

If the particles do not interact with one another, *e.g. if we drop the e-e repulsion*, we call them "noninteracting".

In this case,  $V(\mathbf{r}_1, \mathbf{r}_2, t) = V(\mathbf{r}_1, t) + V(\mathbf{r}_2, t) + \cancel{V(\mathbf{r}_1, \mathbf{r}_2)}$ .

Example: two particles inside a capacitor, far from each other. Then, each electron is just immersed in the potential  $V$  of the capacitor.

Amazingly, "noninteracting", a CRUDE approx., is sometimes a GOOD approx. qualitatively even in atoms.

For non-interacting particles a wave function **solution** of the Sch. Eq. is just the **product**  $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_a(\mathbf{r}_1, t)\Psi_b(\mathbf{r}_2, t)$  where  $a$  and  $b$  are quantum numbers, such as those of the H atom or the square well.

E.g., in the H atom we could have,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_{100}(\mathbf{r}_1, t) \Psi_{21-1}(\mathbf{r}_2, t).$$

Its energy is  $E = E_{100} + E_{21-1}$ .

Another eigenstate:  $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \Psi_{530}(\mathbf{r}_1, t) \Psi_{321}(\mathbf{r}_2, t)$ .

Its energy is  $E = E_{530} + E_{321}$ . Please check!

NOTE: Linear combinations can also be made. E.g., consider  $\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = (3/5) \Psi_{100}(\mathbf{r}_1, t) \Psi_{21-1}(\mathbf{r}_2, t) + (4/5) \Psi_{530}(\mathbf{r}_1, t) \Psi_{321}(\mathbf{r}_2, t)$ . Normalized to one already.

But now the electrons are "entangled" because if by measuring we find particle 1 is in 100, then particle 2 must be in 21-1. The electrons instantly know about what is happening to the other one.

So far all was for noninteracting electrons.

The e-e repulsion, makes everything far more “**complicated**” because it “**correlates**” the electrons: if one electron is say on the left, by mere repulsion the other tends to be on the right. There is an entire field of current research called “**strongly correlated electrons**”. Here the wave function is not just linear combinations of products of H atom wavefunctions. We will return to this in later chapters.

Finally, as usual, in all cases we must **normalize** to 1 because of the probabilistic interpretation:

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

## 5.1.1 Bosons and Fermions

First, for **simplicity**, let us **neglect the e-e repulsion**. The energy levels are the **same** as in the H atom.

Assume one particle is in state "a" (e.g. 1s, spin up) and the other particle is in state "b" (e.g. 2s, spin down).

Then, **ONLY** in this particular case when e-e is neglected, the wave function is the product:

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

As already explained, to prove this, use as potential  $V$  simply the sum of two H-atom terms, one per particle i.e. just the  $p-e_1$  and  $p-e_2$  attractions.

However, the key new concept is that if electrons are **identical**, then we **cannot** say "electron 1 is in  $(1s, \uparrow)$ ". We can only say "**an electron is in  $(1s, \uparrow)$** ".

In **classical physics** we can always "follow" particles and tell them apart, even if identical.  
**READ discussion in book page 201.**

In **quantum physics** we **cannot** follow particles.  
We only know probabilities.

Thus, if a particle is in state "a" and a particle in state "b", we need to **symmetrize** the wave function to account for particles being identical.

One way to symmetrize is to **add** the two cases:

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

In what sense this has been "symmetrized"?

When  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are exchanged, the first term becomes the second, and the second the first.

Then:

$$\psi_{+}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{+}(\mathbf{r}_2, \mathbf{r}_1)$$

Elementary particles where the "+" applies are called **bosons**.

Because in QM we only care about the wave function in absolute value, there is **another** possible combination!

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_b(\mathbf{r}_1)\psi_a(\mathbf{r}_2)]$$

In this case, when  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are exchanged, we collect a minus sign in front:

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = -\psi_{-}(\mathbf{r}_2, \mathbf{r}_1)$$

Elementary particles where the "-" applies are called **fermions**.

In summary, we have to accept as **another law of Nature** that elementary particles are either **bosons**, for the + case, or **fermions**, for the - case.

Moreover, there is a link between the sign +- in the combination and the value of the spin. This can be shown within relativistic QM.

**bosons**  $\leftrightarrow$  **integer spin** (example: photon)

**fermions**  $\leftrightarrow$  **half-integer spin** (example: electron).



If two electrons are in the same state, such as  $(1s, \uparrow)$ , i.e. including spin, then the "-" wave function cancels:

$$\psi_{-}(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2) - \psi_a(\mathbf{r}_1)\psi_a(\mathbf{r}_2)] = 0$$

Then, the famous **Pauli principle** can be deduced from the fact that electrons are fermions.

This is somewhat similar to the case when we deduced the uncertainty principle in QM411.

*It is important to keep the number of arbitrary laws to a minimum!*

Let us define the exchange operator  $\hat{P}$ .


$$\hat{P} \psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$$

Applying  $\hat{P}$  twice:

$$\hat{P} \hat{P} \psi(\mathbf{r}_1, \mathbf{r}_2) = \hat{P} \psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)$$

Because  $\hat{P}^2 = 1$  as operator, then the eigenvalues are +1 and -1.

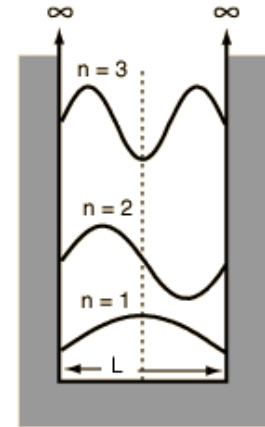
Also  $[\hat{H}, \hat{P}] = 0$ :

$$\hat{H} = \left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{1}{4\pi\epsilon_0} \frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$


Example 5.1: Consider two particles **without spin** in the 1D infinite square well

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

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

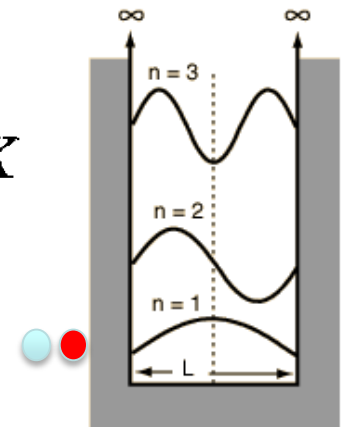


$x = 0$  at left wall of box.

(1) If particles were **distinguishable**, then

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

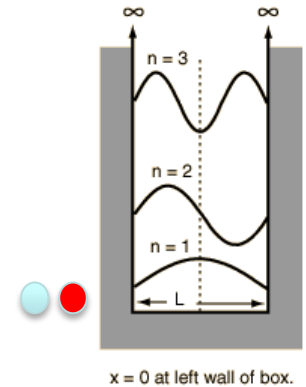
For ground state  $n_1 = n_2 = 1$ :



$x = 0$  at left wall of box.

Ground state  $n_1 = n_2 = 1$ :

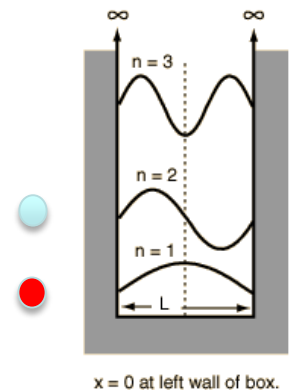
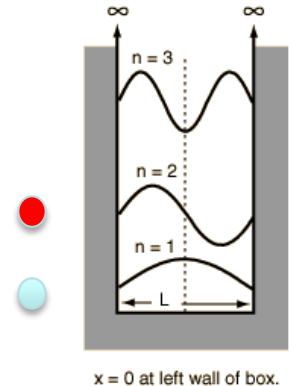
$$\psi_{11} = \frac{2}{a} \sin(\pi x_1/a) \sin(\pi x_2/a), \quad E_{11} = 2K$$



First excited state  $n_1 = 1, n_2 = 2$  or  $n_1 = 2, n_2 = 1$

$$\psi_{12} = \frac{2}{a} \sin(\pi x_1/a) \sin(2\pi x_2/a), \quad E_{12} = 5K$$

$$\psi_{21} = \frac{2}{a} \sin(2\pi x_1/a) \sin(\pi x_2/a), \quad E_{21} = 5K$$

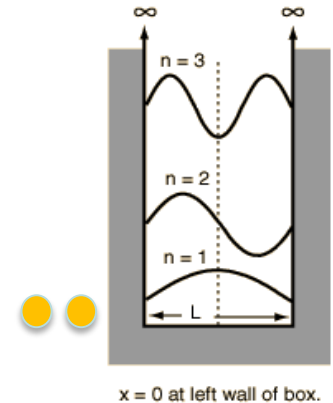


Degeneracy = 2

(2) If particles are **bosons**:

Ground state ( $E=2K$ ) is the same  $n_1 = n_2 = 1$ :

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



$$\hat{P} \psi(x_1, x_2) = \psi(x_2, x_1) = +\psi(x_1, x_2)$$

First excited state ( $E=5K$ ) is now **nondegenerate**

$$\psi^{\text{excited}}(x_1, x_2) = \frac{\sqrt{2}}{a} \left[ \sin(\pi x_1/a) \sin(2\pi x_2/a) + \sin(2\pi x_1/a) \sin(\pi x_2/a) \right]$$

$$\hat{P} \psi^{\text{excited}}(x_1, x_2) = \psi^{\text{excited}}(x_2, x_1) = +\psi^{\text{excited}}(x_1, x_2)$$

