Lecture 3

Two-particle systems

State of the two-particle system is described by the wave function

$$\Psi(\vec{r}_1, \vec{r}_2, t).$$

The Hamiltonian for the two-particle system is

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t).$$

Of course, as usual, the time evolution of the system is described by the Schrödinger equation:

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

The probability to find particle one in volume $d^3\vec{r}_1$ and particle two in volume $d^3\vec{r}_2$ is given by

$$|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 \, d^3\vec{r}_1 \, d^3\vec{r}_2,$$

where the wave function has to be normalized in the following way:

$$\int |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 \, d^3\vec{r}_1 \, d^3\vec{r}_2 = 1.$$

If the potential does not depend on time, then we can separate variables

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(\vec{r}_1, \vec{r}_2) \, e^{-iEt/\hbar},$$

where the spatial wave function obeys the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V\psi = E\psi.$$

total energy of the system

So far, nothing new comparing to one-particle case.

Bosons and fermions

If the particle one is in state $\psi_a(\vec{r})$ and particle two is in state $\psi_b(\vec{r})$, then the total state can be written as the simple product (we will ignore spin for now):

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\, \psi_b(\vec{r}_2), \qquad Eq.\ (1)$$

Note of caution: by no means assume that all two-particle states can be separated into simple product states. All entangled states can not be separated into product states. Here is example of the entangled state.

Suppose each of two particles can be in spin state up $\uparrow$ or down $\downarrow$, then the following state can not be separated into product states:

$$\psi_{12} = \frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow \right)$$

#1   #2   #1   #2

This state means that if the spin of one particle is up, then the spin of the other particle must be down. Such state can not be separated into the product state as neither particle is in definite state of being spin up or spin down.

Equation (1) above assumes that we can tell which particle is particle one and which particle is particle two. In classical mechanics, you can always identify which particle is which. In quantum mechanics, you simply can't say which electron is which as you can not put any labels on them to tell them apart.

There are two possible ways to deal with indistinguishable particles, i.e. to construct two-particle wave function that is non committal to which particle is in which state:

$$\psi_+(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right]$$

$$\psi_-(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \right].$$

Therefore, quantum mechanics allows for two kinds of identical particles: **bosons** (for the "+" sign) and **fermions** (for the "-" sign). In our non-relativistic quantum mechanics we accept the following statement as an axiom:

**All particles with integer spin are bosons,
all particles with half integer spin are fermions.**

From the above, two identical fermions can not occupy the same state:

$$\Psi_-(\vec{r}_1, \vec{r}_2) = A\left[\psi_a(\vec{r}_1)\,\psi_a(\vec{r}_2) - \psi_a(\vec{r}_2)\,\psi_a(\vec{r}_1)\right] = 0.$$

$$\underbrace{\qquad\qquad}_{\text{same state}}$$

It is called **Pauli exclusion principle**.

We introduce operator P that interchanges two particles (exchange operator)

$$P\,f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1). \qquad\qquad P^2 = 1$$

If particles are identical $\quad [P, H] = 0 \qquad (PH - HP = 0).$

Then, we can find solutions to Schrödinger equation that are either symmetric or antisymmetric:

$$\boxed{\Psi(\vec{r}_1, \vec{r}_2) = \pm\,\Psi(\vec{r}_2, \vec{r}_1).} \qquad (2)$$

Wave function is required to satisfy (2) for identical particles.

Example

Suppose we have two non-interacting mass m particles in the infinite square well. The one-particle states are:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

$$E_n = n^2 \left[\frac{\pi^2 \hbar^2}{2ma^2}\right] = n^2 K.$$

$$\sideset{}{}{\underbrace{}_{K}}$$

Case 1: distinguishable particles

Total wave function:
$$\psi_{n_1 n_2}(x_1, x_2) = \psi_{n_1}(x_1)\,\psi_{n_2}(x_2)$$

$$E_{n_1 n_2} = (n_1^2 + n_2^2)\,K$$

Ground (lowest) state:
$n_1 = 1$
$n_2 = 1$

$$\psi_{11} = \frac{2}{a} \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right)$$

$$E_{11} = 2K$$

First excited energy state:
$$n_1 = 1 \quad n_2 = 2 \qquad E_{12} = (1+4)\,K = 5K$$
$$n_1 = 2 \quad n_2 = 1 \qquad E_{21} = (4+1)\,K = 5K$$

The state is doubly degenerate, i.e. two states ψ_{12} and ψ_{21} have the same energy

$$\psi_{12} = \frac{2}{a} \sin\left(\frac{\pi x_1}{a}\right) \sin\left(\frac{2\pi x_2}{a}\right)$$

$$\psi_{21} = \frac{2}{a} \sin\left(\frac{2\pi x_1}{a}\right) \sin\left(\frac{\pi x_2}{a}\right)$$

Case 2: identical bosons

Ground state:
$$\psi_{11} = A\left(\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right) + \frac{2}{a}\sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{\pi x_1}{a}\right)\right)$$

$$= 2A\,\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)$$

$$E_{11} = 2K \quad (\text{same as before})$$

First excited state:
$$\psi_{[12]} = A\left(\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right) + \frac{2}{a}\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\right)$$

$$E_{[12]} = 5K, \text{ but the state is non-degenerate.}$$

Class exercise: find the ground state wave function and energy for the case of identical fermions.

Solution:

There is no state with energy 2K as two fermions can not occupy the same state (they can't both have n=1) as

$$\psi_{11} = A\left(\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right) - \frac{2}{a}\sin\left(\frac{\pi x_2}{a}\right)\sin\left(\frac{\pi x_1}{a}\right)\right) = 0$$

The ground state is

$$\psi = A\left(\frac{2}{a}\sin\left(\frac{\pi x_1}{a}\right)\sin\left(\frac{2\pi x_2}{a}\right) - \frac{2}{a}\sin\left(\frac{2\pi x_1}{a}\right)\sin\left(\frac{\pi x_2}{a}\right)\right]$$

$$E = 5K.$$

Exchange forces

Let's consider another example of what symmetrization actually does. We will consider again three cases: distinguishable particles, identical bosons, and identical fermions and calculate the expectation value of the square of the separation between two particles.

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

ψ_a and ψ_b are othogonal and normalized.

Case 1: distinguishable particles

$$\psi(x_1, x_2) = \psi_a(x_1) \, \psi_b(x_2)$$

$$\langle x_1^2 \rangle = \underbrace{\int x_1^2 \, |\psi_a(x_1)|^2 \, dx_1}_{\langle x^2 \rangle_a} \underbrace{\int |\psi_b(x_2)|^2 \, dx_2}_{= 1} = \langle x^2 \rangle_a$$

$\uparrow$

| expectation value of x^2 in the one-particle state ψ_a |

$$\langle x_2^2 \rangle = \underbrace{\int |\psi_a(x_1)|^2 \, dx_1}_{= 1} \int x_2^2 \, |\psi_b(x_2)|^2 \, dx_2 = \langle x^2 \rangle_b$$

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

$\uparrow$

| expectation value of x in the one-particle state ψ_a |

| expectation value of x in the one-particle state ψ_b |

Result: $\langle (x_1 - x_2)^2 \rangle = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x_b \rangle$

Case 2: Identical bosons

$$\psi_+(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right)$$

$$\langle x_1^2 \rangle = \frac{1}{2}\iint x_1^2 \, |\psi_+(x_1, x_2)|^2 \, dx_1 \, dx_2 =$$

$$= \frac{1}{2}\iint x_1^2 \left[\psi_a^*(x_1)\psi_b^*(x_2) + \psi_b^*(x_1)\psi_a^*(x_2)\right]$$
$$\left[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)\right] dx_1 \, dx_2$$

$$= \frac{1}{2}\Bigg\{ \iint x_1^2 \, |\psi_a(x_1)|^2 \, |\psi_b(x_2)|^2 \, dx_1 \, dx_2$$

$$+ \iint x_1^2 \, |\psi_b(x_1)|^2 \, |\psi_a(x_2)|^2 \, dx_1 \, dx_2$$

$$+ \iint x_1^2 \, \psi_a^*(x_1)\psi_b(x_1) \, \psi_b^*(x_2)\psi_a(x_2) \, dx_1 \, dx_2$$

$$+ \iint x_1^2 \, \psi_b^*(x_1)\psi_a(x_1) \, \psi_a^*(x_2)\psi_b(x_2) \, dx_1 \, dx_2 \Bigg\}$$

$$= \frac{1}{2}\underbrace{\int x_1^2 \, |\psi_a(x_1)|^2 \, dx_1}_{\langle x^2 \rangle_a} \underbrace{\int |\psi_b(x_2)^2| \, dx_2}_{1}$$

$$+ \frac{1}{2}\underbrace{\int x_1^2 \, |\psi_b(x_1)|^2 \, dx_1}_{\langle x^2 \rangle_b} \underbrace{\int |\psi_a(x_2)|^2 \, dx_2}_{1}$$

$$+ \int x_1^2 \, \psi_a^*(x_1)\psi_2(x_1) \, dx_1 \underbrace{\int \psi_b^*(x_2)\psi_a(x_2) \, dx_2}_{=0 \text{ (states are orthogonal)}}$$

$$+ \int x_1^2 \, \psi_b^*(x_1)\psi_a(x_1) \, dx_1 \underbrace{\int \psi_a^*(x_2)\psi_b(x_2) \, dx_2}_{=0}$$

$$= \frac{1}{2}\left(\langle x^2 \rangle_a + \langle x^2 \rangle_b\right)$$

Similarly, $\langle x_2^2 \rangle = \langle x_1^2 \rangle = \frac{1}{2}\left(\langle x^2 \rangle_a + \langle x^2 \rangle_b \right).$

That makes perfect since we can not tell them apart.

$$\langle x_1 x_2 \rangle = \frac{1}{2} \iint x_1 x_2 | \psi_+ (x_1, x_2)|^2 \, dx_1 \, dx_2$$

$$= \frac{1}{2} \Big[\int x_1 | \psi_a (x_1)|^2 \, dx_1 \quad \int x_2 | \psi_b (x_2)|^2 \, dx_2$$

$$+ \int x_1 | \psi_b (x_1)|^2 \, dx_1 \quad \int x_2 | \psi_a (x_2)|^2 \, dx_2$$

$$+ \int x_1 \psi_a^* (x_1) \psi_b (x_1) \, dx_1 \quad \int x_2 \psi_b^* (x_2) \psi_a (x_2) \, dx_2$$

$$+ \int x_1 \psi_b^* (x_1) \psi_a (x_1) \, dx_1 \quad \int x_2 \psi_a^* (x_2) \psi_b (x_2) \, dx_2 \Big]$$

$$= \frac{1}{2} \left(\langle x \rangle_a \langle x \rangle_b + \langle x \rangle_b \langle x \rangle_a + \langle x \rangle_{ab} \langle x \rangle_{ba} + \langle x \rangle_{ba} \langle x \rangle_{ab} \right)$$

$$= \langle x \rangle_a \langle x \rangle_b + |\langle x \rangle_{ab}|^2$$

where $\quad \langle x \rangle_{ab} \equiv \int x \, \psi_a^* (x) \, \psi_b (x) \, dx$

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

That was the result for distinguishable particles, let's call it $\langle (x_1 - x_2)^2 \rangle_d$.

This is an extra term.

Case 3: identical fermions.

Just repeating the case 2 calculations for $\psi_- (x_1, x_2) = \frac{1}{\sqrt{2}} \left(\psi_a (x_1) \psi_b (x_2) - \psi_b (x_1) \psi_a (x_2) \right)$
and we get

$$\langle (x_1 - x_2)^2 \rangle_- = \langle (x_1 - x_2)^2 \rangle_d + 2|\langle x \rangle_{ab}|^2$$

opposite sign comparing to identical bosons

Conclusions:

(1) If there is no overlap between two functions $\psi_a(x)$ and $\psi_b(x)$, then the integral
$$\langle x \rangle_{ab} = \int \psi_a^*(x) \, \psi_b(x) \, x \, dx = 0$$
is zero and all three cases are the same.

Practical conclusion: it is ok to assume that particles with non-overlapping wave functions are distinguishable.

(2) If there is an overlap, identical bosons tend to be somewhat closer, and identical fermions tend to be somewhat further apart than distinguishable particles in the same two states.

Note on spin: **total** wave function has to be symmetric or antisymmetric, we have to put together complete two-electron state:
$$\psi(\vec{r}) \, \chi(s).$$