\text{FCI}}\rangle = \sum_I c_I |\Phi_I\rangle. \quad (4.1)$$

<sup>17</sup>The index  $I$  is also called a *string* of indices  $I = \{i_1, i_2, \dots, i_N\}$  that indicate the occupied spin orbitals.

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

$$\begin{aligned} \Phi_{i_1 i_2 \dots i_N}(x_1, x_2, \dots, x_N) &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(x_1) & \psi_{i_1}(x_2) & \dots & \psi_{i_1}(x_N) \\ \psi_{i_2}(x_1) & \psi_{i_2}(x_2) & \dots & \psi_{i_2}(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_N}(x_1) & \psi_{i_N}(x_2) & \dots & \psi_{i_N}(x_N) \end{vmatrix} \\ &= \frac{1}{\sqrt{N!}} \sum_{\pi}^{N!} (-1)^{p_{\pi}} P_{\pi} [\psi_{i_1}(x_1) \psi_{i_2}(x_2) \dots \psi_{i_N}(x_N)], \end{aligned} \quad (4.2)$$

where  $\pi$  labels a permutation,  $(-1)^{p_{\pi}}$  is the parity of the permutation  $\pi$ , and  $P_{\pi}$  is a permutation operator that acts on the electron coordinates.<sup>18</sup>

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

$$\begin{aligned} \langle \Phi_I | \Phi_I \rangle &= \frac{1}{N!} \sum_{\pi}^{N!} \sum_{\pi'}^{N!} (-1)^{p_{\pi} + p_{\pi'}} \int dx_1 dx_2 \dots dx_N \\ &\quad P_{\pi} [\psi_{i_1}^*(x_1) \dots \psi_{i_N}^*(x_N)] P_{\pi'} [\psi_{i_1}(x_1) \dots \psi_{i_N}(x_N)]. \end{aligned} \quad (4.3)$$

Since the spin-orbital basis is assumed to be orthonormal, 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:

$$\int dx_1 dx_2 \dots dx_N P_{\pi} [|\psi_{i_1}(x_1)|^2 |\psi_{i_2}(x_2)|^2 \dots |\psi_{i_N}(x_N)|^2] = 1. \quad (4.4)$$

<sup>18</sup>For example, for two indices  $\pi = [(1, 2), (2, 1)]$  and  $p_{\pi} = [0, 1]$ .

Summing over all permutations we have

$$\langle \Phi_I | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi} 1 = \frac{N!}{N!} = 1. \quad (4.5)$$

**Problem 4.1.1 – Orthogonality of Slater determinants.** Show that two determinants  $\Phi_I$  and  $\Phi_J$  that differ by one or more spin orbital have zero overlap

$$\langle \Phi_I | \Phi_J \rangle = 0. \quad (4.6)$$

To do so, plug in the definition of Slater determinants in  $\langle \Phi_I | \Phi_J \rangle$ , break down this integral as a product of one-electron integrals, and then show that each term contains one integral that is always zero.

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

$$\langle \Phi_I | \Phi_J \rangle = \delta_{IJ}. \quad (4.7)$$

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

$$\hat{H} \sum_I c_I |\Phi_I\rangle = E \sum_I c_I |\Phi_I\rangle. \quad (4.8)$$

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

$$\sum_I \langle \Phi_J | \hat{H} | \Phi_I \rangle c_I = E \sum_I \underbrace{\langle \Phi_J | \Phi_I \rangle}_{\delta_{IJ}} c_I, \quad (4.9)$$

which may be simplified to

$$\sum_I H_{IJ} c_I = E c_J, \quad (4.10)$$

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

$$\mathbf{H}\mathbf{C} = \mathbf{C}E, \quad (4.11)$$

where  $\mathbf{H}$  is a matrix of dimension  $N_{\text{FCI}} \times N_{\text{FCI}}$ , where  $N_{\text{FCI}}$  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**.

## 4.2 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  $\Phi_I$  and  $\Phi_J$  are two determinants built out of the same orthonormal spin orbital basis.

<sup>19</sup> For convenience we will write the electronic Hamiltonians as

$$\hat{H} = V_{\text{NN}} + \hat{H}_1 + \hat{H}_2, \quad (4.12)$$

<sup>19</sup>More general rules exist for nonorthonormal spin orbitals, and when  $\Phi_I$  and  $\Phi_J$  use different set of spin orbitals.



where

$$V_{\text{NN}} = \sum_A^M \sum_{B>A}^M \frac{Z_A Z_B}{r_{AB}} \quad (4.13)$$

$$\hat{H}_1 = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{r_{iA}} = \sum_i \hat{h}(i) \quad (4.14)$$

$$\hat{H}_2 = \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} = \sum_i^N \sum_{j>i}^N \hat{v}(i, j). \quad (4.15)$$

#### 4.2.1 Matrix elements of the scalar term

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

$$\langle \Phi_I | V_{\text{NN}} | \Phi_J \rangle = V_{\text{NN}} \langle \Phi_I | \Phi_J \rangle = V_{\text{NN}} \delta_{IJ}. \quad (4.16)$$

#### 4.2.2 Matrix elements of the one-electron Hamiltonian

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

$$\begin{aligned} \langle \Phi_I | \hat{H}_1 | \Phi_I \rangle &= \frac{1}{N!} \sum_{\pi \pi'}^{N!} \sum_j (-1)^{p_\pi + p_{\pi'}} \int dx_1 dx_2 \cdots dx_N \\ &\quad P_\pi [\psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N)] \hat{h}(x_j) P_{\pi'} [\psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N)]. \end{aligned} \quad (4.17)$$

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, consider the case of a permutation  $\pi'$  that swaps coordinates  $x_1 \leftrightarrow x_2$  while  $\pi$  is the identity. The term with the operator  $\hat{h}(x_1)$

$$\begin{aligned} &\int dx_1 dx_2 \cdots \psi_{i_1}^*(x_2) \psi_{i_2}^*(x_1) \cdots \hat{h}(x_1) \psi_{i_1}(x_1) \psi_{i_2}(x_2) \cdots \\ &= \int dx_1 \psi_{i_2}^*(x_1) \hat{h}(x_1) \psi_{i_1}(x_1) \times \underbrace{\int dx_2 \psi_{i_1}^*(x_2) \psi_{i_2}(x_2) \times \cdots}_{=0} = 0. \end{aligned} \quad (4.18)$$

We also get zero if the permutation mixes two variables not involved with the operator  $\hat{h}$  as in the case of the permutation  $\pi' \equiv (x_2 \leftrightarrow x_3)$

$$\begin{aligned} &\int dx_1 dx_2 \cdots \psi_{i_1}^*(x_1) \psi_{i_3}^*(x_2) \cdots \hat{h}(x_1) \psi_{i_1}(x_1) \psi_{i_2}(x_2) \cdots \\ &= \int dx_1 \psi_{i_1}^*(x_1) \hat{h}(x_1) \psi_{i_1}(x_1) \times \underbrace{\int dx_2 \psi_{i_3}^*(x_2) \psi_{i_2}(x_2) \times \cdots}_{=0} = 0. \end{aligned} \quad (4.19)$$

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

$$\begin{aligned} \langle \Phi_I | \hat{H}_1 | \Phi_I \rangle &= \frac{1}{N!} \sum_{\pi}^{N!} \int dx_1 dx_2 \cdots dx_N \\ &\quad P_\pi \left\{ \psi_{i_1}^*(x_1) \cdots \psi_{i_N}^*(x_N) \left[ \sum_j \hat{h}(x_j) \right] \psi_{i_1}(x_1) \cdots \psi_{i_N}(x_N) \right\}. \end{aligned} \quad (4.20)$$

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

$$\sum_j^N \int dx \psi_{i_j}^*(x) \hat{h}(x) \psi_{i_j}(x) = \sum_j^N \langle \psi_{i_j} | \hat{h} | \psi_{i_j} \rangle = \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \psi_i \rangle, \quad (4.21)$$

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

$$\langle \Phi_I | \hat{H}_1 | \Phi_I \rangle = \frac{1}{N!} \sum_{\pi}^N \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \psi_i \rangle = \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle. \quad (4.22)$$

In the last term we introduced the abbreviated notation  $\langle i | \hat{h} | i \rangle \equiv \langle \psi_i | \hat{h} | \psi_i \rangle$ .

### 4.2.3 Matrix elements of the two-electron Hamiltonian

The derivation of the two-electron contribution is more involved, and it gives the following result:

$$\langle \Phi_I | \hat{H}_2 | \Phi_I \rangle = \sum_i \sum_{j < i} [\langle ij | ij \rangle - \langle ij | ji \rangle], \quad (4.23)$$

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

$$\langle ij | kl \rangle = \int dx_1 dx_2 \psi_i^*(x_1) \psi_j^*(x_2) \hat{v}(x_1, x_2) \psi_k(x_1) \psi_l(x_2). \quad (4.24)$$

If we introduce the antisymmetrized two-electron integral:

$$\langle ij || kl \rangle = \langle ij | kl \rangle - \langle ij | lk \rangle, \quad (4.25)$$

then it is possible to rewrite as an unconstrained double sum

$$\langle \Phi_I | \hat{H}_2 | \Phi_I \rangle = \sum_i \sum_{j < i} \langle ij || ij \rangle = \frac{1}{2} \sum_{ij} \langle ij || ij \rangle, \quad (4.26)$$

<sup>20</sup>This is simple to see:  $\langle ii || ii \rangle = \langle ii | ii \rangle - \langle ii | ii \rangle = 0$ . since the term that corresponds to  $i = j$  is null<sup>20</sup> and  $\langle ji || ji \rangle = \langle ij || ij \rangle$ .

### 4.2.4 Slater rule for a diagonal matrix element

In summary we can express the diagonal element of the Hamiltonian matrix as

$$\begin{aligned} \langle \Phi_I | \hat{H} | \Phi_I \rangle &= V_{\text{NN}} + \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle, \\ &= V_{\text{NN}} + \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \sum_{i < j}^{\text{occ}} \langle ij || ij \rangle, \end{aligned} \quad (4.27)$$

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

#### ■ Example 4.2.1 | Energy of a single electron.

Consider the determinant for a single electron:

$$|\psi_1\rangle. \quad (4.28)$$

The energy is then given by:

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = \langle 1 | \hat{h} | 1 \rangle + \frac{1}{2} \underbrace{\langle 11 || 11 \rangle}_{=0} = \langle 1 | \hat{h} | 1 \rangle. \quad (4.29)$$

■ **Example 4.2.2 | Energy of a pair of electrons in a closed-shell configuration.**

Let us consider the determinant:

$$|\Phi_I\rangle = |\psi_1\psi_{\bar{1}}\rangle \quad (4.30)$$

The energy is given by:

$$\begin{aligned} \langle \Phi_I | \hat{H} | \Phi_I \rangle &= \langle \psi_1 | \hat{h} | \psi_1 \rangle + \langle \psi_{\bar{1}} | \hat{h} | \psi_{\bar{1}} \rangle \\ &\quad + \frac{1}{2} [\langle \psi_1\psi_1 || \psi_1\psi_1 \rangle + \langle \psi_1\psi_{\bar{1}} || \psi_1\psi_{\bar{1}} \rangle + \langle \psi_{\bar{1}}\psi_1 || \psi_{\bar{1}}\psi_1 \rangle + \langle \psi_{\bar{1}}\psi_{\bar{1}} || \psi_{\bar{1}}\psi_{\bar{1}} \rangle] \\ &= 2 \langle \phi_1 | \hat{h} | \phi_1 \rangle + \langle \phi_1\phi_1 | \phi_1\phi_1 \rangle, \end{aligned} \quad (4.31)$$

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** ( $J_{ij}$ )

$$J_{ij} = \langle ij | ij \rangle = \int dx_1 dx_2 \frac{|\psi_i(x_1)|^2 |\psi_j(x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int dx_1 dx_2 \frac{|\phi_i(\mathbf{r}_1)|^2 |\phi_j(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4.32)$$

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

$$K_{ij} = \langle ij | ji \rangle = \int dx_1 dx_2 \frac{\psi_i^*(x_1) \psi_j^*(x_1) \psi_j(x_2) \psi_i(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (4.33)$$

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

$$\langle \Phi_I | \hat{H} | \Phi_I \rangle = V_{NN} + \sum_i^{\text{occ}(\Phi_I)} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}(\Phi_I)} (J_{ij} - K_{ij}). \quad (4.34)$$

### 4.3 Slater rules for off-diagonal terms

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

#### 4.3.1 Single replacement

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

$$|\Phi_I\rangle = |\psi_1 \cdots \psi_i \cdots \psi_N\rangle \quad (4.35)$$

$$|\Phi_J\rangle = |\psi_1 \cdots \psi_a \cdots \psi_N\rangle, \quad (4.36)$$

where the spin orbital  $\psi_i$  is replaced by  $\psi_a$ . 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

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle = \langle i | \hat{h} | a \rangle + \sum_k^{\text{occ}(\Phi_I)} \langle ik || ak \rangle. \quad (4.37)$$

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

### 4.3.2 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

$$|\Phi_I\rangle = |\psi_1 \cdots \psi_i \psi_j \cdots \psi_N\rangle \quad (4.38)$$

$$|\Phi_J\rangle = |\psi_1 \cdots \psi_a \psi_b \cdots \psi_N\rangle. \quad (4.39)$$

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

$$\langle \Phi_I | \hat{H} | \Phi_J \rangle = \langle ij || ab \rangle. \quad (4.40)$$

Equations (4.27), (4.37), and (4.40) 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.

## 4.4 Structure of the FCI wave function and Hamiltonian

In many cases, the FCI wave function is well approximated by a single Slater determinant, say  $\Phi_0$ , where

$$|\Phi_0\rangle = |\psi_1 \psi_2 \cdots \psi_N\rangle. \quad (4.41)$$

This is called the **reference** determinant and it plays an important role because we can define all other Slater determinants in the FCI expansion in terms of **excitations** of electrons starting from  $\Phi_0$ . These excitations promote electrons from the occupied orbitals in  $\Phi_0$

$$\text{occupied} = \{\psi_1, \psi_2, \cdots, \psi_N\}, \quad (4.42)$$

to those that are unoccupied

$$\text{unoccupied} = \{\psi_{N+1}, \psi_{N+2}, \cdots, \psi_{2K}\}. \quad (4.43)$$

Determinants that differ from  $\Phi_0$  by one spin orbital, for example, by replacing  $\psi_N \rightarrow \psi_{N+1}$

$$|\psi_1 \psi_2 \cdots \psi_{N-1} \psi_{N+1}\rangle, \quad (4.44)$$

are called **singly excited**. We can similarly define determinants with two, three, etc. spin orbital replaced as doubly, triply, etc. excited determinants. In physics, especially in the field of condensed matter, occupied orbitals are also called **holes** while the unoccupied orbitals are called **particles**. This language is consistent with the view that an excited determinant can be seen as combination of creating holes (by removing electrons from occupied orbitals) and particles (by adding electrons to the unoccupied orbitals). Therefore, excited determinants are also referred to as **particle-hole** excitations.<sup>21</sup>

This classification of determinants allows us to rearrange the FCI wave function as

$$|\Psi_{\text{FCI}}\rangle = c_0 |\Phi_0\rangle + \sum_S c_S |\Phi_S\rangle + \sum_D c_D |\Phi_D\rangle + \sum_T c_T |\Phi_T\rangle + \cdots, \quad (4.45)$$

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  $c_0 = 1$

$$|\Psi_{\text{FCI}}\rangle = |\Phi_0\rangle + \sum_S c_S |\Phi_S\rangle + \sum_D c_D |\Phi_D\rangle + \sum_T c_T |\Phi_T\rangle + \cdots \quad (4.46)$$

<sup>21</sup>In band theory another convention is used. Occupied orbitals are referred to as **valence bands** while unoccupied ones as **conduction bands**.

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

$$\langle \Psi_0 | \Phi_{\text{FCI}} \rangle = 1, \quad (4.47)$$

and the wave function is not normalized

$$\langle \Psi_{\text{FCI}} | \Phi_{\text{FCI}} \rangle \neq 1. \quad (4.48)$$

Note also that in intermediate normalization we have that

$$\langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | E | \Psi_{\text{FCI}} \rangle = E \langle \Phi_0 | \Psi_{\text{FCI}} \rangle = E. \quad (4.49)$$

Writing this expression as  $E = \langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle$  and plugging in the definition of  $\Psi_{\text{FCI}}$  in intermediate normalization [Eq. (4.46)] we can express the energy in terms of only FCI coefficients for single and double excitations

$$E = \langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_S c_S \langle \Phi_0 | \hat{H} | \Phi_S \rangle + \sum_D c_D \langle \Phi_0 | \hat{H} | \Phi_D \rangle. \quad (4.50)$$

Terms like  $\langle \Phi_0 | \hat{H} | \Phi_T \rangle$  that arise in this expansion are zero due to Slater rules ( $\Phi_T$  and  $\Phi_0$  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 ( $\Phi_S$ ) and quadruply ( $\Phi_Q$ ) excited determinants

$$H_{SQ} = \langle \Phi_S | \hat{H} | \Phi_Q \rangle = 0, \quad (4.51)$$

because  $\Phi_S$  and  $\Phi_Q$  differ by more than two spin orbitals. The general structure of the Hamiltonian matrix is indicated below

$$\mathbf{H} = \begin{array}{c|ccccc} & 0 & S & D & T & Q \\ \hline 0 & & & & & \\ S & & & & & \\ D & & & & & \\ T & & & & & \\ Q & & & & & \end{array} \quad (4.52)$$

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)

$$N(2K - N) + \frac{1}{4}N^2(2K - N)^2. \quad (4.53)$$

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

$$\text{fraction of nonzero elements} = \frac{N(2K - N) + \frac{1}{4}N^2(2K - N)^2}{\binom{2K}{N}}. \quad (4.54)$$

This quantity becomes smaller as  $N$  and  $K$  increase showing that  $\mathbf{H}$  is mostly empty.

## 4.5 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

$$\mathbf{c} = \tilde{\mathbf{c}} + \delta\mathbf{c}. \quad (4.55)$$

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

$$\tilde{E} = \frac{\tilde{\mathbf{c}}^T \mathbf{H} \tilde{\mathbf{c}}}{\tilde{\mathbf{c}}^T \tilde{\mathbf{c}}} \quad (4.56)$$

and write  $E = \tilde{E} + \delta E$ , where  $\delta E$  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

$$\mathbf{H}(\tilde{\mathbf{c}} + \delta\mathbf{c}) = E(\tilde{\mathbf{c}} + \delta\mathbf{c}), \quad (4.57)$$

from which we get

$$(\mathbf{H} - \tilde{E} - \delta E)\delta\mathbf{c} = -(\mathbf{H} - \tilde{E} - \delta E)\tilde{\mathbf{c}} = -(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}} + \delta E\tilde{\mathbf{c}}. \quad (4.58)$$

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

$$\delta\mathbf{c} = -(\mathbf{H} - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \quad (4.59)$$

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

$$\delta\mathbf{c} = -(\mathbf{H}_d - \tilde{E})^{-1}(\mathbf{H} - \tilde{E})\tilde{\mathbf{c}}. \quad (4.60)$$

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.

### ■ Advanced topic | 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

$$E_{\text{RR}}[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (4.61)$$

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  $\Psi$ . 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  $\Psi$  will give the lowest eigenvalue and eigenstate ( $\Psi_0$ ) of the Hamiltonian

$$\min_{\Psi} E_{\text{RR}}[\Psi] = E_0. \quad (4.62)$$

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

$$\frac{\partial E_{\text{RR}}[\Psi]}{\partial c_I} = 0. \quad (4.63)$$

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.

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

$$\begin{aligned}\mathcal{L}[\Psi] &= \underbrace{\langle \Psi | \hat{H} | \Psi \rangle}_{\text{energy}} - \underbrace{\lambda(\langle \Psi | \Psi \rangle - 1)}_{\text{normalization constraint}} \\ &= \sum_{IJ} c_I^* H_{IJ} c_J - \lambda \left( \sum_I |c_I|^2 - 1 \right).\end{aligned}\quad (4.64)$$

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

$$\frac{\partial \mathcal{L}[\Psi]}{\partial c_I^*} = \sum_J H_{IJ} c_J - \lambda c_I, \quad (4.65)$$

from which we conclude that the FCI vector  $\mathbf{c}$  must satisfy the eigenvalue equation

$$\sum_J H_{IJ} c_J = \lambda c_I. \quad (4.66)$$

■

#### ■ Example 4.5.1 | 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  $(x, y, \lambda)$ :

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda g(x, y) = x^2 + 2y^2 - \lambda(x + y - 2). \quad (4.67)$$

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

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial x} = 2x - \lambda = 0 \quad (4.68)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial y} = 4y - \lambda = 0 \quad (4.69)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial \lambda} = g(x, y) = 0. \quad (4.70)$$

From Eqs. (5.6) and (5.7) we obtain:

$$x = 2y, \quad (4.71)$$

which combined with Eq. (5.8) gives:

$$g(2y, y) = 2y + y - 2 = 0 \quad \Rightarrow \quad y = \frac{2}{3}, \quad (4.72)$$

and  $x = \frac{4}{3}$ .

■

## Study Questions

1. What is the value of  $\langle \Phi_I | \Phi_J \rangle$  for two arbitrary Slater determinants  $\Phi_I$  and  $\Phi_J$ ?
2. What is the equation that determines the FCI energy and eigenvector?
3. What are Slater rules?
4. What is a one-electron integral?
5. What is a two-electron integral?
6. What is the expectation value of the Hamiltonian for a Slater determinant?
7. What are Slater rules for off-diagonal terms?
8. What is a reference determinant?
9. What is an excited determinant?
10. How do we write the FCI wave function using singly, doubly, etc. excited determinants?

11. What is the structure of the Hamiltonian matrix?
12. What are direct diagonalization methods?



# Hartree–Fock theory

## 5.1 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  $\{\psi_1, \psi_2, \dots, \psi_N\}$ :

$$|\Phi_0\rangle = |\psi_1, \psi_2, \dots, \psi_N\rangle. \quad (5.1)$$

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

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle, \quad (5.2)$$

then the Hartree–Fock energy is given by:

$$E_0 = \min_{\Phi} E[\Phi] \quad \text{enforcing} \quad \langle \Phi | \Phi \rangle = 1, \quad (5.3)$$

where we assume that the determinant  $\Phi$  is normalized.

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

$$E_0[\{\psi_i\}] = \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij | ij \rangle. \quad (5.4)$$

### 5.1.1 Minimization of the Hartree–Fock energy functional

As we have seen in the previous section, if the spin orbitals are orthonormal then  $\Phi$  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 5.1.1 | 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  $(x, y, \lambda)$ :

$$\mathcal{L}(x, y, \lambda) = f(x, y) - \lambda g(x, y) = x^2 + 2y^2 - \lambda(x + y - 2). \quad (5.5)$$

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

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial x} = 2x - \lambda = 0 \quad (5.6)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial y} = 4y - \lambda = 0 \quad (5.7)$$

$$\frac{\partial \mathcal{L}(x, y, \lambda)}{\partial \lambda} = g(x, y) = 0. \quad (5.8)$$

From Eqs. (5.6) and (5.7) we obtain:

$$x = 2y, \quad (5.9)$$

which combined with Eq. (5.8) gives:

$$g(2y, y) = 2y + y - 2 = 0 \Rightarrow y = \frac{2}{3}, \quad (5.10)$$

and  $x = \frac{4}{3}$ . ■

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

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \forall i, j \in \text{occupied}. \quad (5.11)$$

To enforce this constraint we consider the following Lagrangian:

$$\mathcal{L}[\{\psi_i\}] = E_0[\{\psi_i\}] - \sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_i | \psi_j \rangle - \delta_{ij}), \quad (5.12)$$

<sup>22</sup>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.

<sup>23</sup>That is  $\lambda_{ji} = \lambda_{ji}^*$ .

<sup>24</sup>A complex Lagrangian cannot be minimized because there is no such a thing as the minimum of a complex function.

where  $\lambda_{ji}$  is a matrix of Lagrange multipliers.<sup>22</sup> Note that  $\lambda_{ji}$  must be a Hermitian matrix<sup>23</sup>, which is a consequence of requiring the Lagrangian to be a real function.<sup>24</sup> 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 means that for any arbitrary variation of the spin orbitals  $\{\delta\psi_i\}$  the Lagrangian must satisfy:

$$\mathcal{L}[\{\psi_i + \delta\psi_i\}] = \mathcal{L}[\{\psi_i\}], \quad (5.13)$$

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

$$\begin{aligned} E_0[\{\psi_i + \delta\psi_i\}] &= \sum_i^{\text{occ}} \langle \psi_i + \delta\psi_i | \hat{h} | \psi_i + \delta\psi_i \rangle \\ &\quad + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle (\psi_i + \delta\psi_i)(\psi_j + \delta\psi_j) | | (\psi_i + \delta\psi_i)(\psi_j + \delta\psi_j) \rangle \\ &= E_0[\{\psi_i\}] + \sum_i^{\text{occ}} \langle \psi_i | \hat{h} | \delta\psi_i \rangle + \sum_i^{\text{occ}} \langle \delta\psi_i | \hat{h} | \psi_i \rangle \\ &\quad + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \delta\psi_i \psi_j | | \psi_i \psi_j \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \delta\psi_j | | \psi_i \psi_j \rangle \\ &\quad + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \psi_j | | \delta\psi_i \psi_j \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle \psi_i \psi_j | | \psi_i \delta\psi_j \rangle \\ &\quad + (\text{higher order}) \\ &= E_0[\{\psi_i\}] + \sum_i^{\text{occ}} \left[ \langle \delta\psi_i | \hat{h} | \psi_i \rangle + \sum_j^{\text{occ}} \langle \delta\psi_i \psi_j | | \psi_i \psi_j \rangle \right] \\ &\quad + \text{h.c.} + (\text{higher order}), \end{aligned} \quad (5.14)$$

where “h.c.” stands for Hermitian conjugate.

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

$$\begin{aligned} -\sum_{ij}^{\text{occ}} \lambda_{ji}(\langle \psi_i + \delta\psi_i | \psi_j + \delta\psi_j \rangle - \delta_{ij}) &= -\sum_{ij}^{\text{occ}} \lambda_{ji}(\langle \psi_i | \psi_j \rangle - \delta_{ij}) \\ &\quad -\sum_{ij}^{\text{occ}} \lambda_{ji} \langle \delta\psi_i | \psi_j \rangle - \sum_{ij}^{\text{occ}} \lambda_{ji} \langle \psi_i | \delta\psi_j \rangle \\ &\quad + (\text{higher order}). \end{aligned} \quad (5.15)$$

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

$$\delta\mathcal{L} = \mathcal{L}[\{\psi_i + \delta\psi_i\}] - \mathcal{L}[\{\psi_i\}] \quad (5.16)$$

$$\delta\mathcal{L} = \sum_i^{\text{occ}} \left[ \langle \delta\psi_i | \hat{h} | \psi_i \rangle + \sum_j^{\text{occ}} \langle \delta\psi_i \psi_j | | \psi_i \psi_j \rangle - \sum_{ij}^{\text{occ}} \lambda_{ji} \langle \delta\psi_i | \psi_j \rangle \right] + \text{h.c.} \quad (5.17)$$

We now rewrite this expression in terms of integrals:

$$\begin{aligned} \delta\mathcal{L} &= \sum_i^{\text{occ}} \int dx_1 \delta\psi_i^*(x_1) \times \\ &\quad \times \left[ \hat{h}\psi_i(x_1) + \sum_j^{\text{occ}} \int dx_2 \frac{|\psi_j(x_2)|^2 \psi_i(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{\text{occ}} \int dx_2 \frac{\psi_j^*(x_2) \psi_i(x_2) \psi_j(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{\text{occ}} \lambda_{ji} \psi_j(x_1) \right]. \end{aligned} \quad (5.18)$$

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 an eigenvalue problem:

$$\hat{h}\psi_i(x_1) + \sum_j^{\text{occ}} \int dx_2 \frac{|\psi_j(x_2)|^2 \psi_i(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \sum_j^{\text{occ}} \int dx_2 \frac{\psi_j^*(x_2) \psi_i(x_2) \psi_j(x_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_j^{\text{occ}} \lambda_{ji} \psi_j(x_1). \quad (5.19)$$

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

$$\hat{J}_j(x_1)\psi_i(x_1) = \int dx_2 \frac{|\psi_j(x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_i(x_1) \quad (5.20)$$

$$\hat{K}_j(x_1)\psi_i(x_1) = \int dx_2 \frac{\psi_j^*(x_2) \psi_i(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_j(x_1), \quad (5.21)$$

we may rewrite the stationary conditions as:

$$\left[ \hat{h}(x_1) + \sum_j^{\text{occ}} \hat{J}_j(x_1) - \hat{K}_j(x_1) \right] \psi_i(x_1) = \sum_j^{\text{occ}} \lambda_{ji} \psi_j(x_1), \quad (5.22)$$

or

$$\hat{f}(x_1)\psi_i(x_1) = \sum_j^{\text{occ}} \lambda_{ji} \psi_j(x_1). \quad (5.23)$$

Eq. (5.23) is called the **Hartree-Fock equation in noncanonical form** and the operator  $\hat{f}(x_1) = \hat{h}(x_1) + \sum_j^{\text{occ}} \hat{J}_j(x_1) - \hat{K}_j(x_1)$  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 equation 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.

### 5.1.2 Hartree–Fock equations in the canonical form

Consider a unitary transformation of the occupied orbitals:

$$|\psi'_i\rangle = \sum_j^{\text{occ}} |\psi_j\rangle U_{ji}, \quad (5.24)$$

<sup>25</sup> $\mathbf{U}^{-1} = \mathbf{U}^\dagger$

where the matrix  $\mathbf{U}$  is unitary.<sup>25</sup> It is possible to prove that a determinant built from the spin orbitals  $\psi'_i$  is related to the determinant in the original basis by a complex phase factor:

$$|\Phi'\rangle = |\psi'_1 \psi'_2 \cdots \psi'_N\rangle = e^{i\theta} |\Phi\rangle. \quad (5.25)$$

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

$$\langle \Phi' | \hat{A} | \Phi' \rangle = \langle \Phi | \hat{A} | \Phi \rangle e^{-i\theta} e^{i\theta} = \langle \Phi | \hat{A} | \Phi \rangle. \quad (5.26)$$

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

$$\sum_j \hat{J}'_j(x_1) = \sum_j \hat{J}_j(x_1), \quad (5.27)$$

$$\sum_j \hat{K}'_j(x_1) = \sum_j \hat{K}_j(x_1) \quad (5.28)$$

and consequently the Fock operator is invariant with respect to this orbital rotation, that is,  $\hat{f}' = \hat{f}$ . From Eq. (5.23) it is easy to show that:

$$\langle \psi_j | \hat{f} | \psi_i \rangle = \lambda_{ji}. \quad (5.29)$$

In the unitarily-transformed basis this condition reads:

$$\langle \psi'_j | \hat{f}' | \psi'_i \rangle = \lambda'_{ji} = \sum_{kl} U_{lj}^* \langle \psi_l | \hat{f}' | \psi_k \rangle U_{ki} = \sum_{kl} U_{lj}^* \lambda_{lk} U_{ki}, \quad (5.30)$$

which may be written in the equivalent form:

$$\boldsymbol{\lambda}' = \mathbf{U}^\dagger \boldsymbol{\lambda} \mathbf{U}. \quad (5.31)$$

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:

$$\hat{f}'(x_1) \psi'_i(x_1) = \lambda'_{ii} \psi'_i(x_1). \quad (5.32)$$

Eq. (5.32) 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  $\lambda'_{ii}$  with  $\epsilon_i$ :

$$\hat{f}(x_1) \psi_i(x_1) = \epsilon_i \psi_i(x_1). \quad (5.33)$$

The quantity  $\epsilon_i$  is called the canonical orbital energy.

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

From the canonical Hartree–Fock equation [Eq. (5.33)] we can derive an expression for the energy of an orbital:

$$\epsilon_i = \langle \psi_i | \hat{f} | \psi_i \rangle = \langle i | \hat{h} | i \rangle + \sum_k^{\text{occ}} \langle ik || ik \rangle. \quad (5.34)$$

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

$$\begin{aligned}
 E_0[\{\psi_i\}] &= \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle \\
 &= \sum_i^{\text{occ}} \langle i | \hat{h} | i \rangle + \sum_{ij}^{\text{occ}} \langle ij || ij \rangle - \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle \\
 &= \sum_i^{\text{occ}} \epsilon_i - \frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle.
 \end{aligned} \tag{5.35}$$

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:

$$|\Phi_0^{N-1}\rangle = |\psi_1, \psi_2, \dots, \psi_{N-1}\rangle. \tag{5.36}$$

The energy of  $\Phi_0^{N-1}$  is:

$$E_0^{N-1}[\{\psi_i\}] = \sum_i^{N-1} \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{ij}^{N-1} \langle ij || ij \rangle. \tag{5.37}$$

and the difference  $E_0 - E_0^{N-1}$  is given by:<sup>26</sup>

$$\begin{aligned}
 E_0 - E_0^{N-1} &= \langle N | \hat{h} | N \rangle + \frac{1}{2} \sum_i^{N-1} \langle iN || iN \rangle + \frac{1}{2} \sum_j^{N-1} \langle Nj || Nj \rangle \\
 &\quad + \langle NN || NN \rangle \\
 &= \langle N | \hat{h} | N \rangle + \sum_i^{N-1} \langle iN || iN \rangle = \epsilon_N.
 \end{aligned} \tag{5.38}$$

<sup>26</sup>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 ( $\psi_i$ ):

$$\text{Ionization potential} = \text{IP} = E_0^{N-1} - E_0^N = -\epsilon_i. \tag{5.39}$$

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

$$\text{Electron affinity} = \text{EA} = E_0^N - E_0^{N+1} = -\epsilon_a. \tag{5.40}$$

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  $\psi_i \rightarrow \psi_a$  to give the determinant  $\Phi_i^a$ . The energy of this excited determinant is:

$$\begin{aligned}
 \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle &= \sum_j^N \langle j | \hat{h} | j \rangle + \langle a | \hat{h} | a \rangle - \langle i | \hat{h} | i \rangle \\
 &\quad + \frac{1}{2} \sum_{ij}^N \langle ij || ij \rangle + \sum_j^N \langle aj || aj \rangle - \sum_j^N \langle ij || ij \rangle \\
 &\quad - \langle ia || ia \rangle,
 \end{aligned} \tag{5.41}$$

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

$$\langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle = E_0 + \epsilon_a - \epsilon_i - \underbrace{\langle ia||ia \rangle}_{\text{hole/electron interaction}}. \quad (5.42)$$

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  $\psi_i$  and the electron in  $\psi_a$ .

### 5.1.4 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:

$$\psi_p^{\text{GHF}}(\mathbf{r}, \omega) = \phi_{p,\alpha}(\mathbf{r})\alpha(\omega) + \phi_{p,\beta}(\mathbf{r})\beta(\omega). \quad (5.43)$$

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:

$$\begin{aligned} \psi_{2p-1}^{\text{UHF}}(\mathbf{r}, \omega) &= \phi_{2p-1}(\mathbf{r})\alpha(\omega), \\ \psi_{2p}^{\text{UHF}}(\mathbf{r}, \omega) &= \phi_{2p}(\mathbf{r})\beta(\omega), \end{aligned} \quad (5.44)$$

with  $p = 1, \dots, K$ , 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:

$$\psi_p^{\text{UHF}}(\mathbf{r}, \omega) = \phi_p(\mathbf{r}) \begin{cases} \alpha(\omega) & \text{if } p < K \\ \beta(\omega) & \text{if } p \geq K \end{cases}, \quad (5.45)$$

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

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

$$\begin{aligned} \psi_{2p-1}^{\text{RHF}}(\mathbf{r}, \omega) &= \phi_p(\mathbf{r})\alpha(\omega), \\ \psi_{2p}^{\text{RHF}}(\mathbf{r}, \omega) &= \phi_p(\mathbf{r})\beta(\omega), \end{aligned} \quad (5.46)$$

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

$$\psi_p^{\text{RHF}}(\mathbf{r}, \omega) = \begin{cases} \phi_p(\mathbf{r})\alpha(\omega) & \text{if } p < K \\ \phi_{p-K}(\mathbf{r})\beta(\omega) & \text{if } p \geq K \end{cases}, \quad (5.47)$$

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

### 5.1.5 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:

$$|\Phi_0^{\text{RHF}}\rangle = |\phi_1\alpha, \dots, \phi_{N/2}\alpha, \phi_1\beta, \dots, \phi_{N/2}\beta\rangle. \quad (5.48)$$

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:

$$\sum_i^N \psi_i = \sum_i^{N/2} \phi_i \alpha + \sum_i^{N/2} \phi_i \beta. \quad (5.49)$$

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

$$\begin{aligned} E_0 = & \sum_{i=1}^{N/2} \langle i | \hat{h} | i \rangle + \sum_{i=1}^{N/2} \langle \bar{i} | \hat{h} | \bar{i} \rangle \\ & \frac{1}{2} \sum_{ij}^{N/2} \langle ij | ij \rangle + \frac{1}{2} \sum_{i\bar{j}}^{N/2} \langle i\bar{j} | i\bar{j} \rangle + \frac{1}{2} \sum_{\bar{i}j}^{N/2} \langle \bar{i}j | \bar{i}j \rangle + \frac{1}{2} \sum_{\bar{i}\bar{j}}^{N/2} \langle \bar{i}\bar{j} | \bar{i}\bar{j} \rangle. \end{aligned} \quad (5.50)$$

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

$$\langle i | \hat{h} | i \rangle = \langle \bar{i} | \hat{h} | \bar{i} \rangle, \quad (5.51)$$

while for the two-electron integrals:

$$\langle ij | ij \rangle = \langle \bar{i}\bar{j} | \bar{i}\bar{j} \rangle = \langle ij | ij \rangle - \langle ij | ji \rangle, \quad (5.52)$$

and

$$\langle i\bar{j} | i\bar{j} \rangle = \langle \bar{i}j | \bar{i}j \rangle = \langle ij | ij \rangle, \quad (5.53)$$

to write the energy expression as:

$$E_0 = 2 \sum_{i=1}^{N/2} \langle i | \hat{h} | i \rangle + \sum_{ij}^{N/2} [2 \langle ij | ij \rangle - \langle ij | ji \rangle]. \quad (5.54)$$

Similarly, we can express the Fock matrix as:

$$\langle i | \hat{f} | j \rangle = \langle i | \hat{h} | j \rangle + \sum_k^{N/2} [2 \langle ik | jk \rangle - \langle ik | kj \rangle]. \quad (5.55)$$

### 5.1.6 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:

$$\phi_i(\mathbf{r}) = \sum_{\mu} \chi_{\mu}(\mathbf{r}) C_{\mu i}. \quad (5.56)$$

Let us consider the Hartree-Fock equation:

$$\hat{f} |\psi_i\rangle = |\psi_i\rangle \epsilon_i, \quad (5.57)$$

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

$$\sum_{\mu} \langle \chi_\nu | \hat{f} | \chi_\mu \rangle C_{\mu i} = \sum_{\mu} \langle \chi_\nu | \chi_\mu \rangle C_{\mu i} \epsilon_i. \quad (5.58)$$

In general, the computational basis may not be orthonormal. Therefore, we write  $\langle \chi_\nu | \chi_\mu \rangle = S_{\nu\mu}$ , 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:

$$\sum_{\mu} F_{\nu\mu} C_{\mu i} = \sum_{\mu} S_{\nu\mu} C_{\mu i} \epsilon_i, \quad (5.59)$$

or in matrix notation

$$\mathbf{F}\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \quad (5.60)$$

where  $\epsilon$  is a diagonal matrix. This is Roothan's form of the Hartree-Fock equations. Note that due to the presence of  $\mathbf{S}$ , this is a generalized eigenvalue problem.

The matrix  $\mathbf{F}$  is the Fock operator expressed in the computational basis and is given by:

$$\begin{aligned} (\mathbf{F})_{\mu\nu} &= f_{\mu\nu} = \langle \chi_\mu | \hat{h} | \chi_\nu \rangle + \sum_k^{N/2} [2 \langle \chi_\mu \phi_k | \chi_\nu \phi_k \rangle - \langle \chi_\mu \phi_k | \phi_k \chi_\nu \rangle] \\ &= h_{\mu\nu} + \sum_k^{N/2} [2 \langle \chi_\mu \chi_\rho | \chi_\nu \chi_\sigma \rangle - \langle \chi_\mu \chi_\rho | \chi_\sigma \chi_\nu \rangle] C_{\rho k}^* C_{\sigma k}. \end{aligned} \quad (5.61)$$

If we introduce the density matrix:

$$P_{\rho\sigma} = \sum_k^{N/2} C_{\rho k}^* C_{\sigma k}, \quad (5.62)$$

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

$$f_{\mu\nu}(\mathbf{P}) = h_{\mu\nu} + \underbrace{\sum_{\rho\sigma} [2 \langle \chi_\mu \chi_\rho | \chi_\nu \chi_\sigma \rangle - \langle \chi_\mu \chi_\rho | \chi_\sigma \chi_\nu \rangle] P_{\rho\sigma}}_{G_{\mu\nu}}. \quad (5.63)$$

Since the Fock matrix depends on  $\mathbf{P}$  and ultimately on  $\mathbf{C}$ , the Hartree-Fock equations are nonlinear and require an iterative solution:

$$\mathbf{F}(\mathbf{C})\mathbf{C} = \mathbf{S}\mathbf{C}\epsilon, \quad (5.64)$$

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

$$\chi_\mu \rightarrow \chi'_\mu = \sum_\nu \chi_\nu X_{\nu\mu}. \quad (5.65)$$

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

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} = \sum_\mu \chi'_\mu C'_{\mu i} = \sum_{\mu\nu} \chi_\nu X_{\nu\mu} C'_{\mu i}, \quad (5.66)$$

from which we get

$$\mathbf{C} = \mathbf{X}\mathbf{C}'. \quad (5.67)$$

Suppose we choose  $\mathbf{X}$  to satisfy the condition:

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}, \quad (5.68)$$

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:

$$\underbrace{\mathbf{X}^\dagger \mathbf{F} \mathbf{X}}_{\mathbf{F}'} \mathbf{C}' = \underbrace{\mathbf{X}^\dagger \mathbf{S} \mathbf{X}}_{\mathbf{1}} \mathbf{C}' \epsilon \quad (5.69)$$

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

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 chosen to be the (matrix) square root of  $\mathbf{S}$ :

$$\mathbf{X} = \mathbf{S}^{-\frac{1}{2}}. \quad (5.70)$$

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

$$\mathbf{S}^{-\frac{1}{2}} \mathbf{S} \mathbf{S}^{-\frac{1}{2}} = \mathbf{S}^{-\frac{1}{2}} \mathbf{S}^{\frac{1}{2}} = \mathbf{1}. \quad (5.71)$$

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

$$\mathbf{S} \mathbf{U} = \mathbf{U} \mathbf{s}, \quad (5.72)$$

and then building

$$\mathbf{S}^{-\frac{1}{2}} = \mathbf{U} \mathbf{s}^{-\frac{1}{2}} \mathbf{U}^\dagger. \quad (5.73)$$

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

$$\mathbf{X} = \mathbf{U} \mathbf{s}^{-\frac{1}{2}}. \quad (5.74)$$

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

$$\mathbf{s}^{-\frac{1}{2}} \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \mathbf{s}^{-\frac{1}{2}} = \mathbf{s}^{-\frac{1}{2}} \mathbf{s} \mathbf{s}^{-\frac{1}{2}} = \mathbf{1}. \quad (5.75)$$

### 5.1.7 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:

$$S_{\mu\nu} = \int d\mathbf{r} \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}), \quad (5.76)$$

$$V_{\mu\nu} = \int d\mathbf{r} \chi_\mu^*(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + V_{eN}(\mathbf{r}) \right] \chi_\nu(\mathbf{r}), \quad (5.77)$$

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

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

$$\mathbf{S} \mathbf{U} = \mathbf{U} \mathbf{s}. \quad (5.78)$$

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

$$\mathbf{X} = \mathbf{U} \mathbf{s}^{-\frac{1}{2}}. \quad (5.79)$$

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

$$\mathbf{P}^{(0)} = \mathbf{0}. \quad (5.80)$$

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:

$$\mathbf{G} = \mathbf{G}[\mathbf{P}^{(k)}, \langle \mu\nu | \rho\sigma \rangle]. \quad (5.81)$$

6. **Formation the Fock matrix.**

$$\mathbf{F} = \mathbf{H} + \mathbf{G}. \quad (5.82)$$

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

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X}. \quad (5.83)$$

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

$$\mathbf{F}' \mathbf{C}' = \mathbf{F}' \epsilon. \quad (5.84)$$

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

$$\mathbf{C} = \mathbf{X} \mathbf{C}'. \quad (5.85)$$

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

$$P_{\mu\nu}^{(k+1)} = \sum_i^N C_{\mu i}^* C_{\nu i}. \quad (5.86)$$

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

$$\Delta E^{(k+1)} = E^{(k+1)} - E^{(k)}, \quad (5.87)$$

and the change in the density matrix:

$$\Delta \mathbf{P}^{(k+1)} = \mathbf{P}^{(k+1)} - \mathbf{P}^{(k)}, \quad (5.88)$$

are used to determine if the Hartree-Fock equation have converged. If  $|\Delta E^{(k+1)}| \leq \eta_E$  and  $\|\Delta \mathbf{P}^{(k+1)}\| \leq \eta_P$ , where  $\eta_E$  and  $\eta_P$  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.

## Study Questions

1. What are the basic assumptions of the Hartree-Fock method?
2. What mathematical condition is imposed on the wave function in the Hartree-Fock method?
3. How are the Fock, Coulomb, and exchange operators defined?
4. What is the energy expression of the Hartree-Fock wave function?
5. What is the Hartree-Fock Lagrangian?
6. What does the Hartree-Fock equation in canonical form look like?
7. What is the meaning of the Hartree-Fock orbital energies?
8. What approximations are made in Koopman's theorem?
9. What is the difference between generalized, unrestricted, and restricted HF?
10. What are the Roothan equations?
11. What is the mathematical expression of the Roothan equations?
12. What is the overlap matrix?

## CHAPTER 6

# Molecular properties and characterization of stationary points

## 6.1 Density matrices and molecular properties

In this section we will discuss the information that can be extracted from the wave function. One of the simplest and most fundamental quantities that we can compute from the full  $N$ -electron wave function is the **electron density**  $\rho(x_1)$ , also called the **one-body density**

$$\rho(x_1) = N \int dx_2 \cdots dx_N \Psi(x_1, x_2, \dots, x_N)^* \Psi(x_1, x_2, \dots, x_N). \quad (6.1)$$

The electron density is multiplied by  $N$  so that the integral over all space is the total number of electrons

$$\int dx_1 \rho(x_1) = N. \quad (6.2)$$

In addition to the electron density, we can define the one-electron density matrix  $\gamma(x'_1; x_1)$ :<sup>27</sup>

$$\gamma(x'_1; x_1) = N \int dx_2 \cdots dx_N \Psi(x'_1, x_2, \dots, x_N)^* \Psi(x_1, x_2, \dots, x_N). \quad (6.3)$$

<sup>27</sup>Note that the one-electron density matrix depends on two variables:  $x_1$  and  $x'_1$ .

The electron density can be obtained from the one-electron density matrix by setting  $x'_1$  equal to  $x_1$

$$\rho(x_1) = \gamma(x_1; x_1), \quad (6.4)$$

that is, the density is the diagonal component of the density matrix.

Given a one-electron operator  $\hat{O}_1$ , defined as:

$$\hat{O}_1(x) = \sum_i^N \hat{o}(x_i), \quad (6.5)$$

the expectation value of  $\hat{O}_1$  may be obtained from the one-particle density matrix. To see this let us compute the expectation value:

$$\langle \Psi | \hat{O}_1 | \Psi \rangle = \sum_i^N \int dx_1 \cdots dx_N \Psi(x_1, x_2, \dots, x_N)^* \hat{o}(x_i) \Psi(x_1, x_2, \dots, x_N). \quad (6.6)$$

Consider one element of this sum with the operator  $\hat{o}(x_i)$ . It is easy to show that it may be written in terms of the one-electron density matrix by relabeling the coordinates  $x_1 \leftrightarrow x_i$ ,

then using the anti-symmetry of the wave function, and lastly, by introducing the auxiliary variable  $x'_1$

$$\begin{aligned}
 & \int dx_1 \cdots dx_N \Psi^*(x_1, \dots, x_i, \dots) \hat{o}(x_i) \Psi(x_1, \dots, x_i, \dots) \\
 &= \int dx_1 \cdots dx_N \Psi^*(x_i, \dots, x_1, \dots) \hat{o}(x_1) \Psi(x_i, \dots, x_1, \dots) \\
 &= \int dx_1 \cdots dx_N \Psi^*(x_1, \dots, x_i, \dots) \hat{o}(x_1) \Psi(x_1, \dots, x_i, \dots) \\
 &= \int dx_1 \left[ \hat{o}(x_1) \int dx_2 \cdots dx_N \Psi^*(x'_1, \dots, x_i, \dots)^* \Psi(x_1, \dots, x_i, \dots) \right]_{x'_1=x_1} \\
 &= \frac{1}{N} \int dx_1 [\hat{o}(x_1) \gamma(x'_1; x_1)]_{x'_1=x_1}.
 \end{aligned} \tag{6.7}$$

Here we take advantage of the fact that we can relabel electron indices, and that if we simultaneously permute indices in the  $\Psi^*$  and  $\Psi$  functions the overall permutation factor is one. In considering the action of  $\hat{o}(x_1)$  onto the product  $\Psi^* \Psi$  we have to be careful to consider that  $\hat{o}(x_1)$  only acts on the term on the right  $\Psi$ . This can be easily accounted for if we introduce an auxiliary variable  $x'_1$  which, after the application of  $\hat{o}(x_1)$  to  $\Psi^* \Psi$ , we set equal to  $x_1$ . This result allows us to write:

$$\langle \Psi | \hat{O}_1 | \Psi \rangle = \int dx_1 [\hat{o}(x_1) \gamma(x'_1; x_1)]_{x'_1=x_1}. \tag{6.8}$$

For a single Slater determinant it is possible to show that the density matrix is given by:

$$\gamma(x'_1; x_1) = \sum_i^N \psi_i^*(x'_1) \psi_i(x_1), \tag{6.9}$$

so that the expectation value of a one-electron operator is equal to:

$$\begin{aligned}
 \langle \Psi | \hat{O}_1 | \Psi \rangle &= \int dx_1 \left[ \hat{o}(x_1) \sum_i^N \psi_i^*(x'_1) \psi_i(x_1) \right]_{x'_1=x_1} \\
 &= \sum_i^N \int dx_1 [\psi_i^*(x'_1) \hat{o}(x_1) \psi_i(x_1)]_{x'_1=x_1} \\
 &= \sum_i^N \langle \psi_i | \hat{o} | \psi_i \rangle.
 \end{aligned} \tag{6.10}$$

Note that this result is consistent with the energy expression for a Slater determinant. If we substitute  $\hat{o}(x_1)$  for the one-electron Hamiltonian  $\hat{h}$  we recover the first contribution to the energy of a determinant.

### ■ Example 6.1.1 | Dipole moment.

Consider the expectation value of the dipole moment operator  $\hat{\mu} = q\vec{r}$ . For a molecule with  $N$  electrons and  $M$  nuclei

$$\hat{\mu} = \sum_i^N \hat{\mu}_i + \sum_A^M \hat{\mu}_A = -e \sum_i^N \vec{r}_i + e \sum_A^M Z_A \vec{R}_A. \tag{6.11}$$

The expectation value of the dipole moment operator for a single Slater determinant  $|\Phi\rangle = |\psi_1 \cdots \psi_N\rangle$

is

$$\begin{aligned}\langle \Phi | \hat{\mu} | \Phi \rangle &= -e \langle \Phi | \sum_i^N \vec{r}_i | \Phi \rangle + e \sum_A^M Z_A \vec{R}_A \langle \Phi | \Phi \rangle \\ &= -e \sum_i^N \langle \psi_i | \vec{r} | \psi_i \rangle + e \sum_A^M Z_A \vec{R}_A.\end{aligned}\quad (6.12)$$

Let us expand the orbitals in the computational basis  $\{\chi_\mu\}$  and integrate over the spin variable  $\omega$ . Then the electronic contribution reads:

$$\begin{aligned}\sum_i^N \langle \psi_i | \vec{r} | \psi_i \rangle &= \sum_i^N \sum_{\mu\nu}^K \langle \chi_\mu | \vec{r} | \chi_\nu \rangle C_{\mu i}^* C_{\nu i} \\ &= \sum_{\mu\nu}^K \langle \chi_\mu | \vec{r} | \chi_\nu \rangle \underbrace{\sum_i^N C_{\mu i}^* C_{\nu i}}_{P_{\mu\nu}} \\ &= \sum_{\mu\nu}^K \langle \chi_\mu | \vec{r} | \chi_\nu \rangle P_{\mu\nu} \\ &= \sum_{\mu}^K (\vec{\mathbf{r}} \mathbf{P}^*)_{\mu\mu} = \text{Tr}(\vec{\mathbf{r}} \mathbf{P}^*),\end{aligned}\quad (6.13)$$

where  $\mathbf{r}$  is the matrix representation of the position operator in the computational basis:

$$(\vec{\mathbf{r}})_{\mu\nu} = \langle \chi_\mu | \vec{r} | \chi_\nu \rangle. \quad (6.14)$$

Notice that  $P_{\mu\nu}$  is the same density matrix that we introduced in the Hartree–Fock method. ■

Another important quantity that can be extracted from the wave function is the two-electron density ( $\rho_2$ ), defined as

$$\rho_2(x_1, x_2) = \frac{N(N-1)}{2} \int dx_3 \cdots dx_N \Psi(x_1, x_2, \dots, x_N)^* \Psi(x_1, x_2, \dots, x_N). \quad (6.15)$$

This quantity gives the probability of finding a pair of electrons in positions  $x_1$  and  $x_2$ , and therefore contains information about the correlated motion of electrons. We will see this quantity again when we will study density functional theory. An analogous two-body density matrix can also be defined

$$\gamma_2(x_1, x_2; x'_1, x'_2) = \frac{N(N-1)}{2} \int dx_3 \cdots dx_N \Psi(x'_1, x'_2, \dots, x_N)^* \Psi(x_1, x_2, \dots, x_N), \quad (6.16)$$

which reduces to the two-electron density when the primed coordinates are equal to the unprimed ones

$$\rho_2(x_1, x_2) = \gamma_2(x_1, x_2; x_1, x_2). \quad (6.17)$$

## 6.2 Atomic charges and bond order

In the case of a single Slater determinant, we can perform a simple analysis of the distribution of electrons following an approach developed by Mulliken. Recall that  $i$ -th MO can be expanded in terms of the AOs ( $\chi_\mu = \text{AO}$ ) and the coefficient matrix ( $C_{\mu i}$ ) as:

$$\phi_i(\mathbf{r}) = \sum_{\mu}^N \chi_{\mu}(\mathbf{r}) C_{\mu i}. \quad (6.18)$$

Since each MO is normalized we can write:<sup>28</sup>

<sup>28</sup>Recall that in quantum mechanics  $|\Psi|^2 = \Psi^* \Psi$  is a probability density.

$$\begin{aligned}
N &= \int d\mathbf{r} \rho(\mathbf{r}) = \sum_i^{\text{occ}} \langle \psi_i | \psi_i \rangle = \sum_i^{\text{occ}} \sum_{\mu\nu}^N C_{\mu i}^* \underbrace{\langle \chi_\mu | \chi_\nu \rangle}_{S_{\mu\nu}} C_{\nu i} \\
&= \sum_{\mu\nu}^N S_{\mu\nu} \underbrace{\sum_i^{\text{occ}} C_{\mu i} C_{\nu i}^*}_{D_{\nu\mu}} = \sum_{\mu\nu}^N S_{\mu\nu} D_{\nu\mu} = \sum_{\mu}^N (SD)_{\mu\mu}
\end{aligned} \tag{6.19}$$

<sup>29</sup>To simplify the notation we will write  $\sum_{\mu} \sum_{\nu \neq \mu}^N$  as  $\sum_{\mu \neq \nu}^N$  and omit the superscript  $N$ .

Using these quantities we define:

- **Total density on atom  $\mu$  ( $q_\mu$ ):**

$$q_\mu = \sum_i^{\text{MO}} n_i |C_{\mu i}|^2 = \sum_i^{\text{MO}} n_i q_\mu^i \quad n_i = \text{occupation (2, 1, or 0)} \tag{6.20}$$

- **Total charge on atom  $\mu$  ( $N_\mu$ ):**

$$N_\mu = (\text{number of } \pi \text{ electrons donated by atom } \mu) - q_\mu \tag{6.21}$$

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

$$p_{\mu\nu} = \sum_i^{\text{MO}} n_i C_{\mu i}^* C_{\nu i} = \sum_i^{\text{MO}} n_i p_{\mu\nu}^i \tag{6.22}$$

### 6.3 Energy gradients

Another useful property that we would like to extract from quantum chemistry computations is the gradient of the energy with respect to the position of the nuclei ( $R_\alpha$ ):

$$g_\alpha(\mathbf{R}) = \frac{\partial V(\mathbf{R})}{\partial R_\alpha} \quad \alpha = 1, \dots, 3M. \tag{6.23}$$

Energy gradients can be obtained either by using numeral methods, for example, by taking finite differences of the energy, or by analytical methods that directly compute the gradients of the energy.

In the finite difference method, the gradient and second derivatives are computed by repeatedly evaluating the energy at different geometries around a reference geometry  $\mathbf{R}_0$ . Suppose we are interested in computing the gradient of a function  $f(x)$  at a point  $x_0$ . In the finite difference method we expand  $f(x)$  as a Taylor series at a point  $x_0 + h$ , where  $h$  is a small displacement

$$f(x_0 + h) = f(x_0) + f'(x_0)h + \frac{1}{2}f''(x_0)h^2 + O(h^3), \tag{6.24}$$

, from which we can obtain  $f'(x_0)$

$$f'(x_0) = \frac{f(x_0 + h) - f(x_0)}{h} - \frac{1}{2}f''(x_0)h + O(h^2). \tag{6.25}$$

For a sufficiently small value of  $h$  we can write

$$f'(x_0) = \frac{f(x_0 + h) - f(x_0)}{h} + O(h), \tag{6.26}$$

which shows that the error in the gradient is proportional to  $h$ . A more accurate finite difference scheme may be obtained by considering the Taylor series centered around  $x_0 - h$

$$f(x_0 - h) = f(x_0) - f'(x_0)h + \frac{1}{2}f''(x_0)h^2 + O(h^3), \tag{6.27}$$

and subtracting this from the expression for  $f(x_0 + h)$

$$f(x_0 + h) - f(x_0 - h) = 2f'(x_0)h + O(h^3). \quad (6.28)$$

From this expression we get an estimate of the gradient with an error that is now proportional to order  $h^2$

$$f'(x_0) = \frac{f(x_0 + h) - f(x_0 - h)}{2h} + O(h^2). \quad (6.29)$$

Analogous formulas can be obtained to determine the energy with higher accuracy. For example, the following equation provides the gradient approximate to order  $h^4$

$$f'(x_0) = \frac{-f(x_0 + 2h) + 8f(x_0 + h) - 8f(x_0 - h) + f(x_0 - 2h)}{12h} + O(h^4). \quad (6.30)$$

These equations may be generalized to second derivative and to the case where there is more than one variable.

The theory behind analytical gradients is well established but highly technical, so it will not be covered in these notes. In general, the cost to compute analytical gradients is similar to that of an energy evaluation. Compare this to the cost of computing the gradient via finite difference, where for each direction ( $3M - 5$  or  $3M - 6$ ) we have to compute 2, 4, or more energies to obtain the gradient. The numerical method is clearly more expensive, but sometimes it is the only option available because the analytical gradients may have not been developed and implemented.

## 6.4 Stationary points and geometry optimization

Gradients are important because they allow us to find stationary points of the potential energy surface  $E(\mathbf{R})$ . Stationary points are defined as those geometries ( $\tilde{\mathbf{R}}$ ) for which all gradients are zero:

$$g_\alpha(\tilde{\mathbf{R}}) = 0 \quad \alpha = 1, \dots, 3M. \quad (6.31)$$

A stationary point can be found by an optimization algorithm like the Newton–Raphson method.

### ■ Example 6.4.1 | Newton–Raphson method in one dimension.

In one dimension the gradient is a scalar  $g$ . If we expand the potential around an arbitrary point  $x_0$  in a Taylor expansion

$$\begin{aligned} V(x) &= V(x_0) + \left. \frac{dV(x)}{dx} \right|_{x=x_0} (x - x_0) + \frac{1}{2!} \left. \frac{d^2V(x)}{dx^2} \right|_{x=x_0} (x - x_0)^2 + \dots \\ &= V(x_0) + g_0(x - x_0) + \frac{1}{2!} h_0(x - x_0)^2 + \dots, \end{aligned} \quad (6.32)$$

where  $g_0 = \left. \frac{dV(x)}{dx} \right|_{x=x_0}$  and  $h_0 = \left. \frac{d^2V(x)}{dx^2} \right|_{x=x_0}$  are the gradient and hessian, respectively.

To find a stationary point we need to impose  $\frac{dV(x)}{dx} = 0$ . Differentiating the Taylor expansion once we obtain

$$\frac{dV(x)}{dx} = g_0 + h_0(x - x_0) + \dots \quad (6.33)$$

Neglecting the terms quadratic in  $(x - x_0)$  and imposing  $\frac{dV(x)}{dx} = 0$  we get:

$$g_0 + h_0(x - x_0) = 0, \quad (6.34)$$

or:

$$x = x_0 - \frac{g_0}{h_0}. \quad (6.35)$$

Thus we can find an approximation to the stationary point using the gradient and the Hessian of the energy. If we apply this equation we are unlikely to land right away onto the stationary point, and an iterative procedure is usually required. ■

For a general molecule, we can derive the Newton–Raphson method by expanding the energy  $V(\mathbf{R})$  as a Taylor series

$$\begin{aligned} V(\mathbf{R}) &= V(\mathbf{R}_0) + \sum_{\alpha} \frac{\partial V}{\partial R_{\alpha}} \bigg|_{\mathbf{R}=\mathbf{R}_0} \Delta R_{\alpha} \\ &\quad + \frac{1}{2!} \sum_{\alpha\beta} \frac{\partial^2 V}{\partial R_{\alpha} \partial R_{\beta}} \bigg|_{\mathbf{R}=\mathbf{R}_0} \Delta R_{\alpha} \Delta R_{\beta} + \dots \\ &= V(\mathbf{R}_0) + \mathbf{g}^T \Delta \mathbf{R} + \frac{1}{2} \Delta \mathbf{R}^T \mathbf{F} \Delta \mathbf{R} + \dots, \end{aligned} \quad (6.36)$$

where we introduced the displacement vector  $(\Delta \mathbf{R})_{\alpha} = \Delta R_{\alpha} = R_{\alpha} - R_{0,\alpha}$ , the gradient vector

$$g_{\alpha} = \frac{\partial V}{\partial R_{\alpha}}, \quad (6.37)$$

and the Hessian matrix (force constant):

$$F_{\alpha\beta} = \frac{\partial^2 V}{\partial R_{\alpha} \partial R_{\beta}}. \quad (6.38)$$

The gradient of  $V(\mathbf{R})$  is then

$$\nabla V(\mathbf{R}) = \mathbf{g} + \mathbf{F} \Delta \mathbf{R} + \dots, \quad (6.39)$$

and imposing  $\nabla V(\mathbf{R}) = 0$  we get (after neglecting higher-order terms):

$$\Delta \mathbf{R} = -\mathbf{F}^{-1} \mathbf{g}, \quad (6.40)$$

or

$$\mathbf{R} = \mathbf{R}_0 - \mathbf{F}^{-1} \mathbf{g}. \quad (6.41)$$

This procedure for optimizing the geometry is called the Newton–Raphson method. It requires both the energy gradient ( $\mathbf{g}$ ) and the Hessian ( $\mathbf{F}$ ). In a typical quantum chemistry code the Hessian might not be computed exactly. Instead, one may start from a guess and update the Hessian with information from the gradient as one explores the potential energy surface during an optimization.

## 6.5 Normal Coordinate Analysis and Harmonic Frequencies

Once we identify a stationary point, it is possible to characterize its nature (minimum, saddle point, maximum) by performing a normal mode analysis. In a normal mode analysis we will solve the nuclear Schrödinger equation at a minimum geometry by expanding the potential up to quadratic terms. Recall that the nuclear Schrödinger equation in the Born–Oppenheimer approximation is:

$$\hat{H}_{\text{nuc}} \chi_v(\mathbf{R}) = E_v \chi_v(\mathbf{R}), \quad (6.42)$$

where  $\hat{H}_{\text{nuc}}$  is the nuclear Hamiltonian for a given electronic state (we omit the index  $k$  to simplify the notation)

$$\hat{H}_{\text{nuc}} = \hat{T}_N + V(\mathbf{R}). \quad (6.43)$$

For small vibrations around a minimum (or any other type of stationary point), the potential can be expanded up to quadratic terms as

$$V(\mathbf{R}) \approx V(\mathbf{R}_0) + \frac{1}{2} \Delta \mathbf{R}^T \mathbf{F} \Delta \mathbf{R} = V(\mathbf{R}_0) + \frac{1}{2!} \sum_{\alpha\beta} \Delta R_{\alpha} F_{\alpha\beta} \Delta R_{\beta}, \quad (6.44)$$



while the kinetic energy operator (in atomic units) is:

$$\hat{T}_N = -\frac{1}{2} \sum_{\alpha}^{3M} \frac{1}{M_{\alpha}} \frac{\partial^2}{\partial R_{\alpha}^2}. \quad (6.45)$$

Unfortunately, the potential couples different atomic Cartesian coordinates together, which prevents a direct solution of the Schrödinger equation. To solve this problem we first rewrite the kinetic energy operators in terms of Cartesian displacements. Using the chain rule we can show that taking the derivative with respect to a coordinate  $R_{\alpha}$  is equivalent to taking the derivative with respect to its corresponding displacement  $\Delta R_{\alpha}$

$$\frac{\partial}{\partial R_{\alpha}} = \sum_{\beta} \frac{\partial \Delta R_{\beta}}{\partial R_{\alpha}} \frac{\partial}{\partial \Delta R_{\beta}} = \sum_{\beta} \delta_{\alpha\beta} \frac{\partial}{\partial \Delta R_{\beta}} = \frac{\partial}{\partial \Delta R_{\alpha}}. \quad (6.46)$$

Using Cartesian displacements, the Hamiltonian operator may be written as

$$\hat{H}_{\text{nuc}} = -\frac{1}{2} \sum_{\alpha}^{3M} \frac{1}{M_{\alpha}} \frac{\partial^2}{\partial \Delta R_{\alpha}^2} + \frac{1}{2} \sum_{\alpha\beta}^{3M} \Delta R_{\alpha} F_{\alpha\beta} \Delta R_{\beta}. \quad (6.47)$$

Next, we want to hide the mass dependence. To this end, introduce mass-weighted coordinates ( $q_{\alpha}$ ), defined as

$$q_{\alpha} = \sqrt{M_{\alpha}} \Delta R_{\alpha}. \quad (6.48)$$

With this transformation the derivative with respect to  $\Delta R_{\alpha}$  may be written as

$$\frac{\partial}{\partial \Delta R_{\alpha}} = \sum_{\beta} \frac{\partial q_{\beta}}{\partial \Delta R_{\alpha}} \frac{\partial}{\partial q_{\beta}} = \sum_{\beta} \sqrt{M_{\beta}} \delta_{\alpha\beta} \frac{\partial}{\partial q_{\beta}} = \sqrt{M_{\alpha}} \frac{\partial}{\partial q_{\alpha}}. \quad (6.49)$$

Plugging in this result into the Hamiltonian we get

$$\hat{H}_{\text{nuc}} = -\frac{1}{2} \sum_{\alpha}^{3M} \frac{\partial^2}{\partial q_{\alpha}^2} + \frac{1}{2} \sum_{\alpha\beta}^{3M} q_{\alpha} \tilde{F}_{\alpha\beta} q_{\beta}, \quad (6.50)$$

where  $\tilde{F}_{\alpha\beta}$  is the mass-weighted Hessian:

$$\tilde{F}_{\alpha\beta} = \frac{F_{\alpha\beta}}{\sqrt{M_{\alpha} M_{\beta}}}. \quad (6.51)$$

If we introduce the diagonal mass matrix  $\mathbf{W}$ :

$$W_{\alpha\beta} = M_{\alpha} \delta_{\alpha\beta}, \quad (6.52)$$

we can write the mass-weighted Hessian as:

$$\tilde{\mathbf{F}} = \mathbf{W}^{-1/2} \mathbf{F} \mathbf{W}^{-1/2} \quad (6.53)$$

The last step consists in diagonalizing the mass-weighted Hessian. Consider the orthogonal matrix  $\mathbf{L}$  that diagonalizes  $\tilde{\mathbf{F}}$ :

$$\tilde{\mathbf{F}} \mathbf{L} = \mathbf{L} \boldsymbol{\lambda}. \quad (6.54)$$

If we express the mass-weighted Hessian as  $\tilde{\mathbf{F}} = \mathbf{L} \boldsymbol{\lambda} \mathbf{L}^T$ , we can rewrite the potential energy term as:

$$\frac{1}{2} \sum_{\alpha\beta\gamma}^{3M} q_{\alpha} L_{\alpha\gamma} \lambda_{\gamma} L_{\beta\gamma} q_{\beta} = \frac{1}{2} \sum_{\gamma}^{3M} \left( \sum_{\alpha} q_{\alpha} L_{\alpha\gamma} \right) \lambda_{\gamma} \left( \sum_{\beta} q_{\beta} L_{\beta\gamma} \right), \quad (6.55)$$

which suggests introducing a new set of variables, the normal modes ( $Q_\gamma$ ):

$$Q_\gamma = \sum_{\alpha} q_{\alpha} L_{\alpha\gamma}. \quad (6.56)$$

Since  $\mathbf{L}$  is an orthogonal transformation, the structure of the kinetic energy operator does not change when transforming the coordinate systems. Hence, we can finally write the Hamiltonian as

$$\hat{H}_{\text{nuc}} = -\frac{1}{2} \sum_{\alpha} \frac{\partial^2}{\partial Q_{\alpha}^2} + \frac{1}{2} \sum_{\alpha} \lambda_{\alpha} Q_{\alpha}^2 = \sum_{\alpha} \left[ -\frac{1}{2} \frac{\partial^2}{\partial Q_{\alpha}^2} + \frac{1}{2} \lambda_{\alpha} Q_{\alpha}^2 \right]. \quad (6.57)$$

Note that in the normal coordinate system the potential is a quadratic function:

$$V(\mathbf{Q}) = \sum_{\alpha} \lambda_{\alpha} Q_{\alpha}^2. \quad (6.58)$$

Therefore, if all  $\lambda_{\alpha}$  are positive ( $\lambda_{\alpha} > 0$ ), then the stationary point is a minimum. If one or more  $\lambda_{\alpha} < 0$  we have a saddle point. If all  $\lambda_{\alpha} < 0$  then we are at a maximum. Thus, a harmonic vibrational analysis can be used after geometry optimization to characterize the nature of a stationary point. Note that for saddle points and maxima the concept of vibrational frequency breaks down because we have to take the square root of a negative number. In this case we talk about **imaginary frequencies**. Minima are said to have no imaginary frequencies.

In the normal mode coordinates, the Hamiltonian is a sum of terms of the form

$$\hat{H}_{\alpha} = -\frac{1}{2} \frac{\partial^2}{\partial Q_{\alpha}^2} + \frac{1}{2} \lambda_{\alpha} Q_{\alpha}^2, \quad (6.59)$$

which is the Hamiltonian for a harmonic oscillator with unity mass and force constant  $k = \lambda_{\alpha}$ . The eigenvalues for this Hamiltonian are given by

$$E_{\alpha}^{(v_{\alpha})} = \sqrt{\lambda_{\alpha}} \left( \frac{1}{2} + v_{\alpha} \right), \quad (6.60)$$

where  $v_{\alpha} = 0, 1, \dots$  is the vibrational quantum number for the normal mode  $Q_{\alpha}$ . The total nuclear energy is given by:

$$E^{\text{v}} = \sum_{\alpha} E_{\alpha}^{(v_{\alpha})} = \frac{1}{2} \sum_{\alpha} \sqrt{\lambda_{\alpha}} + \sum_{\alpha} \sqrt{\lambda_{\alpha}} v_{\alpha}. \quad (6.61)$$

The first term in this expansion is the zero-point vibrational energy (ZPVE) in the harmonic approximation. This is the energy of the nuclei in the ground vibrational state.

The normal modes may be related to the Cartesian displacements by combining all the coordinate transformations. Starting from the normal modes one finds that:

$$\mathbf{Q}^T = \mathbf{q}^T \mathbf{L} = \Delta \mathbf{R}^T \mathbf{W}^{1/2} \mathbf{L} \quad (6.62)$$

and taking the transpose:

$$\mathbf{Q} = \mathbf{L}^T \mathbf{W}^{1/2} \Delta \mathbf{R}. \quad (6.63)$$

Now after solving for  $\Delta \mathbf{R}$  we get:

$$\Delta \mathbf{R} = \mathbf{W}^{-1/2} \mathbf{L} \mathbf{Q}. \quad (6.64)$$

## CHAPTER 7

# Density Functional Theory

### 7.1 What is a functional?

You are very familiar with the concept of a function. In its simplest form, a function  $f(x)$  is a rule to map a number  $x$  to another number  $f(x)$ . The hydrogen atom wave functions are a function that maps points in  $\mathbb{R}^3$  to a complex number.

Functionals generalize the concept of function. In a functional the input is a function, say  $f(x)$ , and the output is a number. For example, consider the following functional  $F$ :

$$F[\rho(x)] = \int_a^b dx |\rho(x)|^2, \quad (7.1)$$

takes a generic function  $\rho(x)$  and returns the integral of its modulus square integrated in the range  $[a, b]$ . We will often encounter functionals of the form:

$$F[\rho(x)] = \int_a^b dx f(\rho(x), \rho'(x)), \quad (7.2)$$

where  $\rho'(x)$  is the derivative of  $\rho(x)$ .

As in the case of functions, we may define the derivative of a functional. Consider a function  $\rho(x)$  and an arbitrary small variation  $\delta\rho(x) = \epsilon\phi(x)$ . We define the functional derivative  $\frac{\delta F[\rho]}{\delta\rho}$  as the function that satisfies the following condition:

$$\lim_{\epsilon \rightarrow 0} \frac{F[\rho + \epsilon\phi] - F[\rho]}{\epsilon} = \int dx \frac{\delta F(x)}{\delta\rho(x)} \phi(x). \quad (7.3)$$

In other words, for a small variation in the function  $\rho(x)$ ,  $\delta\rho(x)$ , the difference in the value of the functional is linear in the functional derivative:

$$\delta F[\rho] = F[\rho + \delta\rho] - F[\rho] = \int dx \frac{\delta F[\rho]}{\delta\rho(x)} \delta\rho(x) + \text{terms of order } [\delta\rho(x)]^2 \text{ and higher.} \quad (7.4)$$

### 7.2 Early developments in DFT

The central idea of DFT is to replace the complex wave function for a  $N$  electron system,  $\Psi(x_1, \dots, x_N)$  with the electron density  $\rho(\mathbf{r})$ . This would allow to reduce the problem of optimizing a function of  $4^N$  variables to the simpler case of a function of 3 dimensions.

It is easy to see that one can write the energy of a system of  $N$  electrons using only the one- and two-particle density matrices. In the case of the kinetic energy operator:

$$\begin{aligned}
 \langle \Psi | \hat{T} | \Psi \rangle &= \sum_i^N \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* \left( -\frac{1}{2} \nabla_i^2 \right) \Psi(x_1, \dots, x_N) \\
 &= -\frac{N}{2} \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* \nabla_1^2 \Psi(x_1, \dots, x_N) \\
 &= -\frac{N}{2} \int dx_1 \left[ \nabla_1^2 \int dx_2 \cdots dx_N \Psi(x'_1, \dots, x_N)^* \Psi(x_1, \dots, x_N) \right]_{x'_1=x_1} \\
 &= \int dx_1 \left[ -\frac{1}{2} \nabla_1^2 \gamma(x'_1; x_1) \right]_{x'_1=x_1}.
 \end{aligned} \tag{7.5}$$

The nuclear-electron potential

$$\begin{aligned}
 \langle \Psi | \hat{V}_{\text{ex}} | \Psi \rangle &= \sum_i^N \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* v_{\text{ex}}(x_i) \Psi(x_1, \dots, x_N) \\
 &= N \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* v_{\text{ex}}(x_1) \Psi(x_1, \dots, x_N) \\
 &= N \int dx_1 \left[ v_{\text{ex}}(x_1) \int dx_2 \cdots dx_N \Psi(x_1, \dots, x_N)^* \Psi(x_1, \dots, x_N) \right] \\
 &= \int dx_1 v_{\text{ex}}(x_1) \rho(x_1).
 \end{aligned} \tag{7.6}$$

Similarly for the electron-electron repulsion energy we have:

$$\begin{aligned}
 \langle \Psi | \hat{V}_{\text{ee}} | \Psi \rangle &= \frac{1}{2} \sum_{ij}'^N \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* \frac{1}{r_{ij}} \Psi(x_1, \dots, x_N) \\
 &= \frac{N(N-1)}{2} \int dx_1 \cdots dx_N \Psi(x_1, \dots, x_N)^* \frac{1}{r_{12}} \Psi(x_1, \dots, x_N) \\
 &= \frac{N(N-1)}{2} \int dx_1 dx_2 \left[ \frac{1}{r_{12}} \int dx_3 \cdots dx_N \Psi(x_1, \dots, x_N)^* \Psi(x_1, \dots, x_N) \right] \\
 &= \int dx_1 dx_2 \frac{1}{r_{12}} \rho_2(x_1, x_2),
 \end{aligned} \tag{7.7}$$

where  $\rho_2(x_1, x_2)$  is the two-electron density:

$$\rho_2(x_1, x_2) = \frac{N(N-1)}{2} \int dx_3 \cdots dx_N \Psi(x_1, \dots, x_N)^* \Psi(x_1, \dots, x_N). \tag{7.8}$$

Combined together, these three equations may be written as the sum of three functionals:

$$E = T[\rho_1(x'_1; x_1)] + V_{\text{ex}}[\rho(x_1)] + V_{\text{ee}}[\rho_2(x_1, x_2)]. \tag{7.9}$$

One may be tempted to try to minimize this functional over  $\rho_1$  and  $\rho_2$ . However, this solution is not as simple as it looks. Without any constraint, the minimization of this functional gives energies that significantly below those of FCI. The issue is the fact that by integrating out the majority of the electrons we loose information regarding the sign of the wave function. In other words, not all  $\rho_1$  and  $\rho_2$  that we can conceive correspond to a  $N$ -electron wave function. One needs to augment the energy minimization with  $N$ -representability constraints, that is, constraints that make sure that  $\rho_1$  and  $\rho_2$  come from a  $N$ -electron wave function.

Thomas and Fermi were the first to propose a way to compute the energy of a system of electrons via a functional of the electron density  $\rho(x_1)$  alone. By assuming the uniform electron gas model, they derived the following kinetic energy functional:

$$T \approx T_{\text{TF}}[\rho(x_1)] = C_{\text{F}} \int d\mathbf{r} \rho^{5/3}(\mathbf{r}), \quad (7.10)$$

where  $C_{\text{F}}$  is a constant. Furthermore, they approximated the electron-electron repulsion term with the classical Coulomb repulsion energy:

$$V_{\text{ee}} \approx J[\rho] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}. \quad (7.11)$$

Note that  $T$  is difficult to approximate, and  $T_{\text{TF}}$  is generally not very accurate. The Thomas–Fermi model has problems describing molecular systems. It cannot describe bonding.

This functional was later improved by Dirac by adding electron exchange effects:

$$E_{\text{x}}[\rho] = -C_{\text{x}} \int d\mathbf{r} \rho^{4/3}(\mathbf{r}). \quad (7.12)$$

The combination of the Thomas–Fermi functional with Dirac exchange is usually called the local density approximation (LDA) because it assumes a uniform electron density.

### 7.3 Theoretical foundations of DFT: the Hohenberg–Kohn theorems

DFT was put on solid grounds by the work of Hohenberg and Kohn (1964). The HK theorems establish a one-to-one relationship between the ground state density  $\rho_{\text{gs}}$  and the external potential  $v_{\text{ex}}$ . Moreover, they state that there is a universal functional of the density  $F[\rho]$  such that the total functional:

$$E[\rho] = F[\rho] + \int d\mathbf{r} v_{\text{ex}}(\mathbf{r})\rho(\mathbf{r}), \quad (7.13)$$

has a minimum that corresponds to the ground state energy:

$$\min E[\rho] = E_{\text{gs}}, \quad (7.14)$$

$$\arg \min E[\rho] = \rho_{\text{gs}}. \quad (7.15)$$

The HK theorems are both trivial and nontrivial, and they do not provide a recipe to find  $F[\rho]$ . Currently, the exact  $F[\rho]$  is unknown and it is likely that we will not be able to write a closed form expression for it. Contrast this with the functionals based on the one- and two-electron density matrices where the functionals are exactly known. Here we will not give a proof of the HK theorems. In the next section we will take a look at a different proof proposed by Levy.

### 7.4 Levy's variational functional

Recall that the ground state energy is defined as:

$$E_{\text{gs}} = \min_{\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = 1} \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle. \quad (7.16)$$

Let us introduce a functional that searches all possible wave functions  $\tilde{\Psi}$  of  $N$  electrons and minimizes the energy, subject to the constraint that the density of  $\tilde{\Psi}$  is equal to a given density  $\rho$ :

$$E[\rho] = \min_{\tilde{\Psi} \rightarrow \rho} \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = \min_{\tilde{\Psi} \rightarrow \rho} \langle \tilde{\Psi} | \hat{T} + \hat{V}_{\text{ee}} | \tilde{\Psi} \rangle + V_{\text{ex}}[\rho]. \quad (7.17)$$

Note that the last term,  $V_{\text{ex}}[\rho]$ , is the only component that includes information about the arrangement of the atoms. If we identify the first term with the universal functional:

$$F[\rho] = \min_{\tilde{\Psi} \rightarrow \rho} \langle \tilde{\Psi} | \hat{T} + \hat{V}_{\text{ee}} | \tilde{\Psi} \rangle, \quad (7.18)$$

<sup>30</sup>Here we use the *infimum*, which is similar to the concept of *minimum*. The infimum is the greatest lower bound of a set. This concept is useful, for example, when considering the positive real numbers  $\mathbb{R}_{>0} = \{x \in \mathbb{R} : x > 0\}$ . This set has no minimum but it does have a infimum, the number 0.

we may write the ground state energy as:<sup>30</sup>

$$E = \inf_{\rho} \left( F[\rho] + \int d\mathbf{r} v_{\text{ex}}(\mathbf{r}) \rho(\mathbf{r}) \right). \quad (7.19)$$

Note that  $E[\rho]$  is only defined for ground-state densities obtained by minimizing the expectation value of an antisymmetric wave function. Thus, this approach does not suffer from the problem of  $N$ -representability. The Levy approach also solves the  $v$ -representability problem and guarantees that there are not other densities that are not  $v$ -representable and yield the same ground state energy.

## 7.5 The Kohn–Sham method

As we have seen in the previous section, the kinetic energy functional in DFT depends only on the electron density  $\rho$ . This formulation of DFT is often called pure or orbital-free DFT. This approach does not work too well in practical applications. The kinetic energy is a major component of the total energy. From the virial theorem one can prove that the expectation value of the kinetic energy  $\langle \hat{T} \rangle$  is related to the expectation value of the potential energy  $\langle \hat{V} \rangle$  by:

$$\langle \hat{T} \rangle = -\frac{1}{2} \langle \hat{V} \rangle. \quad (7.20)$$

Hence a large error in  $\langle \hat{T} \rangle$  can lead to a large error in the total energy  $\langle \hat{T} \rangle + \langle \hat{V} \rangle$ .

In the method proposed by Kohn and Sham, molecular orbitals are reintroduced. In this way, the kinetic energy functional can be expressed in a form that is significantly more accurate than that of orbital-free functionals.

The Kohn–Sham formalism starts by defining two systems. The first one, is the real system in which all electrons interact with each other in an external potential  $v_{\text{ex}}$ . In this case  $\hat{V}_{\text{ee}} \neq 0$ . From the Hohenberg–Kohn theorem we know that given  $v_{\text{ex}}$  there is a unique ground electronic state  $\Psi$  (unless the ground state is degenerate) with electron density  $\rho$ . In addition, Kohn and Sham consider an auxiliary system of non-interacting electrons in a potential  $v_s$ , which in general is not equal to  $v_{\text{ex}}$ . In the auxiliary system  $\hat{V}_{\text{ee}} = 0$ , so the Hamiltonian is given by a sum of one-electron operators:

$$\hat{H}_s = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N v_s(x_i) = \sum_i^N \hat{h}_s(x_i). \quad (7.21)$$

The non-interacting system satisfies the Schrödinger equation:

$$\hat{H}_s \Psi_s = E_s \Psi_s, \quad (7.22)$$

where  $\Psi_s$  is a single Slater determinant,  $|\Psi_s\rangle = |\psi_1 \cdots \psi_N\rangle$ , and the orbitals  $\psi_i$  satisfy one-electron Schrödinger equations:

$$\hat{h}_s(x) \psi_i(x) = \epsilon_i \psi_i(x). \quad (7.23)$$

The energy of the auxiliary system is given by the sum of the one-electron energies:

$$E_s = \langle \Psi_s | \hat{H}_s | \Psi_s \rangle = \sum_i^N \epsilon_i. \quad (7.24)$$

For this system we can write the exact density ( $\rho_s$ ):

$$\rho_s(x) = \sum_i^N |\psi_i(x)|^2, \quad (7.25)$$

and density matrix:

$$\gamma_s(x; x') = \sum_i^N \psi_i(x) \psi_i^*(x'). \quad (7.26)$$

Kohn and Sham now make the following assumption. They impose that the exact ground state density and the density of the auxiliary system are equal

$$\rho = \rho_s. \quad (7.27)$$

The above condition is satisfied by finding an appropriate external potential  $v_s$ . Note, that this does not imply that the density matrix of the real and auxiliary systems coincide, that is, in general we will have that  $\gamma \neq \gamma_s$ .

For the auxiliary we can write the energy as a functional of the Kohn-Sham orbitals:

$$E[\{\psi_i\}] = T_s[\{\psi_i\}] + \int dx v_s(x) \rho(x), \quad (7.28)$$

where the kinetic energy of the auxiliary system is given by

$$T_s[\{\psi_i\}] = \langle \Psi_s | \hat{T} | \Psi_s \rangle = \sum_i^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle. \quad (7.29)$$

Note, that the exact kinetic energy  $T[\rho] = \langle \Psi | \hat{T} | \Psi \rangle$  in general differs from  $T_s[\{\psi_i\}]$ . So why do we introduce the auxiliary system? So that we can approximate  $T[\rho]$  using an expression that depends on orbitals. Functionals of the kinetic energy that contain orbitals are significantly more accurate than approximations bases only on the electron density.

Now we can manipulate the energy expression to explicitly contain the KS kinetic energy. Starting from the exact density functional we rewrite it in terms of quantities that are known plus an unknown exchange-correlation functional ( $E_{xc}[\{\psi_i\}]$ ):

$$\begin{aligned} E[\{\psi_i\}] &= T[\{\psi_i\}] + V_{ex}[\rho] + V_{ee}[\{\psi_i\}] \\ &= T_s[\{\psi_i\}] + V_{ex}[\rho] + J[\rho] + \underbrace{T[\{\psi_i\}] - T_s[\{\psi_i\}] + V_{ee}[\{\psi_i\}] - J[\rho]}_{E_{xc}[\{\psi_i\}]} \\ &= T_s[\{\psi_i\}] + V_{ex}[\rho] + J[\rho] + E_{xc}[\{\psi_i\}]. \end{aligned} \quad (7.30)$$

The exchange-correlation functional contain contributions from exchange and correlation (which are missing from the Coulomb functional  $J[\rho]$ ) and corrections to the kinetic energy ( $T[\{\psi_i\}] - T_s[\{\psi_i\}]$ ).

To obtain the ground state energy and density we minimize the KS functional subject to orthonormality of the spin orbitals. Note, that the Hohenberg-Kohn theorems justify this procedure since minimization of the exact functional  $E[\rho]$  leads to the ground state energy and density [see Eqs. (7.14)-(7.15)]. This goal may be achieved by a Lagrangian analogous to the one used in Hartree-Fock theory:

$$\mathcal{L}_{KS}[\{\psi_i\}] = E_{KS}[\{\psi_i\}] - \sum_{ij}^{\text{occ}} \lambda_{ji} (\langle \psi_i | \psi_j \rangle - \delta_{ij}). \quad (7.31)$$

At this point, we can derive Hartree-Fock-like equations by impose that this Lagrangian is stationary with respect to changes in the orbitals. One new aspect in this derivation is that

we have to compute the variation in the exchange-correlation functional when the orbitals are changed from  $\{\psi_i\}$  to  $\{\psi_i + \delta\psi_i\}$

$$\begin{aligned} E_{\text{xc}}[\{\psi_i + \delta\psi_i\}] - E_{\text{xc}}[\{\psi_i\}] &= \sum_i \int dx \frac{\delta E_{\text{xc}}}{\delta \psi_i^*} \delta\psi_i = \sum_i \int dx \frac{\delta E_{\text{xc}}}{\delta \rho} \frac{\delta \rho}{\delta \psi_i^*} \delta\psi_i \\ &= \sum_i \int dx v_{\text{xc}}(x) \psi_i(x) \delta\psi_i, \end{aligned} \quad (7.32)$$

where we have introduced the exchange-correlation potential ( $v_{\text{xc}}$ ), which is the functional derivative of  $E_{\text{xc}}$  with respect to the density.

If we impose the stationarity condition on  $\mathcal{L}_{\text{KS}}[\{\psi_i\}]$  we obtain the following eigenvalue equation

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{ex}}(\mathbf{r}) + \hat{J}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_i(x) = \sum_j^{\text{occ}} \lambda_{ji} \psi_j(x), \quad (7.33)$$

which, after performing a rotation to the basis that diagonalizes the matrix  $\lambda_{ij}$  yields the canonical Kohn–Sham equations

$$\left[ -\frac{1}{2} \nabla^2 + v_{\text{ex}}(\mathbf{r}) + \hat{J}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_i(x) = \epsilon_i \psi_i(x). \quad (7.34)$$

We can collect all the potential energy terms together and identify them with the potential of the auxiliary system ( $v_s$ )

$$v_s(\mathbf{r}) = v_{\text{ex}}(\mathbf{r}) + \hat{J}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}). \quad (7.35)$$

## 7.6 Approximate density functionals

The simplest way to approximate the exact exchange-correlation density functional is to assume that the electron density is homogeneous. This leads to the so-called local density approximation (LDA). For a homogeneous density, all derivatives of  $\rho(\mathbf{r})$  are zero, so one assumes a parametric form that includes only this variable. In the LDA, the density functional is written as

$$E_{\text{ex}}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) [\epsilon_x(\rho) + \epsilon_c(\rho)], \quad (7.36)$$

where  $\epsilon_x(\rho)$  and  $\epsilon_c(\rho)$  are the exchange and correlation energy density. The exchange contribution derived by Dirac is given by

$$\epsilon_x^{\text{Dirac}}(\rho) = -C_x \rho^{1/3}, \quad (7.37)$$

while for the correlation part a common choice is the functional by Vosko–Wilk–Nusair (VWN),  $\epsilon_c^{\text{VWN}}$ , which was obtained by fitting the energy of the homogeneous electron gas computed with highly-accurate quantum Monte Carlo methods.

Further improvements can be introduced if one considers the derivatives of the density. A common way to introduce the first derivative is via the dimensionless quantity

$$x = \frac{|\nabla \rho|}{\rho}. \quad (7.38)$$

For example, Becke’s exchange function (B88) takes the form

$$\epsilon_x^{\text{B88}}(\rho) = -\beta \rho^{1/3} \frac{x}{1 + 6\beta \sinh^{-1} x}. \quad (7.39)$$



# Single-reference wave function methods

Wave function methods are a class of quantum chemistry approaches that try to build the exact solution to the electronic Schrödinger equation in a systematic way. Most methods start with the assumption that the Hartree–Fock solution ( $\Phi_0$ ) is accurate and that the exact wave function ( $\Psi$ ) can be obtained from it by adding a small correction.

To be more rigorous we have to introduce the notion of correlation energy. One definition of electron correlation is the difference between the FCI ( $E_{\text{FCI}}$ ) and Hartree–Fock ( $E_{\text{HF}}$ ) energy

$$E_{\text{corr}} = E_{\text{FCI}} - E_{\text{HF}} \leq 0. \quad (8.1)$$

This difference is negative because the Hartree–Fock energy is variational, that is,  $E_{\text{HF}} \geq E_{\text{FCI}}$ . Note that the HF energy is exact ( $E_{\text{HF}} = E_{\text{FCI}}$ ) only for one electron systems, or certain other special cases. The correlation energy is further divided into two components

- **Dynamical or weak correlation.** These are correlation effects that result from the short-range Coulomb repulsion of electrons and long-range London dispersion interactions.
- **Static, strong, or nondynamical correlation.** These are correlation effects that arise from the interaction of near-degenerate electronic states, for example, when breaking a bond, in excited states, in systems with coupled localized spins. In this case the HF single determinant approximation is qualitatively incorrect and one needs to use a **multireference approach**.

We have already seen an example where static correlation plays an important role: the dissociation of the  $\text{H}_2$  molecule. In this case, we saw that the ground state requires two determinants to correctly describe the covalent configuration in the dissociation limit ( $\text{H}^\bullet + \text{H}^\bullet$ ). Another case where the HF approximation fails is symmetry forbidden processes. For example consider a reaction in which the reactant is well described by the Slater determinant

$$|\Phi_R\rangle = |(\phi_S)^2\rangle, \quad (8.2)$$

where  $\phi_S$  is a symmetric orbital, while the product is described by the Slater determinant

$$|\Phi_P\rangle = |(\phi_A)^2\rangle, \quad (8.3)$$

where  $\phi_A$  is an antisymmetric orbital. Because  $\phi_S$  and  $\phi_A$  have different symmetry, they cannot continuously transform one into the other. Therefore, a wave function that describes the reaction at all points must be a linear combination

$$|\Psi\rangle = C_R |\Phi_R\rangle + C_P |\Phi_P\rangle. \quad (8.4)$$

## 8.1 Truncated configuration interaction

Perhaps one of the simplest approximations of the FCI wave function consists in truncating the basis of Slater determinants. In truncated CI methods, one expresses the FCI wave function as a sum of a reference HF determinant and all of its singly, doubly, and so on, substituted determinants. If we write the reference HF determinant as

$$|\Phi_0\rangle = |\psi_1 \cdots \psi_N\rangle, \quad (8.5)$$

then we write a determinant where the spin orbital  $\psi_i$  has been replaced with  $\psi_a$  as

$$|\Phi_i^a\rangle = |\psi_1 \cdots \cancel{\psi_i} \psi_a \cdots \psi_N\rangle. \quad (8.6)$$

In this notation, the indices at the bottom show the spin orbitals from which electrons have been removed, while the indices at the top show the empty orbitals that have been occupied by electrons. At times we may use an alternative notation based on **second quantization**. In this equivalent approach, we introduce two new operators,  $\hat{a}_p^\dagger$  and  $\hat{a}_p$ , that create and annihilate an electron in a generic spin orbital  $\psi_p$ . In second quantization we can write a singly-substituted determinant from the HF reference by first removing an electron from  $\psi_i$  via the operator  $\hat{a}_i$  and then creating an electron in  $\psi_a$  via  $\hat{a}_a^\dagger$

$$|\Phi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i |\Phi_0\rangle. \quad (8.7)$$

Doubly-substituted determinant are similarly defined as

$$|\Phi_{ij}^{ab}\rangle = \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |\Phi_0\rangle, \quad (8.8)$$

where we use the convention that upper indices are read from left to right, while lower indices are read from right to left.

Using this notation the FCI wave function may be written as

$$|\Psi_{\text{FCI}}\rangle = |\Phi_0\rangle + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a |\Phi_i^a\rangle + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \frac{1}{36} \sum_{ijk}^{\text{occ}} \sum_{abc}^{\text{vir}} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \dots \quad (8.9)$$

Note that we assigned a coefficient equal to one to the HF determinant  $\Phi_0$ . This way of writing  $\Psi_{\text{FCI}}$  is called **intermediate normalization**. Instead of being normalized,  $\Psi_{\text{FCI}}$  is such that the projection of the HF determinant onto  $\Psi_{\text{FCI}}$  is one, that is,

$$\langle \Phi_0 | \Psi_{\text{FCI}} \rangle = 1. \quad (8.10)$$

To derive equations for the energy we can simply project the Schrödinger equation on the left with  $\Phi_0$

$$\langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle = \langle \Phi_0 | \Psi_{\text{FCI}} \rangle E = E. \quad (8.11)$$

Therefore,  $E = \langle \Phi_0 | \hat{H} | \Psi_{\text{FCI}} \rangle$ . We can rewrite this condition in a more detailed way by plugging in the expansion of  $\Psi_{\text{FCI}}$  in terms of determinants

$$\begin{aligned} E &= \langle \Phi_0 | \hat{H} \left( |\Phi_0\rangle + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a |\Phi_i^a\rangle + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots \right) \\ &= \underbrace{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}_{E_{\text{HF}}} + \underbrace{\sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle}_{E_{\text{corr}}}. \end{aligned} \quad (8.12)$$

Here we can directly identify the Hartree–Fock energy and the contribution due to electron correlation. Although the FCI expansion includes triply and higher-substituted determinants,

Slater's rules imply that the matrix elements between the reference and a generic excited determinant ( $|\Phi_{ij\cdots}^{ab\cdots}\rangle$ ),  $\langle\Phi_0|\hat{H}|\Phi_{ij\cdots}^{ab\cdots}\rangle$ , are nonzero only when a determinant is at most a double substitution with respect to  $\Phi_0$ . This is what determines this expansion to terminate. This result is interesting because depending on what we want to compute, we may not need to know the entire wave function. In the case of the energy, knowledge of only the coefficients for the singly- and doubly-substituted determinants is sufficient to recover the exact correlation energy. This result, however, does not mean that the FCI wave function can be approximated only with singles and doubles, but it does suggest that such an approximation may be accurate.

In truncated CI methods, the FCI expansion is truncated at a certain excitation level  $n$ . If we introduce the excitation operator  $\hat{C}$

$$\hat{C} = \hat{C}_1 + \hat{C}_2 + \dots + \hat{C}_n, \quad (8.13)$$

where a generic  $k$ -body excitation operator  $\hat{C}_k$  is defined as

$$\hat{C}_k = \frac{1}{(k!)^2} \sum_{ij\cdots}^{\text{occ}} \sum_{ab\cdots}^{\text{vir}} c_{ij\cdots}^{ab\cdots} \underbrace{\hat{a}_a^\dagger \hat{a}_b^\dagger \cdots \hat{a}_j \hat{a}_i}_{k\text{-fold excitation}}, \quad (8.14)$$

we can rewrite a truncated CI wave function as

$$|\Psi_{\text{CI}}\rangle = (1 + \hat{C}) |\Phi_0\rangle. \quad (8.15)$$

The simplest truncated CI approach is CI singles (CIS), which consists in the approximation  $\hat{C} \approx \hat{C}_1$

$$|\Psi_{\text{CIS}}\rangle = |\Phi_0\rangle + \sum_i^{\text{occ}} \sum_a^{\text{vir}} c_i^a |\Phi_i^a\rangle. \quad (8.16)$$

To solve for the CI coefficients  $c_i^a$  one has to diagonalize the Hamiltonian in the basis of the reference and all of its singly substituted determinant. Interestingly, if the reference is a Hartree–Fock determinant, the CIS wave function one finds that the matrix elements between the reference and any single is a matrix element of the Fock operator

$$\langle\Phi_i^a|\hat{H}|\Phi_0\rangle = h_{ai} + \sum_k^{\text{occ}} \langle ak||ik\rangle \equiv f_{ai} = \langle\psi_a|\hat{f}|\psi_i\rangle. \quad (8.17)$$

Now recall that the Hartree–Fock equation could be written in the most general form as

$$\hat{f}|\psi_i\rangle = \sum_j^{\text{occ}} |\psi_j\rangle \lambda_{ji}. \quad (8.18)$$

This equation shows that when we apply  $\hat{f}$  onto an occupied orbital we get back a linear combination of orbitals that are occupied. Therefore, when we left-project a virtual orbital  $\psi_a$  onto  $\hat{f}|\psi_i\rangle$ , the matrix element is null

$$\langle\psi_a|\hat{f}|\psi_i\rangle = \sum_j^{\text{occ}} \langle\psi_a|\psi_j\rangle \lambda_{ji} = 0. \quad (8.19)$$

This result is known as **Brillouin's theorem**, and it implies that for HF orbitals  $\langle\Phi_i^a|\hat{H}|\Phi_0\rangle = 0$ . Consequently, the Hamiltonian matrix in CIS does not have off-diagonal blocks that couple the reference to the singles and the CIS ground state energy is simply the Hartree–Fock energy. Although CIS does not improve the description of the Hartree–Fock solution for the ground state, it can be used to compute excited states.

Brillouin's theorem applies only to single substituted determinants, so double substitutions can mix with the reference. The simplest CI methods that includes ground-state correlation corrections is CI with doubles (CID), which corresponds to the wave function approximation

$$|\Psi_{\text{CID}}\rangle = |\Phi_0\rangle + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle. \quad (8.20)$$

When both singles and doubles are included in CI, we have CI with singles and doubles (CISD). One can also define higher order approximations that additionally include triples (CISDT) and quadruples (CISDTQ).

Despite its simplicity, truncated CI suffers from a major deficiency: the energy and other properties lack size consistency, that is, they are not additive for separate fragments. Consider two fragments, A and B. We say that a computational method is size consistent if a computation of the energy of A and B held at infinite distance  $[E(A \cdots B)]$  is equal to the sum of the energy of A  $[E(A)]$  plus the energy of B  $[E(B)]$

$$E(A \cdots B) = E(A) + E(B). \quad (8.21)$$

For truncated CIs, in general one has that  $E(A \cdots B) \neq E(A) + E(B)$ , and we therefore say that they lack size consistency. The reason why truncated CI is not size consistent is that the wave function is not **multiplicatively separable**. For FCI, if we know the wave function of molecules A ( $\Psi^A$ ) and B ( $\Psi^B$ ), the total wave function for  $A \cdots B$  should be the product

$$|\Psi^{AB}\rangle = |\Psi^A \Psi^B\rangle. \quad (8.22)$$

To see why this is not the case consider a CID wave function for both systems, for example,  $|\Psi_{\text{CID}}^A\rangle = (1 + \hat{C}_2^A) |\Phi_0^A\rangle$ , and similarly for B. A CID computation on  $A \cdots B$  still includes only double and has the form

$$|\Psi_{\text{CID}}^{AB}\rangle = (1 + \hat{C}_2^A + \hat{C}_2^B) |\Phi_0^A \Phi_0^B\rangle. \quad (8.23)$$

However, the total wave function for  $A \cdots B$  at infinite separation should be

$$|\Psi_{\text{CID}}^A \Psi_{\text{CID}}^B\rangle = (1 + \hat{C}_2^A)(1 + \hat{C}_2^B) |\Phi_0^A \Phi_0^B\rangle = (1 + \hat{C}_2^A + \hat{C}_2^B + \hat{C}_2^A \hat{C}_2^B) |\Phi_0^A \Phi_0^B\rangle. \quad (8.24)$$

The last term,  $\hat{C}_2^A \hat{C}_2^B |\Phi_0^A \Phi_0^B\rangle$ , contains so called **unlinked terms** that correspond to quadruply substituted determinants. These quadruples are missing from the CID wave function of  $A \cdots B$  and that is why this method does not yield the correct energy. Size consistency is a necessary requirement of any electronic structure theory, because otherwise we could not compute consistent reaction energies. Note that corrections for the lack of size consistency in truncated CI do exist, for example, **Davidson's size-consistency correction**.

## 8.2 Møller–Plesset perturbation theory

A second approach to approximate the FCI wave function is to use perturbation theory. Recall that the Hamiltonian in second quantization reads

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r, \quad (8.25)$$

where the quantities  $h_{pq} = \langle \psi_p | \hat{h} | \psi_q \rangle$  are matrix elements of the one-body operator while  $\langle pq || rs \rangle$  are two-electron integrals.

In the **Møller–Plesset** formalism, the Hamiltonian is first partitioned into a zeroth-order part ( $\hat{H}_0$ ) plus a perturbation ( $\hat{V}$ ), and  $\hat{H}_0$  is chosen to be the Fock operator

$$\hat{H}_0 = \hat{f} = \sum_p \epsilon_p \hat{a}_p^\dagger \hat{a}_p. \quad (8.26)$$

Here we assume that the orbitals have been variationally optimized via the Hartree–Fock method and rotated to the canonical basis (so that  $f_{pq} = \epsilon_p \delta_{pq}$ ). It follows that the perturbation contains one- and two-body terms

$$\hat{V} = \hat{H} - \hat{f} = \sum_{pq} (h_{pq} - \epsilon_p \delta_{pq}) \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r. \quad (8.27)$$

This choice is convenient since the HF determinant is an eigenfunction of  $\hat{H}_0$ <sup>31</sup>

$$\hat{H}_0 |\Phi_0\rangle = \left( \sum_i^{\text{occ}} \epsilon_i \right) |\Phi_0\rangle. \quad (8.28)$$

<sup>31</sup> As a matter of fact, any determinant is an eigenfunction of a diagonal one-body operator like  $\hat{H}_0$  with eigenvalue given by the sum of the orbital energies  $\epsilon_i$  of all the occupied spin orbitals.

Using this result we find that the first-order energy is given by

$$E_0^{(1)} = \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = E_{\text{HF}} - \sum_i^{\text{occ}} \epsilon_i = -\frac{1}{2} \sum_{ij}^{\text{occ}} \langle ij || ij \rangle, \quad (8.29)$$

so that the sum of zeroth- and first-order energies is the Hartree–Fock energy

$$E_0^{(0)} + E_0^{(1)} = \langle \Phi_0 | \hat{H}_0 + \hat{V} | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle = E_{\text{HF}}. \quad (8.30)$$

Recall that in standard perturbation theory, the first-order correction to the wave function  $[\Psi_0^{(1)}]$  is given by the sum

$$|\Psi_0^{(1)}\rangle = \sum_{k \neq 0} |\Psi_k^{(0)}\rangle \frac{\langle \Psi_k^{(0)} | \hat{V} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} \quad (8.31)$$

where the set of states  $\{\Psi_k^{(0)}\}$  are eigenstates of the zeroth-order Hamiltonian. In our case the state that we want to improve is the Hartree–Fock determinant, that is,  $\Psi_0^{(0)} = \Phi_0$ , and the other states in the set  $\{\Psi_k^{(0)}\}$  are all singly, doubly, etc., substituted determinants,  $\{\Phi_i^a, \Phi_{ij}^{ab}, \dots\}$ . The matrix element between singly excited determinants  $[\Psi_k^{(0)} = \Phi_i^a]$  and the reference are zero

$$\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle = 0. \quad (8.32)$$

The only matrix elements  $\langle \Psi_k^{(0)} | \hat{V} | \Psi_0^{(0)} \rangle$  that are nonzero are those between the doubles  $[\Psi_k^{(0)} = \Phi_{ij}^{ab}]$  and the reference  $[\Psi_0^{(0)} = \Phi_0]$

$$\langle \Phi_{ij}^{ab} | \hat{V} | \Phi_0 \rangle = \langle ab || ij \rangle. \quad (8.33)$$

The denominator  $E_0^{(0)} - E_k^{(0)}$  is the difference of the zeroth-order energy of these states and may be written as

$$E_0^{(0)} - E_k^{(0)} = \langle \Phi_0 | \hat{H}_0 | \Phi_0 \rangle - \langle \Phi_{ij}^{ab} | \hat{H}_0 | \Phi_{ij}^{ab} \rangle = \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b. \quad (8.34)$$

This gives us the following expression for the first-order wave function correction

$$|\Psi_0^{(1)}\rangle = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} |\Phi_{ij}^{ab}\rangle \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (8.35)$$

where in the sum we include a factor  $\frac{1}{4}$  to avoid double counting determinants. note that the first-order wave function coefficients

$$c_{ij}^{ab,(1)} = \frac{\langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (8.36)$$

depend on the ratio of a two-electron integral ( $\langle ab||ij\rangle$ ) and a Møller–Plesset denominator ( $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$ ). When the latter is small, the coefficient may diverge, that is  $|c_{ij}^{ab,(1)}| \rightarrow \infty$  when  $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \rightarrow 0$ . This may happen if the virtual orbitals becomes near degenerate with the occupied ones, signaling that we are dealing with a problem in which static correlation effects play an important role.

Corrections to the energy due to electron correlation enter at second order. Recall that the second-order energy is given by

$$E_0^{(2)} = \sum_{k \neq 0} \frac{|\langle \Psi_0^{(0)} | \hat{V} | \Psi_k^{(0)} \rangle|^2}{E_0^{(0)} - E_k^{(0)}}, \quad (8.37)$$

which can be written as

$$E_0^{(2)} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle \Phi_0 | \hat{V} | \Phi_{ij}^{ab} \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle ij||ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (8.38)$$

The sum of the HF energy plus this second-order correction ( $E_{\text{MP2}}$ )

$$E_{\text{MP2}} = E_{\text{HF}} + E_0^{(2)}, \quad (8.39)$$

is known as Møller–Plesset second-order perturbation theory (MP2) and is a commonly employed methods to treat dynamical correlation effects. For a Hartree–Fock reference, this correction is always negative since the energy of virtual orbitals is higher than that of occupied ones, so that the denominator  $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \leq 0$  is a negative quantity. As a consequence  $E_{\text{MP2}} \leq E_{\text{HF}}$ . However, the MP2 energy is not variational and in many cases it may be lower than the FCI energy. It is not too difficult to see that the MP2 energy expression is additive for noninteracting fragments, that is,

$$E_0^{(2)}(A \cdots B) = E_0^{(2)}(A) + E_0^{(2)}(B). \quad (8.40)$$

Some aspects to keep into consideration when using MPn:

- The MP2 energy can be generalized to higher orders (MP3, MP4, etc.). However, this series is not guaranteed to converge. Cases are known where the correlation energy diverges after a certain point.
- MP perturbation theory is well suited for the weak correlation regime and cannot be applied to bond-breaking processes. In this case it is necessary to use a multireference perturbation theory (MRPT).

### 8.3 Coupled Cluster theory

In our discussion of truncated CI we mentioned that it would be desirable for the wave function to be multiplicatively separable for noninteracting fragments. For two fragments A and B this means requiring that  $|\Psi^{AB}\rangle = |\Psi^A \Psi^B\rangle$ . Coupled cluster theory solves this problem by employing an exponential wave function of the form

$$|\Psi_{\text{CC}}\rangle = e^{\hat{T}} |\Phi_0\rangle = \left(1 + \hat{T} + \frac{1}{2!} \hat{T}^2 + \frac{1}{3!} \hat{T}^3 + \dots\right) |\Phi_0\rangle, \quad (8.41)$$

where the operator  $\hat{T}$  is defined as the  $\hat{C}$  operator encountered in CI as the sum of one-, two-, and higher-body operators up to order  $n$

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_n, \quad (8.42)$$

where a generic  $k$ -body excitation operator  $\hat{T}_k$  is defined as

$$\hat{T}_k = \frac{1}{(k!)^2} \sum_{ij \dots}^{\text{occ}} \sum_{ab \dots}^{\text{vir}} t_{ij \dots}^{ab \dots} \underbrace{\hat{a}_a^\dagger \hat{a}_b^\dagger \dots \hat{a}_j \hat{a}_i}_{k\text{-fold excitation}}. \quad (8.43)$$

The quantities  $t_{ij \dots}^{ab \dots}$  are called coupled cluster amplitudes and are the central variables in CC theory.

To see why the CC wave function is multiplicatively separable we can take two individual molecules for which we have solved the CC equations

$$|\Psi_{\text{CC}}^A\rangle = e^{\hat{T}^A} |\Phi_0^A\rangle, \quad (8.44)$$

$$|\Psi_{\text{CC}}^B\rangle = e^{\hat{T}^B} |\Phi_0^B\rangle. \quad (8.45)$$

The product wave function can then be shown to be equivalent to the CC wave function for the system  $A \dots B$

$$|\Psi_{\text{CC}}^A \Psi_{\text{CC}}^B\rangle = e^{\hat{T}^A} e^{\hat{T}^B} |\Phi_0^A \Phi_0^B\rangle = e^{\hat{T}^A + \hat{T}^B} |\Phi_0^A \Phi_0^B\rangle = |\Psi_{\text{CC}}^{AB}\rangle, \quad (8.46)$$

due to the fact that  $\exp(\hat{T}^A) \exp(\hat{T}^B) = \exp(\hat{T}^A + \hat{T}^B)$ . Note that in general, given two operators  $\hat{X}$  and  $\hat{Y}$ , we have that

$$\exp(\hat{X}) \exp(\hat{Y}) = \exp(\hat{X} + \hat{Y}), \quad (8.47)$$

only if  $\hat{X}$  and  $\hat{Y}$  commute, that is,  $[\hat{X}, \hat{Y}] = 0$ . Since cluster operators involve only substitutions from occupied to virtual orbitals, they always commute, and in particular  $[\hat{T}^A, \hat{T}^B] = 0$ .

**Problem 8.3.1** Show that the single ( $\hat{T}_1$ ) and double ( $\hat{T}_2$ ) excitation operators defined as follow commute, that is,  $[\hat{T}_1, \hat{T}_2] = 0$ .

$$\hat{T}_1 = \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \hat{a}_a^\dagger \hat{a}_i. \quad (8.48)$$

$$\hat{T}_2 = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i. \quad (8.49)$$

Remember to avoid using the same dummy index in two independent quantities.

Equations for the CC energy and amplitudes are obtained by plugging in the CC wave function into the Schrödinger equation

$$\hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{\hat{T}} |\Phi_0\rangle, \quad (8.50)$$

followed by premultiplication with  $\exp(-\hat{T})$  on the left

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle = E e^{-\hat{T}} e^{\hat{T}} |\Phi_0\rangle = E |\Phi_0\rangle. \quad (8.51)$$

The energy is given by projecting onto  $\langle \Phi_0 |$

$$E = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle, \quad (8.52)$$

while the CC amplitudes are obtained from projections onto excited determinants  $\langle \Phi_{ij \dots}^{ab \dots} |$

$$0 = \langle \Phi_{ij \dots}^{ab \dots} | e^{-\hat{T}} \hat{H} e^{\hat{T}} |\Phi_0\rangle. \quad (8.53)$$

How can we compute the term  $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ ? Well, there is a very useful formula named after Baker–Campbell–Hausdorff (BCH) that says that this expression can be rewritten as a series of commutators

$$\begin{aligned} e^{-\hat{T}} \hat{H} e^{\hat{T}} &= \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}] + \frac{1}{4!} [[[[ \hat{H}, \hat{T} ], \hat{T}], \hat{T}], \hat{T}] + \dots \\ &= \hat{H} + \sum_{k=1}^{\infty} \underbrace{[\dots [[\hat{H}, \hat{T}], \hat{T}], \dots]}_{k \text{ nested commutators}}. \end{aligned} \quad (8.54)$$

This series is infinite, but because of the structure of the Hamiltonian and the fact that all the components in the  $\hat{T}$  operators commute, we have that the BCH series **truncates after the four-fold commutator term**, and this result is independent on the number of electrons. This is important because it means that we can find all the terms in the CC equations and so we do not need to approximate the expression for  $e^{-\hat{T}} \hat{H} e^{\hat{T}}$ .

To develop a hierarchy of coupled cluster methods that approximate the FCI energy better and better we can truncate the  $\hat{T}$  operator to some low particle number (2-4). Because we do not use any argument from perturbation theory to come up with these schemes, we usually think of CC theory as a **nonperturbative method**. The simplest CC approximation is CC with doubles (CCD), which uses the approximation  $\hat{T} \approx \hat{T}_2$ . In this case the Schrödinger equation reads

$$\hat{H} e^{\hat{T}_2} |\Phi_0\rangle = E_{\text{CCD}} e^{\hat{T}_2} |\Phi_0\rangle, \quad (8.55)$$

which upon projection onto  $\Phi_0$  gives

$$\langle \Phi_0 | \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle = E_{\text{CCD}} \langle \Phi_0 | e^{\hat{T}_2} | \Phi_0 \rangle. \quad (8.56)$$

The matrix element on the left of this expression is given by

$$\begin{aligned} \langle \Phi_0 | e^{\hat{T}_2} | \Phi_0 \rangle &= \langle \Phi_0 | (1 + \hat{T}_2 + \dots) | \Phi_0 \rangle \\ &= \langle \Phi_0 | \Phi_0 \rangle + \underbrace{\frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \langle \Phi_0 | \Phi_{ij}^{ab} \rangle}_{=0} + \dots = 1, \end{aligned} \quad (8.57)$$

where the orthogonality of determinants makes all contributions but the first null. Similarly, the right hand side of Eq. (8.56) gives

$$\begin{aligned} \langle \Phi_0 | \hat{H} e^{\hat{T}_2} | \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} (1 + \hat{T}_2 + \dots) | \Phi_0 \rangle \\ &= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_0 \rangle \\ &= E_{\text{HF}} + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \langle ij || ab \rangle t_{ij}^{ab}. \end{aligned} \quad (8.58)$$

It is interesting to analyze the CCD wave function to understand its structure. Expanding the exponential we get

$$|\Psi_{\text{CCD}}\rangle = e^{\hat{T}_2} |\Phi_0\rangle = |\Phi_0\rangle + \hat{T}_2 |\Phi_0\rangle + \underbrace{\frac{1}{2!} \hat{T}_2^2 |\Phi_0\rangle + \frac{1}{3!} \hat{T}_2^3 |\Phi_0\rangle + \dots}_{\text{unlinked quadruples, hexuples, ...}} \quad (8.59)$$

The leading term in  $\Psi_{\text{CCD}}$  is the Hartree–Fock determinant, followed by double substitutions generated by the  $\hat{T}_2$  operator. However, we also see contributions involving quadruple and



higher substitutions that arise from the higher powers of the cluster operator ( $\hat{T}_2^2$ , etc.). These terms generate the unlinked excitations that were missing in the CID method. The cost of CCD is proportional to  $O^2V^4$ , where  $O$  and  $V$  are the number of occupied and virtual orbitals, respectively.

Because add singles does not change the computational scaling, the CC with singles and doubles (CCSD) approximation is generally preferred to CCD. Note that singles play a special role in CC theory. Consider, for example, the CCSD wave function

$$|\Psi_{\text{CCSD}}\rangle = e^{\hat{T}_1 + \hat{T}_2} |\Phi_0\rangle = e^{\hat{T}_2} e^{\hat{T}_1} |\Phi_0\rangle, \quad (8.60)$$

where we have used the fact that  $\hat{T}_1$  and  $\hat{T}_2$  commute to rearrange this expression. **Thouless' theorem** says that the effect of  $\exp(\hat{T}_1)$  applied onto a determinant  $\Phi_0$  is to generate another (nonnormalized) determinant

$$e^{\hat{T}_1} |\Phi_0\rangle = C |\tilde{\Phi}_0\rangle, \quad (8.61)$$

where  $C$  is a normalization constant. Therefore, the operator  $\hat{T}_1$  in CC theory may be viewed as creating a different Slater determinant than the reference. This observation explains the reason why CCSD is also very insensitive to the choice of orbitals used to form the reference determinant.

Note that the CC energy can be written in general as

$$\begin{aligned} \langle \Phi_0 | \hat{H} e^{\hat{T}} | \Phi_0 \rangle &= \langle \Phi_0 | \hat{H} \left( 1 + \hat{T}_1 + \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \dots \right) | \Phi_0 \rangle \\ &= E_{\text{HF}} + \sum_i^{\text{occ}} \sum_a^{\text{vir}} f_{ia} t_i^a + \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \langle ij || ab \rangle t_{ij}^{ab} + \frac{1}{2} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \langle ij || ab \rangle t_i^a t_j^b. \end{aligned} \quad (8.62)$$

The CCSD method is generally insufficient to achieve chemical high accuracy, defined as an error of 1 kcal mol<sup>-1</sup> or less. To improve the accuracy of CCSD one can add triples and arrive at the CCSDT method defined by the wave function

$$|\Psi_{\text{CCSDT}}\rangle = e^{\hat{T}_1 + \hat{T}_2 + \hat{T}_3} |\Phi_0\rangle, \quad (8.63)$$

however, the cost of this method is now proportional to  $O^3V^5$ ! A practical alternative is to introduce triples via perturbation theory. The most successful way to achieve this goal is the CCSD(T) method, which is considered by many the gold standard of quantum chemistry. In CCSD(T) one determines second-order triples,  $\hat{T}_3^{(2)}$ , and these are used to obtain fourth-order perturbative corrections to the energy [ $E^{(4)}$ ] that involve singles, double, and triples, which are added to the CCSD energy

$$E_{\text{CCSD(T)}} = E_{\text{CCSD}} + E_T^{(4)} + E_{ST}^{(4)} + E_{DT}^{(4)}. \quad (8.64)$$

The cost to evaluate  $E_{\text{CCSD(T)}}$  scales as  $O^3V^4$  and this method yields results that are generally of equal or better quality than CCSDT.

## Appendix: derivation of second-order perturbation theory

In Rayleigh–Schrödinger perturbation theory we partition the Hamiltonian into a zeroth-order part ( $\hat{H}^{(0)}$ ) plus a first-order perturbation ( $\hat{H}^{(1)}$ )

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}, \quad (8.65)$$

where  $\lambda$  is a parameter that ranges from 0 to 1. When  $\lambda = 0$  the Hamiltonian is equal to  $\hat{H}(0) = \hat{H}^{(0)}$ , while when  $\lambda = 1$  we recover the full Hamiltonian  $\hat{H}(1) = \hat{H}$ .

In perturbation theory we expand a given exact state  $\Psi_0$  and its corresponding eigenvalue  $E_0$  as a power series in  $\lambda$

$$|\Psi_0(\lambda)\rangle = |\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \lambda^2 |\Psi_0^{(2)}\rangle + \dots = \sum_{n=0}^{\infty} \lambda^n |\Psi_0^{(n)}\rangle, \quad (8.66)$$

$$E_0(\lambda) = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots = \sum_{n=0}^{\infty} \lambda^n E_0^{(n)}, \quad (8.67)$$

where  $|\Psi_0^{(n)}\rangle$  and  $E_0^{(n)}$  indicate a generic  $n$ -th order correction to the wave function and energy, respectively. For convenience, we assume that the zeroth-order wave function is normalized,

$$\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle = 1, \quad (8.68)$$

and that all corrections are orthogonal to  $|\Psi_0^{(0)}\rangle$ , that is

$$\langle \Psi_0^{(0)} | \Psi_0^{(n)} \rangle = 0, \quad n = 1, 2, \dots \quad (8.69)$$

This implies that the wave function satisfies the **intermediate normalization** convention, that is

$$\langle \Psi_0^{(0)} | \Psi_0 \rangle = 1. \quad (8.70)$$

To obtain order-by-order expressions for perturbation theory we plug in the definition of  $|\Psi_0(\lambda)\rangle$  and  $E_0(\lambda)$  into the Schrödinger equation

$$[\hat{H}^{(0)} + \lambda \hat{H}^{(1)}] |\Psi_0(\lambda)\rangle = E_0(\lambda) |\Psi_0(\lambda)\rangle, \quad (8.71)$$

more explicitly

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}) (|\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \dots) = (E_0^{(0)} + \lambda E_0^{(1)} + \dots) (|\Psi_0^{(0)}\rangle + \lambda |\Psi_0^{(1)}\rangle + \dots). \quad (8.72)$$

Next, we proceed to collect terms with the same value of  $\lambda$ . For example, we can explicitly identify the terms of order zero and one

$$\hat{H}^{(0)} |\Psi_0^{(0)}\rangle + \lambda (\hat{H}^{(0)} |\Psi_0^{(1)}\rangle + \hat{H}^{(1)} |\Psi_0^{(0)}\rangle) + \dots = E_0^{(0)} |\Psi_0^{(0)}\rangle + \lambda (E_0^{(1)} |\Psi_0^{(0)}\rangle + E_0^{(0)} |\Psi_0^{(1)}\rangle) + \dots \quad (8.73)$$

This equation must be valid for every value of  $\lambda$ , so terms with equal power of  $\lambda$  must be equal for each order of perturbation. The zeroth-order terms on both sides of this equation are

$$\hat{H}^{(0)} |\Psi_0^{(0)}\rangle = E_0^{(0)} |\Psi_0^{(0)}\rangle. \quad (8.74)$$

This equation tells us two things. First, it tells us that the zeroth-order wave function  $|\Psi_0^{(0)}\rangle$  must be an eigenfunction of  $\hat{H}^{(0)}$ . Second, if we apply  $\langle \Psi_0^{(0)} |$  from the left we get an expression for  $E_0^{(0)}$

$$\langle \Psi_0^{(0)} | \hat{H}^{(0)} | \Psi_0^{(0)} \rangle = \langle \Psi_0^{(0)} | E_0^{(0)} | \Psi_0^{(0)} \rangle = E_0^{(0)}. \quad (8.75)$$

The first-order terms give the equation

$$\hat{H}^{(0)} |\Psi_0^{(1)}\rangle + \hat{H}^{(1)} |\Psi_0^{(0)}\rangle = E_0^{(1)} |\Psi_0^{(0)}\rangle + E_0^{(0)} |\Psi_0^{(1)}\rangle. \quad (8.76)$$

Applying  $\langle \Psi_0^{(0)} |$  from the left to both sides we get

$$\langle \Psi_0^{(0)} | \hat{H}^{(0)} | \Psi_0^{(1)} \rangle + \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle = E_0^{(1)} \underbrace{\langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle}_{=1} + E_0^{(0)} \underbrace{\langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle}_{=0}, \quad (8.77)$$

and the last term drops because we assumed that  $\langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle = 0$ . The first term of this expression is zero as well because  $\langle \Psi_0^{(0)} | \hat{H}^{(0)} | \Psi_0^{(1)} \rangle = E_0^{(0)} \langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle = 0$ . Therefore, we get (after rearranging terms)

$$E_0^{(1)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle. \quad (8.78)$$

So we can compute the first-order energy correction from the zeroth-order wave function! That is like getting something for nothing.

To derive the first-order wave function we rearrange the terms in the Schrödinger equation

$$(\hat{H}^{(0)} - E_0^{(0)}) | \Psi_0^{(1)} \rangle = (E_0^{(1)} - \hat{H}^{(1)}) | \Psi_0^{(0)} \rangle. \quad (8.79)$$

Next we will project this expression onto the basis of eigenfunctions of  $\hat{H}^{(0)}$ . These are the states  $|\Psi_k^{(0)}\rangle$  with  $k = 0, 1, \dots$  that satisfy

$$\hat{H}^{(0)} | \Psi_k^{(0)} \rangle = E_k^{(0)} | \Psi_k^{(0)} \rangle. \quad (8.80)$$

After projection we need to simplify the expression a bit using Eq. (8.80)

$$\begin{aligned} \langle \Psi_k^{(0)} | (\hat{H}^{(0)} - E_0^{(0)}) | \Psi_0^{(1)} \rangle &= \langle \Psi_k^{(0)} | (E_0^{(1)} - \hat{H}^{(1)}) | \Psi_0^{(0)} \rangle \\ \langle \Psi_k^{(0)} | (E_k^{(0)} - E_0^{(0)}) | \Psi_0^{(1)} \rangle &= - \langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle \\ (E_k^{(0)} - E_0^{(0)}) \langle \Psi_k^{(0)} | \Psi_0^{(1)} \rangle &= - \langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle. \end{aligned} \quad (8.81)$$

Assuming that  $\Psi_0^{(0)}$  is not degenerate with any of the excited states  $\Psi_k^{(0)}$ , all of the terms with  $k \neq 0$  of the last expression can be divided by  $(E_k^{(0)} - E_0^{(0)})$  to obtain

$$\langle \Psi_k^{(0)} | \Psi_0^{(1)} \rangle = \frac{\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}}. \quad (8.82)$$

Note, however, that when  $k = 0$ , the term  $\langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle = 0$  because we assumed it so when we choose to use intermediate normalization.

With this information we can now construct the first-order wave function correction. If we multiply  $|\Psi_0^{(1)}\rangle$  by the resolution of the identity  $\hat{1} = \sum_{k=0}^{\infty} |\Psi_k^{(0)}\rangle \langle \Psi_k^{(0)}|$  we can write [using Eq. (8.82) to express  $\langle \Psi_k^{(0)} | \Psi_0^{(1)} \rangle$ ]

$$\begin{aligned} |\Psi_0^{(1)}\rangle &= \sum_{k=0}^{\infty} |\Psi_k^{(0)}\rangle \langle \Psi_k^{(0)} | \Psi_0^{(1)} \rangle \\ &= \sum_{k>0}^{\infty} \frac{\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} |\Psi_k^{(0)}\rangle \\ &= \sum_{k>0}^{\infty} C_k^{(1)} |\Psi_k^{(0)}\rangle. \end{aligned} \quad (8.83)$$

Note that the sum excludes the term with  $k = 0$  because  $\langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle = 0$ . The quantity  $\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle$  that appears in this expression is nothing else than the first-order wave function coefficient  $C_k^{(1)}$  for determinant  $|\Psi_k^{(0)}\rangle$

$$C_k^{(1)} = \frac{\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}}. \quad (8.84)$$

This quantity is proportional to the off-diagonal matrix element of the first-order Hamiltonian  $\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle$  (also called a coupling term), and inversely proportional to  $E_0^{(0)} - E_k^{(0)}$ , which is an energy difference between two zeroth-order states.

At second-order the Schrödinger equation gives

$$\hat{H}^{(0)} |\Psi_0^{(2)}\rangle + \hat{H}^{(1)} |\Psi_0^{(1)}\rangle = E_0^{(2)} |\Psi_0^{(0)}\rangle + E_0^{(1)} |\Psi_0^{(1)}\rangle + E_0^{(0)} |\Psi_0^{(2)}\rangle. \quad (8.85)$$

From this expression we can derive  $E_0^{(2)}$  by projecting on the left by  $\langle \Psi_0^{(0)} |$  and removing all the zero terms

$$E_0^{(2)} = \langle \Psi_0^{(0)} | \hat{H}^{(1)} | \Psi_0^{(1)} \rangle = \sum_{k>0}^{\infty} \frac{|\langle \Psi_k^{(0)} | \hat{H}^{(1)} | \Psi_0^{(0)} \rangle|^2}{E_0^{(0)} - E_k^{(0)}}. \quad (8.86)$$

The last term was obtained using the expression for  $|\Psi_0^{(1)}\rangle$  we derived before.

## CHAPTER 9

# General Advice for Running Quantum Chemistry Computations

### 9.1 Choosing the right units, geometry input, and selecting the electronic state

As you setup a computation you will have several options for providing information about your molecule to a quantum chemistry program. The molecular geometry is usually specified by either in xyz or zmat format. In the xyz format you provide a list of the element symbol (AtomI) and the  $(x, y, z)$  coordinates (XI YI ZI):

```
Atom1 X1 Y1 Z1
Atom2 X2 Y2 Z2
...
AtomM XM YM ZM
```

In the zmat format, the geometry is specified via internal coordinates, that is, via bond lengths (RIJ), bond angles (ThetaIJK), and , bond dihedral angles (PhiIJKL):

```
Atom1
Atom2 I R2I
Atom3 I R3I J Theta3IJ
Atom4 I R4I J Theta4IJ K Phi4IJK
Atom5 I R5I J Theta5IJ K Phi5IJK
...
```

Most programs assume that the  $(x, y, z)$  coordinates are given in units of Ångstrom (Å), but keywords may be provided to switch to atomic units (bohr).

Other important inputs to quantum chemistry computations are the charge and spin multiplicity of the electronic state we are interested in studying. The charge determines the total number of electrons, since

$$\text{charge} = \sum_{\alpha=1}^M Z_{\alpha} - N_{\alpha} - N_{\beta}, \quad (9.1)$$

while the spin multiplicity  $S = 2M_S + 1$  determines the difference  $N_{\alpha} - N_{\beta}$  since

$$M_S = \frac{1}{2}(N_{\alpha} - N_{\beta}). \quad (9.2)$$

The charge and spin multiplicity are specified at the beginning of an input file. For example, to run a computation on a singlet state of the methane molecule ( $\text{CH}_4$ ), we indicate a charge equal to 0 (first number in the second line) and a multiplicity  $S = 2M_s + 1 = 2 \times 0 + 1 = 1$  ( $M_S = 0$  because there are equal number of alpha and beta electron in a singlet state)

```

set molecule methane {
0 1 # <- charge multiplicity
C      -0.7174019291      0.3273733834      0.0000000000
H       0.3525980709      0.3273733834      0.0000000000
H      -1.0740647110      1.3198547045     -0.1807553242
H      -1.0740695669     -0.0123274364      0.9498902827
H      -1.0740708618     -0.3254059329     -0.7691335623
}

```

For a tutorial on the Psi4 package check out this link:

[http://www.psi4.org/psi4manual/master/index\\_tutorials.html](http://www.psi4.org/psi4manual/master/index_tutorials.html)

## 9.2 Choice of the basis set

Next, you will have to select a basis set to perform your computations. In this case it is important to distinguish between DFT and wave function computations.

- For DFT and Hartree–Fock computations common choices include Pople’s 6-31G\* and 6-31G\*\* basis sets but I would discourage you from using these because they are now obsolete. Better, use the Karlsruhe basis sets (def2-SVP, def2-TZVP, def2-QZVP, def2-TZVPD, ...). For routine computations, a def2-TZVP basis should provide nearly-converged results.
- For wave function methods like MP2, CCSD, CCSD(T), etc., Dunning’s correlation-consistent basis sets (cc-pVXZ, with  $X = D, T, Q, 5$ ) are recommended. These are families of basis sets that systematically converge to the full basis set limit. The cc-pVDZ basis is likely to provide reasonable, but potentially inaccurate results. A cc-pVTZ basis is generally recommended for routine applications. For highly-accurate benchmark results it is necessary to use the cc-pVQZ or cc-pV5Z basis sets.
- Note that to describe Rydberg states, long range interactions, and anions it is generally recommended to add diffuse functions to your basis. For the Pople/Karlsruhe basis sets you will see the symbols “+” and “D”, while the correlation-consistent basis sets add the “aug-” prefix to the basis set name.
- Dunning’s basis sets (cc-pVXZ) are meant to correlate only valence electrons, so core electrons should be frozen in computations that use them. To account for core electron correlation it is necessary to use a core-valence set, usually indicated with the symbol cc-pCVXZ, or the newer weighted core-valence sets (cc-pwCVXZ).
- Other variants of Dunning’s basis sets include basis extended for period 3 atoms [cc-pV(X+d)Z], pseudopotential basis sets for heavy elements [cc-pVXZ-PP], and basis sets for relativistic computations [cc-pVXZ-DK].

**Note, that is common practice in Quantum Chemistry to cite the original reference to the basis sets employed in a computation. Crafting a basis set for a large number of elements in the periodic table takes a lot of work and the people that invested the time doing so deserve credit.**

A great resource for finding the definition of basis sets and the papers in which they were introduced is the Basis Set Exchange website:

<https://www.basissetexchange.org>.

## 9.3 Methods for ground-state computations

Any exploratory study should start with a DFT computation using a modest basis set (e.g., def2-SVP) using well-established functionals like (B3LYP). Density functional theory, with their low computational scaling ( $N^4$ , where  $N$  is the number of electrons), are generally applicable to numerous problems where one is interested only in the ground state. Hartree–Fock theory, is generally not sufficiently accurate for any application, unless it is followed by a correlated wave function computation.

Møller–Plessett perturbation theory methods (MP2, MP3, etc.) are more expensive than DFT as they scale as  $N^5$  or higher. MP2 is in many case qualitatively correct and gives particularly good results for geometries. Beyond second order, the MP series is not guaranteed to converge and it is preferable to use coupled cluster methods.

Coupled cluster theory with singles and double (CCSD) is generally regarded as a very good method, but cannot provide energies with chemical accuracy (defined as a relative error less than 1 kcal/mol). This method scales as  $N^6$  and is already quite expensive. The gold standard in correlated wave function computations is the CCSD(T) method, which augments CCSD with perturbative corrections for triple substitutions [(T)].

## 9.4 Excited state methods

When one is interested in going beyond the ground state there are fewer options. A common choice is time-dependent DFT (TD-DFT). TD-DFT can provide excitation energies of good quality, although it is known to fail in many instances. Special functionals have been developed to describe Rydberg and charge-transfer excitations (range separated) and you should use one of them if you are interested in computing spectra.

At the wave function level, a common method for excited states is configuration interaction with singles (CIS). CIS uses a combination of singly substituted Slater determinants obtained by promoting an electron in an occupied orbital to a virtual one. CIS is not very accurate but it is economical. In coupled cluster theory, excited states may be obtained via the equation-of-motion approach (EOM-CC) or the very similar linear-response formalism (LR-CC). EOM-CCSD is a good choice (although expensive) for computing accurate excitation energies. Other methods include the second- and third- order algebraic-diagrammatic construction [ADC(2)/ADC(3)] and the CC2/CC3 methods, which are approximations of EOM-CC theory.

## 9.5 Troubleshooting computations

### 9.5.1 Self-consistent-field (SCF) procedure

What could go wrong in a quantum chemistry computation? Well, there are several aspects that can fail, but the most important and frequent is failure of the self-consistent-field (SCF) procedure in Hartree–Fock and DFT to converge. When this part of the computation does not converge, the rest of the results may be meaningless. Be careful, because some programs will continue to run even if the SCF procedure did not converge!

There are several things that you can try to do if your SCF computation does not converge:

- Increase the number of SCF iterations that the code is allowed to perform.
- Change the initial orbital guess. A program may have different ways to guess the initial orbitals used in a SCF procedure.
- Change the basis set. In general large basis sets or basis sets with diffuse functions will be more problematic to converge. Another solution is to converge the SCF procedure with a small basis set and then to use these orbitals as guesses for a computation with a larger basis.

- In certain cases, it is possible to use other convergence tricks. One is level shift, which consists in shifting the energy of unoccupied orbitals. This works for certain cases (diradicals and triplet states). Some code may implement some more refined methods to improve convergence, check the manual.

### 9.5.2 Finding the right SCF solution, symmetry, and orbital occupation

Even if the SCF procedure converges, sometimes the solution found is wrong. This can happen if you are stretching bonds, or have many diffuse functions, or if the molecule has symmetry. When you find a wrong SCF solution you may find some strange outcomes, for example, the energy of the LUMO may be lower than that of the HOMO, like in the calculation below on  $N_2$ :

```
==> Iterations <==
                        Total Energy      Delta E      RMS |[F,P]|
@DF-RHF iter   1:  -104.05276519746047  -1.04053e+02  1.84072e-01 DIIS
...
@DF-RHF iter   8:  -107.84466525047402  -3.15438e-10  2.08693e-07 DIIS
Energy and wave function converged.

Orbital Energies [Eh]
-----

Doubly Occupied:

      1Ag  -15.685996      1B1u  -15.682880      2Ag   -1.391910
      1B3u  -0.658683      1B2u   -0.588756      3Ag   -0.529034
      1B2g   -0.235918

Virtual:

      2B1u   -0.390811      1B3g    0.185252      3B1u    0.580952
```

In this example, the LUMO ( $2B_{1u}$ ) has orbital energy  $\epsilon_{\text{LUMO}} = -0.391E_h$  lower than the HOMO  $\epsilon_{\text{HOMO}} = -0.236E_h$ .

In this case the SCF procedure converged to the wrong solution because of an incorrect guess of the occupation of orbitals due to symmetry. For  $N_2$  there are 8 irreducible representations in the large Abelian point group ( $D_{2h}$ ). The SCF program has to guess how many orbital of each irrep should be occupied with electrons. If it guesses wrong, then the SCF procedure may get stuck and you end up with the wrong occupation numbers. In this case the program guessed the following occupation for the doubly occupied orbitals (DOCC):

```
      Ag  B1g  B2g  B3g  Au  B1u  B2u  B3u
DOCC = [  3,   0,   1,   0,   0,   1,   1,   1 ]
```

If we change the occupation so that the LUMO is occupied and the HOMO not, that is, we set

```
      Ag  B1g  B2g  B3g  Au  B1u  B2u  B3u
DOCC = [  3,   0,   0,   0,   0,   2,   1,   1 ]
```

then we get the correct solution

```
@DF-RHF iter   1:  -99.92277294845300  -9.99228e+01  2.54521e-01 DIIS
...
@DF-RHF iter   9:  -108.95348837895291  -1.85295e-10  1.00773e-07 DIIS
Energy and wave function converged.
```



## Orbital Energies [Eh]

-----

Doubly Occupied:

1Ag	-15.687294	1B1u	-15.683937	2Ag	-1.469609
2B1u	-0.774890	3Ag	-0.626042	1B2u	-0.607131
1B3u	-0.607131				

Virtual:

1B2g	0.174361	1B3g	0.174361	3B1u	0.593802
------	----------	------	----------	------	----------

You can see that the final energy in this computation is significantly smaller than the previous one ( $-108.953488$  vs.  $-107.844665250 E_h$ ).

In other cases, changing occupation numbers is not enough and you might have to run a **stability analysis**. A stability analysis is similar to a harmonic frequency analysis, but instead of moving the nuclei around we test if the SCF solution is stable with respect to changes in the orbitals. In a stability analysis one computes the Hessian with respect to orbital rotations. The presence of one or more negative eigenvalues of the Hessian indicate that the SCF solution is unstable. Some programs allow you to use the information from a stability analysis to find a better (more stable) solution.

As a first example consider the following computation on  $O_2$

```
molecule h2 {
  0 1
  0
  0 1 1.22220
  symmetry c1
}

set basis cc-pVDZ
set reference uhf
set stability_analysis follow
energy ('scf')
```

Initially the SCF procedure finds a singlet (multiplicity = 1) solution

	Total Energy	Delta E	RMS   [F,P]
@DF-UHF iter SAD:	-148.80750855152425	-1.48808e+02	0.00000e+00
...			
@DF-UHF iter 6:	-149.53968837671806	-5.73920e-08	9.50024e-07 DIIS

Energy and wave function converged.

==> Post-Iterations <==

@Spin Contamination Metric:	-2.842170943E-14
@S <sup>2</sup> Expected:	0.000000000E+00
@S <sup>2</sup> Observed:	-2.842170943E-14

We can tell this is a singlet solution because the expectation value of  $\hat{S}^2$  is practically zero. However, this solution is not stable as the following analysis reveals

Negative totally symmetric eigenvalue detected: -0.111172

```
Wavefunction unstable!
Lowest UHF->UHF stability eigenvalues:
A -0.111172
```

```
Rotating orbitals by 0.500000 * pi / 2 radians along unstable eigenvector.
Running SCF again with the rotated orbitals.
@DF-UHF iter 7: -149.58236352738325 -1.49582e+02 2.51289e-03 DIIS
...
@DF-UHF iter 14: -149.59625391005312 -1.61574e-08 7.49422e-07 DIIS

==> Post-Iterations <==
```

```
@Spin Contamination Metric: 1.064489505E+00
@S^2 Expected: 0.000000000E+00
@S^2 Observed: 1.064489505E+00
```

The end of this computation shows that the final UHF wave function is spin contaminated, that is, the expectation value of  $\hat{S}^2$  is quite different from the allowed values  $S(S+1) \in \{0, 2, 6, \dots\}$ . The value of  $\hat{S}^2$  between 0 and 2 indicates that it is possible that a triplet solution may be more stable. We can check this easily by running a triplet computation

```
molecule h2 {
  0 3
  0
  0 1 1.22220
  symmetry c1
}
```

```
set basis cc-pVDZ
set reference uhf
energy ('scf')
```

The following output shows that the final energy is even lower than the previous computation and that the observed average value of  $\hat{S}^2$  (2.0338) is close to the one expected for a triplet state (2.0)

	Total Energy	Delta E	RMS  [F,P]
@DF-UHF iter SAD:	-148.80750855152425	-1.48808e+02	0.00000e+00
...			
@DF-UHF iter 7:	-149.62449435085691	-1.13297e-08	8.35935e-07 DIIS

Energy and wave function converged.

```
==> Post-Iterations <==
```

```
@Spin Contamination Metric: 3.383018297E-02
@S^2 Expected: 2.000000000E+00
@S^2 Observed: 2.033830183E+00
```

### 9.5.3 Failure of the mean-field approximation

In certain cases, a stability analysis can reveal issues with the assumption that the wave function is well described by a single determinant. In general, a single Slater determinant is insufficient to describe states that are near-degenerate. This may happen when there are several near-degenerate orbitals that can be occupied in several ways. When a single Slater determinant is

insufficient we need a method like CASSCF that uses a linear combination of determinants to describe an electronic state.

As an example, consider  $H_2$  with a bond distance (1.5 Å) that is twice the equilibrium one. If we run a restricted Hartree–Fock (RHF) computation we get

```
==> Iterations <==

                Total Energy          Delta E          RMS | [F,P] |
@DF-UHF iter SAD:    -0.76784932808581  -7.67849e-01    0.00000e+00
@DF-UHF iter   1:    -1.00141998955223  -2.33571e-01    2.75241e-03 DIIS
...
@DF-UHF iter   4:    -1.00219852882535  -2.24884e-08    2.49903e-08 DIIS
Energy and wave function converged.
```

However, a stability analysis reveals that this wave function is unstable and that an unrestricted HF (UHF) solution exists

```
Negative totally symmetric eigenvalue detected: -0.107448
Wavefunction unstable!
Lowest RHF->UHF stability eigenvalues:
  A -0.107448

Rotating orbitals by 0.500000 * pi / 2 radians along unstable eigenvector.
Running SCF again with the rotated orbitals.
@DF-UHF iter   5:    -1.00996434718943  -1.00996e+00    8.98053e-03 DIIS
...
@DF-UHF iter  11:    -1.02138009771254  -5.27588e-09    1.55929e-07 DIIS
```

The solution found after following the mode with negative eigenvalue is lower in energy. A second stability analysis reveals that the UHF solution we found is now stable:

```
Wavefunction stable under totally symmetric rotations.
Lowest totally symmetric eigenvalue: 0.177523
Lowest UHF->UHF stability eigenvalues:
  A 0.177523

Stability analysis over.
```

```
==> Post-Iterations <==
```

```
@S^2 Expected:          0.000000000E+00
@S^2 Observed:          5.824960917E-01
```

The UHF solution is spin contaminated since the expectation value of  $\hat{S}^2$  is ca. 0.5825 instead of 0, as it should be for a singlet state. In this case, the problem is that a single Slater determinant cannot properly describe bond breaking in  $H_2$ . As we have seen in the section on FCI, we need at least two determinants to describe the wave function of  $H_2$  correctly in the dissociation limit. This can be done by running a multiconfigurational SCF calculation, where one optimizes both the orbitals and determinant coefficients of a FCI computation done on a small subset of so-called active orbitals. When we consider all determinants generated by distributing the active electrons in all possible ways we talk of a complete-active-space SCF (CASSCF) computation. Running a CASSCF computation on  $H_2$  with two electrons in two orbitals we get a singlet solution that is lower than the RHF and UHF solutions

```
==> Starting MCSCF iterations <==
```

	Iter	Total Energy	Delta E	Orb RMS	CI RMS
@MCSCF	1:	-1.035694387154	-3.3496e-02	2.82e-02	4.23e-16
...					
@MCSCF	8:	-1.056125382298	-2.8041e-08	6.30e-06	1.67e-15

The 4 most important determinants:

*	1	-0.951333	20>
*	2	0.308164	02>

In the last two lines of this output we can read the coefficients associated with the determinants included in the CASSCF procedure, where the determinants are indicated as a list of number with the occupation of each orbital (0, +, -, or 2 for empty, single alpha electron, single beta electron, and doubly occupied, respectively).

### 9.5.4 Geometry optimization

Another common failure is lack of convergence in geometry optimizations. Here is a list of things to consider:

- Do not use an optimized geometry unless you have verified that the geometry optimization has actually converged.
- Geometry optimization can be slow to converge, especially if the atoms have to “go around a corner”. Since geometry optimizers usually estimate the Hessian instead of computing the exact one, starting the optimization with the full Hessian may improve convergence. This is particularly true of transition state searches. Most of the time, you can significantly reduce the cost to compute the Hessian by using smaller basis or less expensive method.
- Some molecules are hard to optimize due to the choice of optimization coordinates. Sometimes you can improve convergence by using more complex coordinate systems.
- Once you have found a stationary point, run a frequency analysis to verify that the geometry is a local minimum or a transition state.
- Another aspect to keep in mind is that in certain codes, geometry optimization cannot proceed from a geometry with high symmetry (e.g.,  $D_{2h}$ ) to low symmetry (e.g.,  $C_1$ ). If you want to find a minimum, it is generally a good idea to start with a guess geometry that has no symmetry and let the optimizer determine if the minimum is symmetric. Again, this is why it is important to run a frequency analysis after a geometry optimization to verify the nature of the stationary point.

## CHAPTER 10

# Multireference wave function methods

In this chapter we will discuss methods can be used to treat bond break process and electronically excited states.

### 10.1 Multiconfigurational self-consistent-field theory

As we have seen previously, in many cases the Hartree–Fock method is usually captures a large fraction of the total electronic energy. This is usually true of closed-shell molecules and high-spin open-shells. However, we have also encountered cases, like for example, the  $H_2$  molecule the dissociation limit, where a single determinant wave function fails to capture even the correct qualitative behavior of the electrons.

In this section we will discuss multiconfigurational self-consistent-field (MCSCF) methods, which may be viewed as generalizations of Hartree–Fock theory. In MCSCF methods, an electronic state is approximated with a small configuration interaction wave function

$$|\Psi_{\text{MCSCF}}\rangle = \sum_I C_I |\Phi_I\rangle, \quad (10.1)$$

in which both the orbitals ( $\phi_i$ ) from which the determinants ( $\Phi_I$ ) and the determinant coefficients ( $C_I$ ) are variationally optimized. Note, that in general, that they determinants employed to expand the MCSCF wave function (understood as occupation patterns of electrons) are not changed in the optimization process.

The MCSCF energy is obtained by performing a simultaneous optimization of the orbitals and the determinant coefficients

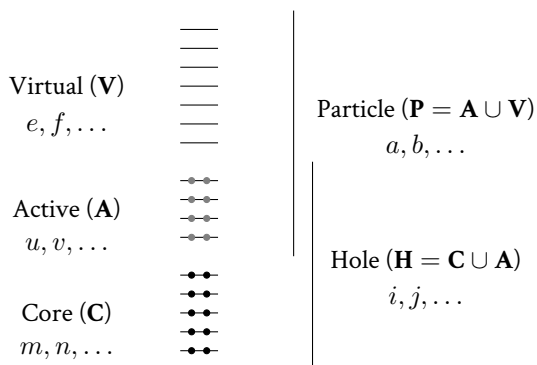
$$E_{\text{MCSCF}} = \min_{C_I, \{\psi_i\}} \langle \Psi_{\text{MCSCF}} | \hat{H} | \Psi_{\text{MCSCF}} \rangle, \quad (10.2)$$

imposing that the determinant vector is normalized ( $\sum_I |C_I|^2 = 1$ ) and the orbitals are orthonormal. It is always implicitly assumed that the MCSCF wave function is constructed using restricted spin orbitals so that the alpha and beta spatial parts of a given orbital are the same.

Different MCSCF methods are defined by the way the determinant are selected. The most widely used approach is the complete-active-space self-consistent-field (CASSCF) method, which basically forms all the MCSCF determinant by performing a FCI in a limited number of orbitals. In CASSCF one starts by partitioning the orbitals into three spaces:

- **Core (or doubly occupied) orbitals (C).** These orbitals are generally the lowest one in energy and are kept doubly occupied in all the determinants in the CASSCF wave function.

- **Active orbitals (A).** These orbitals have variable occupation in the CASSCF wave function. In most cases these are chosen to be valence orbital associated with the particular aspect we want to model. For example, for to describe the wave function for the single bond-breaking reaction  $A-B \longrightarrow A+B$  it is sufficient to include a single pair of A-B bonding/antibonding orbitals.
- **Virtual orbitals (V).** These orbitals are not occupied in the CASSCF wave function. These are usually high-energy orbitals that are typically irrelevant to description of a chemical reaction or an excited state.



In CASSCF one generates determinants with the core orbitals occupied and  $n_A$  active electrons distributed in the active orbitals. Therefore, a generic CASSCF determinant has the form

$$|\Phi_I\rangle = \underbrace{\hat{a}_u^\dagger \hat{a}_v^\dagger \cdots \hat{a}_z^\dagger}_{\text{active}} \prod_m^{\mathbf{C}} \hat{a}_m^\dagger |\rangle. \quad (10.3)$$

In the literature, and active space in which a given number of electrons ( $n_{\text{el}}$ ) is distributed in a given number of active orbitals ( $n_A$ ) is abbreviated with  $\text{CAS}(n_{\text{el}}, n_A)$ . For example, an active space with two electrons in two orbitals is denoted  $\text{CAS}(2e, 2o)$ .

In CASSCF, the space of determinants is **complete**, in the sense that all possible determinants are included. One consequence of this choice is that the wave function is invariant with respect to unitary transformations of the active orbitals. This means that if we transform the active orbitals via a unitary transformation  $\mathbf{U}$

$$\psi_u \rightarrow \psi'_u = \sum_v \psi_v U_{vu}, \quad (10.4)$$

and consequently all the determinant change according to

$$|\Phi_I\rangle = |\psi_{i_1} \psi_{i_2} \cdots \psi_{i_N}\rangle \rightarrow |\Phi'_I\rangle = |\psi'_{i_1} \psi'_{i_2} \cdots \psi'_{i_N}\rangle, \quad (10.5)$$

there is a corresponding set of CI coefficients  $C'_I$  such that the transformed CASSCF wave function is identical to the original one

$$\sum_I C_I |\Phi_I\rangle = \sum_I C'_I |\Phi'_I\rangle. \quad (10.6)$$

This property implies that we are free to work with any unitarily transformed version of the CASSCF active orbitals (e.g., delocalized, localized).

Note that since the CAS space includes all possible determinants, its size grows very quickly with the number of active orbitals and electrons. If we ignore point group symmetry, we can compute the number of determinants with a given number of alpha ( $n_\alpha$ ) and beta ( $n_\beta$ ) electrons in the active orbitals just by counting how many arrangements of electrons are possible for the two spin cases. For each spin case, the number of ways we can distribute  $n$  electrons is

given by the number of ways we can choose  $n$  spin orbitals to occupy and taking into account that permutations are equivalent. This quantity is given by the binomial coefficient

$$\binom{n}{k} = \frac{n!}{(n-k)!k!}, \quad (10.7)$$

where  $n! = 1 \times 2 \times \dots \times n$ , and  $0! = 1$  by definition. The total number of determinants ( $d$ ) is given by the product of the number of arrangements of alpha and beta electrons

$$d = \binom{n_A}{n_\alpha} \binom{n_A}{n_\beta}. \quad (10.8)$$

As shown in Tab. 10.1, this quantity grows very quickly, and therefore, practical computations are typically limited to active spaces of size CAS(16e,16o).

Size of the active space		
Active electrons	Active orbitals	CAS determinants
2	2	4
4	4	36
6	6	400
8	8	4,900
10	10	63,504
12	12	853,776
14	14	11,778,624
16	16	165,636,900
18	18	2,363,904,400
20	20	34,134,779,536

Table 10.1: Number of determinants in a CAS space at half filling. These numbers ignore the reduction in size due to point group symmetry.

Note that one can also define a corresponding CASCI approach in which one generated a CAS space and performs the variational optimization of the CI coefficients **without** optimizing the orbitals.

## 10.2 Multireference configuration interaction

The CASSCF method can only account for static correlation effects, which in practice is not enough to accurately describe multideterminantal electronic states. The simplest way to include dynamical correlation effects on top of a CASSCF reference is via a configuration interaction wave function. In the multireference configuration interaction (MRCI) approach, one starts with a CASSCF reference and adds excited determinants that account for dynamical correlation effects. The simplest approach is **uncontracted** MRCI with singles and doubles (u-MRCISD), in which one simply augments the CASSCF determinant space with all singly and doubly excited determinants of each reference determinant. The u-MRCISD wave function is given by

$$|\Psi_{\text{u-MRCI}}\rangle = \sum_I^{\text{CAS}} C_I |\Phi_I\rangle + \sum_A^{\text{EXT}} C_A |\Phi_A\rangle, \quad (10.9)$$

where the space of external determinants is generated by applying the operators  $\hat{a}_a^\dagger \hat{a}_i$  and  $\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i$  to all the CAS determinants

$$\text{EXT} = \{|\Phi_A\rangle | \Phi_A = \hat{a}_a^\dagger \hat{a}_i |\Phi_I\rangle, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |\Phi_I\rangle \forall \Phi_I \in \text{CAS}\}. \quad (10.10)$$

In defining the EXT space, the orbital indices  $i, j$  run over the core and active orbitals, while  $a, b$  run over the active and virtuals. The u-MRCISD method provides very accurate results, but it has a computational scaling that becomes quickly unmanageable when the number of CAS determinants is large. The approximate number of u-MRCISD determinants depends on the number of hole ( $N_H$ ) and particle ( $N_P$ ) orbitals and is proportional to

$$N_{\text{det}}^{\text{u-MRCISD}} = d N_H^2 N_P^2, \quad (10.11)$$

which is limited both by the size of the active space ( $d$ ) and the number of electrons and basis functions used.

A more economical alternative to the u-MRCISD method is the **internally-contracted** MRCISD (ic-MRCISD) method. In ic-MRCISD, one still generates all possible singles and doubles out of a CAS; however, an excitation operator is applied to the entire CAS reference all at once. For example, internally-contracted singly excited configurations are defined as

$$|\Psi_i^a\rangle = \hat{a}_a^\dagger \hat{a}_i |\Psi_{\text{CAS}}\rangle = \sum_I C_I \hat{a}_a^\dagger \hat{a}_i |\Phi_I\rangle. \quad (10.12)$$

The right hand side of this equation shows that  $|\Psi_i^a\rangle$  is a linear combination of excited determinants ( $\hat{a}_a^\dagger \hat{a}_i |\Phi_I\rangle$ ) with coefficients fixed to the value of the CAS wave function ( $C_I$ ).

The ic-MRCISD wave function is defined by the following wave function guess

$$\begin{aligned} |\Psi_{\text{ic-MRCISD}}\rangle &= (1 + \hat{C}) |\Psi_{\text{CAS}}\rangle \\ &= \sum_I C_I |\Phi_I\rangle + \sum_i \sum_a c_i^a \hat{a}_a^\dagger \hat{a}_i |\Psi_{\text{CAS}}\rangle + \frac{1}{4} \sum_{ij} \sum_{ab} c_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i |\Psi_{\text{CAS}}\rangle \\ &= \sum_I C_I |\Phi_I\rangle + \sum_i \sum_a c_i^a |\Psi_i^a\rangle + \frac{1}{4} \sum_{ij} \sum_{ab} c_{ij}^{ab} |\Psi_{ij}^{ab}\rangle, \end{aligned} \quad (10.13)$$

where the coefficients  $c_i^a$  and  $c_{ij}^{ab}$  are obtained by minimizing the energy of the ic-MRCISD wave function. Therefore, the number of variational parameters in the ic-MRCISD wave function is of the order of  $N_H^2 N_P^2$ , which is significantly less than the corresponding for u-MRCISD. The lower scaling of ic-MRCISD makes it the methods of choice among all variants of MRCI. Note, however, that there are several very important variants of MRCI that only partially contract the wave function.

### 10.3 Multireference perturbation theory and coupled cluster theory

It is also possible to generalize perturbation theory to the case of a multideterminantal reference. As for standard Møller–Plesset perturbation theory, one has to select a partitioning of the Hamiltonian into zeroth- plus first-order terms. In the case of multideterminantal references this choice is not straightforward and several choices have been considered. The simplest strategy is to employ a **diagonal** one-body zeroth-order operator, like in Møller–Plesset perturbation theory, for example

$$\hat{H}_0 = \sum_p \epsilon_p \hat{a}_p^\dagger \hat{a}_p, \quad (10.14)$$

however, a more common choice employs a general one-body operator

$$\hat{F} = \sum_{pq} f_{pq} \hat{a}_p^\dagger \hat{a}_q, \quad (10.15)$$



where  $f_{pq}$  are matrix elements of the average Fock matrix and are computed as

$$f_{pq} = \langle \Psi^{(0)} | [\hat{a}_p, [\hat{H}, \hat{a}_q^\dagger]]_+ | \Psi^{(0)} \rangle. \quad (10.16)$$

Then the corresponding zeroth-order Hamiltonian is expressed as

$$\hat{H}_0 = \hat{P}_{\text{CAS}} \hat{H} \hat{P}_{\text{CAS}} + \hat{P}_{\text{SD}} \hat{F} \hat{P}_{\text{SD}}, \quad (10.17)$$

where  $\hat{P}_{\text{CAS}}$  and  $\hat{P}_{\text{SD}}$  are projection operators defined in terms of the CAS determinants and all singly and doubly excited determinants generated from the CAS (SD). For example,  $\hat{P}_{\text{CAS}}$  is defined as

$$\hat{P}_{\text{CAS}} = \sum_I^{\text{CAS}} |\Phi_I\rangle \langle \Phi_I|. \quad (10.18)$$

Another way to define  $\hat{F}$  is using the Dyll partitioning, which includes two-body terms in the active space. Note that it was also found beneficial to apply a shift to the active orbital energies (IPEA shift) to

Like for MRCI, one can develop various contracted variants of MRPT: uncontracted, partially-contracted, internally-contracted, and strongly contracted. All of these differ in the number of variational degrees of freedom. The most common formulation of MRPT are the second-order CAS perturbation theory (CASPT2) and second-order  $n$ -electron valence perturbation theory (NEVPT2). Describing these approaches in detail is beyond the scope of these notes and the interested reader is urged to consult the primary literature.

Many variants of multireference coupled cluster (MRCC) methods have also been proposed. These can be divided in four broad categories. The first is Fock-space multireference coupled cluster methods, which aim to describe states with different number of electrons. The second one is Jeziorski–Monkhorst methods, which employ an uncontracted ansatz of the form

$$|\Psi_{\text{JM-MRCC}}\rangle = \sum_I^{\text{CAS}} C_I e^{\hat{T}^I} |\Phi_I\rangle. \quad (10.19)$$

The third type is internally-contracted MRCC theories, which generalize the ic-MRCI method and are based on the following ansatz

$$|\Psi_{\text{ic-MRCC}}\rangle = e^{\hat{T}} |\Psi_{\text{CAS}}\rangle = \sum_I^{\text{CAS}} C_I e^{\hat{T}} |\Phi_I\rangle. \quad (10.20)$$

There are also a large number of methods that use the single-reference CC ansatz but modify it so that it can describe some type of wave functions with mild multideterminantal character. Some example include methods-of-moment CC, equation-of-motion spin-flip CC, and the CCSDt/CCSDtq methods.