

18 Permutation symmetry

1. One of the first things we notice in Eq. (17.6), that is the full molecular Hamiltonian, is that it remains the same when we interchange any two electrons. In fact this is true for any observable. Why?
2. Say we have a Helium atom that has two electrons. And I want to name the two electrons A and B. I am pretending I can say which one is A and which one is B. And if I could then perform an experiment with A in the 1s orbital of He and B in the 2s orbital of Helium and make an observation. I follow this up by moving A to the 2s orbital and B to the 1s orbital, and if I could make another observation I would have to get the same result as the previous time around. And this should be true for any kind of observation that we make. This is what I mean when I say the two electrons are indistinguishable.
3. Hence the probability (which is also an observable quantity) associated with the wavefunction, $\phi(r_i, \{R_I\})$ should also remain the same if I were to interchange any two electrons. That is:

$$|\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\})|^2 = |\phi(r_2, r_1, \dots, r_i, \dots, \{R_I\})|^2 \quad (18.1)$$

where on the right hand side we have exchanged the positions of electrons 1 and 2 and as per our previous discussion these probabilities must be the same.

4. Hence the electronic wavefunction, $\phi(r_i, \{R_I\})$, must satisfy the following condition:

$$\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\}) = \pm \phi(r_2, r_1, \dots, r_i, \dots, \{R_I\}) \quad (18.2)$$

that is the wavefunction can either be symmetric (+) or anti-symmetric (-) with exchange (or permutation) of particles.

5. It turns out that in nature we have two different kinds of particles. One set of particles have wavefunctions that are symmetric with respect to exchange of particles. This set of particles are called *bosons*. The reason they are called so is because they obey what is known as the Bose-Einstein statistics. The other set of particles that have wavefunctions that are anti-symmetric with respect to exchange of particles are called *fermions* since they obey Fermi-Dirac statistics. (These statistics are means that one uses to find out how the energy levels are populated. Based on the symmetry properties that these particles obey, that is symmetry with respect to permutation, the energy levels are populated differently and these two statistics tell us how so.)
6. By contrast classical particles obey what is known as the Maxwell-Boltzmann statistics.
7. Therefore, for *bosons*:

$$\phi_B(r_1, r_2, \dots, r_i, \dots, \{R_I\}) = \phi_B(r_2, r_1, \dots, r_i, \dots, \{R_I\}) \quad (18.3)$$

and for *fermions*:

$$\phi_F(r_1, r_2, \dots, r_i, \dots, \{R_I\}) = -\phi_F(r_2, r_1, \dots, r_i, \dots, \{R_I\}) \quad (18.4)$$

where we have used subscript B to represent boson and subscript F to represent fermions.

8. One more important result that comes in from relativistic quantum mechanics is that *fermions* can only have half-integer spins and *bosons* can only have integer spins. This is something that one cannot get from non-relativistic quantum mechanics, hence we will take this result for granted at this time.
9. Electrons, protons and neutrons are *fermions*. Photons are *bosons*. In addition, a collection of two fermions has a net spin of 0 or 1 and hence is a *boson*. For this reason a ${}^4\text{He}$, since it has an even number of electrons, protons and neutrons, is a *boson*. We will see more on this a little later.
10. Another important result that we find from permutation symmetry of *fermions* is that two fermions cannot be at the same point, since if r_1 is the position of electrons 1 and 2

$$\phi_F(r_1, r_1, \dots, r_i, \dots, \{R_I\}) = -\phi_F(r_1, r_1, \dots, r_i, \dots, \{R_I\}) = 0. \quad (18.5)$$

Hence, if two fermions were to occupy the same position, the corresponding state wavefunction would have to be zero, if not it would violate the permutation anti-symmetry property of fermions. This is called the *Pauli's exclusion principle* and states that two electrons (or more generally fermions) cannot occupy the same point in space simultaneously and hence cannot have the same set of quantum numbers. This is a very powerful result that we will get back to in a little while, but more importantly this is a result that really rules the whole of chemistry and is obtained entirely from permutation symmetry.

11. As for bosons, two bosons can occupy the same position since:

$$\phi_B(r_1, r_1, \dots, r_i, \dots, \{R_I\}) = \phi_B(r_1, r_1, \dots, r_i, \dots, \{R_I\}) \quad (18.6)$$

does not have to be zero in this case. Thus bosons can occupy the same point in space and can occupy the same energy level, etc and hence are very *sociable* particles unlike fermions. This leads to a very important property at low temperatures. Since, many bosons can occupy the same energy level, a collection of these at low temperatures can *condense* together to form a **Bose-Einstein condensate**. Probably many of you have heard about this very new and interesting phenomenon. (New in the sense that it was first seen experimentally in 1995 but it was in fact predicted by Bose back in 1920, using permutation symmetry just as we did here!!)

12. Classical particles obey Maxwell-Boltzmann statistics and have intermediate *sociability* :-), between fermions and bosons.

19 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. (17.8).
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:

$$\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\}) = \eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N) \quad (19.1)$$

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 η_1 , electron 2 whose position is given by r_2 is in orbital η_2 and so on. The approximate form of the wavefunction represented in Eq. (19.1) is often known as the **Hartree product**.

3. However, Eq. (19.1) 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:

$$\begin{aligned} \mathcal{P}_{1,2}[\phi(r_1, r_2, \dots, r_i, \dots, \{R_I\})] &= \mathcal{P}_{1,2}[\eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N)] \\ &= [\eta_1(r_2)\eta_2(r_1) \cdots \eta_N(r_N)] \\ &\neq \pm [\eta_1(r_1)\eta_2(r_2) \cdots \eta_N(r_N)] \end{aligned} \quad (19.2)$$

Hence while Eq. (19.1) 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. (19.1) does have the attractive independent particle property, in that all the N particles represented in Eq. (19.1) are independent of each other, we note that the probability associated with the wavefunction has the following product form:

$$|\phi(r_1, r_1, \dots, r_i, \dots, \{R_I\})|^2 = |\eta_1(r_1)|^2 |\eta_2(r_2)|^2 \cdots |\eta_N(r_N)|^2 \quad (19.3)$$

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. (19.3) has a similar mathematical form. And for this reason the approximation in Eq. (19.1) is termed as the independent particle approximation.

5. So, Eq. (19.1) is *useful* but can we make it better, by including permutation symmetry in it?
6. Let us now consider a new function Φ which is a sum of two terms similar to Eq. (19.1):

$$\Phi = [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] \quad (19.4)$$

where in the second term we have just interchanged particles i and j . Equation (19.4) does satisfy permutation symmetry but only for particle i and j since:

$$\begin{aligned} \mathcal{P}_{i,j}\Phi &= \mathcal{P}_{i,j} \{[\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots]\} \\ &= [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_j)\cdots\eta_j(r_i)\cdots] - [\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots] \\ &= -\Phi \end{aligned} \quad (19.5)$$

However, Eq. (19.4) 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. (19.4) so that permutation symmetry is obeyed for all set of particles. Let us propose the following definition for the wavefunction:

$$\Phi = \sum_p (-1)^p \{\eta_1(r_1)\eta_2(r_2)\cdots\eta_i(r_i)\cdots\eta_j(r_j)\cdots\} \quad (19.6)$$

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. (19.4)) we note that this equation is indeed a generalization of Eq. (19.4).

8. Let us illustrate Eq. (19.6) on the board for a few simple cases and convince ourselves that Eq. (19.6) indeed obeys permutation symmetry.
9. As we will see on the board Eq. (19.6) is in fact a short hand notation for a determinant. Hence the wavefunction in Eq. (19.6) has a determinantal form. This was first noted by Slater and hence is called the Slater determinant.
10. The Slater determinant in Eq. (19.6) is closest a Fermionic system can get to an independent particle system, without violating permutation symmetry.
11. In fact, we can also write Eq. (19.6) 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. (17.8)