

25.1: Many-Electron Wave Functions

When we have more than one electron, the sixth postulate that we discussed in [chapter 24](#) comes into place. In other words, we need to account for the spin of the electrons and we need the wave function to be antisymmetric with respect to exchange of the coordinates of any two electrons. In order to do so, we can define a new variable \mathbf{x} which represents the set of all four coordinates associated with an electron: three spatial coordinates \mathbf{r} , and one spin coordinate s , i.e., $\mathbf{x} = \{\mathbf{r}, s\}$. We can then write the electronic wave function as $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$, and we require the sixth postulate to hold by writing:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \dots, \mathbf{x}_N) \quad (25.1.1)$$

A very important step in simplifying $\Psi(\mathbf{x})$ is to expand it in terms of a set of one-electron functions. Since we need to take into account the spin coordinate as well, we can define a new function, called **spin-orbital**, by multiplying a spatial orbital by one of the two spin functions:

$$\begin{aligned} \chi(\mathbf{x}) &= \psi(\mathbf{r})\phi_{\uparrow}(s), \\ \chi(\mathbf{x}) &= \psi(\mathbf{r})\phi_{\downarrow}(s). \end{aligned} \quad (25.1.2)$$

Notice that for a given spatial orbital $\psi(\mathbf{r})$, we can form two spin orbitals, one with \uparrow spin, and one with \downarrow spin (since the spin coordinate s has only two possible values, as already discussed in [chapter 23](#)). For the spatial orbitals we can use the same one-particle functions that solve the TISEq for the hydrogen atom, $\psi_{n\ell m_{\ell}}(\mathbf{r})$ (eq. 21.7 in [chapter 21](#)). Notice how each spin-orbital now depends on four quantum numbers, the three for the spatial part, n, ℓ, m_{ℓ} , plus the spin quantum number m_s . We need to keep in mind, however, that the spin-orbitals, $\chi_{n\ell m_{\ell} m_s}$, are *not* analytic solutions to the TISEq, so the resulting wave function is *not* the exact wave function of the system, but just an approximation.

Once we have defined one-electron spin-orbitals for each electron in the system, we can use them as the basis for our many-electron wave function. While doing so, we need to make sure to enforce the antisymmetry property of the overall wave function. We will start from the simplest case of an atom with two electrons with coordinates \mathbf{x}_1 and \mathbf{x}_2 , which we put in two spin-orbitals χ_1 and χ_2 . We can write the total wave function as a linear combination of the two spin-orbitals as:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) &= b_{11}\chi_1(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{12}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \\ &\quad b_{21}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) + b_{22}\chi_2(\mathbf{x}_1)\chi_2(\mathbf{x}_2). \end{aligned} \quad (25.1.3)$$

We then notice that in order for the antisymmetry principle to be obeyed, we need $b_{12} = -b_{21}$ and $b_{11} = b_{22} = 0$, which give:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = b_{12} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2)]. \quad (25.1.4)$$

This wave function is sufficient to describe two-electron atoms and ions, such as helium. The numerical coefficient can be determined imposing the normalization condition, and is equal to $b_{12} = \frac{1}{\sqrt{2}}$. For the ground state of helium, we can replace the spatial component of each spin-orbital with the $1s$ hydrogenic orbital, ψ_{100} , resulting in:

$$\begin{aligned} \Psi(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}} [\psi_{100}(\mathbf{r}_1)\phi_{\uparrow}\psi_{100}(\mathbf{r}_2)\phi_{\downarrow} - \psi_{100}(\mathbf{r}_1)\phi_{\downarrow}\psi_{100}(\mathbf{r}_2)\phi_{\uparrow}] \\ &= \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) \frac{1}{\sqrt{2}} [\phi_{\uparrow}\phi_{\downarrow} - \phi_{\downarrow}\phi_{\uparrow}], \end{aligned} \quad (25.1.5)$$

which clearly shows how we need just one spatial orbital, ψ_{100} , to describe the system, while the antisymmetry is taken care by a suitable combination of spin functions, $\frac{1}{\sqrt{2}}[\phi_{\uparrow}\phi_{\downarrow} - \phi_{\downarrow}\phi_{\uparrow}]$. Notice also that we commit a small inaccuracy when we say: “two electron occupies one spin-orbital, one electron has spin up, and the other electron has spin down, with configuration: $[\uparrow\downarrow]$ ”, as is typically found in general chemistry textbooks. The reality of the spin configuration is indeed more complicated, and the ground state of helium should be represented as $\frac{1}{\sqrt{2}}[\uparrow\downarrow - \downarrow\uparrow]$.

In order to generalize from two electrons to N , we can first observe how Equation (26.1.4) could be easily constructed by placing the spin-orbitals into a 2×2 matrix and calculating its determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}, \quad (25.1.6)$$

where each column contains one spin-orbital, each row contains the coordinates of a single electron, and the vertical bars around the matrix mean that we need to calculate its determinant. This notation is called the **Slater determinant**, and it is the preferred way of building any N -electron wave function. Slater determinants are useful because they can be easily built for any case of N electrons in N spin-orbitals, and they also automatically enforce the antisymmetry of the resulting wave function. A general Slater determinant is written:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} = |\chi_1, \chi_2, \dots, \chi_N\rangle, \quad (25.1.7)$$

where the notation $|\dots\rangle$ is a shorthand to indicate the Slater determinant where only the diagonal elements are reported.

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