Appendix B

1. Properties of the Many-Electron Wavefunction

Probabilistic interpretation of the many-electron wavefunction

The many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, which describes the electronic state of the molecule, must be "quadratic integrable"

$$\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d^{3N}\mathbf{r} = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d^{3N}\mathbf{r} = 1$$

and $|\Psi^2(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|$ has the physical interpretation that

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d^{3N}\mathbf{r} = |\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, \ldots\, d^3\mathbf{r}_N$$

is the "*probability of finding electrons* $1, 2, \ldots, N$ *simultaneously in volume elements* $d^3\boldsymbol{r}_1, d^3\boldsymbol{r}_2, \ldots d^3\boldsymbol{r}_N$".

Indistinguishability

The fact that electrons are indistinguishable particles places important restrictions on the form of the wavefunction.
In order to preserve the probability

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d^{3N}\mathbf{r}$$

the many body wavefunctions of indistiguishable particles must be either **symmetric** or **antisymmetric** under interchange of two particles. This because all observables must remain unchanged upon interchange of two particles in the system (which is exactly the definition of indistinguishability!).

2. The two electrons case

The fact that electrons are indistinguishable means that the many-body wavefunction has to fulfill the symmetric restriction required by the conservation of the probability $|\Psi|^2\, d\mathbf{r}$ unter interchange of particles.

In the case of a two electrons system with wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2)$,

$$P(\mathbf{r}_1, d^3\mathbf{r}_1; \mathbf{r}_2, d^3\mathbf{r}_2) = \Psi(\mathbf{r}_1, \mathbf{r}_2)\Psi^*(\mathbf{r}_1, \mathbf{r}_2)d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

is the probability of electron 1 in the volume $d\mathbf{r}_1$, electron 2 simultaneously in $d\mathbf{r}_2$, and

$$P_1(\mathbf{r}_1, d^3\mathbf{r}_1) = d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \Psi(\mathbf{r}_1, \mathbf{r}_2)\Psi^*(\mathbf{r}_1, \mathbf{r}_2)$$

is the probability to find electron 1 in $d^3\mathbf{r}_1$ and the other *anywhere* else.

The probability of finding *any* of the 2 electrons in $d^3\mathbf{r}_1$ is $2P_1(\mathbf{r}_1, d^3\mathbf{r}_1)$, since the product $\Psi(\mathbf{r}_1, \mathbf{r}_2)\Psi^*(\mathbf{r}_1, \mathbf{r}_2)$ is completely symmetrical in the variables $\mathbf{r}_i$ and therefore each one has the same probability of being in a given volume.

In order to fulfill the requirements of indistinguishibility the two-electron wavefunction must satisfy

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1,) \qquad (symmetric)$$

$$\text{or}$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = -\Psi(\mathbf{r}_2, \mathbf{r}_1) \quad (antisymmetric)$$

Since electrons are **fermions** we know that we have to take the second option.

In general, the many electron wavefunction of N electrons is described by

an anti-symmetric function in the position variables $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_2$. [1]

3. The Slater Determinant

The main problem with the simple guess $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \cdot \phi_1(\mathbf{r}_1) \cdot \phi_2(\mathbf{r}_2) \ldots \phi_N(\mathbf{r}_N)$ for a many-electron wavefunction starting from single electron orbitals is that this does not take into account that the electrons are indistinguishable. It violates therefore one of the fundamental principles of quantum theory. In order to constract N electrons wavefunctions with the correct symmetry (anti-symmetry upon exchange of two electrons) we can proceed in the following way:

1. construct a set of one-electron molecular orbitals. To this end we can use for example linear combinations of atomic orbitals or, even better, Hartree-Fock orbitals, which are solution of the Hartree Fock equation (In Hartree-Fock one makes the assumption that the many-electron wavefunction is a Slater determinant of unknown molecular orbitals, and then one solves the Schrödinger equation to get such orbitals).

2. construct *products* of the one electron orbitals, which possess the right symmetry.

You can easily convince yourself that the simple product of one electron orbitals doesn't have the required anti-symmetric property

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \neq -\phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) = -\Phi(\mathbf{r}_2, \mathbf{r}_1)$$

---

[1] For the case of N electrons the result can be generalized in the following way:

$$\mathcal{P}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \qquad (symmetric)$$
$$\text{or}$$
$$\mathcal{P}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \varepsilon_P\, \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \quad (antisymmetric)$$

where $\mathcal{P}$ effects any permutation of the arguments $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ and ε_p is ± 1 according as the perturbation is equivalent to an even or odd number of interchanges.

In *linear algebra* you learnt about an object that shows this particular property: the *determinant* of a matrix.

$$\det A = \begin{vmatrix} a_{11} & \ldots & a_{1N} \\ \vdots & & \vdots \\ a_{N1} & \ldots & a_{NN} \end{vmatrix} = \sum_{i=1}^{N!} (-1)^{\alpha} a_{1p_1} a_{2p_2} \ldots a_{1p_N}$$

where the sum runs over all permutations $(p_1, p_2, \ldots, p_N)$ of the set $(1, 2, \ldots, N)$, and α is the number of permuted pairs (p_i, p_j) with $p_i > p_j$ and $i < j$.

It is simple to look at an example. For $N = 2$ we have

$$\det A = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}$$

According to the rules of determinants, we know that upon exchange of two columns the determinant changes sign:

$$\det A' = \begin{vmatrix} a_{12} & a_{11} \\ a_{22} & a_{21} \end{vmatrix} = a_{12}a_{21} - a_{11}a_{22} = -\det A$$

This is exactly what we need to construct the N electrons wavefunction!

Consider again the case of a 2 electrons wavefunction. The Slater determinant

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) \end{vmatrix}$$

has precisely the correct symmetry,

$$\Psi(\mathbf{r}_2, \mathbf{r}_1) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_2(\mathbf{r}_1) & \psi_1(\mathbf{r}_1) \\ \psi_2(\mathbf{r}_2) & \psi_1(\mathbf{r}_2) \end{vmatrix} = -\Psi(\mathbf{r}_1, \mathbf{r}_2) \quad .$$

We can now generalize the result to the case of N-electrons wavefunctions. The Slater determinant in terms of N one-electron wavefunctions $\psi_1, \ldots \psi_N$

is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_2) \\ . & . & . & . \\ . & . & . & . \\ . & . & . & . \\ \psi_1(\mathbf{r}_N) & \psi_2(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} .$$

4. A One Dimensional Example

Imagine you have two electrons in a one dimensional box, and that one is in the ground state, the other in the first excited state. The square of the corresponding one-particle wavefunctions, $\phi_1(r)$ and $\phi_2(r)$, are shown here:
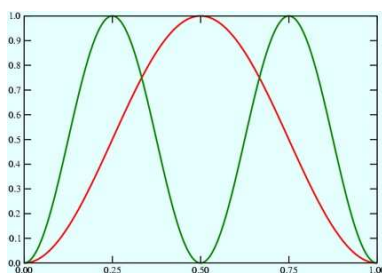
Below are shown two different 2D-plots of the square of the two electron wavefunction obtained from the "product" of the ground state and first excited state one electron wavefunctions.

The first (on the left) is constructed as a simple product of the two one-electron wavefunctions

$$\Phi_1(r_1, r_2) = \phi_1(r_1)\, \phi_2(r_2)$$

But we have just shown that this expression is incorrect because it has no symmetry. The picture on the right shows the correct antisymmetrized difference of products

$$\Phi_2(r_1, r_2) = \phi_1(r_1)\, \phi_2(r_2) - \phi_1(r_2)\, \phi_2(r_1)$$
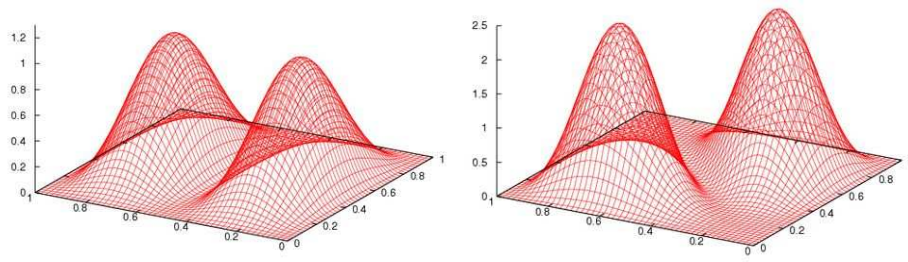
Figure 1: Plot of $\Phi_1(r_1, r_2)$ (left) and $\Phi_2(r_1, r_2)$ (right).

What is the main difference between these two wavefunctions?.