

III. Many-electron wave functions

A. The electron spin

Zeeman has shown that a small magnetic field causes the splitting of energy levels in atoms. Each atomic level is split into a doublet. The amount of splitting is proportional to the field. At zero field these doublets are degenerate. The conclusion is that the electron has an intrinsic magnetic moment which can take two values. The states of the internal magnetic moment of the electron are assumed to be proportional to an internal angular momentum called “spin”. The spin of an electron can be assumed to have two values $\pm \frac{\hbar}{2}$. This is an additional “degree of freedom”. It is not continuous, but is nevertheless a degree of freedom. We denote a spin-orbital $\psi_n(\mathbf{x}) = \psi_n(\mathbf{r}, s)$ where $\mathbf{r}$ is a point in 3D space and s is a “spin variable”, which allows us to perform an inner product of spin as explained now. There are two possible spin functions for an electron, $\alpha(s)$ denotes spin up and $\beta(s)$ spin down. These two states are complete and orthonormal:

$$\int \alpha(s)^* \alpha(s) ds = \langle \alpha | \alpha \rangle = 1$$

$$\int \beta(s)^* \alpha(s) ds = \langle \beta | \alpha \rangle = 0$$

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The variable s is just a mnemonic. With new notation, we have:

$$\langle \psi | \phi \rangle = \int \psi(\mathbf{x})^* \phi(\mathbf{x}) d\mathbf{x} = \int \int \psi(\mathbf{r}, s)^* \phi(\mathbf{r}, s) ds d^3r \quad (3.1.1)$$

B. The Pauli principle

The electronic wavefunctions are functions of N_e electronic coordinates and spins $\psi(\mathbf{x}_1, \dots, \mathbf{x}_{N_e})$. Here $\mathbf{x}_j \equiv (\mathbf{r}_j, s_j)$. The Pauli principle states that this wavefunction must be antisymmetric with respect to interchange of two electrons:

$$\psi(\dots \mathbf{x}_i, \dots, \mathbf{x}_j, \dots) \equiv -\psi(\dots \mathbf{x}_j, \dots, \mathbf{x}_i, \dots) \quad (3.2.1)$$

This is a “boundary condition” we impose while solving for any electronic wave function.

C. The Excited states of the Helium atom

How should we represent the, in an approximate form, the low lying excited states of the Helium atom. He^+ has two low lying orbitals 1s and 2s (the 2p orbitals are degenerate with the 2s, but we will not consider them because in the Helium atom they are of much higher energy. We can form a 2-electron wavefunction by: $\psi(\mathbf{x}_1, \mathbf{x}_2) = \psi_{1s}(r_1)\psi_{1s}(r_2)[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)]$.

The excited states will involve excitation of an electron to the 2s orbital. We can then write:

$$\begin{aligned} \psi_2(x_1, x_2) &= [\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{1s}(r_2)\psi_{2s}(r_1)]\alpha(s_1)\beta(s_2) \\ \psi_3(x_1, x_2) &= [\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{1s}(r_2)\psi_{2s}(r_1)][\alpha(s_1)\beta(s_2) \\ &\quad + \alpha(s_2)\beta(s_1)] \\ \psi_4(x_1, x_2) &= [\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{1s}(r_2)\psi_{2s}(r_1)][\beta(s_1)\beta(s_2)] \\ \psi_5(x_1, x_2) &= [\psi_{1s}(r_1)\psi_{2s}(r_2) + \psi_{1s}(r_2)\psi_{2s}(r_1)][\alpha(s_1)\beta(s_2) \\ &\quad - \alpha(s_2)\beta(s_1)] \end{aligned} \quad (3.3.1)$$

The first 3 states form a triplet the total spin is 1. The last is again a singlet (like the ground state).

D. The Slater wave function is the basic anti-symmetric function describing N electrons in N orbitals

The previous example is difficult to generalize. In order to develop a way to easily represent antisymmetric functions of all types, we consider the following 2-electron function, composed of 2 1-electron spin-orbitals:

$$\begin{aligned}\Psi(x_1, x_2) &= \frac{1}{\sqrt{2}} [\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) \\ \phi_2(x_1) & \phi_2(x_2) \end{vmatrix}\end{aligned}\tag{3.4.1}$$

If we choose the orbitals to be orthonormal, $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ then:

$$\begin{aligned}\langle \Psi | \Psi \rangle &= \iint \Psi(x_1, x_2)^* \Psi(x_1, x_2) dx_1 dx_2 \\ &= \frac{1}{2} \iint [\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)]^2 dx_1 dx_2 \\ &= \frac{1}{2} \iint [\phi_1(x_1)^2 \phi_2(x_2)^2 + \phi_1(x_2)^2 \phi_2(x_1)^2 \\ &\quad + 2\phi_1(x_2)\phi_2(x_1)\phi_1(x_2)\phi_2(x_1)] dx_1 dx_2 = 1\end{aligned}\tag{3.4.2}$$

E. Without loss of generality, we may assume the orbitals of a Slater wave function are orthogonal

But what happens if the orbitals are not orthogonal? Suppose that the orbitals were not orthonormal:

$$\langle \phi_i | \phi_j \rangle = S_{ij}\tag{3.5.1}$$

It is then possible to “orthonormalize” them. i.e define two linear combinations which are orthonormal. Define:

$$\xi_n = \sum_m \phi_m A_{mn} \quad (3.5.2)$$

and demand: $\langle \xi_i | \xi_j \rangle = \delta_{ij}$. Then:

$$\delta_{ij} \langle \xi_i | \xi_j \rangle = \sum_{m,n} A_{mi}^* \langle \phi_i | \phi_j \rangle A_{nj} = (A^\dagger S A)_{ij} \quad (3.5.3)$$

Thus: $A^\dagger S A = I$ or $AA^\dagger = S^{-1}$. Note also that $\det A = (\det S)^{-1/2}$. There are many solutions to this equation. (For example, if A_0 is a solution then so is $A_0 U$ where U is any unitary matrix.) Each solution will give us a different set of orthonormal orbitals. The Slater wave function made out from these new orbitals is:

$$\begin{aligned} \det\{\xi_i(x_j)\} &= \det\{(A^T)_{ni} \phi_i(x_j)\} = \det A \times \det\{\phi_i(x_j)\} \\ &= \frac{1}{\sqrt{\det S}} \det\{\phi_i(x_j)\} \end{aligned} \quad (3.5.4)$$

Thus, the new wavefunction is the same as the old one, up to multiplication by constant! Yet, it is always more convenient to work with normalized orbitals, so we can assume the orbitals are orthonormal without any loss of generality. This development also shows that given any set of N orbitals from which the Slater wave function has been constructed, we can take N linear combinations of the orbitals to obtain new orbitals that give the same Slater wave function up to a constant factor.

F. Any antisymmetric function can be expanded as a sum of basic Slater (determinantal) functions

For orthonormal orbitals, the normalization is easy to compute. We write explicitly the determinant as:

$$\det[\phi_1 \dots \phi_N](\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{i_1 \dots i_N} (-)^{P_{i_1 \dots i_N}} \prod_{k=1}^N \phi_{i_k}(\mathbf{x}_k) \quad (3.6.1)$$

Where $(i_1 \dots i_N)$ is a permutation of the numbers $1 \dots N$ (there are $N!$ such permutations). Each permutation can be obtained from a series of pair swapping operations. For example: (132) is obtained from (123) by switching the pair of numbers in position 2 and 3. We write this as: $(132) = S_{23}(123)$. (2413) is obtained from (1234) by three operations:

$$S_{23}S_{34}S_{12}(1234) = S_{23}S_{34}(2134) = S_{23}(2143) = (2413) \quad (3.6.2)$$

If the number of switches is odd the permutation is odd and $P_{i_1 \dots i_N} = 1$; if the number of switches is even, the permutation is even and $P_{i_1 \dots i_N} = 0$. The normalization of a determinantal wave function composed of orthonormal orbitals is:

$$\begin{aligned} & \int |\det[\phi_1 \dots \phi_N](\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \sum_{i_1 \dots i_N j_1 \dots j_N} (-)^{P_{i_1 \dots i_N}} (-)^{P_{j_1 \dots j_N}} \int \prod_{k=1}^N \phi_{i_k}(\mathbf{x}_k) \prod_{q=1}^N \phi_{j_q}(\mathbf{x}_q) d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \sum_{i_1 \dots i_N j_1 \dots j_N} (-)^{P_{i_1 \dots i_N}} (-)^{P_{j_1 \dots j_N}} \prod_{k=1}^N \langle \phi_{i_k} | \phi_{j_k} \rangle \end{aligned} \quad (3.6.3)$$

Because of orthonormality the orbital integral $\langle \phi_{i_k} | \phi_{j_k} \rangle$ is zero unless $i_k = j_k$. These integrals appear in products so the product is non-zero only if $i_k = j_k$ for *all* $k = 1 \dots N$. The only conclusion is, that the two permutations *must* be identical and:

$$\int |\det[\xi_1 \dots \xi_N](\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N = \sum_{i_1 \dots i_N j_1 \dots j_N} 1 = N! \quad (3.6.4)$$

We conclude that the normalization factor of a determinantal wave function of orthonormal orbitals is $\frac{1}{\sqrt{N!}}$ and write:

$$\frac{1}{\sqrt{N!}} \det[\xi_{i_1} \dots \xi_{i_N}] \equiv |i_1 \dots i_N\rangle \quad (3.6.5)$$

Given a set of $M > N$ orthonormal single-electron spin-orbitals $\phi_n(\mathbf{x}) = \phi_n(\mathbf{r}, s)$ $n = 1, 2, \dots, M$, we can consider the space of all linear combinations of all N -particle determinants that can be made. There are $\binom{M}{N} = \frac{M!}{N!(M-N)!}$ ways to select determinants so this is the dimension of the space. The dimension grows factorially with M . A typical antisymmetric wave function can be approached by linear combinations of these determinants:

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \sum_{\{i_1, \dots, i_N\}} C_{i_1, \dots, i_N} \det[\phi_{i_1}(\mathbf{x}_1) \dots \phi_{i_N}(\mathbf{x}_N)] \quad (3.6.6)$$

The sum is over all selections of N integers, where each selection is ordered so that $i_1 < i_2 < \dots$. If the orbitals are orthogonal, the constants $C_{i_1, \dots, i_N}$ are obtained from:

$$C_{i_1, \dots, i_N} = \frac{1}{\sqrt{N!}} \int \det[\phi_{i_1}(\mathbf{x}_1) \dots \phi_{i_N}(\mathbf{x}_N)] \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_1 \dots d\mathbf{x}_N \quad (3.6.7)$$

G. Determinant expectation values

In this section we discuss the calculation of expectation values of many-electron operators for N electrons within a given Slater wave function $\Psi_S(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)]$. We assume the orbitals $\phi_i(\mathbf{x})$ are orthonormal: $\langle \phi_i | \phi_j \rangle = \delta_{ij}$.

i. One-body operators

Consider an operator $\hat{o}_1(\mathbf{x})$ which operates on an electron with spin-coordinates $\mathbf{x}$. For N electrons we define the sum of $\hat{o}_1$ for each electron

$$\hat{O} = \sum_{n=1}^N \hat{o}_1(\mathbf{x}_n), \quad (3.6.8)$$

Examples: when electrons are in a potential well $v(\mathbf{r})$, the total potential energy operator is $\hat{V} = \sum_{n=1}^N v(\mathbf{r}_n)$; the total kinetic energy is: $\hat{T} = \sum_{n=1}^N \hat{T}_1(n) = \sum_{n=1}^N \left(-\frac{\hbar^2}{2\mu_e} \frac{\partial^2}{\partial x_n^2} \right)$.

When the system of N electrons is in a given Slater wave function $\Psi_S(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)]$, then using the notation of (3.6.3), we have:

$$\begin{aligned} & \langle \Psi_S | \hat{O} | \Psi_S \rangle \\ &= \frac{1}{N!} \int \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)] \hat{O} \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)] d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \frac{1}{N!} \sum_{n=1}^N \sum_{\substack{i_1 \dots i_N \\ j_1 \dots j_N}} (-)^{P_i + P_j} \prod_{\substack{k=1 \\ k \neq n}}^N \langle \phi_{i_k} | \phi_{j_k} \rangle \langle \phi_{i_n} | \hat{o}_1 | \phi_{j_n} \rangle \end{aligned} \quad (3.6.9)$$

Once again, a massive cancellation of terms happens in the first integral. Inspection shows that both permutations, i and j , must be equal otherwise there is always an orbital integral for which the integrals $\langle \xi_{i_k} | \xi_{j_k} \rangle$ is zero. When the permutations are identical we have:

$$\langle \Psi_S | \hat{O} | \Psi_S \rangle = \frac{1}{N!} \sum_{n=1}^N \sum_{i_1 \dots i_N} \langle \phi_{i_n} | \hat{o}_1 | \phi_{j_n} \rangle = \sum_{n=1}^N \langle \phi_j | \hat{o}_1 | \phi_n \rangle \quad (3.6.10)$$

As an example, let us take the electron density $\hat{n}(\mathbf{r}) = \sum_{n=1}^N \delta(\mathbf{r} - \mathbf{r}_n)$. Thus:

$$n(\mathbf{r}) = \sum_{n=1}^N |\phi_n(\mathbf{r}, s)|^2 \quad (3.6.11)$$

Conclusion: The matrix element of a 1-particle operator is the sum of its single-electron matrix elements.

ii. Two-body operators

Consider an operator $\hat{o}_{12}(\mathbf{x}_1, \mathbf{x}_2)$ which operates on two electrons with spin-coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$. For N electrons we define the sum of $\hat{o}_{12}$ on all pairs of electrons

$$\hat{O} = \sum_{n < m = 1}^N \hat{o}_{12}(\mathbf{x}_n, \mathbf{x}_m) = \frac{1}{2} \sum_{n \neq m = 1}^N \hat{o}_{12}(\mathbf{x}_n, \mathbf{x}_m), \quad (3.6.12)$$

Examples: The 2-electron interaction potential is $u_{12}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\kappa e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$. The total interaction energy operator is: $\hat{U} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N u_{12}(\mathbf{r}_i, \mathbf{r}_j)$.

We compute the expectation value

$$\begin{aligned} & \langle \Psi_S | \hat{U} | \Psi_S \rangle \\ &= \frac{1}{N!} \int \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)] \hat{U} \det[\phi_1(\mathbf{x}_1) \dots \phi_N(\mathbf{x}_N)] d\mathbf{x}_1 \dots d\mathbf{x}_N \\ &= \frac{1}{N!} \frac{1}{2} \sum_{\substack{n, m=1 \\ n \neq m}}^N \sum_{\substack{i_1 \dots i_N \\ j_1 \dots j_N}} (-)^{P_i + P_j} \prod_{\substack{k \neq n \\ k \neq m}}^N \langle \phi_{i_k} | \phi_{j_k} \rangle \langle \phi_{i_m} \phi_{j_m} | u_{12} | \phi_{i_n} \phi_{j_n} \rangle \end{aligned} \quad (3.6.13)$$

Where we used the notation:

$$\langle \phi_i \phi_j | u_{12} | \phi_{i'} \phi_{j'} \rangle \equiv \int \phi_i(\mathbf{x}) \phi_j(\mathbf{x}') u_{12}(\mathbf{r}, \mathbf{r}') \phi_{i'}(\mathbf{x}) \phi_{j'}(\mathbf{x}') d\mathbf{x} d\mathbf{x}' \quad (3.6.14)$$

The following symmetry properties hold from the above definition:

$$\begin{aligned}
\langle \phi_i \phi_j | u_{12} | \phi_{i'} \phi_{j'} \rangle &= \langle \phi_{i'} \phi_j | u_{12} | \phi_i \phi_{j'} \rangle = \langle \phi_i \phi_{j'} | u_{12} | \phi_{i'} \phi_j \rangle \\
&= \langle \phi_{i'} \phi_{j'} | u_{12} | \phi_i \phi_j \rangle = etc
\end{aligned} \tag{3.6.15}$$

For a pair of permutations to contribute to the integral in Eq. (3.6.13), the permutations must either be identical or involve the permutation of a single pair of orbitals. Thus:

$$\langle \Psi_S | \hat{U} | \Psi_S \rangle = \frac{1}{2} \sum_{\substack{n,m=1 \\ n \neq m}}^N [\langle \phi_n \phi_m | u_{12} | \phi_n \phi_m \rangle - \langle \phi_n \phi_m | u_{12} | \phi_m \phi_n \rangle] \tag{3.6.16}$$