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

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

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

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

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

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

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

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

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

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

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

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

$$\hat{s}_z |s, m_s\rangle = \hbar m_s |s, m_s\rangle. \tag{3.7}$$

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]

$$|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle, \tag{3.8}$$

$$|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle. \tag{3.9}$$

[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:

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1, \tag{3.10}$$

$$\langle \alpha | \beta \rangle = 0. \tag{3.11}$$

A general spin state of an electron $|\sigma\rangle$ can be represented in the basis of states $\{|\alpha\rangle, |\beta\rangle\}$ as

$$|\sigma\rangle = c_\alpha |\alpha\rangle + c_\beta |\beta\rangle = (|\alpha\rangle, |\beta\rangle) \begin{pmatrix} c_\alpha \\ c_\beta \end{pmatrix}. \tag{3.12}$$

When written in this way, then the basis states are represented by the vectors

$$|\alpha\rangle \leftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |\beta\rangle \leftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{3.13}$$

In this representation, the operators $\hat{s}_x$, $\hat{s}_y$, and $\hat{s}_z$ can be represented by the matrices

$$\mathbf{s}_x = \frac{\hbar}{2}\boldsymbol{\sigma}_x, \quad \mathbf{s}_y = \frac{\hbar}{2}\boldsymbol{\sigma}_y, \quad \mathbf{s}_z = \frac{\hbar}{2}\boldsymbol{\sigma}_z, \tag{3.14}$$

where $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, and $\boldsymbol{\sigma}_z$ are called Pauli matrices. The Pauli matrices are defined as

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.15}$$

At times, we might write these functions as

$$\alpha(\omega) = \langle \omega | \alpha \rangle \tag{3.16}$$

$$\beta(\omega) = \langle \omega | \beta \rangle, \tag{3.17}$$

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

$$\langle \alpha | \beta \rangle = \int d\omega \, \alpha^*(\omega)\beta(\omega) = 0. \tag{3.18}$$

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

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \tag{3.19}$$

$$\hat{s}_- = \hat{s}_x - i\hat{s}_y \tag{3.20}$$

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

$$\hat{s}_+ |\alpha\rangle = 0, \tag{3.21}$$

$$\hat{s}_+ |\beta\rangle = |\alpha\rangle \quad (m_s : -\frac{1}{2} \to \frac{1}{2}), \tag{3.22}$$

$$\hat{s}_- |\alpha\rangle = |\beta\rangle \quad (m_s : \frac{1}{2} \to -\frac{1}{2}), \tag{3.23}$$

$$\hat{s}_- |\beta\rangle = 0. \tag{3.24}$$

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

$$\hat{s}^2 = \hat{s}_+\hat{s}_- + \hat{s}_z^2 - \hat{s}_z. \tag{3.25}$$

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

$$\hat{S}_x = \sum_i^N \hat{s}_x(i), \quad \hat{S}_y = \sum_i^N \hat{s}_y(i), \quad \hat{S}_z = \sum_i^N \hat{s}_z(i),$$

$$\hat{S}^2 = \sum_i^N \hat{s}^2(i), \quad \hat{S}_+ = \sum_i^N \hat{s}_+(i), \quad \hat{S}_- = \sum_i^N \hat{s}_-(i),$$

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

$$\hat{S}^2 |S, M_S\rangle = S(S+1) |S, M_S\rangle , \tag{3.26}$$

$$\hat{S}_z |S, M_S\rangle = M_S |S, M_S\rangle , \quad M_S = -S, -S+1, \ldots, S-1, S. \tag{3.27}$$

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

$$\text{multiplicity} = 2S + 1 \tag{3.28}$$

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 $\{\phi_i(\vec{r})\}$

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

$$f(\vec{r}) = \sum_i^\infty a_i \phi_i(\vec{r}). \tag{3.29}$$

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

By combining spin functions with spatial orbitals we get **spin orbitals**. The most general form of a spin orbital is[4]

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

$$\psi(x) \equiv \psi(\vec{r}, \sigma) = \psi^\alpha(\vec{r})\alpha(\omega) + \psi^\beta(\vec{r})\beta(\omega), \tag{3.30}$$

which we can represent equivalently in terms of a wave function that looks like a vector multiplied by the spin basis:

$$\psi(x) = (|\alpha\rangle , |\beta\rangle) \begin{pmatrix} \psi^\alpha(\vec{r}) \\ \psi^\beta(\vec{r}) \end{pmatrix}. \tag{3.31}$$

This representation of a spin orbital is the most general and often it is not used in practice. More commonly, we take spin orbitals to be specific combination of a spatial orbital with either the α or β spin function. That is, we write

$$\psi_\sigma(x) = \psi_\sigma(\vec{r}, \omega) = \phi^\sigma(\vec{r})\sigma(\omega), \tag{3.32}$$

where $\sigma(\omega) \in \{\alpha(\omega), \beta(\omega)\}$ indicates a generic spin function. Here the functions $\phi^\alpha(\vec{r})$ and $\phi^\beta(\vec{r})$ can be different.

This notation can be extended to a basis of spin orbitals, which in the most general case will consists of two groups of functions, one for each spin case, $\{\psi_{i,\alpha}(x)\}$ and $\{\psi_{i,\beta}(x)\}$, each expressed using a basis of spatial orbitals $\{\phi_i^\alpha(\vec{r})\}$ and $\{\phi_i^\beta(\vec{r})\}$ (note that these two bases can be different!)

$$\psi_{i,\sigma}(x) = \psi_{i,\sigma}(\vec{r}, \omega) = \phi_i^\sigma(\vec{r})\sigma(\omega). \tag{3.33}$$

Note that if each set of spatial orbitals is orthonormal, that is

$$\int d\vec{r}\, \phi_i^\alpha(\vec{r})^* \phi_j^\alpha(\vec{r}) = \delta_{ij}, \tag{3.34}$$

and

$$\int d\vec{r}\, \phi_i^\beta(\vec{r})^* \phi_j^\beta(\vec{r}) = \delta_{ij}, \tag{3.35}$$

then the spin orbital basis is also orthonormal in the following sense

$$
\begin{aligned}
\langle \psi_{i,\sigma} | \psi_{j,\sigma'} \rangle &= \int d\vec{r}\, d\omega\, \psi_{i,\sigma}^*(\vec{r}, \omega)\psi_{j,\sigma'}(\vec{r}, \omega) \\
&= \int d\vec{r}\, \phi_i^\sigma(\vec{r})^* \phi_j^{\sigma'}(\vec{r}) \int d\omega\, \sigma^*(\omega)\sigma'(\omega) \\
&= \delta_{ij}\delta_{\sigma\sigma'}.
\end{aligned}
\tag{3.36}
$$

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 will use a shorthand notation and collect the indices (i, σ) into one index k and specify the way spin orbitals are ordered. For example, for basis of K spatial orbitals we can define $2K$ spin orbitals as:

$$\psi_{2i-1}(x) = \phi_i^\alpha(\vec{r})\alpha(\omega), \tag{3.37}$$

$$\psi_{2i}(x) = \phi_i^\beta(\vec{r})\beta(\omega), \tag{3.38}$$

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

$$(\psi_1, \psi_2, \psi_3, \psi_4, \ldots) = (\phi_1^\alpha \alpha, \phi_1^\beta \beta, \phi_2^\alpha \alpha, \phi_2^\beta \beta, \ldots). \tag{3.39}$$

3.3 N-electron wave functions

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

$$\Phi(\ldots, x_i, \ldots, x_j, \ldots, x_N) = -\Phi(\ldots, x_j, \ldots, x_i, \ldots, x_N). \tag{3.40}$$

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

$$\Phi(x_2, x_1) = -\Phi(x_1, x_2). \tag{3.41}$$

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

using the spin orbital basis as:

$$\Phi(x_1, x_2) = \sum_i^\infty a_i(x_2)\psi_i(x_1), \tag{3.42}$$

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

$$a_i(x_2) = \sum_j^\infty a_{ij}\psi_j(x_2), \tag{3.43}$$

and introduced the quantity a_{ij}, which carries both the indices for the x_1 and x_2 expansions. Combining Eqs. (3.42)–(3.43) we obtain:

$$\Phi(x_1, x_2) = \sum_{ij}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2). \tag{3.44}$$

This functions may satisfy the antisymmetry condition if:

$$\sum_{ij}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) = -\sum_{ij}^\infty a_{ij}\psi_i(x_2)\psi_j(x_1). \tag{3.45}$$

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

$$\sum_{ij}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) = -\sum_{ij}^\infty a_{ji}\psi_j(x_2)\psi_i(x_1), \tag{3.46}$$

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

$$\sum_{ij}^\infty (a_{ij} + a_{ji})\psi_i(x_1)\psi_j(x_2) = 0. \tag{3.47}$$

Equation (3.47) must hold for any value of $\psi_i(x_1)\psi_j(x_2)$, and this is possible only if

$$a_{ij} + a_{ji} = 0. \tag{3.48}$$

This conditions may also be written as

$$a_{ij} = -a_{ji}. \tag{3.49}$$

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. (3.48) 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 $a_{i_1 i_2 i_3 \cdots i_N}$.

Using Eq. (3.48) we may write the two-electron wave function as:

$$\begin{aligned} \Phi(x_1, x_2) &= \sum_{i<j}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) + \sum_{i>j}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) \\ &= \sum_{i<j}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) + \sum_{j>i}^\infty a_{ji}\psi_j(x_1)\psi_i(x_2) \\ &= \sum_{i<j}^\infty a_{ij}\psi_i(x_1)\psi_j(x_2) - \sum_{i<j}^\infty a_{ij}\psi_i(x_2)\psi_j(x_1) \\ &= \sum_{i<j}^\infty a_{ij}[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)]. \end{aligned} \tag{3.50}$$

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:

$$\det \begin{bmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{bmatrix} \equiv \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix} = \psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1). \quad (3.51)$$

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

$$\Phi(x_1, x_2) = \sum_{i<j}^{\infty} a_{ij} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) \\ \psi_j(x_1) & \psi_j(x_2) \end{vmatrix}. \quad (3.52)$$

Recall that using the wedge product notation this quantity can be written also as

$$|\Phi\rangle = \sum_{i<j}^{\infty} a_{ij} |\psi_i\rangle \wedge |\psi_j\rangle. \quad (3.53)$$

∎

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

$$\Phi_{ijk\ldots}(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_i(x_1) & \psi_i(x_2) & \cdots & \psi_i(x_N) \\ \psi_j(x_1) & \psi_j(x_2) & \cdots & \psi_j(x_N) \\ \psi_k(x_1) & \psi_k(x_2) & \cdots & \psi_k(x_N) \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix}. \quad (3.54)$$

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

$$|\Phi_{ijk\ldots}\rangle = |\psi_i\rangle \wedge |\psi_j\rangle \wedge |\psi_k\rangle \wedge \cdots = |\psi_i\psi_j\psi_k\cdots\rangle, \quad (3.55)$$

omitting the labels of the electrons. The basis of Slater determinants $\{|\psi_i\psi_j\psi_k\cdots\rangle\}$ with $i, j, k, \ldots \in \{0, 1, 2, \ldots\}$ is complete.[5] Therefore, we may expand any electronic wave function Ψ using the Slater determinant basis:

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

$$|\Psi\rangle = \sum_{i<j<k\cdots}^{\infty} C_{ijk\ldots} |\psi_i\psi_j\psi_k\cdots\rangle. \quad (3.56)$$

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:

$$N_{\text{FCI}} = \binom{2K}{N}. \quad (3.57)$$

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:

$$\Phi^{\mathrm{HP}}(x_1, x_2) = \psi_i(x_1)\psi_j(x_2). \tag{3.58}$$

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

$$|\Phi^{\mathrm{HP}}(x_1, x_2)|^2 = |\psi_i(x_1)|^2|\psi_j(x_2)|^2 = P_i(x_1)P_j(x_2). \tag{3.59}$$

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

A Slater determinant:

$$\Phi^{\mathrm{SD}}(x_1, x_2) = \frac{1}{\sqrt{2}}[\psi_i(x_1)\psi_j(x_2) - \psi_i(x_2)\psi_j(x_1)]. \tag{3.60}$$

has a probability distribution equal to:

$$\begin{aligned}
|\Phi^{\mathrm{SD}}(x_1, x_2)|^2 = \frac{1}{2}[&P_i(x_1)P_j(x_2) + P_j(x_1)P_i(x_2) \\
&- \psi_i^*(x_1)\psi_j(x_1)\psi_j^*(x_2)\psi_i(x_2) \\
&- \psi_j^*(x_1)\psi_i(x_1)\psi_j(x_2)\psi_i^*(x_2)].
\end{aligned} \tag{3.61}$$

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 $|\Phi^{\mathrm{SD}}(x_1, x_2)|^2$ over the spin variables ω_1 and ω_2 we can derive a probability distribution that depends only on the positions of the electrons:

$$P(\mathbf{r}_1, \mathbf{r}_2) = \int d\omega_1 d\omega_2 |\Phi^{\mathrm{SD}}(x_1, x_2)|^2. \tag{3.62}$$

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

$$P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2)]. \tag{3.63}$$

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

$$\begin{aligned}
P(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2}[&P_i(\mathbf{r}_1)P_j(\mathbf{r}_2) + P_j(\mathbf{r}_1)P_i(\mathbf{r}_2) \\
&- \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\
&- \phi_j^*(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_i^*(\mathbf{r}_2)].
\end{aligned} \tag{3.64}$$

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 H₂

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, $\chi_{1s}^{\mathrm{A}}(\mathbf{r})$ and $\chi_{1s}^{\mathrm{B}}(\mathbf{r})$. Note that these two orbitals are not necessarily orthogonal as their overlap (S) is in general not equal to zero

$$S = \int d\mathbf{r}\chi_{1s}^{\mathrm{A}} * (\mathbf{r})\chi_{1s}^{\mathrm{B}}(\mathbf{r}) \neq 0. \tag{3.65}$$

From these atomic orbitals we can form two spatial orbitals:

$$\phi_{\mathrm{g}}(\mathbf{r}) = N_{\mathrm{g}}[\chi_{1\mathrm{s}}^{\mathrm{A}}(\mathbf{r}) + \chi_{1\mathrm{s}}^{\mathrm{B}}(\mathbf{r})], \tag{3.66}$$

$$\phi_{\mathrm{u}}(\mathbf{r}) = N_{\mathrm{u}}[\chi_{1\mathrm{s}}^{\mathrm{A}}(\mathbf{r}) - \chi_{1\mathrm{s}}^{\mathrm{B}}(\mathbf{r})]. \tag{3.67}$$

> **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 $\phi_{\mathrm{g}}(\mathbf{r})$ and $\phi_{\mathrm{u}}(\mathbf{r})$ in terms of the overlap integral S.

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

$$\psi_1(x) = \psi_{\mathrm{g}}(x) = \phi_{\mathrm{g}}(\mathbf{r})\alpha(\omega), \tag{3.68}$$

$$\psi_2(x) = \psi_{\bar{\mathrm{g}}}(x) = \phi_{\mathrm{g}}(\mathbf{r})\beta(\omega), \tag{3.69}$$

$$\psi_3(x) = \psi_{\mathrm{u}}(x) = \phi_{\mathrm{u}}(\mathbf{r})\alpha(\omega), \tag{3.70}$$

$$\psi_4(x) = \psi_{\bar{\mathrm{u}}}(x) = \phi_{\mathrm{u}}(\mathbf{r})\beta(\omega). \tag{3.71}$$

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

$$|\psi_{\mathrm{g}}\psi_{\mathrm{g}}\rangle = 0, \tag{3.72}$$

is zero because we have placed two electrons in the same spin orbital.[6] We may form six unique determinants:

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

$$|\Phi_1\rangle = |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{g}}}\rangle = \overline{\uparrow\downarrow} \tag{3.73}$$

$$|\Phi_2\rangle = |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle = \begin{matrix}\downarrow\\\uparrow\end{matrix} \tag{3.74}$$

$$|\Phi_3\rangle = |\psi_{\mathrm{u}}\psi_{\bar{\mathrm{g}}}\rangle = \begin{matrix}\uparrow\\\downarrow\end{matrix} \tag{3.75}$$

$$|\Phi_4\rangle = |\psi_{\mathrm{u}}\psi_{\bar{\mathrm{u}}}\rangle = \underline{\uparrow\downarrow} \tag{3.76}$$

$$|\Phi_5\rangle = |\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = \begin{matrix}\uparrow\\\uparrow\end{matrix} \tag{3.77}$$

$$|\Phi_6\rangle = |\psi_{\bar{\mathrm{g}}}\psi_{\bar{\mathrm{u}}}\rangle = \begin{matrix}\downarrow\\\downarrow\end{matrix} \tag{3.78}$$

[7]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.

[8]Recall that for molecules that possess a center of inversion the following rules apply: g × g = g, g × u = u × g = u, u × u = g.

Symmetry greatly simplifies this problem.[7] The determinants $|\Phi_1\rangle$ and $|\Phi_4\rangle$ are gerade since the product $\psi_{\mathrm{g}}\psi_{\bar{\mathrm{g}}}$ has symmetry equal to g × 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	$\psi_{\mathrm{g}}\psi_{\bar{\mathrm{g}}}$	g	0	
Φ_2	$\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}$	u	0	
Φ_3	$\psi_{\mathrm{u}}\psi_{\bar{\mathrm{g}}}$	u	0	(3.79)
Φ_4	$\psi_{\mathrm{u}}\psi_{\bar{\mathrm{u}}}$	g	0	
Φ_5	$\psi_{\mathrm{g}}\psi_{\mathrm{u}}$	u	1	
Φ_6	$\psi_{\bar{\mathrm{g}}}\psi_{\bar{\mathrm{u}}}$	u	−1	

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

$$C_1 \left| \Phi_1 \right\rangle + C_4 \left| \Phi_4 \right\rangle , \tag{3.80}$$

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 $-S, -S+1, \ldots, S-1, S$, 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 $C_1 \left| \Phi_1 \right\rangle + C_4 \left| \Phi_4 \right\rangle$ are singlet states.

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

$$C_2 \left| \Phi_2 \right\rangle + C_3 \left| \Phi_3 \right\rangle , \tag{3.81}$$

plus we have two ungerade states with $M_S = \pm 1$ ($\left| \Phi_5 \right\rangle, \left| \Phi_6 \right\rangle$) 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:

$$
\begin{aligned}
\left| \Phi_1 \right\rangle = \left| \psi_\mathrm{g} \psi_{\bar{\mathrm{g}}} \right\rangle &= N_\mathrm{g}^2 \left| (\chi_\mathrm{1s}^\mathrm{A} + \chi_\mathrm{1s}^\mathrm{B})\alpha(\chi_\mathrm{1s}^\mathrm{A} + \chi_\mathrm{1s}^\mathrm{B})\beta \right\rangle \\
&= N_\mathrm{g}^2 [\left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle + \left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle + \left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle + \left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle].
\end{aligned}
\tag{3.82}
$$

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

$$\left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle \equiv \enspace \textcircled{$\uparrow\downarrow$} \quad \bigcirc \tag{3.83}$$

and

$$\left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle \equiv \enspace \bigcirc \quad \textcircled{$\uparrow\downarrow$} \tag{3.84}$$

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:

$$\left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle \equiv \enspace \textcircled{$\uparrow$} \quad \textcircled{$\downarrow$} \tag{3.85}$$

and

$$\left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle \equiv \enspace \textcircled{$\downarrow$} \quad \textcircled{$\uparrow$} \tag{3.86}$$

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:

$$
\begin{aligned}
\left| \Phi_4 \right\rangle = \left| \psi_\mathrm{u} \psi_{\bar{\mathrm{u}}} \right\rangle &= N_\mathrm{u}^2 \left| (\chi_\mathrm{1s}^\mathrm{A} - \chi_\mathrm{1s}^\mathrm{B})\alpha(\chi_\mathrm{1s}^\mathrm{A} - \chi_\mathrm{1s}^\mathrm{B})\beta \right\rangle \\
&= N_\mathrm{u}^2 [\left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle - \left| \chi_\mathrm{1s}^\mathrm{A}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle - \left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{A}\beta \right\rangle + \left| \chi_\mathrm{1s}^\mathrm{B}\alpha\chi_\mathrm{1s}^\mathrm{B}\beta \right\rangle].
\end{aligned}
\tag{3.87}
$$

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:

$$
\begin{aligned}
|\Phi_5\rangle = |\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle &= N_{\mathrm{g}}N_{\mathrm{u}}\,|(\chi_{1\mathrm{s}}^{\mathrm{A}} + \chi_{1\mathrm{s}}^{\mathrm{B}})\alpha(\chi_{1\mathrm{s}}^{\mathrm{A}} - \chi_{1\mathrm{s}}^{\mathrm{B}})\alpha\rangle \\
&= N_{\mathrm{g}}N_{\mathrm{u}}[\underbrace{|\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\rangle}_{=0} - |\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\rangle + |\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\rangle - \underbrace{|\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\rangle}_{=0}] \\
&= 2N_{\mathrm{g}}N_{\mathrm{u}}\,|\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\rangle .
\end{aligned}
\tag{3.88}
$$

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

$$
|\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\rangle = -\,|\chi_{1\mathrm{s}}^{\mathrm{B}}\alpha\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\rangle .
\tag{3.89}
$$

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

$$
|\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\chi_{1\mathrm{s}}^{\mathrm{A}}\alpha\rangle \equiv \text{(↑↑)} \quad \text{(—)}
\tag{3.90}
$$

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:

$$
\hat{S}^2\,|\Phi_5\rangle = \hat{S}^2\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = (\hat{S}_+\hat{S}_- + \hat{S}_z^2 - \hat{S}_z)\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle .
\tag{3.91}
$$

[9] $\hat{S}_- = \hat{s}_-(1) + \hat{s}_-(2)$.   Let us consider these terms in detail[9]

$$
\hat{S}_+\hat{S}_-\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = \hat{S}_+(|\psi_{\bar{\mathrm{g}}}\psi_{\mathrm{u}}\rangle + |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle) = 2\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle .
\tag{3.92}
$$

$$
\hat{S}_z\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = \left(\frac{1}{2} + \frac{1}{2}\right)|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = |\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle .
\tag{3.93}
$$

Putting all together we get

$$
\begin{aligned}
\hat{S}^2\,|\Phi_5\rangle &= (\hat{S}_+\hat{S}_- + \hat{S}_z^2 - \hat{S}_z)\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle \\
&= 2\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle + |\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle - |\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle = 2\,|\psi_{\mathrm{g}}\psi_{\mathrm{u}}\rangle .
\end{aligned}
\tag{3.94}
$$

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 the determinants Φ_2 and Φ_3. Let us compute $\hat{S}^2\,|\Phi_2\rangle$. We will need the quantity:

$$
\hat{S}_+\hat{S}_-\,|\Phi_2\rangle = \hat{S}_+\hat{S}_-\,|\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle = \hat{S}_+\,|\psi_{\bar{\mathrm{g}}}\psi_{\bar{\mathrm{u}}}\rangle = |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle + |\psi_{\bar{\mathrm{g}}}\psi_{\mathrm{u}}\rangle,
\tag{3.95}
$$

and

$$
\hat{S}_z\,|\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle = \left(\frac{1}{2} - \frac{1}{2}\right)|\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle = 0.
\tag{3.96}
$$

From these results we find that:

$$
\hat{S}^2\,|\Phi_2\rangle = |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle + |\psi_{\bar{\mathrm{g}}}\psi_{\mathrm{u}}\rangle = |\psi_{\mathrm{g}}\psi_{\bar{\mathrm{u}}}\rangle - |\psi_{\mathrm{u}}\psi_{\bar{\mathrm{g}}}\rangle = |\Phi_2\rangle - |\Phi_3\rangle .
\tag{3.97}
$$

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:

$$
\hat{S}^2\,|\Phi_3\rangle = |\Phi_3\rangle - |\Phi_2\rangle .
\tag{3.98}
$$

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

$$|\Phi_\pm\rangle = \frac{1}{\sqrt{2}}\left(|\Phi_2\rangle \pm |\Phi_3\rangle\right). \tag{3.99}$$

These two states are such that

$$\hat{S}^2|\Phi_+\rangle = 0, \tag{3.100}$$

and

$$\hat{S}^2|\Phi_-\rangle = 2|\Phi_-\rangle. \tag{3.101}$$

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
$\frac{1}{\sqrt{2}}\left(|\Phi_2\rangle + |\Phi_3\rangle\right)$	u	0	0	Excited singlet state
$|\Phi_5\rangle$	u	1	1	
$\frac{1}{\sqrt{2}}\left(|\Phi_2\rangle - |\Phi_3\rangle\right)$	u	1	0	Triplet state (degenerate)
$|\Phi_6\rangle$	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 $m_l = -1, 0, 1$.

$$2p_{-1}, 2p_0, 2p_1 \tag{3.102}$$

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

$$\begin{aligned}
2p_{-1} &= 2p_x - i2p_y \\
2p_0 &= 2p_z \\
2p_{+1} &= 2p_x + i2p_y
\end{aligned} \tag{3.103}$$

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

Number	Determinant	M_L	M_S
1	$\lvert(2\mathrm{p}_{-1}\alpha)(2\mathrm{p}_0\alpha)\rangle$	-1	1
2	$\lvert(2\mathrm{p}_{-1}\alpha)(2\mathrm{p}_1\alpha)\rangle$	0	1
3	$\lvert(2\mathrm{p}_0\alpha)(2\mathrm{p}_1\alpha)\rangle$	1	1
4	$\lvert(2\mathrm{p}_{-1}\alpha)(2\mathrm{p}_{-1}\beta)\rangle$	-2	0
5	$\lvert(2\mathrm{p}_{-1}\alpha)(2\mathrm{p}_0\beta)\rangle$	-1	0
6	$\lvert(2\mathrm{p}_{-1}\alpha)(2\mathrm{p}_1\beta)\rangle$	0	0
7	$\lvert(2\mathrm{p}_0\alpha)(2\mathrm{p}_{-1}\beta)\rangle$	-1	0
8	$\lvert(2\mathrm{p}_0\alpha)(2\mathrm{p}_0\beta)\rangle$	0	0
9	$\lvert(2\mathrm{p}_0\alpha)(2\mathrm{p}_1\beta)\rangle$	1	0
10	$\lvert(2\mathrm{p}_1\alpha)(2\mathrm{p}_{-1}\beta)\rangle$	0	0
11	$\lvert(2\mathrm{p}_1\alpha)(2\mathrm{p}_0\beta)\rangle$	1	0
12	$\lvert(2\mathrm{p}_1\alpha)(2\mathrm{p}_1\beta)\rangle$	2	0
13	$\lvert(2\mathrm{p}_{-1}\beta)(2\mathrm{p}_0\beta)\rangle$	-1	-1
14	$\lvert(2\mathrm{p}_{-1}\beta)(2\mathrm{p}_1\beta)\rangle$	0	-1
15	$\lvert(2\mathrm{p}_0\beta)(2\mathrm{p}_1\beta)\rangle$	1	-1

(3.104)

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		•	

(3.105)

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		•	

$\rightarrow$

$M_L \backslash M_S$	-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			

$\rightarrow$

$M_L \backslash M_S$	-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 nondegerate 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:

$$1\sigma_g \propto 1s_A + 1s_B$$
$$1\sigma_u \propto 1s_A - 1s_B \qquad (3.106)$$

These orbitals have been labeled "σ" 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

$$2\sigma_g \propto 2s + 2s$$
$$2\sigma_u \propto 2s - 2s \qquad (3.107)$$

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

$$3\sigma_u \propto 2p_0 - 2p_0$$
$$3\sigma_g \propto 2p_0 + 2p_0 \qquad (3.108)$$

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 π orbitals (named so because $|m_l| = 1$).

$$1\pi_{u_1} \propto 2p_1 + 2p_1, \quad 1\pi_{u_{-1}} \propto 2p_{-1} + 2p_{-1}$$
$$1\pi_{g_1} \propto 2p_1 - 2p_1, \quad 1\pi_{g_{-1}} \propto 2p_{-1} - 2p_{-1} \qquad (3.109)$$

The energetic order of these orbitals is

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_u < 1\pi_u < 1\pi_g < 3\sigma_g \qquad (3.110)$$

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

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^2 \qquad (3.111)$$

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	$\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\alpha)\rangle$	0	1	g
2	$\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_{-1}}\beta)\rangle$	-2	0	g
3	$\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\beta)\rangle$	0	0	g
4	$\lvert (1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\beta)\rangle$	0	0	g
5	$\lvert (1\pi_{g_1}\alpha)(1\pi_{g_1}\beta)\rangle$	2	0	g
6	$\lvert (1\pi_{g_{-1}}\beta)(1\pi_{g_1}\beta)\rangle$	0	-1	g

$$(3.112)$$

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
-2		•	
-1			
0	•	••	•
1			
2		•	

$\rightarrow$

$M_L\backslash M_S$	-1	0	1
-2			
-1			
0	•	••	•
1			
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: Σ ($|M_L| = 0$), Π ($|M_L| = 1$), Δ ($|M_L| = 2$), Φ ($|M_L| = 3$), 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 Σ 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 π orbitals. One can show that the corresponding symmetry operator ($\hat{\sigma}_v$) switches the two $1\pi_g$ orbitals

$$\hat{\sigma}_v(1\pi_{g_1}) \propto \hat{\sigma}_v(2p_1^A - 2p_1^B) = 2p_{-1}^A - 2p_{-1}^B = 1\pi_{g_{-1}} \qquad (3.113)$$

and similarly $\hat{\sigma}_v(1\pi_{g_{-1}}) = 1\pi_{g_1}$. 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 $\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\alpha)\rangle$. When we apply the $\hat{\sigma}_v$ operation to this determinant, we distribute this operator to all of its orbitals

$$\hat{\sigma}_v \lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\alpha)\rangle = \lvert \hat{\sigma}_v(1\pi_{g_{-1}}\alpha)\hat{\sigma}_v(1\pi_{g_1}\alpha)\rangle = \lvert (1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\alpha)\rangle = -\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\alpha)\rangle$$
$$(3.114)$$

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,

$$\frac{1}{\sqrt{2}} \left[\lvert (1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\beta)\rangle + \lvert (1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\beta)\rangle \right] \qquad (3.115)$$

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

$$\hat{\sigma}_v \frac{1}{\sqrt{2}} \left[|(1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\beta)\rangle + |(1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\beta)\rangle \right]$$

$$= \frac{1}{\sqrt{2}} \left[|(1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\beta)\rangle + |(1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\beta)\rangle \right] \qquad (3.116)$$

$$= \frac{1}{\sqrt{2}} \left[|(1\pi_{g_{-1}}\alpha)(1\pi_{g_1}\beta)\rangle + |(1\pi_{g_1}\alpha)(1\pi_{g_{-1}}\beta)\rangle \right]$$

Therefore, the singlet state is of type "+" and it 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?