

13 Multi-particle systems

13.1 Two identical particles

One particle is described by the wavefunction

$$\Psi(r, t)$$

Two particles are described by the wavefunction

$$\Psi(r_1, r_2, t)$$

where r_1 and r_2 are the coordinates for the first and second particle respectively. Everything else follows from this. We still have the Schroedinger Equation

$$i\hbar \frac{\partial}{\partial t} \Psi = H\Psi$$

The Hamiltonian is now a bit more complicated, but in the straightforward way:

$$H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r_1, r_2, t)$$

The operator ∇_1 is only acting on the first coordinate r_1 and the operator ∇_2 is only acting on the second coordinate r_2 . We can, as before, split of the time dependent part as

$$\Psi(r_1, r_2, t) = \psi(r_1, r_2) e^{-Et/\hbar}$$

The time-independent Schroedinger equation is yet again

$$H\psi = E\psi$$

The general statistical interpretation is now as follows. The expression

$$|\Psi(r_1, r_2, t)|^2 d^3r_1 d^3r_2$$

is the probability of finding the particle 1 in the volume d^3r_1 and the particle 2 in the volume d^3r_2 at the same time. This leads to the normalization of the wavefunction in the form

$$\int |\Psi(r_1, r_2, t)|^2 d^3r_1 d^3r_2 = 1$$

13.2 Fermions and Bosons

Let's look again at the two particle wavefunction. If we have one particle in state $\psi_a(r_1)$ and another one in state $\psi_b(r_2)$, then the wavefunction would be a simply product

$$\psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2)$$

But this assume that we can tell the two particles appart. Imagine both particles in different states in the hydrogen atom. They could easily swap their orbits and we would never notice. Clasically, this is not an issue. We can always paint a particle red and another particle green. Quantum mechanically, this does not work.

So, we need to do something clever. Luckily quantum mechanics is clever and we can construct a wave function that works out just the way we want it. The new wavefunction should be non-commital to accomodate particle which are indistinguishable in principle.

It turns out there are in fact two solutions

$$\psi_{\pm}(r_1, r_2) = A [\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)]$$

The two solutions have names: Bosons (+) and Fermions (-). Because we are not doing relativistic Quantum Mechanics, we have to call the following an axiom (rather than being able to prove it): Particles with integer spin are bosons, particles with half integer spin are fermions. This is called spin statistics.

What we have just done has important consequences. For example, it follows immediately that two fermions cannot occupy the same state:

$$\psi_{-}(r_1, r_2) = \psi_a(r_1)\psi_a(r_2) - \psi_a(r_1)\psi_a(r_2) = 0$$

This is the Pauli exclusion principle. It applies to all identical fermions.

Another way to look at this is with the exchange operator:

$$P f(r_1, r_2) = f(r_2, r_1)$$

This operator is idempotent. The eigenvalues are ± 1 . It commutes with the Hamiltonian

$$[H, P] = 0$$

Thus, we can find a complete set of simultaneous eigenfunctions. This means that the solutions are either symmetric (eigenvalue +1) or anti-symmetric (eigenvalue -1). Because they commute, it also follows that if a particle is in one of these states, it will stay there.

Griffith calls this the symmetrization requirement.

Example 15. Let's work with two non-interacting particles. And let's look at the infinite square well. The solutions for one particle were

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), \quad E_n = n^2 K$$

If the particles are distinguishable, then we just have

$$\psi_{n_1, n_2}(x_1, x_2) = \psi_{n_1}(x_1)\psi_{n_2}(x_2), \quad E_{n_1, n_2} = (n_1^2 + n_2^2)K$$

The ground state would be

$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a), \quad E_{11} = 2K$$

The first excited state is degenerate with

$$\begin{aligned} \psi_{12} &= \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a), & E_{12} &= 5K \\ \psi_{21} &= \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a), & E_{21} &= 5K \end{aligned}$$

If we have two identical particles which are bosons, then the ground state is unchanged (both particles can be in the same state), but the first excited state is now non-degenerate

$$\psi = \frac{\sqrt{2}}{a} [\sin(2\pi x_1/a) \sin(\pi x_2/a) + \sin(\pi x_1/a) \sin(2\pi x_2/a)], \quad E = 5K$$

If we have two identical particles which are fermions, then there is no ground state with energy $2K$. The lowest energy state is

$$\psi = \frac{\sqrt{2}}{a} [\sin(2\pi x_1/a) \sin(\pi x_2/a) - \sin(\pi x_1/a) \sin(2\pi x_2/a)]$$

which has an energy of $5K$.

13.3 Exchange Forces

Let's do a bit more ground work to find out what these symmetrization requirement actually do. As the name of the section suggests, we'll look at them in the form of exchange forces. Let's write down the different wave functions for the different cases

$$\begin{aligned}\psi(x_1, x_2) &= \psi_a(x_1)\psi_b(x_2) \quad \text{distinguishable particles} \\ \psi_+(x_1, x_2) &= \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)] \quad \text{Bosons} \\ \psi_-(x_1, x_2) &= \frac{1}{\sqrt{2}} [\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)] \quad \text{Fermions}\end{aligned}$$

We'll assume that the states ψ_a and ψ_b are normalized and orthogonal. We will now calculate the expectation value of the square separation between the two particles

$$\langle (x_1 - x_2)^2 \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle - 2 \langle x_1 x_2 \rangle$$

13.3.1 Distinguishable particles

We have

$$\langle x_1^2 \rangle = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_a$$

as well as

$$\langle x_2^2 \rangle = \int |\psi_a(x_1)|^2 dx_1 \int x_2^2 |\psi_b(x_2)|^2 dx_2 = \langle x^2 \rangle_b$$

and

$$\langle x_1 x_2 \rangle = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$$

Thus

$$\langle (x_1 - x_2)^2 \rangle_d = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b$$

13.3.2 Non-Distinguishable particles

$$\begin{aligned}\langle x_1^2 \rangle &= \frac{1}{2} \left[\int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 + \int x_1^2 |\psi_b(x_1)|^2 dx_1 \int |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1^2 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int \psi_b(x_2)^2 \psi_a(x_2) dx_2 \pm \int x_1^2 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int \psi_a(x_2)^2 \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b \pm 0 \pm 0]\end{aligned}$$

Because the particles are non-distinguishable, we also have

$$\langle x_2^2 \rangle = \frac{1}{2} [\langle x^2 \rangle_a + \langle x^2 \rangle_b]$$

The cross term gives:

$$\begin{aligned}\langle x_1 x_2 \rangle &= \frac{1}{2} \left[\int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 + \int x_1 |\psi_b(x_1)|^2 dx_1 \int x_2 |\psi_a(x_2)|^2 dx_2 \right. \\ &\quad \left. \pm \int x_1 \psi_a(x_1)^* \psi_b(x_1) dx_1 \int x_2 \psi_b(x_2)^2 \psi_a(x_2) dx_2 \pm \int x_1 \psi_b(x_1)^* \psi_a(x_1) dx_1 \int x_2 \psi_a(x_2)^2 \psi_b(x_2) dx_2 \right] \\ &= \frac{1}{2} [\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a \pm \langle x \rangle_{ab} \langle x \rangle_{ba} \pm \langle x \rangle_{ab} \langle x \rangle_{ba}] \\ &= \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2\end{aligned}$$

where

$$\langle x \rangle_{ab} = \int x \psi_a(x)^* \psi_b(x) dx$$

Thus,

$$\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \mp 2 |\langle x \rangle_{ab}|^2$$

The last term is the difference to the case with distinguishable particles. Let's discuss this term. Bosons are feeling an attraction force, while fermions are pushed apart. Note that this is not actually a force, it is a purely geometrical effect. And purely quantum mechanical!

Now, there is a big thing that we've been ignoring: Spin! The total wavefunction of an electron looks like

$$\psi(r)\chi(s)$$

Where the last part is the spinor. If we exchange the particles, the wavefunction needs to be antisymmetric (for fermions such as the electron) with respect to the entire wavefunction.

This means that it matters whether the spinor part of the wavefunction is symmetric or not. Remember the Clebsch-Gordon stuff? Which combination of spinors was symmetric? The singlet! This means that the singlet configuration leads to bonding.

14 Atoms

We now discuss Atoms beyond hydrogen. We use the letter Z to describe the atomic number. And we consider neutral atoms which means that Z is also the number of the electrons. The Hamiltonian of such a system is

$$H = \sum_{j=1}^Z \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{Ze^2}{r_j} \right) + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq k}^Z \frac{e^2}{|r_j - r_k|}$$

The wavefunction looks like

$$\psi(r_1, r_2, \dots, r_Z) \chi(s_1, s_2, \dots, s_Z)$$

and all we have to do is solve

$$H\psi = E\psi$$

and take the antisymmetric solutions (because electrons are fermions).

Of course, we can't do that. This Hamiltonian cannot be solved exactly. What kills us is the interaction term. We can try to solve it in a perturbation theory approach, but for now we'll just ignore it. I know, it's a bad approximation, but we get the other things qualitatively right.

Other things that are not in the above equation

- Accounting for the motion of the nucleus (reduced mass works only for two particles).
- Magnetic interactions due to spin.
- Relativistic corrections.
- Finite size of the nucleus.

LECTURE 11 ENDS
