

Multi-particle Wavefunctions and the Importance of a Minus Sign

R. M. Suter

May 1, 2015

Wavefunctions and identical particles. For multiple particle wavefunctions, there are substantial notational complications. For N particles, we need N coordinates, $\{x\}$ or $\{\mathbf{r}\}$. For distinguishable particles, we can specify positions x_1, x_2, \dots, x_N and ask questions such as, what is the probability for a multi-particle configuration in which particle 1 is at position x_1 within dx_1 , **and** particle 2 is at position x_2 within dx_2 , etc. We write this as $P(x_1, x_2, \dots, x_N)dx_1 dx_2 \dots dx_N$ and the corresponding wavefunction is $\psi(x_1, x_2, \dots, x_N)$. In this notation, you should think of the position in the list of arguments as referring to the list of particles and the values of the corresponding arguments as giving the appropriate position value for that particle. That is, the subscripts on the x 's simply denote entries in $\{x\}$ whereas the first argument says we are asking about particle 1 being at position x_1 . In the above expressions, the subscripts and the positions in the list correspond, so the distinction seems unnecessary.

If the particles are indistinguishable, we have to re-phrase the probability question as, what is the probability that there is **a** particle at position x_1 within dx_1 and **a** particle is at position x_2 within dx_2 , etc. There are N of these coordinates, but they are just a list of positions, not positions of specific particles. We still write the probability as $P(x_1, x_2, \dots, x_N)$ (still the probability density for finding particle 1 position at x_1 , particle 2 at position x_2 , etc) and $P(x_2, x_1, \dots, x_N)$ the corresponding quantity for finding particle 1 at position x_2 , particle 2 at x_1 , etc. If the particles are truly indistinguishable, we must insist that the last two probabilities are the same: permuting which particle is where cannot give a different probability. In fact, any random re-ordering of the position variables must give the same probability.

Multiparticle wavefunctions must obey either

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = \psi(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (1)$$

or

$$\psi(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = - \psi(x_1, \dots, x_j, \dots, x_i, \dots, x_N) \quad (2)$$

in order that the probability behave properly. While one could imagine a complex phase factor, $e^{i\theta}$, as being a more general solution that gives the probability the correct behavior, performing another exchange on the right side of (1) or (2) has to return the function we started with, so $e^{i2\theta} = 1$ and $\theta = 0$ or π (+1 or -1) are the only choices.

Product wavefunctions for non-interacting identical particles. For two non-interacting particles, the Schrodinger equation takes the form

$$-\frac{\hbar^2}{2m} [\nabla_1^2 + \nabla_2^2] \psi(x_1, x_2) + [V(x_1) + V(x_2)] \psi(x_1, x_2) = E\psi(x_1, x_2), \quad (3)$$

with E being the energy of the two particle system. Operations on ψ involve only one position variable at a time, so we expect to be able to form solutions as products:

$$\tilde{\psi}_{n,m}(x_1, x_2) = u_n(x_1) u_m(x_2), \quad (4)$$

where u_n and u_m are solutions to the one particle equation in potential $V(x)$. The energy is simply

$$E = E_n + E_m. \quad (5)$$

The left side of (4) indicates that we have two particles with one in state n and one in state m and we are asking about particle 1 being at x_1 , particle 2 being at x_2 . The right side implies that particle 1 is in state n and particle 2 is in state m – this already appears to overstate our knowledge of the two particle system (unless, in fact, $n = m$)! Note that exchanging the position coordinates yields

$$\tilde{\psi}_{n,m}(x_2, x_1) = u_n(x_2) u_m(x_1). \quad (6)$$

Equation 6 gives the probability amplitude that particle 1 is in state n and is at coordinate x_2 and particle 2 is in state m and is at coordinate x_1 . This could equally well be interpreted as reversing the particles' state assignments, keeping the coordinates the same.

We noted that the product functions overstate our knowledge and this is reflected in the two expressions, (4) and (6), which appear equally valid (or invalid) but which do not satisfy either (1) or (2). As an example, take the potential to be the infinite square well and take $n = 1$ and $m = 2$ (keeping in mind that for $n = m$ the two product functions are identical) and take $x_1 = a/2$, $x_2 = 2a/3$. Then (4) becomes

$$\tilde{\psi}_{1,2}(x_1, x_2) = \frac{2}{a} \sin \left[\frac{\pi a}{a} \right] \sin \left[\frac{2\pi 2a}{a} \right] = \frac{2}{a} (1) \sin(4\pi/3) = \frac{2}{a} \left(-\frac{\sqrt{3}}{2}\right), \quad (7)$$

whereas

$$\tilde{\psi}_{1,2}(x_2, x_1) = \frac{2}{a} \sin \left[\frac{\pi 2a}{a} \right] \sin \left[\frac{2\pi a}{a} \right] = \frac{2}{a} (\sqrt{3}/2) \sin \pi = 0. \quad (8)$$

This is clearly inconsistent with (1) and (2).

The bottom line is that we have two possible product wavefunctions that correspond to alternate assignments of particles to states or position coordinates. Both overstate our knowledge of the system but both are energy eigenfunctions. In any such situation, quantum mechanics tells us to sum the amplitudes for things we do not know and allow for interference effects that occur when we square the amplitude to obtain a probability function. This is directly analogous to the double slit experiment (or any diffraction experiment): we sum the amplitudes associated with each possible path to obtain the observed interference pattern. We form two possible linear combinations that satisfy either (1) or (2):

$$\psi_{n,m}(x_1, x_2) = \frac{1}{\sqrt{2}} [u_n(x_1) u_m(x_2) \pm u_n(x_2) u_m(x_1)]. \quad (9)$$

The pre-factor maintains the normalization of ψ (assuming the u 's are normalized). This function explicitly demonstrates our ignorance by including terms associated with each indistinguishable assignment combination of particles to states or positions: either the particle at x_1 is in state n or it is the one in state m .

The above simple argument (even if the notation is not so straightforward) yields an astounding result. The choice of + or – in the linear combination leads to quite different behavior and experimental observation leads to the conclusion that some types of objects use

the + and some types use the –! Any particle with half-integer spin (electrons, protons, neutrons, quarks, muons, taus, neutrinos,...) uses the – and these particles are called Fermions (as we will see, they obey the Pauli exclusion principle). Integer spin particles (photons, pions, Kon's,... and now the Higgs) use the + and are called Bosons (they do not obey the Pauli principle). This choice of sign leads to completely different behavior of collections of particles. Composite objects (nuclei, atoms,...) that have well-defined spin obey the same rules. For example, ${}^4\text{He}$, composed of two protons, two neutrons, and two electrons has spin zero and is a Boson whereas ${}^3\text{He}$ with two protons, one neutron, and two electrons has spin $1/2$ and is a Fermion (these statements apply to the ground electronic and nuclear states).

To see that the choice of sign leads to different behavior, let's ask about the probability of finding the two *non-interacting* particles at the same position. We have

$$\psi_{n,m}(x_1, x_1) = \frac{1}{\sqrt{2}} [u_n(x_1) u_m(x_1) \pm u_n(x_1) u_m(x_1)]. \quad (10)$$

For Bosons, with the +, we find $\psi_{n,m}(x_1, x_1) = \frac{1}{\sqrt{2}} 2u_n(x_1) u_m(x_1)$ which means that $P_{n,m}(x_1, x_1) = 2|u_n(x_1)|^2|u_m(x_1)|^2$ or twice what we would have expected from the individual one particle wavefunctions. For Fermions, we find that $\psi_{n,m}(x_1, x_1) = P_{n,m}(x_1, x_1) = 0!$ The Fermions avoid each other whereas Bosons are much friendlier. These “correlations” are present even though we have assumed no interaction potential between the particles. Also, note that the probability is still normalized so the enhanced or reduced probability of finding the particles in the same place must be compensated by the opposite trend for more separated coordinates.

Next, let's ask about the probability for finding the two particles in the same state. In this case, we can make a symmetric wavefunction from just the product of single particle wavefunctions:

$$\psi_{n,n}(x_1, x_2) = u_n(x_1) u_n(x_2) = u_n(x_2) u_n(x_1). \quad (11)$$

The two terms we needed in the linear combination wavefunctions are the same, so there is no need to form that combination. If we try to form an anti-symmetric function by using the linear combination, we get zero:

$$\psi_{n,n}(x_1, x_2) = \frac{1}{\sqrt{2}} [u_n(x_1) u_n(x_2) - u_n(x_2) u_n(x_1)] = 0. \quad (12)$$

The conclusion is that we simply cannot form such a wavefunction – this is the “strong statement” of the Pauli exclusion principle. It is the basis for the statement that no two Fermions can occupy the same quantum state.

The distinction in the above behaviors can hardly be more dramatic or more important. It is due to the anti-symmetric nature of Fermion wavefunctions that nature has to put electrons into different quantum states in multi-electron atoms. This leads directly to the structure of the Periodic Table and all the properties of atoms, molecules, solids, etc. Bosons, on the other hand, have ground states in which all the particles go to the same single particle ground state – this is Bose condensation, a subject of great current interest (due to the recently developed ability to cool collections of atoms in magnetic and optical traps to extremely low temperatures and thus to achieve condensation). This condensation is responsible for superfluidity in liquid ${}^4\text{He}$ (not seen in ${}^3\text{He}$ where the only difference is buried down inside the nucleus) and for superconductivity where electron pairs form spin

zero, Bosonic states (“Cooper pairs”) that condense. There is recent evidence that ^3He can have a similar pairing and condensation phenomenon at extremely low temperatures.

Try to imagine what the world would be like if electrons were bosons – all it would take is to reverse a single minus sign!

Inclusion of spin states. We found above that spin is critically important, but the notation used there did not explicitly include spin degrees of freedom. Here, we assume that the spin degrees of freedom are independent of the spatial variables (for example, there are no spatially varying magnetic fields, including no interactions between magnetic moments) and that spin up and spin down states have the same energy (i.e., there is no magnetic field at all and we neglect interactions between magnetic moments). In this case, the variables separate and we can write total wavefunctions as products of space and spin parts, for example,

$$\psi(x_1, x_2, \uparrow, \uparrow) = u_n(x_1)u_m(x_2)|\uparrow\rangle|\uparrow\rangle$$

or

$$\psi(x_1, x_2, \uparrow, \uparrow) = \frac{1}{\sqrt{2}}[u_n(x_1)u_m(x_2) \pm u_n(x_2)u_m(x_1)]|S, m_S\rangle$$

where, in this case, the spin states are described in terms of total spin angular momentum and its z component.

It is shown in Chapter 8 (p. 182, 183) that the total spins states can be written in terms of the individual spin’s up and downs states:

$$|S, m_S\rangle = |1, 1\rangle \Leftrightarrow |\uparrow, \uparrow\rangle \tag{13}$$

$$|S, m_S\rangle = |1, 0\rangle \Leftrightarrow \frac{1}{\sqrt{2}}[|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle] \tag{14}$$

$$|S, m_S\rangle = |1, -1\rangle \Leftrightarrow |\downarrow, \downarrow\rangle \tag{15}$$

and

$$|S, m_S\rangle = |0, 0\rangle \Leftrightarrow \frac{1}{\sqrt{2}}[|\uparrow, \downarrow\rangle - |\downarrow, \uparrow\rangle]. \tag{16}$$

The three spin $S = 1$ states are all symmetric under exchange of particles whereas the single spin $S = 0$ state is antisymmetric. Since the total wavefunction is a product of spin and space parts and it is the exchange symmetry of the total wavefunction that matters, we see that, for two Fermions, if the spin is in the singlet, $S = 0$ state, then the space part must be symmetric under exchange. The symmetric space part allows the possibility that both particles can be in the same orbital (i.e., having the same orbital quantum numbers – the space part here will be a simple product) or they can be in different orbitals (represented by the linear combination of orbital functions, summed with a + sign). For the two $s = 1/2$ Fermions in the triplet of $S = 1$ states, the space function must be antisymmetric which requires a linear combination summed with the – sign (and this disallows the particles from being in the same state). Among other things, this explains why the He atom in its ground state has its two electrons in the $S = 0$ configuration: the anti-symmetric spin function allows both electrons to be in the $n = 1, l = 0, m_l = 0$ orbital which clearly minimizes the dominant Coulomb energy.