24 Permutation symmetry

1. One of the first things we notice in Eq. (23.6), 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:

$$|\phi(r_1, r_2, \cdots, r_i, \cdots, \{R_I\})|^2 = |\phi(r_2, r_1, \cdots, r_i, \cdots, \{R_I\})|^2 \tag{24.1}$$

   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:

$$\phi(r_1, r_2, \cdots, r_i, \cdots, \{R_I\}) = \pm\phi(r_2, r_1, \cdots, r_i, \cdots, \{R_I\}) \tag{24.2}$$

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*:

$$\phi_B(r_1, r_2, \cdots, r_i, \cdots, \{R_I\}) = \phi_B(r_2, r_1, \cdots, r_i, \cdots, \{R_I\}) \tag{24.3}$$

   and for *fermions*:

$$\phi_F(r_1, r_2, \cdots, r_i, \cdots, \{R_I\}) = -\phi_F(r_2, r_1, \cdots, r_i, \cdots, \{R_I\}) \tag{24.4}$$

   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}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

$$\phi_F(r_1, r_1, \cdots, r_i, \cdots, \{R_I\}) = -\phi_F(r_1, r_1, \cdots, r_i, \cdots, \{R_I\}) = 0. \tag{24.5}$$

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:

$$\phi_B(r_1, r_1, \cdots, r_i, \cdots, \{R_I\}) = \phi_B(r_1, r_1, \cdots, r_i, \cdots, \{R_I\}) \tag{24.6}$$

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.

