

Determinants

A determinant is a square array of numbers used to represent a specific combination of those numbers. Here is the explicit definition for the two smallest determinants, 2×2 and 3×3 :

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

$$\begin{aligned} \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} &= a \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \begin{vmatrix} d & e \\ g & h \end{vmatrix} \\ &= a(ei - fh) - b(dg - if) + c(dh - eg) \end{aligned}$$

Note that there are 6 terms in a 3×3 determinant, 3 with + sign and 3 with - sign. A $N \times N$ determinant has $N!$ terms, half of them carry the + sign and the other half carry a - sign. The symbols a, b, \dots, i , could also be functions instead of numbers.

Slater determinants

The elements in a Slater determinant are spin-orbitals. A Slater determinant can be thought of as the simplest way to construct a wavefunction for N electrons that is guaranteed to be antisymmetric wrt interchange of any two set of electron coordinates. Here's the method for making a Slater determinant:

- given N electrons labeled $1, 2, 3, \dots$
- and given N spin-orbitals $\chi_1, \chi_2, \chi_3, \dots$
- make a $N \times N$ determinant where the entries at position (i, j) are $\chi_j(i)$. In other words, you put the function “spin-orbital j ” acting on the “variables of electron i ” at the position (i, j) in the determinant, and you do that for each of the N^2 positions in the determinant.

Consider the ground state of the Li atom for example, electronic configuration $1s^2 2s^1$. The 3 spin-orbitals are:

- $(n = 1, \ell = 0, m = 0, m_s = +\frac{1}{2})$, denoted by the symbol “ $1s$ ”;
- $(n = 1, \ell = 0, m = 0, m_s = -\frac{1}{2})$, denoted by the symbol “ $\overline{1s}$ ”;
- $(n = 2, \ell = 0, m = 0, m_s = +\frac{1}{2})$, denoted by the symbol “ $2s$ ”.

There are 6 ways of “putting” 3 electrons (1,2,3) in 3 spin-orbitals ($1s, \overline{1s}, 2s$) and these will give the 6 terms when we expand the Slater determinant:

$$\begin{aligned} & \sqrt{1/3!} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix} \\ &= \sqrt{1/6} \{ 1s(1) [\overline{1s}(2)2s(3) - 2s(2)\overline{1s}(3)] \\ & \quad - \overline{1s}(1) [1s(2)2s(3) - 2s(2)1s(3)] \\ & \quad + 2s(1) [1s(2)\overline{1s}(3) - \overline{1s}(2)1s(3)] \} \end{aligned}$$

You can verify that this function is antisymmetric. For example, let's interchange everywhere the electron labels 1 and 3, we get:

$$\begin{aligned}
 &= \sqrt{1/6} \{ 1s(3) [\overline{1s}(2)2s(1) - 2s(2)\overline{1s}(1)] \\
 &\quad - \overline{1s}(3) [1s(2)2s(1) - 2s(2)1s(1)] \\
 &\quad + 2s(3) [1s(2)\overline{1s}(1) - \overline{1s}(2)1s(1)] \}
 \end{aligned}$$

compare with the previous expression and you'll see they are equal but with opposite sign.

Slater determinants are conceptually very useful because they are the simplest qualitatively correct wavefunctions for atoms and molecules with more than one electron, ie, almost everything! By “qualitatively correct” I mean “obeying the Pauli exclusion principle” which is a **necessary** property of any N -electron wavefunction. But Slater determinants are almost never written in the fully expanded form like above, and they don't have to be. All calculations involving Slater determinants Ψ such as $\int \Psi^* \Psi d\tau$ or $\int \Psi^* \hat{H} \Psi d\tau$ are done using some rules about determinants, and the calculations are almost always done with computer programs. Just imagine: the Slater determinant for the ground state of the benzene molecule (42 electrons) is a 42×42 determinant, it has 1.4×10^{51} terms! Even a computer can not handle such large numbers of terms. But that is not necessary. In a more advanced course in electronic structure you would see that integrals involving Slater determinants like above simplify *greatly* because of the permutation symmetry, and other properties, of determinants. These integrals, and all expressions that contain Slater determinants, can be reduced to only one or a few terms, not 1.4×10^{51} .