

Identical Particles

Multiple particle systems

The Hamiltonian of a multi-particle system can be written in general as:

$$H(x_1, x_2, \dots, x_N, t) = \sum_{i=1, N} \frac{p_i^2}{2 m_i} + V(x_1, x_2, \dots, x_N, t)$$

Suppose that the particles do not interact with one another. This implies that each particle moves in a common potential:

$$V(x_1, x_2, \dots, x_N, t) = \sum_{i=1, N} V(x_i, t) \quad \text{and hence} \quad H(x_1, x_2, \dots, x_N, t) = \sum_{i=1, N} H_i(x_i, t)$$

In other words, for the case of non-interacting particles, the multi-particle Hamiltonian of the system can be written as the sum of N independent single-particle Hamiltonians. Then, the multi-particle wavefunction can be written as the product of N independent single-particle wavefunctions:

$$\psi(x_1, x_2, \dots, x_N, t) = \psi_1(x_1, t) \psi_2(x_2, t) \dots \psi_N(x_N, t)$$

Two particles system

- ▶ Statistical interpretation:

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

Is the probability density of finding particle 1 in volume d^3r_1 and particle 2 in d^3r_2

Thus:

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

If the potential $V(r_1, r_2)$ is time-independent, we can obtain the t.d. solutions by separation of variables:

$$\Psi(r_1, r_2, t) = \Psi(r_1, r_2) e^{-i\bar{E}t/\hbar}$$

Two particles system

► Where:

$$\Psi(r_1, r_2)$$

Satisfies the t.i.S.E.:

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

For instance, for the Helium atom

$$V(r_1, r_2) = -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|r_2 - r_1|}\right)$$

Two particles system

- ▶ Suppose particle 1 is in the (one-particle) state $\psi_a(\mathbf{r})$, and particle 2 is in the state $\psi_b(\mathbf{r})$, If the two particles are distinguishable and non interacting, than the wf. Can be written as a simple product:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi_a(\mathbf{r}_1) \Psi_b(\mathbf{r}_2)$$

- ▶ But in quantum mechanics we have identical particles, such as electrons, that cannot be distinguished each other, but they are utterly identical. There is nothing (any of their properties) that can be used to distinguish the electrons, and if one imagine to have a way to do it, this will not work because when we try to observe the electrons, we alter them and we cannot be sure if for instance they switched places.

Indistinguishable particles

- ▶ To mathematically describe this indistinguishable principle, there are two ways to build the wf.:

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

The \pm makes a distinction between two kinds of identical particle:

- ▶ Bosons, with plus sign (e.g. photons and phonons)
- ▶ Fermions, with minus sign (e.g. electrons and protons)

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

Pauli exclusion principle

- ▶ To describe mathematically the indistinguishable principle, there are two ways to build the wf.:

$$\psi_{-}(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_a(r_1) \psi_b(r_2) - \psi_b(r_1) \psi_a(r_2)]$$

Fermions, with minus sign (e.g. electrons and protons)

- ▶ Two identical fermions cannot occupy the same state.

For $\psi_a = \psi_b$, then:

$$\psi_{-}(r_1, r_2) = \frac{1}{\sqrt{2}} [\psi_a(r_1) \psi_a(r_2) - \psi_a(r_1) \psi_a(r_2)] = 0$$

This is the famous Pauli exclusion principle

Pauli exclusion principle

- ▶ More in general and formally we can define the exchange operator:

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

The eigenvalue of P are ± 1 and P and H are compatible: $[P, H]=0$
They have a common set of eigenstates.

This means that the solutions of the S.E. are symmetric (eigenvalue $+1$) or antisymmetric (eigenvalue -1) under exchange of particles:

$$\psi(r_1, r_2) = \pm \psi(r_2, r_1) \quad (\text{the } + \text{ refers to bosons, } - \text{ to fermions})$$

THIS MEANS THAT ACCORDING TO THE KIND OF PARTICLES (BOSONS OR FERMIONS), I'LL HAVE A SYMMETRIZATION REQUIREMENT FOR THEIR WFs.

Pauli exclusion principle

- ▶ The anti-symmetry requirement for the WF of fermions can be extended to N fermions systems. For a system containing N identical and non-interacting fermions, the anti-symmetric stationary wavefunction of the system is written as:

$$\psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(x_1) & \psi_b(x_1) & \dots & \psi_n(x_1) \\ \psi_a(x_2) & \psi_b(x_2) & \dots & \psi_n(x_2) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_a(x_N) & \psi_b(x_N) & \dots & \psi_n(x_N) \end{vmatrix}$$

This expression is known as the *Slater determinant*, and automatically satisfies the symmetry requirements on the wavefunction.

Exchange Force

- ▶ Suppose one particle is in state $\psi_a(x)$, and the other is in state $\psi_b(x)$, and these two states are orthogonal and normalized. If the two particles are indistinguishable, then the combined wave function is :

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

If you calculate the expectation value of the square of the distance between the two particles:

$$\langle (x_a - x_b)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2 \langle x \rangle_a \langle x \rangle_b \pm 2 |\langle x \rangle_{ab}|^2$$

The last term is what differentiates it from the case of distinguishable particles

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The last term is what differentiates it from the case of distinguishable particles:

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 |\langle x \rangle_{ab}|^2$$

↓
distinguishable
particle distance

↓ due to the
exchange
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Exchange Force

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 \langle x \rangle_{ab}^2$$

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$\langle x \rangle_{ab} = \langle \Psi_a | x | \Psi_b \rangle$
↓ due to the
exchange
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$$\int x \Psi_a^* \Psi_b dx$$

- ▶ Identical bosons (the upper signs) tend to be somewhat closer together
- ▶ Identical fermions (the lower signs) somewhat farther apart as compared to distinguishable particles in the same two states.

Exchange Force

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 \langle x \rangle_{ab}^2$$

\downarrow
distinguishable
particle distance

$\langle x \rangle_{ab} = \langle \Psi_a | x | \Psi_b \rangle$
 \rightarrow due to the
exchange
"force"

Notice that $\langle x \rangle_{ab}$ vanishes unless the two wave functions actually overlap, in fact:

$$\langle x \rangle_{ab} = \int x \Psi_a^* \Psi_b(x) dx$$

\rightarrow if Ψ_a and Ψ_b are not overlapping
 $\Psi_a = 0$ where $\Psi_b \neq 0$ and vice versa

The integral is then = 0

Exchange Force

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 \langle x \rangle_{ab}^2 = \phi$$

\downarrow
distinguishable
particle distance

if no overlap
between ψ_a and ψ_b

- ▶ If two electrons are very far each other (and their wf do not overlap), then it's not going to make any difference whether the wfs are antisymmetrized or not...

Exchange Force

$$\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_d \mp 2 \underline{\underline{|\langle x \rangle_{ab}|^2}} \neq \phi$$

with overlap between Ψ_a and Ψ_b

- ▶ When there is some overlap of the wave functions, the system behaves as though there were a "force of attraction" between identical bosons, pulling them closer together,
- ▶ and a "force of repulsion" between identical fermions, pushing them apart.

We call this an exchange force, although it's not really a force at all, because no physical agency is pushing on the particles; but it is a purely geometrical consequence of the symmetrization requirement.

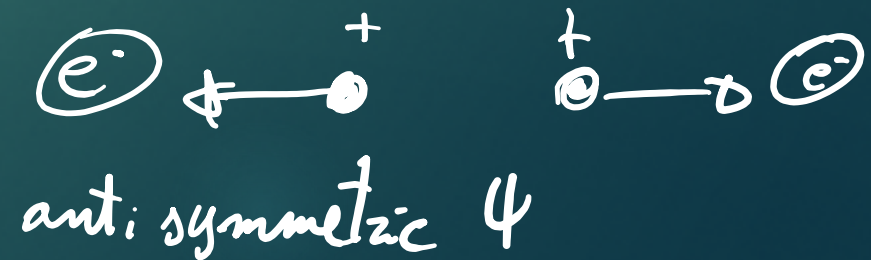
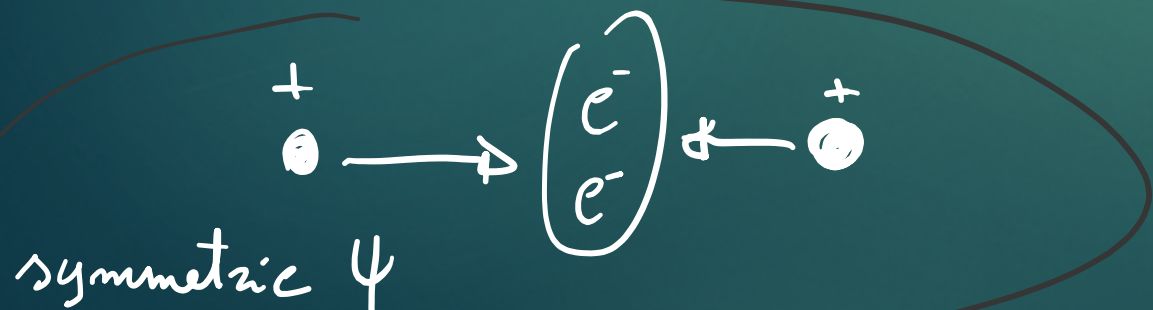
Exchange Force

We call this an exchange force, although it's not really a force at all, because no physical agency is pushing on the particles; but it is a purely geometrical consequence of the symmetrization requirement.

Still, this "force" has important consequences. For instance, consider the H_2 molecule.

At a first approximation, we have two electrons centered at two different nuclei in their ground state.

If we consider symmetric wf for these electrons, the "exchange force" will push the electrons each other and the accumulation of negative charge will attract protons inward, explaining the covalent bond

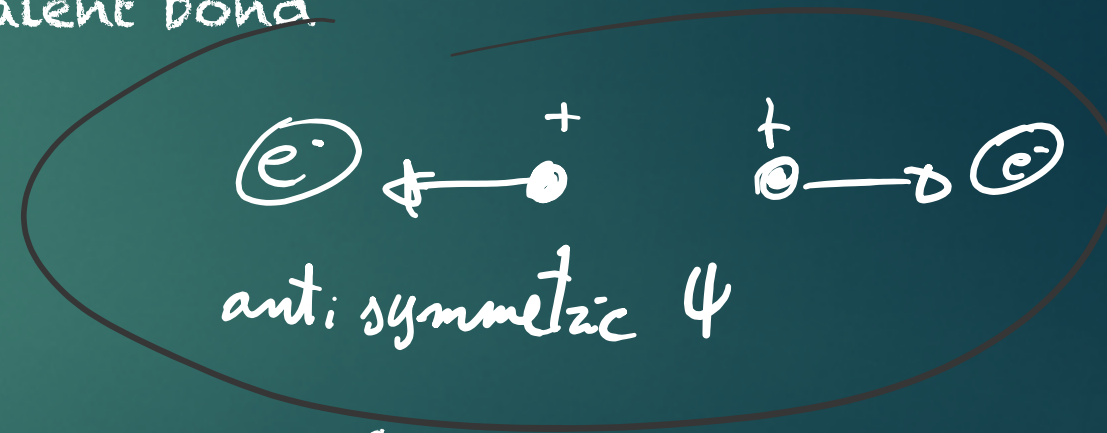
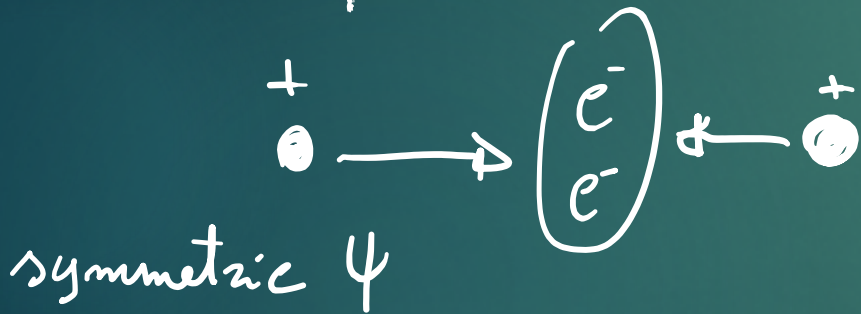


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But electrons are Fermions and have antisymmetric wf.

What is wrong with that? ...we miss spin!

Exchange Force

The complete state of the electron includes not only its position wave function, but also a spinor, describing the orientation of its spin:

$$\Psi(\mathbf{r}) \chi(s)$$

When we put together the two-electron state, it is the whole works, not just the spatial part, that has to be antisymmetric with respect to exchange.

Let's go back to singlet and triplet combinations...

Sum of angular momenta

Suppose that the two operators J_1 and J_2 are spin operators with $s=1/2$:

Thus, if $S=S=1$

$$\left. \begin{array}{l} m_j=1 \quad |1\ 1\rangle = \uparrow\uparrow \\ m_j=0 \quad |1\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ m_j=-1 \quad |1\ -1\rangle = \downarrow\downarrow \end{array} \right\} \text{triplet state}$$

SYMMETRIC

if $S=S=0$

$$m_j=0 \quad |0\ 0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \left. \right\} \text{Singlet state}$$

ANTISYMMETRIC

Exchange Force

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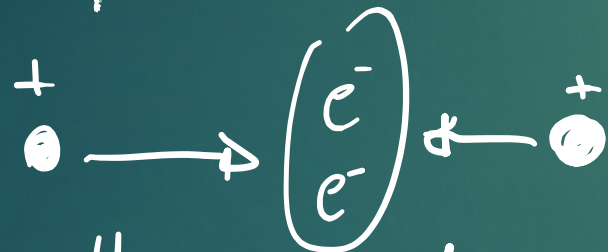
- ▶ the singlet combination is antisymmetric and hence would have to be joined with a symmetric spatial function
- ▶ the three triplet states are all symmetric and would require an antisymmetric spatial function.

Exchange Force

For instance, consider the H_2 molecule.

At a first approximation, we have two electrons centered at two different nuclei in their ground state.

If we consider symmetric wf for these electrons, the "exchange force" will push the electrons each other and the accumulation of negative charge will attract protons inward, explaining the covalent bond.



symmetric $\psi(1,2)$ anti-symmetric $\chi(s)$

The electrons are Fermions and have antisymmetric wf:

Antisymmetric spinor (singlet) but symmetric spatial wf.

Exchange Force

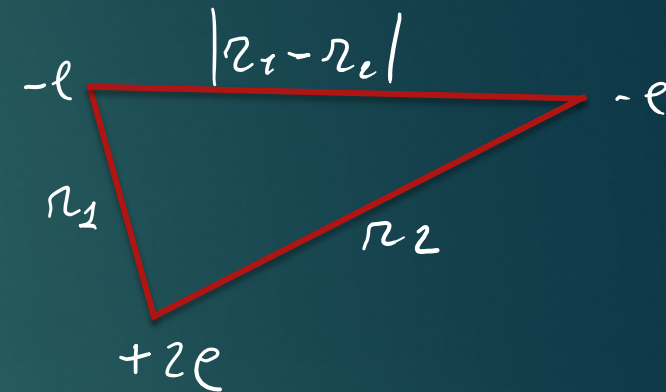
With a similar approach you can think at an exchange energy, which is a term in the total energy due to the symmetric constrain of the wf. and differentiating the energy of two-particle systems that are distinguishable or undistinguishable...

Now Lets' consider again the Helium atom

Helium atom

In seeking an approximation to the ground state, we might first work out the solution in the absence of this last term...

$$\begin{aligned}\Psi_0(r_1, r_2) &= \Psi_{1s}(r_1) \Psi_{1s}(r_2) = \\ &= \Psi_{100}(r_1) \Psi_{100}(r_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}\end{aligned}$$

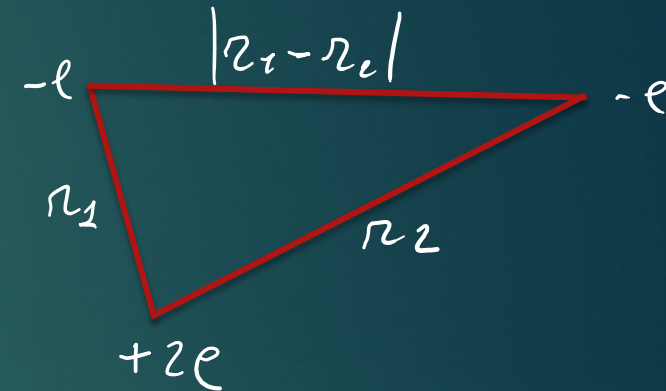


- ▶ Thus, the G.S. WF is symmetric (inverting r_1 and r_2 , its sign is unchanged)
- ▶ Thus, the G.S. of Helium is a singlet configuration.

Helium atom

In seeking an approximation to the ground state, we might first work out the solution in the absence of this last term...

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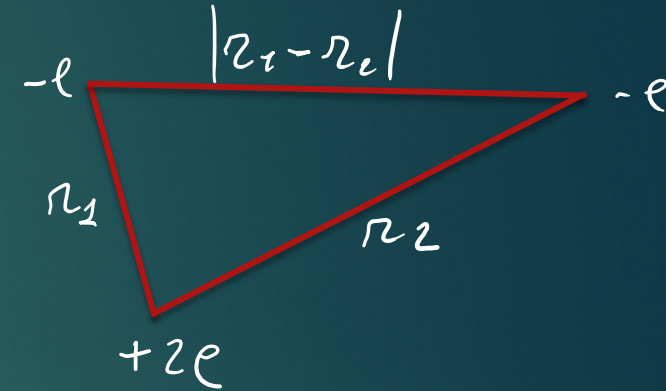
- What about the excited states? They consist of one electron in the hydrogenic G.S. and another in the excited state:

$$\Psi_{100}(r_1) \Psi_{nlm}(r_2)$$

Helium atom

- ▶ What about the excited states? They consist of one electron in the hydrogenic G.S. and another in the excited state:

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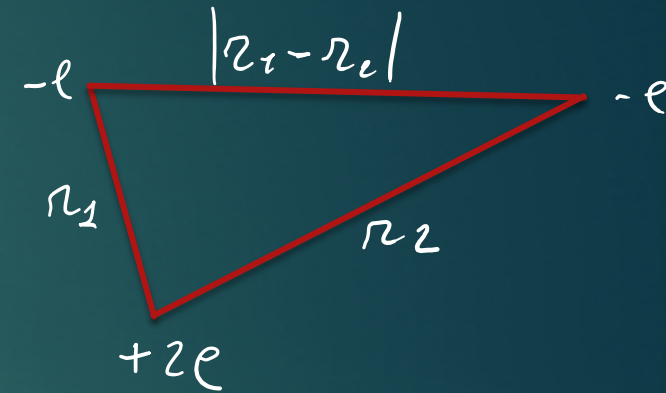
We can construct both symmetric and antisymmetric combinations:

- ▶ the former go with the antisymmetric spin configuration (the singlet), and they are called parahelium
- ▶ the latter require a symmetric spin configuration (the triplet), and they are known as orthohelium

Helium atom

- ▶ What about the excited states? They consist of one electron in the hydrogenic G.S. and another in the excited state:

$$\Psi_{100}(r_1) \quad \Psi_{nlm}(r_2)$$



The ground state is necessarily parahelium; the excited states come in both forms.

Because the symmetric spatial state brings the electrons closer together, we expect a higher energy than their orthohelium counterparts.

The periodic table

Table 5.1: Ground-state electron configurations for the first four rows of the Periodic Table.

Z	Element	Configuration	
1	H	(1s)	$^2S_{1/2}$
2	He	(1s) ²	1S_0
3	Li	(He)(2s)	$^2S_{1/2}$
4	Be	(He)(2s) ²	1S_0
5	B	(He)(2s) ² (2p)	$^2P_{1/2}$
6	C	(He)(2s) ² (2p) ²	3P_0
7	N	(He)(2s) ² (2p) ³	$^4S_{3/2}$
8	O	(He)(2s) ² (2p) ⁴	3P_2
9	F	(He)(2s) ² (2p) ⁵	$^2P_{3/2}$
10	Ne	(He)(2s) ² (2p) ⁶	1S_0
11	Na	(Ne)(3s)	$^2S_{1/2}$
12	Mg	(Ne)(3s) ²	1S_0
13	Al	(Ne)(3s) ² (3p)	$^2P_{1/2}$
14	Si	(Ne)(3s) ² (3p) ²	3P_0
15	P	(Ne)(3s) ² (3p) ³	$^4S_{3/2}$
16	S	(Ne)(3s) ² (3p) ⁴	3P_2
17	Cl	(Ne)(3s) ² (3p) ⁵	$^2P_{3/2}$
18	Ar	(Ne)(3s) ² (3p) ⁶	1S_0

$n=1$

$n=2$

$n=3$



$$2S+1$$

$$L_J$$

$$L=0 \rightarrow S$$

$$1 \rightarrow P$$

$$2 \rightarrow D$$

$$3 \rightarrow F$$

⋮

The n^{th} shell has room for $2n^2$ electrons

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$n=1$

$n=2$

$n=3$

$$2S+1$$

$$L_J$$

$$L=0 \rightarrow S$$

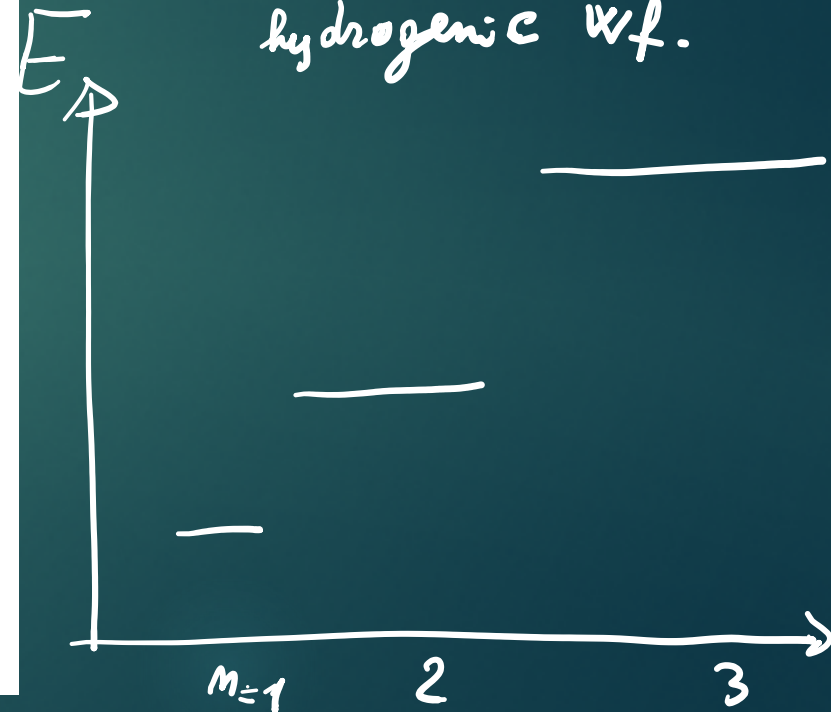
$$1 \rightarrow P$$

$$2 \rightarrow D$$

$$3 \rightarrow F$$

⋮

The n^{th} shell has room for $2n^2$ electrons
 E_n corresponds to n^2 hydrogenic wf.



Quantum statistic

The behaviour of systems consisting of many identical particles is studied by a special field of physics called quantum statistics.

The issue in question is the structure of the ground state and its energy for the system on $N \gg 1$ non-interacting free electrons (an ideal electron gas) confined within a box of volume V .