

9.6: Electron Configurations, The Pauli Exclusion Principle, The Aufbau Principle, and Slater Determinants

To discuss the electronic states of atoms we need a system of notation for multi-electron wavefunctions. As we saw in Chapter 8, the assignment of electrons to orbitals is called the electron configuration of the atom. One creates an electronic configuration representing the electronic structure of a multi-electron atom or ion in its ground or lowest-energy state as follows. First, obey the [Pauli Exclusion Principle](#), which requires that each electron in an atom or molecule must be described by a different spin-orbital. Second, assign the electrons to the lowest energy spin-orbitals, then to those at higher energy. This procedure is called the [Aufbau Principle](#) (which translates from German as build-up principle). The mathematical analog of this process is the construction of the approximate multi-electron wavefunction as a product of the single-electron atomic orbitals.

For example, the configuration of the boron atom, shown schematically in the energy level diagram in Figure 9.6.1, is written in shorthand form as $1s^2 2s^2 2p^1$. As we saw in [previously](#), the degeneracy of the 2s and 2p orbitals is broken by the electron-electron interactions in multi-electron systems.

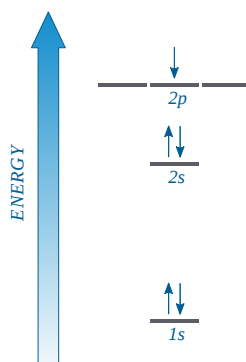


Figure 9.6.1: Orbital energy level diagram that represents the electron configuration of the boron atom. Orbital energy differences are approximately to scale. (CC BY-SA; Ümit Kaya)

Rather than showing the individual spin-orbitals in the diagram or in the shorthand notation, we commonly say that up to two electrons can be described by each spatial orbital, one with spin function α (electron denoted by an arrow pointing up) and the other with spin function β (arrow pointing down). This restriction is a manifestation of the Pauli Exclusion Principle mentioned above. An equivalent statement of the Pauli Exclusion Principle is that each electron in an atom has a unique set of quantum numbers (n, l, m_l, m_s) . Since the two spin functions are degenerate in the absence of a magnetic field, the energy of the two electrons with different spin functions in a given spatial orbital is the same, and they are shown on the same line in the energy diagram.

Exercise 9.6.1

Write the electronic configuration of the carbon atom and draw the corresponding energy level diagram.

Exercise 9.6.2

Write the values for the quantum numbers (n, l, m_l, m_s) for each of the six electrons in carbon.

We can deepen our understanding of the quantum mechanical description of multi-electron atoms by examining the concepts of electron indistinguishability and the Pauli Exclusion Principle in detail. We will use the following statement as a guide to keep our explorations focused on the development of a clear picture of the multi-electron atom: “When a multi-electron wavefunction is built as a product of single-electron wavefunctions, the corresponding concept is that exactly one electron’s worth of charge density is described by each atomic spin-orbital.”

A subtle, but important part of the conceptual picture is that the electrons in a multi-electron system are not distinguishable from one another by any experimental means. Since the electrons are indistinguishable, the probability density we calculate by squaring the modulus of our multi-electron wavefunction also cannot change when the electrons are interchanged (permuted) between different orbitals. In general, if we interchange two identical particles, the world does not change. As we will see below, this

requirement leads to the idea that the world can be divided into two types of particles based on their behavior with respect to permutation or interchange.

For the probability density to remain unchanged when two particles are permuted, the wavefunction itself can change only by a factor of $e^{i\varphi}$, which represents a complex number, when the particles described by that wavefunction are permuted. As we will show below, the $e^{i\varphi}$ factor is possible because the probability density depends on the absolute square of the function and all expectation values involve $\psi\psi^*$. Consequently $e^{i\varphi}$ disappears in any calculation that relates to the real world because $e^{i\varphi}e^{-i\varphi} = 1$.

We could symbolically write an approximate two-particle wavefunction as $\psi(r_1, r_2)$. This could be, for example, a two-electron wavefunction for helium. To exchange the two particles, we simply substitute the coordinates of particle 1 (r_1) for the coordinates of particle 2 (r_2) and vice versa, to get the new wavefunction $\psi(r_2, r_1)$. This new wavefunction must have the property that

$$|\psi(r_1, r_2)|^2 = \psi(r_2, r_1)^* \psi(r_2, r_1) = \psi(r_1, r_2)^* \psi(r_1, r_2) \quad (9.6.1)$$

since the probability density of the electrons in the atom does not change upon permutation of the electrons.

Exercise 9.6.3

Permute the electrons in Equation ??? (the product function for He wavefunction.)

Equation 9.6.1 will be true only if the wavefunctions before and after permutation are related by a factor of $e^{i\varphi}$,

$$\psi(r_1, r_2) = e^{i\varphi} \psi(r_2, r_1) \quad (9.6.2)$$

so that

$$(e^{-i\varphi} \psi(r_1, r_2)^*) (e^{i\varphi} \psi(r_2, r_1)^*) = \psi(r_1, r_2)^* \psi(r_2, r_1) \quad (9.6.3)$$

If we exchange or permute two identical particles twice, we are (by definition) back to the original situation. If each permutation changes the wavefunction by $e^{i\varphi}$, the double permutation must change the wavefunction by $e^{i\varphi}e^{i\varphi}$. Since we then are back to the original state, the effect of the double permutation must equal 1; i.e.,

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \quad (9.6.4)$$

which is true only if $\varphi = 0$ or an integer multiple of π . The requirement that a double permutation reproduce the original situation limits the acceptable values for $e^{i\varphi}$ to either +1 (when $\varphi = 0$) or -1 (when $\varphi = \pi$). Both possibilities are found in nature.

Exercise 9.6.4

Use Euler's Equality to show that $e^{i2\varphi} = 1$ when $\varphi = 0$ or $n\pi$ and consequently $e^{i\varphi} = \pm 1$.

Wavefunctions for which $e^{i\varphi} = +1$ are defined as symmetric with respect to permutation, because the wavefunction is identical before and after a single permutation. Wavefunctions that are symmetric with respect to interchange of the particles obey the following mathematical relationship:

$$e^{i\varphi}e^{i\varphi} = e^{i2\varphi} = 1 \quad (9.6.5)$$

The behavior of some particles requires that the wavefunction be symmetric with respect to permutation. These particles are called bosons and have integer spin such as deuterium nuclei, photons, and gluons.

The behavior of other particles requires that the wavefunction be antisymmetric with respect to permutation ($e^{i\varphi} = -1$). A wavefunction that is antisymmetric with respect to electron interchange is one whose output changes sign when the electron coordinates are interchanged, as shown below:

$$\psi(r_2, r_1) = e^{i\varphi} \psi(r_1, r_2) = -\psi(r_1, r_2) \quad (9.6.6)$$

These particles, called fermions, have half-integer spin and include electrons, protons, and neutrinos.

Exercise 9.6.5

Explain without any equations why there are only two kinds of particles in the world: bosons and fermions.

In fact, an elegant statement of the Pauli Exclusion Principle is simply “electrons are fermions.” This statement means that any wavefunction used to describe multiple electrons must be antisymmetric with respect to permutation of the electrons, providing yet another statement of the Pauli Exclusion Principle. The requirement that the wavefunction be antisymmetric applies to all multi-electron functions $\psi(r_1, r_2, \dots, r_i)$, including those written as products of single electron functions $\varphi_1(r_1)\varphi_2(r_2) \cdots \varphi_i(r_i)$.

Another way to simply restate the Pauli Exclusion Principle is that “electrons are fermions.”

The first statement of the Pauli Exclusion Principle was that two electrons could not be described by the same spin orbital. To see the relationship between this statement and the requirement that the wavefunction be antisymmetric for electrons, try to construct an **antisymmetric wavefunction** for two electrons that are described by the same spin-orbital. We can try to do so for helium. Write the He approximate two-electron wavefunction as a product of identical 1s spin-orbitals for each electron, $\varphi_{1s\alpha}(r_1)$ and $\varphi_{1s\alpha}(r_2)$:

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\alpha}(r_2) \quad (9.6.7)$$

To permute the electrons in this two-electron wavefunction, we simply substitute the coordinates of electron 1 (r_1) for the coordinates of electron 2 (r_2) and vice versa, to get

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\alpha}(r_1) \quad (9.6.8)$$

This is identical to the original function (Equation 9.6.7) since the two single-electron component functions **commute**. The two-electron function has not changed sign, as it must for fermions. We can construct a wavefunction that is antisymmetric with respect to permutation symmetry only if each electron is described by a different function.

Exercise 9.6.6

What is meant by the term permutation symmetry?

Exercise 9.6.7

Explain why the product function $\varphi(r_1)\varphi(r_2)$ could describe two bosons (deuterium nuclei) but can not describe two fermions (e.g. electrons).

Let's try to construct an antisymmetric function that describes the two electrons in the ground state of helium. Blindly following the first statement of the Pauli Exclusion Principle, that each electron in a multi-electron atom must be described by a different spin-orbital, we try constructing a simple product wavefunction for helium using two different spin-orbitals. Both have the 1s spatial component but one has spin function α and the other has spin function β so the product wavefunction matches the form of the ground state electron configuration for He, $1s^2$.

$$\psi(r_1, r_2) = \varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) \quad (9.6.9)$$

After permutation of the electrons, this becomes

$$\psi(r_2, r_1) = \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1) \quad (9.6.10)$$

which is different from the starting function (Equation 9.6.9) since $\varphi_{1s\alpha}$ and $\varphi_{1s\beta}$ are **different** functions. However, an antisymmetric function must produce the same function multiplied by (-1) after permutation, and that is not the case here. We must try something else.

To avoid getting a totally different function when we permute the electrons, we can make a linear combination of functions. A very simple way of taking a linear combination involves making a new function by simply adding or subtracting functions. The function that is created by subtracting the right-hand side of Equation 9.6.10 from the right-hand side of Equation 9.6.9 has the desired antisymmetric behavior.

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} [\varphi_{1s\alpha}(r_1)\varphi_{1s\beta}(r_2) - \varphi_{1s\alpha}(r_2)\varphi_{1s\beta}(r_1)] \quad (9.6.11)$$

The constant on the right-hand side accounts for the fact that the total wavefunction must be normalized.

Exercise 9.6.8

Show that the linear combination in Equation 9.6.11 is antisymmetric with respect to permutation of the two electrons. Replace the minus sign with a plus sign (i.e. take the positive linear combination of the same two functions) and show that the resultant linear combination is symmetric.

Exercise 9.6.9

Write a similar linear combination to describe the $1s^1 2s^1$ excited configuration of helium.

A linear combination that describes an appropriately antisymmetrized multi-electron wavefunction for any desired orbital configuration is easy to construct for a two-electron system. However, interesting chemical systems usually contain more than two electrons. For these multi-electron systems a relatively simple scheme for constructing an antisymmetric wavefunction from a product of one-electron functions is to write the wavefunction in the form of a determinant. John Slater introduced this idea so the determinant is called a **Slater determinant**.

The Slater determinant for the two-electron wavefunction of helium is

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{1s}(1)\alpha(1) & \varphi_{1s}(1)\beta(1) \\ \varphi_{1s}(2)\alpha(2) & \varphi_{1s}(2)\beta(2) \end{vmatrix} \quad (9.6.12)$$

and a shorthand notation for this determinant is

$$\psi(r_1, r_2) = 2^{-\frac{1}{2}} \text{Det}[\varphi_{1s}(r_1)\varphi_{1s}(r_2)] \quad (9.6.13)$$

The determinant is written so the electron coordinate changes in going from one row to the next, and the spin orbital changes in going from one column to the next. The advantage of having this recipe is clear if you try to construct an antisymmetric wavefunction that describes the orbital configuration for uranium! Note that the normalization constant is $(N!)^{-\frac{1}{2}}$ for N electrons.

Exercise 9.6.10

Show that the determinant form is the same as the form for the helium wavefunction that is given in Equation 9.6.11.

Exercise 9.6.11

Expand the Slater determinant in Equation 9.6.12 for the He atom.

Exercise 9.6.12

Write and expand the Slater determinant for the electronic wavefunction of the Li atom.

Exercise 9.6.13

Write the Slater determinant for the carbon atom. If you expanded this determinant, how many terms would be in the linear combination of functions?

Exercise 9.6.14

Write the Slater determinant for the $1s^1 2s^1$ excited state orbital configuration of the helium atom.

Now that we have seen how acceptable multi-electron wavefunctions can be constructed, it is time to revisit the “guide” statement of conceptual understanding with which we began our deeper consideration of electron indistinguishability and the Pauli Exclusion

Principle. What does a multi-electron wavefunction constructed by taking specific linear combinations of product wavefunctions mean for our physical picture of the electrons in multi-electron atoms? Overall, the antisymmetrized product function describes the configuration (the orbitals, regions of electron density) for the multi-electron atom. Because of the requirement that electrons be indistinguishable, we can't visualize specific electrons assigned to specific spin-orbitals. Instead, we construct functions that allow each electron's probability distribution to be dispersed across each spin-orbital. The total charge density described by any one spin-orbital cannot exceed one electron's worth of charge, and each electron in the system is contributing a portion of that charge density.

Exercise 9.6.13

Critique the energy level diagram and shorthand electron configuration notation from the perspective of the indistinguishability criterion. Can you imagine a way to represent the wavefunction expressed as a Slater determinant in a schematic or shorthand notation that more accurately represents the electrons? (This is not a solved problem!)

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