

## IDENTICAL PARTICLES

So far we have studied systems with only a single particle, described by  $\Psi(\vec{r}, t)$ . What if we now have two particles in our system? What consequences does that have?

First of all, we need a two-particle wavefunction  $\Psi(\vec{r}_1, \vec{r}_2, t)$ , depending on the positions of particle 1 and 2. The time-evolution is determined by the SE,

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

with

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

acts on  $\vec{r}_1$   
particle 1

$\vec{r}_2$  acts on  
particle 2.

The statistical interpretation is analogous to one-particle case:

$$|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3 r_1 d^3 r_2$$

is the probability of finding particle 1 in the volume  $d^3 r_1$  and particle 2 in the volume  $d^3 r_2$ .

if the potential is time-independent, we can obtain a complete set of solutions by separation of variables

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

where  $\psi(\vec{r}_1, \vec{r}_2)$  satisfies the TISE

$$\left[ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2) \right] \psi = E \psi.$$

$E$  total energy of system.

Solving this equation is difficult in general, but we will look at one special case:

### Non-interacting particles

The particles are subject to external forces, but do not interact with each other:

$$V(\vec{r}_1, \vec{r}_2) = V_1(\vec{r}_1) + V_2(\vec{r}_2).$$

In this case, we can define

$$\hat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 + V_i(\vec{r}_i)$$

$$\rightarrow \hat{H} = \hat{H}_1 + \hat{H}_2,$$

and use separation of variables

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2)$$

where  $\psi_a$  and  $\psi_b$  satisfy the one-particle SE

$$\hat{H}_1 \psi_a = E_a \psi_a$$

$$\hat{H}_2 \psi_b = E_b \psi_b$$

$$\text{and } E = E_a + E_b.$$

The two-particle wavefunction is then a product of single-particle wavefunctions:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = [\psi_a(\vec{r}_1, t) e^{-iE_a t/\hbar}] [\psi_b(\vec{r}_2, t) e^{-iE_b t/\hbar}] \\ = \Psi_a(\vec{r}_1, t) \Psi_b(\vec{r}_2, t).$$

We can then say that particle 1 is in state a, or particle 2 is in state b.

Linear combinations of such solutions are also solutions of the SE;

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \frac{3}{5} \Psi_a(\vec{r}_1, t) \Psi_b(\vec{r}_2, t) + \frac{4}{5} \Psi_c(\vec{r}_1, t) \Psi_d(\vec{r}_2, t).$$

The state of particle 1 depends on the state of particle 2, and vice versa.

If we measure particle 1 to be in state a, we know particle 2 is in state b! The two particles are entangled.

### Indistinguishable particles - fermions and bosons

In classical physics one can always, in principle, tell two particles apart — paint one red and one blue, or write numbers on them. On the other hand, in quantum mechanics two identical particles are utterly indistinguishable!

It's impossible to tell for instance two electrons apart. This has important consequences!

For two identical particles, we must have:

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

If the particles are indistinguishable, it shouldn't matter which is no. 1 and which is no. 2. In general, we can therefore have  $\Psi(\vec{r}_2, \vec{r}_1) = e^{i\phi} \Psi(\vec{r}_1, \vec{r}_2)$ ,  $\phi \in \mathbb{R}$ . In 3D there are only two possibilities,  $\phi = 0$  or  $\pi$ , meaning

$$\Psi(\vec{r}_2, \vec{r}_1) = \begin{cases} + \Psi(\vec{r}_1, \vec{r}_2) & \text{bosons} \\ - \Psi(\vec{r}_1, \vec{r}_2) & \text{fermions.} \end{cases}$$

Particles which are symmetric under exchange of two particles are called bosons.

Particles which are antisymmetric under exchange of two particles are called fermions.

For non-interacting particles in states  $a$  and  $b$ , we would therefore have the states

$$\Psi(\vec{r}_1, \vec{r}_2) = \begin{cases} \frac{1}{\sqrt{2}} (\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) + \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)), \\ \quad \text{for bosons} \\ \frac{1}{\sqrt{2}} (\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) - \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)), \\ \quad \text{for fermions} \end{cases}$$

### Pauli exclusion principle

From the above two classes of wavefunctions we immediately notice an important consequence. If we try to put the two particles in the same state  $a$ , we get

$$\psi_{aa}^{\text{boson}}(\vec{r}_1, \vec{r}_2) \propto \psi_a(\vec{r}_1) \psi_a(\vec{r}_2)$$

for bosons. However, for fermions, we get

$$\begin{aligned}\psi_{aa}^{\text{fermion}}(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1) \psi_a(\vec{r}_2) - \psi_a(\vec{r}_2) \psi_a(\vec{r}_1)] \\ &= 0!\end{aligned}$$

This is an example of the Pauli exclusion principle, which states that

Fermions cannot be in the same single-particle state.

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For bosons, however, there is no such limitation. This means that, in principle, a macroscopic number of bosons can occupy the same quantum state. This is what happens in a Bose-Einstein condensate.

EXAMPLE - Two noninteracting particles  
in an infinite square well.

We have the one-particle wavefunctions  
and eigenvalues

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L}, \quad n = 1, 2, 3, \dots$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \equiv K n^2.$$

Let's see how the symmetry properties  
affect the possible ground states and  
first excited state. We forget about spin for now.

Distinguishable particles: (classical)

- ground state:  $\psi_{11} = \frac{2}{L} \sin \frac{\pi x_1}{L} \sin \frac{\pi x_2}{L}$

$$E_{11} = 2K$$

- first excited state:

$$\psi_{12} = \frac{2}{L} \sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L}, \quad E_{12} = 5K$$

$$\psi_{21} = \frac{2}{L} \sin \frac{2\pi x_1}{L} \sin \frac{\pi x_2}{L}, \quad E_{21} = 5K$$

Degenerate!

Bosons:

- ground state:  $\psi_{11}$  as above,  $E_{11} = 2K$ .

- first excited state:

$$\psi_1 = \frac{\sqrt{2}}{L} \left[ \sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} + \sin \frac{2\pi x_1}{L} \sin \frac{\pi x_2}{L} \right]$$

$$E = 5K, \quad \text{nondegenerate!}$$

Since the particles are indistinguishable, we cannot label which particle is in which state, and we therefore get a non-degenerate first excited state in this case.

### Fermions

- Ground state:  $E = 5K!$

$$\psi = \frac{1}{\sqrt{2}} \left[ \sin \frac{\pi x_1}{L} \sin \frac{2\pi x_2}{L} - \sin \frac{2\pi x_1}{L} \sin \frac{\pi x_2}{L} \right]$$

Since the fermions cannot occupy the same single particle state, the ground state energy becomes higher than in the other two cases.

We therefore see that the statistical properties, the symmetrisation requirement, leads to differences in the physics. Another example is that of exchange forces:

### Exchange forces

[Gr. 5.1.2, H 8.5.3]

Let us assume the following wavefunctions:

1. Distinguishable particles

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

2. Identical bosons

$$\psi_+ = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) + \psi_b(x_1) \psi_a(x_2)]$$

### 3. Identical fermions

$$\Psi = \frac{1}{\sqrt{2}} [\psi_a(x_1) \psi_b(x_2) - \psi_b(x_1) \psi_a(x_2)]$$

a and b are not the same state!

We will now calculate the expectation value of the square of the separation distance between the two particles

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

For distinguishable particles we get

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

the expectation value of  $x^2$  in the one-particle state  $\psi_a$ . Likewise

$$\begin{aligned} \langle x_2^2 \rangle &= \int dx_1 |\psi_a(x_1)|^2 \cdot \int dx_2 x_2^2 |\psi_b(x_2)|^2 \\ &= \langle x^2 \rangle_b. \end{aligned}$$

and

$$\begin{aligned} \langle x_1 x_2 \rangle &= \int dx_1 x_1 |\psi_a(x_1)|^2 \cdot \int dx_2 x_2 |\psi_b(x_2)|^2 \\ &= \langle x \rangle_a \langle x \rangle_b, \end{aligned}$$

where  $\langle x \rangle_{a/b}$  is the expectation value of  $x$  in the one-particle state a/b.

In case 1, we therefore get

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

In the case of identical particles,  
we get (we treat bosons and fermions simult.)

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

and

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

Finally:

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

where

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

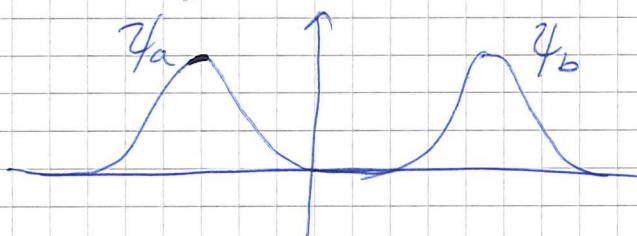
Hence,

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

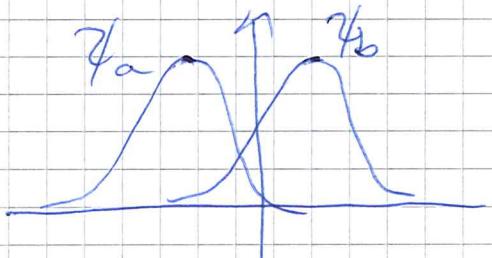
The final term was not thus far

distinguishable particles. Identical bosons (-) tend to be closer together, and identical fermions (+) farther apart compared to distinguishable particles in the same two states.

Note:  $\langle x \rangle_{ab}$  nonzero when wavefunctions overlap:



$$\langle x \rangle_{ab} = 0$$



$$|\langle x \rangle_{ab}| > 0.$$

As a practical matter, this allows us to not have to care about (anti)symmetrization when the identical particles are very far apart. We don't have to antisymmetrize the wavefunction of every electron in the universe every time we do a calculation — phew!

When the wavefunctions of identical particles do overlap, the system behaves as though there is an "attractive force" between bosons, and a "repulsive force" between fermions — an exchange "force".

Note: not an actual force!

## Slater determinant

[H 8.5.2]

If we have to consider multiple fermions, there is a general method to get an antisymmetric wavefunction.

If we have  $Z$  fermions in the one-particle states  $\psi_1, \psi_2, \dots, \psi_Z$ , the wavefunction is given by

$$\psi(1, 2, \dots, Z) = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \dots & \psi_1(Z) \\ \psi_2(1) & \psi_2(2) & \dots & \psi_2(Z) \\ \dots & \dots & \dots & \dots \\ \psi_Z(1) & \psi_Z(2) & \dots & \psi_Z(Z) \end{vmatrix}$$

This is called a Slater determinant, and ensures:

- antisymmetrization
- Pauli principle
- correct normalization.

Note: this wavefunction is an exact solution of the SE only when the fermions don't interact with each other.

## SPIN AND STATISTICS

There is a relation between the spin of a particle and the statistics it obeys:

Particles with integer spin are bosons, and particles with half-integer spin are fermions.

The spin-statistics theorem can be proven in relativistic quantum mechanics — we take it as an axiom.

In 2D systems one can have "quasiparticles" which are neither bosons nor fermions, but rather something in between — anyons. Proposed as building blocks in quantum computers.

## Electrons spin $\frac{1}{2}$

An electron has two possible spin states: up  $| \uparrow \rangle$  and down  $| \downarrow \rangle$ . It can also be classified by other quantum numbers, e.g. which energy eigenstate it is in, and so on. We can write the total electron state as

$$|\Psi\rangle = |\psi, \chi\rangle \equiv |\psi\rangle \otimes |\chi\rangle$$

or analogously

$$\Psi = \psi(\vec{r}) \chi,$$

wavefunction  $\xrightarrow{\text{I}}$   $\Sigma$  spinor, spin part  
spatial part

$\Sigma$  tensor product  
of Hilbert  
spaces.

We now construct the two-electron state

$$|\Psi\rangle = |\Psi_a, \Psi_b\rangle = |\psi_a, \psi_b\rangle \otimes |\chi_a, \chi_b\rangle$$

particle 1  $\uparrow$     particle 2

which has to be anti-symmetric when exchanging particles:

$$|\Psi_a, \Psi_b\rangle = - |\Psi_b, \Psi_a\rangle.$$
$$= |\psi_a, \psi_b\rangle \otimes |\chi_a, \chi_b\rangle = - |\psi_b, \psi_a\rangle \otimes |\chi_b, \chi_a\rangle$$

There are now two ways to make the state antisymmetric:  
either the spatial part is antisymmetric or the spin part is antisymmetric. This means that two electrons can be in the same spatial state as long as they are in different spin states:

$$\Psi(1,2) = \psi_a(\vec{r}_1)\psi_a(\vec{r}_2) \frac{\chi_1^1\chi_2^2 - \chi_1^2\chi_2^1}{\sqrt{2}}$$

spin singlet state.

This is why electronic orbitals in atoms can hold two electrons.