

## *Slater Determinants and the Antisymmetrizing Operator*

Virtually all approximate many electron wavefunctions are constructed from determinants in which the entries are spin orbitals of the form  $\varphi = \phi(\vec{r})\xi$  where  $\xi = \alpha$  or  $\beta$ . These determinants are called Slater Determinants after J. C. Slater who introduced them in 1935. They are very useful because they do not distinguish between electrons (important because they are indistinguishable) and automatically satisfy the requirement that the wavefunction describing them must be antisymmetric with respect to electron interchange (Pauli Principle). Manipulations with Slater Determinants can be made much simpler by using the antisymmetrizing operator that we now discuss.

A Slater determinant for a two-electron system has the form

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} a(1) & a(2) \\ b(1) & b(2) \end{vmatrix} = \frac{1}{\sqrt{2}} (a(1)b(2) - a(2)b(1))$$

where  $a$  &  $b$  are orthonormal spin orbitals for electrons 1&2 and the factor  $\sqrt{2}$  is required for  $\Psi(1,2)$  to be normalized to 1. Indeed as we will show subsequently the normalization factor for an  $N$  electron system is  $\sqrt{N!}$ . If we define a transposition operator,  $\hat{P}_{12}$  by

$$\hat{P}_{12}\chi(1,2) = \chi(2,1)$$

we may write the Slater Determinant as

$$\Psi(1,2) = \frac{1}{\sqrt{2}} (a(1)b(2) - \hat{P}_{12}a(1)b(2)) = \frac{1}{\sqrt{2}} (1 - \hat{P}_{12})a(1)b(2)$$

We define the antisymmetrization operator for this two electron system  $\hat{\mathcal{A}}$  as

$$\hat{\mathcal{A}} = \frac{1}{\sqrt{2}} (1 - \hat{P}_{12})$$

and write the Slater Determinant as

$$\Psi(1,2) = \hat{\mathcal{A}}a(1)b(2)$$

Note

$$\hat{\mathcal{A}}^2 = \frac{1}{\sqrt{2}}(1 - \hat{P}_{12}) \frac{1}{\sqrt{2}}(1 - \hat{P}_{12}) = \frac{1}{2}(1 - 2\hat{P}_{12} + \hat{P}_{12}\hat{P}_{12})$$

and since  $\hat{P}_{12}\hat{P}_{12} = 1$  we have

$$\hat{\mathcal{A}}^2 = (1 - \hat{P}_{12}) = \sqrt{2}\hat{\mathcal{A}}$$

and  $\hat{\mathcal{A}}$  is not idempotent. Now consider a three-electron system

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} a(1) & a(2) & a(3) \\ b(1) & b(2) & b(3) \\ c(1) & c(2) & c(3) \end{vmatrix}$$

Expanding the determinant we have

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \left( a(1)(b(2)c(3) - b(3)c(2)) - a(2)(b(1)c(3) - b(3)c(1)) + a(3)(b(1)c(2) - b(2)c(1)) \right)$$

Which can be written in terms of various transposition operators as

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} (1 - \hat{P}_{23} - \hat{P}_{12} + \hat{P}_{13}\hat{P}_{12} + \hat{P}_{23}\hat{P}_{12} - \hat{P}_{13} + \hat{P}_{23}\hat{P}_{12}) a(1)b(2)c(3)$$

Note that the sign of a term is plus for the identity and double transposition and negative for a single transposition. This sign is called the parity of the permutation, a permutation being a product of transpositions.

We may define an antisymmetrizing operator for this system as

$$\hat{\mathcal{A}} = \frac{1}{\sqrt{3!}} (1 - \hat{P}_{23} - \hat{P}_{12} + \hat{P}_{13}\hat{P}_{12} + \hat{P}_{23}\hat{P}_{12} - \hat{P}_{13} + \hat{P}_{23}\hat{P}_{12}) \text{ and write the SD for a}$$

three electron system as

$$\Psi(1,2,3) = \hat{\mathcal{A}}a(1)b(2)c(3)$$

Note that the number of terms in  $\hat{\mathcal{A}}$  is understood from the number of orbitals being antisymmetrized. It's straight-forward to show that  $\hat{\mathcal{A}}^2 = \sqrt{3!}\hat{\mathcal{A}}$  for this three electron operator. One may extend this idea to an N electron Slater Determinant

$$\Psi(1,2,3,\dots,N) = \hat{\mathcal{A}}a(1)b(2)c(3)\cdots d(N)$$

Where

$$\hat{\mathcal{A}} = \frac{1}{\sqrt{N!}} \sum_P^{N!} \varepsilon_P \hat{P}$$

The sum goes over the  $N!$  elements of the permutation group of order  $N$  and  $\varepsilon_P$  is the parity of the permutation (positive for a permutation composed of an even number of transpositions and negative if composed of an odd number).

### *Some properties of $\hat{\mathcal{A}}$*

1.  $\hat{\mathcal{A}}^2 = \sqrt{N!} \hat{\mathcal{A}} = \sum_P^{N!} \varepsilon_P \hat{P}$ , the operator is not idempotent.
2.  $\hat{\mathcal{A}} = \hat{\mathcal{A}}^+$ , the operator is self adjoint.
3.  $\hat{\mathcal{A}}$  is symmetric with respect to electron interchange and therefore commutes with the Hamiltonian or any other operator that is symmetric with respect to electron interchange.

$$[\hat{\mathcal{A}}, \hat{H}] = 0$$