

## 25 The Independent particle approximation: Slater determinants

1. In this section we will go through a very important concept: the independent particle approximation. This approximation is at the heart of many methods such as Hartree-Fock theory and Density functional theory which are very popular methods to solve the electronic Schrödinger Equation, Eq. (23.8).
2. The first assumption within the independent particle approximation is each particle is independent, ie each particle is in a different orbital, so that we can write the wavefunction in a product form:

$$\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\}) = \eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N) \quad (25.1)$$

where  $\{\eta_i\}$  are  $N$  orbitals (we assume there are  $N$  electrons as well) and we have omitted the dependence on  $\{R_I\}$  on the right hand side. This equation means that electron 1, whose position is given by  $r_1$  is in the orbital  $\eta_1$ , electron 2 whose position is given by  $r_2$  is in orbital  $\eta_2$  and so on. The approximate form of the wavefunction represented in Eq. (25.1) is often known as the **Hartree product**.

3. However, Eq. (25.1) is not an acceptable wavefunction for Fermions since it lacks the anti-symmetry property of Fermions. How do we know this? Let us permute the coordinates for electrons 1 and 2 (that is interchange the positions of electron 1 and 2) using a permutation operator  $\mathcal{P}_{1,2}$ , and see what happens:

$$\begin{aligned}\mathcal{P}_{1,2} [\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\})] &= \mathcal{P}_{1,2} [\eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N)] \\ &= [\eta_1(r_2)\eta_2(r_1) \cdots \eta_N(r_N)] \\ &\neq \pm [\eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N)]\end{aligned}\tag{25.2}$$

Hence while Eq. (25.1) is a useful *independent particle* approximation for the wavefunction, but it does not have the suitable properties to represent Fermionic systems.

4. To see that Eq. (25.1) does have the attractive independent particle property, in that all the  $N$  particles represented in Eq. (25.1) are independent of each other, we note that the probability associated with the wavefunction has the following product form:

$$|\phi(r_1, r_1, \dots, r_i, \dots, \{R_I\})|^2 = |\eta_1(r_1)|^2 |\eta_2(r_2)|^2 \cdots |\eta_N(r_N)|^2 \quad (25.3)$$

and from probability theory we remember that two events A and B are considered independent of each other if the probability of both A and B occurring simultaneously is equal to the product of the probability of A occurring times the probability of B occurring. Eq. (25.3) has a similar mathematical form. And for this reason the approximation in Eq. (25.1) is termed as the independent particle approximation.

5. So, Eq. (25.1) is *useful* but can we make it better, by including permutation symmetry in it?

6. Let us now consider a new function  $\Phi$  which is a sum of two terms similar to Eq. (25.1):

$$\Phi = [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] \quad (25.4)$$

where in the second term we have just interchanged particles  $i$  and  $j$ . Equation (25.4) does satisfy permutation symmetry but only for particle  $i$  and  $j$  since:

$$\begin{aligned} \mathcal{P}_{i,j}\Phi &= \mathcal{P}_{i,j} \{ [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] \} \\ &= [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] \\ &= -\Phi \end{aligned} \quad (25.5)$$

However, Eq. (25.4) obeys permutation symmetry only for particles  $i$  and  $j$  and *no other set of particles*. (We can convince ourselves that this is true by interchanging particle 1 and particle 2 and we would find that permutation symmetry is not obeyed. Please do this for **homework**.)

7. Can we generalize Eq. (25.4) so that permutation symmetry is obeyed for all set of particles. Let us propose the following definition for the wavefunction:

$$\Phi = \sum_p (-1)^p \{ \eta_1(r_1) \eta_2(r_2) \cdots \eta_i(r_i) \cdots \eta_j(r_j) \cdots \} \quad (25.6)$$

where the sum is over all possible permutations. For each permutation there is a negative sign introduced by way of the factor  $(-1)^p$ . Since all permutations are included (instead of just one in Eq. (25.4)) we note that this equation is indeed a generalization of Eq. (25.4).

8. Let us illustrate Eq. (25.6) on the board for a few simple cases and convince ourselves that Eq. (25.6) indeed obeys permutation symmetry.

9. As we will see on the board Eq. (25.6) is in fact a short hand notation for a determinant. Hence the wavefunction in Eq. (25.6) has a determinantal form. This was first noted by Slater and hence is called the Slater determinant.
10. The Slater determinant in Eq. (25.6) is closest a Fermionic system can get to an independent particle system, without violating permutation symmetry.
11. In fact, we can also write Eq. (25.6) as: which looks more like a determinant as we saw on the board for the simpler cases.
12. It is important to note here that both in Hartree-Fock theory and in density functional theory, two commonly used approaches in electronic structure theory, the wavefunction has a Slater determinant form. This form actually affords a great deal of simplification to Eq. (23.8)