

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.¹ 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 ε_{jkl} is the Levi-Civita symbol defined as

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

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 α and β ²

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

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

¹ 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.

² 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 ω is a fictitious spin variable. This allow us to treat $\alpha(\omega)$ and $\beta(\omega)$ as traditional wave functions. For example, the orthogonality condition [Eq. (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.³ 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 $\{\phi_i(\vec{r})\}$

³A 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:⁴

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

⁴We 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 σ and σ' are different.

To avoid having to write the two subscripts i and σ every time we indicated a spin orbital, we will often collect the indices (i, σ) 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 Φ 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:

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

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

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

■

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

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

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.⁵ Therefore, we may expand any electronic wave function Ψ using the Slater determinant basis:

⁵This 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_{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 ω_1 and ω_2 we can derive a probability distribution that depends only on the positions of the electrons:

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

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 H_2

In this section we will do an extensive study of the wave function of H_2 in a minimal basis set. Consider two hydrogen atoms (H_A and H_B) separated by a distance R_{AB} . We will assume that each atom has one atomic basis function, $\chi_{1s}^{\text{A}}(\mathbf{r})$ 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.⁶ We may form six unique determinants:

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

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

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

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

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

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

Symmetry greatly simplifies this problem.⁷ The determinants $|\Phi_1\rangle$ and $|\Phi_4\rangle$ are gerade since the product $\psi_g\psi_{\bar{g}}$ has symmetry equal to $g \times g = g$.⁸ 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
Φ_1	$\psi_g\psi_{\bar{g}}$	g	0
Φ_2	$\psi_g\psi_{\bar{u}}$	u	0
Φ_3	$\psi_u\psi_{\bar{g}}$	u	0
Φ_4	$\psi_u\psi_{\bar{u}}$	g	0
Φ_5	$\psi_g\psi_u$	u	1
Φ_6	$\psi_{\bar{g}}\psi_{\bar{u}}$	u	-1

(3.69)

⁶Just to avoid confusion: a spatial orbital may accommodate two electrons (with opposite spin) a spin orbitals can accommodate only one electron.

⁷Recall 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.

⁸Recall 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 (Φ_1 and Φ_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 Φ_1 , the lowest energy determinant. If we plug in the definitions of the spin orbitals we obtain:

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

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 Φ_1 represents a state that has mixture of 50% covalent and 50% ionic electronic configurations. The determinant Φ_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 Φ_1 and Φ_4 may be used to represent covalent or ionic states because by carefully choosing C_1 and C_4 it is possible to cancel the ionic or covalent contributions.

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

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

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 Φ_5 corresponds to having each atomic orbital occupied by one alpha electron.

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

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

Let us consider these terms in detail⁹

$$^9 \hat{S}_- = \hat{s}_-(1) + \hat{s}_-(2).$$

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

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

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

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

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

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

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

suggests that we consider the plus and minus combination of Φ_2 and Φ_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, Φ_- is a triplet state while Φ_+ 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	

(3.92)

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?