

III Many particle systems

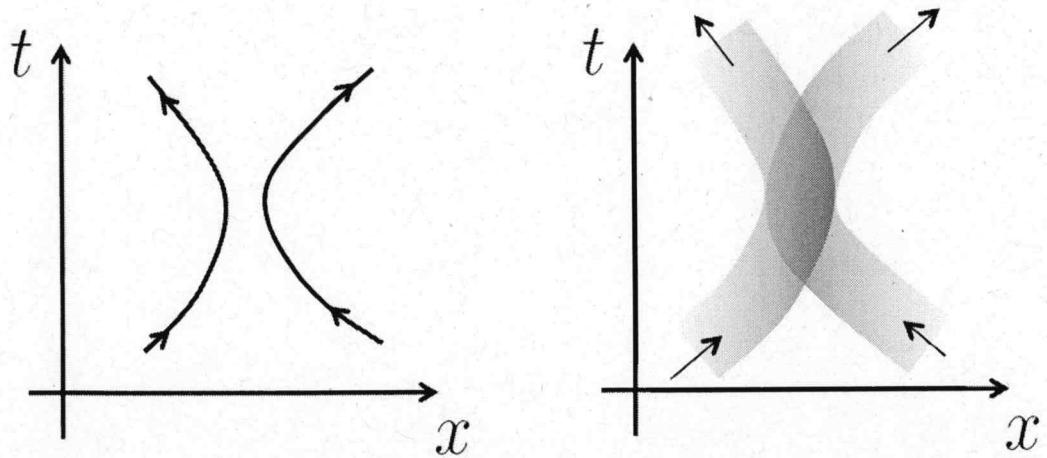
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- In this chapter we will be considering Systems that are composed of many particles, e.g. atoms with many electrons.
- We will show that the concept of exchange symmetry leads to the notion of bosonic and fermionic particles.
- We will also develop the so-called second quantisation formalism, which allows to describe many-body systems through creation and annihilation operators, in close analogy to our treatment of the quantised radiation field.

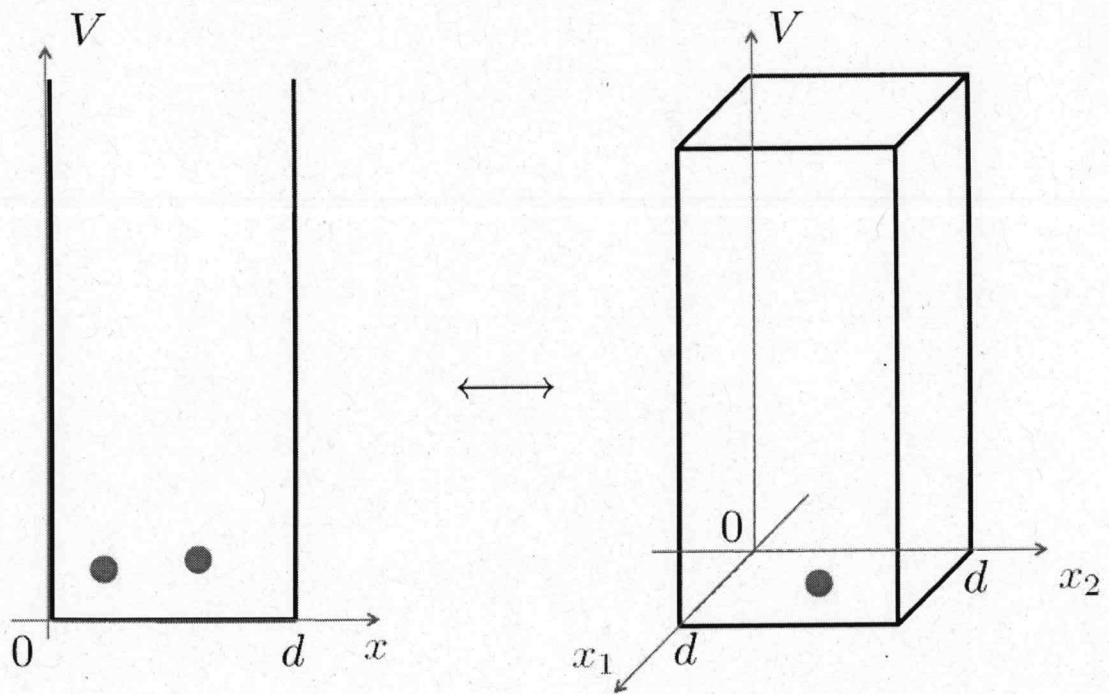
III. 1 Identical particles

- In classical physics two identical particles can be distinguished, i.e. we can observe their trajectories and know at any time which one is which.
- For quantum mechanical particles this is not the case, e.g. two electrons or photons are truly identical and there is not even in principle a way to mark them in order to make them distinguishable.

Identical particles: classical vs. quantum



Two particles in a potential well



In systems composed of identical particles each particle .. follows the exact same physics".

- This means that operators which describe these systems, such as H , \hat{L}^2 or L_z , are symmetric under exchange of particles.
- In order to get an idea of what that means lets consider two identical particles contained in one-dimensional infinitely deep potential well.
- The corresponding potential is

$$V(x) = \begin{cases} 0 & 0 \leq x \leq d \\ \infty & \text{elsewhere} \end{cases}$$

- The stationary Schrödinger equation of this system is

$$\underbrace{\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_2^2} \right]}_{\text{Hamiltonian, } H(x_1, x_2)} u(x_1, x_2) = E u(x_1, x_2)$$

$x_{1,2}$: coordinate of particle 1/2

m .. particle mass

energy

wave function

- The Hamiltonian is indeed symmetric under the exchange of particles.

$$H(x_1, x_2) = H(x_2, x_1)$$

- The problem is formally equivalent to a single particle confined in a two-dimensional potential well, which can be solved by separating variables.
- The normalised solutions are

$$u_{n_1, n_2}(x_1, x_2) = \frac{2}{d} \sin\left(\frac{n_1 \pi}{d} x_1\right) \sin\left(\frac{n_2 \pi}{d} x_2\right),$$

where $n_1, n_2 \in \mathbb{N}$ are the quantum numbers.

- The eigenvalues of the energy are

$$E_{n_1, n_2} = \frac{\hbar^2}{2m} \frac{\pi^2}{d^2} (n_1^2 + n_2^2).$$

- Let us consider the case $n_1 = 2, n_2 = 3$.

- Given that $u_{n_1, n_2}(x_1, x_2)$ solves the Schrödinger equation, one would expect that $|u_{n_1, n_2}(x_1, x_2)|^2$ is the probability for encountering particle 1 at position x_1 and particle 2 at position x_2 .

- However, this does not yield a consistent result, since

$$|u_{23}(x_1, x_2)|^2 \Big|_{\substack{x_1 = \frac{d}{2} \\ x_2 = \frac{d}{3}}} \neq |u_{23}(x_1, x_2)|^2 \Big|_{\substack{x_1 = \frac{d}{3} \\ x_2 = \frac{d}{2}}}$$

probability to
find particle 1(2)
at position $\frac{d}{2}(\frac{d}{3})$
 $= 0$

$$|u_{23}(x_1, x_2)|^2 \Big|_{\substack{x_1 = \frac{d}{3} \\ x_2 = \frac{d}{2}}}$$

probability to
find particle 1(2)
at position $\frac{d}{3}(\frac{d}{2})$
 $\neq 0$

- This result is certainly not compatible with having indistinguishable particles, whose quantum state $|\Psi(x_1, x_2)\rangle$ should obey

$$|\Psi(x_1, x_2)\rangle|^2 = |\Psi(x_2, x_1)\rangle|^2,$$

i.e. it should not matter for the probability density whether particle 1(2) is at position $x_1(x_2)$ or vice versa.

- To fix the problem, we make use of the fact that $u_{23}(x_2, x_1) = u_{32}(x_1, x_2)$, and that both of these wave functions have the same energy eigenvalue

$$E_{23} = E_{32} = \frac{13t^2\pi^2}{2md^2}.$$

- This means that any superposition of those two states is again a valid wave function.

- In particular one finds that

$$u_{23}^{(S)}(x_1, x_2) = \frac{1}{\sqrt{2}} (u_{23}(x_1, x_2) + u_{23}(x_2, x_1))$$

$$u_{23}^{(A)}(x_1, x_2) = \frac{1}{\sqrt{2}} (u_{23}(x_1, x_2) - u_{23}(x_2, x_1)),$$

which obey

$$u_{23}^{(S)}(x_1, x_2) = u_{23}^{(S)}(x_2, x_1) \quad \text{symmetric state}$$

$$u_{23}^{(A)}(x_1, x_2) = -u_{23}^{(A)}(x_2, x_1) \quad \text{anti-symmetric state}$$

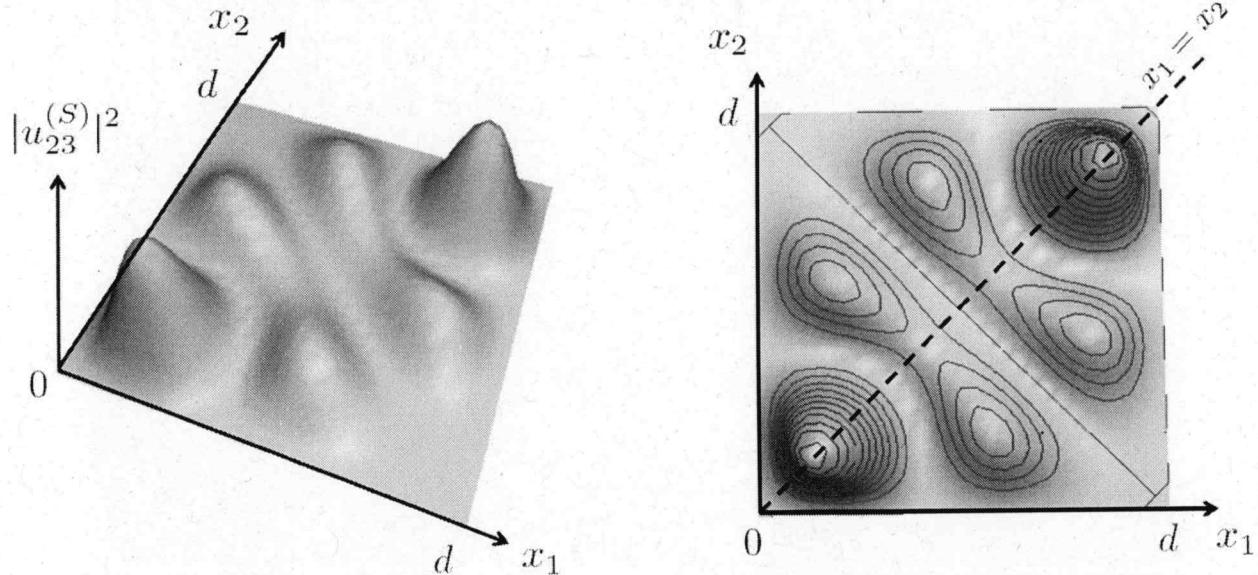
satisfy the required symmetry condition

$$|u_{23}^{(S,A)}(x_1, x_2)|^2 = |u_{23}^{(S,A)}(x_2, x_1)|^2.$$

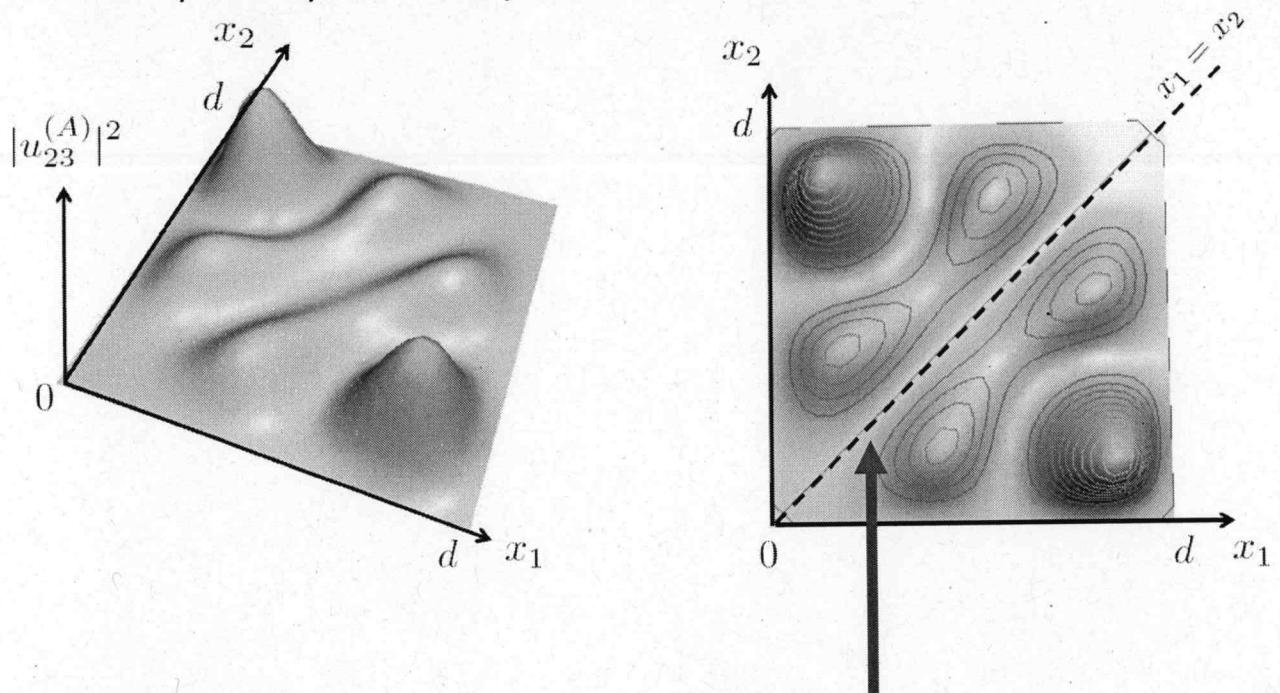
- In principle, one can also construct other superpositions which obey this property, but it turns out that only the symmetric and anti-symmetric ones are realised in nature.
- In fact, the symmetry property is intimately connected with the spin of the particles, which is referred to spin-statistics theorem.

Identical particles

Probability density of a symmetric two-body wave function



Probability density of an antisymmetric two-body wave function



- Particles with integer-valued spin $0, 1, 2, \dots$ (photons, ${}^4\text{He}, \dots$) are so-called bosons and their many-body wave function is symmetric under particle exchange.
- Particles with half-integer-valued spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ (electron, quarks, proton) are referred to as fermions and their many-body wave functions is anti-symmetric under particle exchange.
- Note, that unlike the probability density of the symmetric state, we find that $|U_{22}^{(A)}(\mathbf{x}, \mathbf{x})|^2 = 0$.
- This means that the probability to find two particles with an antisymmetric state at the same spatial position is zero.
- This is a manifestation of the Pauli principle which states that two fermions cannot occupy the same state.

In what follows, we will generalise these considerations to a system consisting of N identical particles.

A general Hamiltonian of a system of indistinguishable particles must be fully symmetric under exchange of the labels, corresponding to the degrees of freedom of these particles, i.e.

$$H(\underbrace{1, 2, 3, \dots, N}_{\text{labels}}) = H(2, 1, 3, \dots, N) = \dots$$

A typical example is a Hamiltonian of an atom with nuclear charge Z :

$$H = \underbrace{\sum_{i=1}^{N=Z} \left(\frac{\vec{p}_i^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i|} \right)}_{\begin{array}{l} \text{kinetic energy} \\ \text{of electrons and} \\ \text{Coulomb interaction} \\ \text{between electrons} \\ \text{and nucleus} \end{array}} + \underbrace{\sum_{\substack{i,j=1 \\ i < j}}^{N=Z} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{Coulomb interaction} \atop \text{among electrons}}$$

For the sake of simplicity we have omitted interactions related to the spin of the electrons.

The wave function of a many-body system can be written in the form

$$\Psi(\xi_1, \dots, \xi_N),$$

where ξ_i contains the variables that characterise a particle, e.g. position, spin, ...

$$\hookrightarrow \xi_i = \{\vec{r}_i, s_{i,z}, \dots\}$$

Like for the Hamiltonian before, we use the short hand notation

$$\Psi(\xi_1, \dots, \xi_N) = \underbrace{\Psi(1, \dots, N)}_{\text{particle labels}}.$$

For the following discussion it is useful to define the transposition operator T_{ij} ,

$$T_{ij} \Psi(\dots, i, \dots, j, \dots) = \Psi(\dots, j, \dots, i, \dots)$$

which swaps the labels i and j in the argument of Ψ .

For example:

$$T_{23} T_{12} \Psi(1, 2, 3) = T_{23} \Psi(2, 1, 3) = \Psi(2, 3, 1).$$

In total there are $\frac{N(N-1)}{2}$ transpositions, with $i < j$.

The transposition operators have the following properties:

i) $T_{ij}^2 = \underline{1}$

ii) Different transposition operators do not commute in general, e.g.

$$T_{12} T_{23} 4(1,2,3) = T_{12} 4(1,3,2) = 4(2,3,1) \neq T_{23} T_{12} 4(1,2,3)$$

iii) The transposition operator commutes with the Hamiltonian, i.e.

$$[H, T_{ij}] = 0$$

This is shown as follows:

$$\begin{aligned} T_{ij} H(\dots, i, \dots, j, \dots) 4(\dots, i, \dots, j, \dots) &= H(\dots, j, \dots, i, \dots) 4(\dots, j, \dots, i, \dots) \\ &\stackrel{\substack{\text{Symmetry} \\ \text{of the} \\ \text{Hamiltonian}}}{=} H(\dots, i, \dots, j, \dots) 4(\dots, j, \dots, i, \dots) \\ &= H(\dots, i, \dots, j, \dots) T_{ij} 4(\dots, i, \dots, j, \dots) \end{aligned}$$

Analogously, any operator O that is symmetric under particle exchange commutes with T_{ij} : $[O, T_{ij}] = 0$.

The next operator that we are going to need for the subsequent discussion is the permutation operator $P_{P(1)\dots P(N)}$, which replaces the labels $1, \dots, N$ in the wave function by $P(1), \dots, P(N)$.

$$\hookrightarrow P_{P(1) \dots P(N)} 4(\dots, 4, \dots, N, \dots, 1, \dots) = 4(\dots, P(4), \dots, P(N), \dots, P(1), \dots)$$

\uparrow \uparrow \uparrow
 $P(4)$ $P(N)$ $P(1)$

- For example: $P_{231} 4(1, 2, 3) = 4(2, 3, 1)$

or $P_{231} 4(2, 3, 1) = 4(3, 1, 2)$.

- In total, there are $N!$ permutations.
- Each permutation can be decomposed into a sequence of transpositions, e.g. $P_{231} = T_{12} T_{23}$.
- The sign (signum or signature) of a permutation is odd (even) when it can be decomposed into an odd (even) number of transpositions

number of
 transpositions
 \downarrow
 $\underbrace{(-1)^{\#P}}$
 sign of
 permutation

$$\left\{ \begin{array}{l} 1, \text{ when } P \text{ is a product of} \\ \text{an even number of transpositions} \\ -1, \text{ when } P \text{ is a product of an} \\ \text{odd number of transpositions} \end{array} \right.$$

- The permutation operator commutes with the Hamiltonian: $[H, P] = 0$.
- When 4 is an eigenfunction of H , then also $P4$ is an eigenfunction with the same eigenvalue:
 $H4 = E4 \rightarrow PH4 = EP4 \rightarrow H(P4) = E(P4)$

- We now come back to the notion of bosons and fermions, whose wave functions have to obey

bosons: $T_{ij} \Psi^{(S)}(1, \dots, N) = + \Psi^{(S)}(1, \dots, N) \delta_{ij}$

fermions: $T_{ij} \Psi^{(A)}(1, \dots, N) = - \Psi^{(A)}(1, \dots, N) \delta_{ij}$

- For $N=2$, there is only one non-trivial transposition, and the corresponding symmetric and anti-symmetric states are

$$\Psi^{(S)} = \mathcal{N} (\Psi(1,2) + \Psi(2,1))$$

↓
normalisation factor

$$\Psi^{(A)} = \mathcal{N} (\Psi(1,2) - \Psi(2,1))$$

- For $N=3$, there are three transpositions (T_{12}, T_{13}, T_{23}) and $3!$ permutations, and the anti-symmetric states are:

$$\Psi^{(S)} = \mathcal{N} (\Psi(1,2,3) + \Psi(2,1,3) + \Psi(2,3,1) + \Psi(1,3,2) + \Psi(3,1,2) + \Psi(3,2,1))$$

$$\Psi^{(A)} = \mathcal{N} (\Psi(1,2,3) - \Psi(2,1,3) + \Psi(2,3,1) - \Psi(1,3,2) + \Psi(3,1,2) - \Psi(3,2,1))$$

- Generalising these results leads to the following wave functions,

Symmetric state (bosons)

$$\Psi^{(S)} = N \sum_P P \Psi(1, \dots, N) \equiv \Psi^B$$

↓ sign of the permutation

$$\Psi^{(A)} = N \sum_P (-1)^{P_P} P \Psi(1, \dots, N) \equiv \Psi^F$$

↑ sum over all permutations

- Let us now discuss the consequences of the fact that in nature we encounter only symmetric or antisymmetric many-body states:

(i) Pauli exclusion principle

- Since $\Psi^F(1, 2, \dots, N) = -\Psi^F(2, 1, \dots, N)$ one has immediately $\Psi^F(1, 1, \dots, N) = 0$.

↳ Two identical fermions must not occupy the same quantum state. This has far-reaching consequences concerning the composition of atoms and matter in general.

(ii) Symmetry properties of wave functions
for spatial and spin degrees of freedom

(P4)

- Let's consider two fermions whose wave function has a spatial and a spin part:

$$\Psi^F(1,2) = \Psi^F(\vec{r}_1, s_{1,z}; \vec{r}_2, s_{2,z}) = \underbrace{\psi(\vec{r}_1, \vec{r}_2)}_{\text{Spatial wave function}} \underbrace{\chi(s_{1,z}, s_{2,z})}_{\text{Spin state}}$$

- Two spin $\frac{1}{2}$ particles can couple to form triplet (total spin $S=1$) or singlet (total spin $S=0$) states.

total spin quantum number \rightarrow s_m spin projection quantum number

$$|1,1\rangle = \begin{matrix} s_{1,z} & s_{2,z} \\ |\uparrow \uparrow\rangle \end{matrix} \quad |1,0\rangle = \frac{1}{\sqrt{2}}(|\uparrow \downarrow\rangle + |\downarrow \uparrow\rangle) \quad |1,-1\rangle = |\downarrow \downarrow\rangle \quad \left. \right\} \text{triplet}$$

$$|0,0\rangle = \frac{1}{2}(|\uparrow \downarrow\rangle - |\downarrow \uparrow\rangle) \quad \text{singlet}$$

- The singlet (triplet) states are antisymmetric (symmetric) under the exchange of particles.

- In order for the total state (combination of spatial and spin part) to be antisymmetric, the spatial wavefunction $\psi(\vec{r}_1, r_2)$ has to be antisymmetric (symmetric), when the spins are in the triplet (singlet) state.
- This has measurable consequences for the structure of multi-electron atoms.

(iii) Composite particles

- When a particle is composed from other particles, the following rule applies:
If the particle is composed of an odd number of fermions it is a fermion, otherwise it is a boson.
- To illustrate this, we consider two hydrogen atoms, whose state is given by

$$\Psi(H_1; H_2) = \Psi(e_1, p_1; e_2, p_2).$$
- Exchanging the two electrons yields

$$\Psi(e_1, p_1; e_2, p_2) \xrightarrow{e_1 \leftrightarrow e_2} -\Psi(e_2, p_1; e_1, p_2)$$
and exchanging the two protons yields

$$\Psi(e_1, p_1; e_2, p_2) \xrightarrow{p_1 \leftrightarrow p_2} -\Psi(e_1, p_2; e_2, p_1).$$

Hence $\Psi(e_1, p_1; e_2, p_2) \xrightarrow[e_1 \leftrightarrow e_2]{p_1 \leftrightarrow p_2} \Psi(e_2, p_2; e_1, p_1)$,
 and thus $\Psi(H_1; H_2) \xrightarrow{H_1 \leftrightarrow H_2} \Psi(H_2; H_1)$.
 ↑ boson!

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- In the following we construct the (anti-)symmetric wave functions of a non-interacting many-particle problem.
- These are usually a good starting point for perturbative expansions of interacting many-particle systems.
- The Hamiltonian we study, has the form

$$H = \sum_{i=1}^N \left(\frac{\vec{p}_i^2}{2m} + V_{\text{ext}}(\vec{r}_i) \right) = \sum_{i=1}^N H_i$$

↑ external potential

- In order to solve the stationary Schrödinger equation $H \Psi(1, \dots, N) = E \Psi(1, \dots, N)$ we make the separation ansatz

$$\Psi(1, \dots, N) = \psi^{(1)}(1) \psi^{(2)}(2) \dots \psi^{(N)}(N),$$

where the $\psi^{(i)}$ are single-particle wave functions that obey the single particle Schrödinger equation

$$H_i \psi^{(i)} = E^{(i)} \psi^{(i)}.$$

- Inserting the ansatz into the many-body Schrödinger equation, one sees that this is indeed solved:

$$H \Psi(1, \dots, N) = \sum_{i=1}^N H_i \psi^{(i)}(1) \dots \psi^{(N)}(N) = \underbrace{\left(\sum_{i=1}^N E^{(i)} \right)}_{\text{energy eigenvalue}} \psi^{(i)}(1) \dots \psi^{(N)}(N).$$

- Each of the functions $\psi^{(i)}$ can be one of the eigenstates u_1, u_2, u_3, \dots with eigenvalues E_1, E_2, E_3, \dots of the single-body Schrödinger equation.
- Therefore, the product wave function is generally of the form

$$\Psi(1, \dots, N) = u_{n_1}(1) u_{n_2}(2) \dots u_{n_N}(N)$$

↗ quantum number(s) labelling
 the energy eigenstate of
 the first particle

- The energy eigenvalue of the many-body system is then composed of the energy eigenvalues of the individual particles via

$$E = E_{n_1} + E_{n_2} + \dots + E_{n_N}.$$

- Let us now construct the symmetric eigenstates of bosons.

- $N=2 : \Psi^B(1,2) = \frac{1}{\sqrt{2}} (u_{n_1}(1) u_{n_2}(2) + u_{n_1}(2) u_{n_2}(1))$
↑ normalisation factor

- $N=3$ with two bosons in state u_{n_1} and one boson in state u_{n_3} :

$$\begin{aligned} \Psi^B(1,2,3) &= N (u_{n_1}(1) u_{n_1}(2) u_{n_3}(3) + u_{n_1}(2) u_{n_1}(1) u_{n_3}(3) \\ &\quad + u_{n_1}(2) u_{n_1}(3) u_{n_3}(1) + u_{n_1}(1) u_{n_1}(3) u_{n_3}(2) \\ &\quad + u_{n_1}(3) u_{n_1}(1) u_{n_3}(2) + u_{n_1}(3) u_{n_1}(2) u_{n_3}(1)) \\ &= 2N (u_{n_1}(1) u_{n_1}(2) u_{n_3}(3) + u_{n_1}(1) u_{n_1}(3) u_{n_3}(2) + u_{n_1}(3) u_{n_1}(2) u_{n_3}(1)) \end{aligned}$$

Since all u_n are normalised and mutually orthogonal, the normalisation factor is given by

$$1 = 4N^2 \cdot 3 \rightarrow N = \frac{1}{\sqrt{2!3!}} = \frac{1}{\sqrt{2!3!}}$$

- Generalising these considerations leads to

$$\Psi^B(1, \dots, N) = \frac{1}{\sqrt{N! N_{n_1}! N_{n_2}! \dots N_{n_N}!}} \sum_P u_{n_1}(P(1)) \dots u_{n_N}(P(N))$$

↑ number of bosons in state u_{n_i} .

- When all bosons occupy the same state, e.g. u_{n_1} , the $N_{n_1}=N$ and all the other $N_m=1$ and the wave function simplifies to

$$\Psi^B(1, \dots, N) = u_{n_1}(1) \dots u_{n_N}(N).$$

- If the state u_n is the ground state $\Psi^{(B)}$ describes a so-called Bose-Einstein condensate (predicted 1924 by Bose and Einstein; experimentally realised in 1995 by Cornell, Ketterle, Wieman (Nobel prize 2001)).

- For the case of fermionic particles, we construct the many-body wave function according to

$$\Psi^{(F)}(1, \dots, N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^{\#P} u_{n_1}(p_1) \dots u_{n_N}(p_N).$$

- For $N=2$ this yields the known result

$$\begin{aligned} \Psi^F(1, 2) &= \frac{1}{\sqrt{2}} (u_{n_1}(1) u_{n_2}(2) - u_{n_1}(2) u_{n_2}(1)) \\ &= \frac{1}{\sqrt{2}} \det \begin{pmatrix} u_{n_1}(1) & u_{n_1}(2) \\ u_{n_2}(1) & u_{n_2}(2) \end{pmatrix}, \end{aligned}$$

whose generalisation yields the so-called Slater determinant:

$$\Psi^F(1, \dots, N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_{n_1}(1) & \dots & u_{n_1}(N) \\ \vdots & \ddots & \vdots \\ u_{n_N}(1) & \dots & u_{n_N}(N) \end{pmatrix}$$

- Here, the Pauli principle is reflected by the fact that the determinant vanishes when two columns or rows are identical.

III. 2 The helium atom

(9D)

- The helium atom contains two electrons and its Hamiltonian reads

$$H = \underbrace{\frac{\vec{p}_1^2}{2\mu} + \frac{\vec{p}_2^2}{2\mu}}_{\text{nuclear charge } Z=2} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_1|} - \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_2|}}_{\text{two non-interacting hydrogen atoms}} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

- We can thus compose the problem into a many-body Hamiltonian, H_0 , of non-interacting particles and an interaction term.
- The ground state of the non-interacting problem is given by

$$\Psi_{1s,1s}(\vec{r}_1, \vec{r}_2) = \Psi_{1s}(\vec{r}_1) \Psi_{1s}(\vec{r}_2),$$

where $\Psi_{1s}(\vec{r}) = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}$ is the ground state (1s-state) of the single-body problem, i.e. the hydrogen atom.

- Since the spatial wave function of the ground state is apparently symmetric, the electrons need to be in an anti-symmetric spin state, i.e. the $S=0$ singlet state.

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- The ground state of the non-interacting problem is thus

$$\Psi(\vec{r}_1, s_{+1}; \vec{r}_2, s_{+2}) = \Psi_{1s}(\vec{r}_1) \Psi_{1s}(\vec{r}_2) \frac{1}{\sqrt{2}} (|1\rangle\langle 1| - |2\rangle\langle 2|).$$

- The ground state energy is given by:

$$\begin{aligned} H_0 \Psi_{1s1s}(\vec{r}_1, \vec{r}_2) &= \underbrace{2 E_{1s}^{(0)} \Psi_{1s1s}(\vec{r}_1, \vec{r}_2)} \\ &= -2 Z^2 E_{Ryd} \\ &= -108.8 \text{ eV} \end{aligned}$$

- This is relatively far from the experimentally measured result, $E_{1s1s}^{(\text{exp})} = -78.98 \text{ eV}$, for helium.

- The discrepancy stems from electron-electron interaction term.

- Its contribution can be estimated through first order perturbative theory, which yields the correction

$$\Delta E_{1s1s}^{(1)} = \frac{e^2}{4\pi\epsilon_0} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \frac{|4_{1s}(\vec{r}_1)|^2 |4_{1s}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{Z=2}{2} E_{Ryd} = 34 \text{ eV}$$

$$\hookrightarrow E_{1s1s}^{(0)} + \Delta E_{1s1s}^{(1)} = -\frac{11}{2} E_{Ryd} = -74.8 \text{ eV}$$

- The agreement of this corrected value with the experiment is fairly good.

- To conclude, we briefly discuss the excited states of helium.
- Here one of the electrons is excited to the state $\psi_{n=2, e, m}(\vec{r})$, and the spatial wave function of the non-interacting two-electron system is

$$\psi_{1s12\text{em}}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\psi_{1s}(\vec{r}_1) \psi_{2\text{em}}(\vec{r}_2) \pm \psi_{1s}(\vec{r}_2) \psi_{2\text{em}}(\vec{r}_1))$$

Sign depends on symmetry of
spin state ↓

- The energy of this state (under the action of H_0) is

$$E_{1s12\text{em}}^{(0)} = -Z^2 E_{\text{Ryd}} \left(1 + \frac{1}{4}\right) = -5 E_{\text{Ryd}} = -68 \text{ eV.}$$

- We can now use again perturbation theory to calculate the energy correction due to the electron-electron interaction:

$$\begin{aligned} \Delta E_{1s12\text{em}}^{(1)} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}_1 \int d\vec{r}_2 \frac{|4_{1s}(\vec{r}_1) 4_{2\text{em}}(\vec{r}_2) \pm 4_{1s}(\vec{r}_2) 4_{2\text{em}}(\vec{r}_1)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ &= \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}_1 \int d\vec{r}_2 \frac{|4_{1s}(\vec{r}_1)|^2 |4_{2\text{em}}(\vec{r}_2)|^2 \pm 4_{1s}^*(\vec{r}_1) 4_{2\text{em}}^*(\vec{r}_2) 4_{1s}(\vec{r}_2) 4_{2\text{em}}(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} \end{aligned}$$

$$= I_{\text{em}} \pm K_{\text{em}}$$

↑
electrostatic
energy

↑
exchange
energy

For an anti-symmetric spatial wave function (the electrons are in the triplet state) the energy correction is

$$\Delta E_{\text{isystem}}^{(1)} = I_{\text{em}} - K_{\text{em}}$$

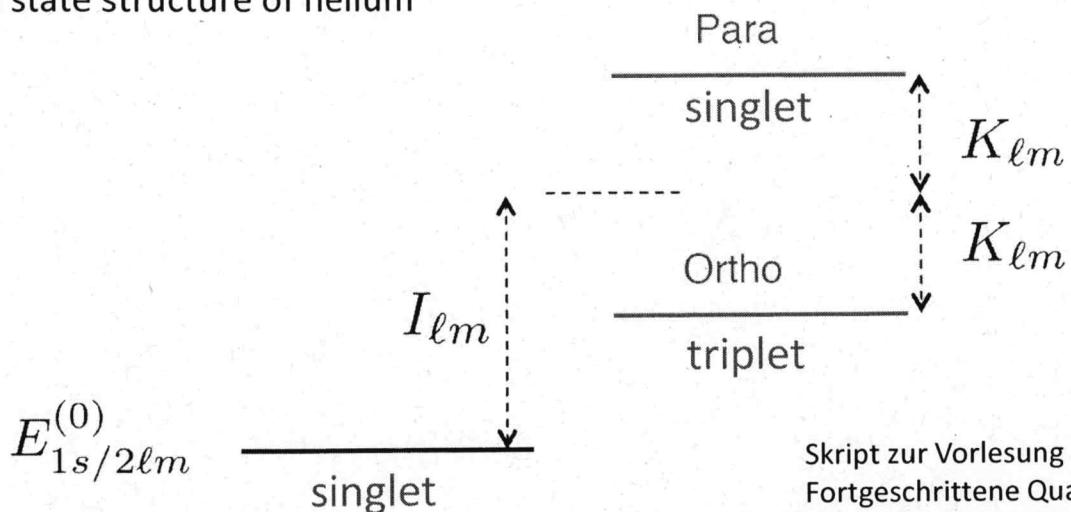
Since $K_{\text{em}} > 0$ this state has a lower energy compared to the state in which the electron spins form a singlet.

The Pauli principle thus introduces a spin-dependence of the energies, although the Hamiltonian that we studied, does not explicitly depend on the spin degrees of freedom.

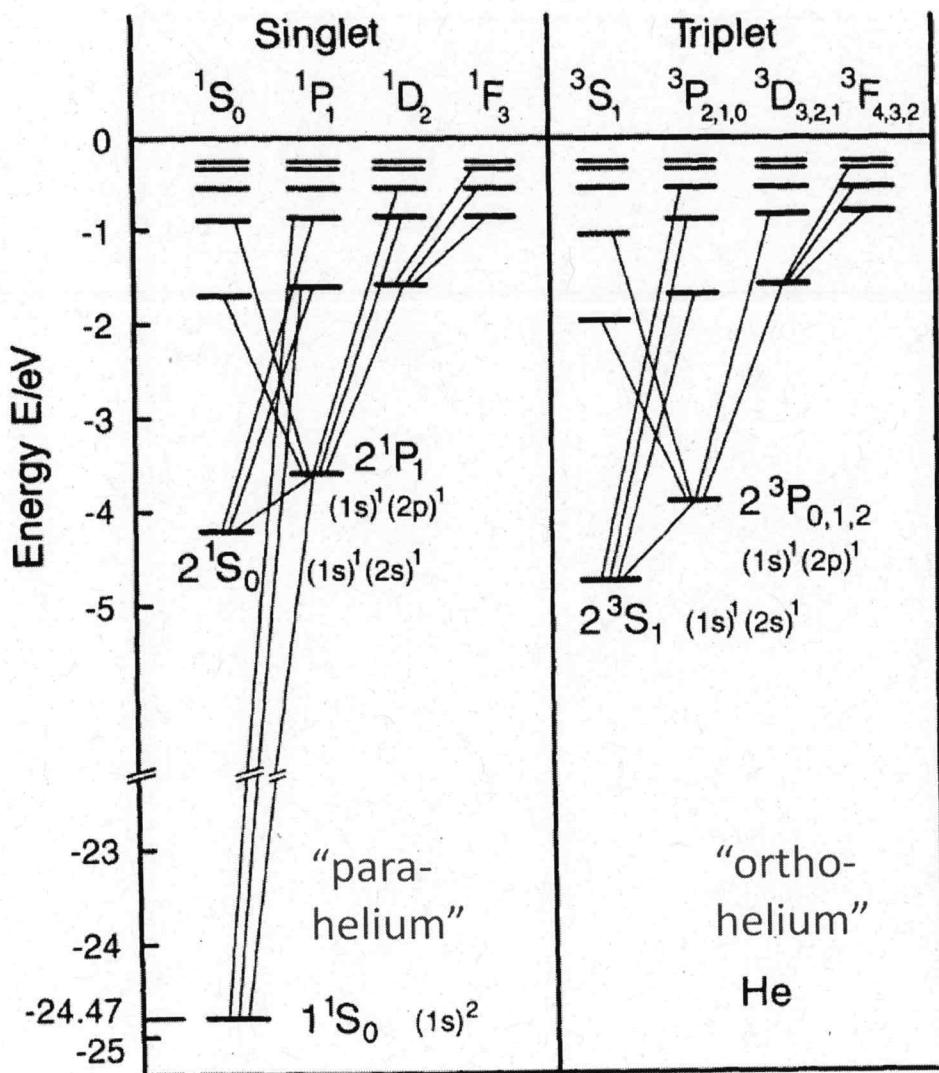
Helium where spins form a singlet (triplet) is also referred to as para (ortho) helium.

The triplet state is extremely long-lived ($\sim 10^8$ s lifetime), which comes from the fact that external perturbations that couple singlet and triplet states are extremely weak.

Ground state structure of helium



Skript zur Vorlesung
Fortgeschrittene Quantentheorie
(Quantenmechanik II)
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Haken and Wolf,
The Physics of Atoms
and Quanta,
Springer

III. 3 Heavier atoms

(94)

- The treatment of heavier atoms, i.e. atoms with a larger number of electrons, becomes increasingly complicated.
- This requires the utilisation of approximation methods, which we discuss in the following.
- Starting point is the Hamiltonian

$$H = \sum_{i=1}^{N=2} \left(-\frac{\hbar^2}{2\mu} \Delta - \frac{ze^2}{4\pi\epsilon_0 |\vec{r}_i|} \right) + \underbrace{\frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N=2} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}}_{\frac{N(N-1)}{2} \text{ interaction terms}}$$

Sum of single electron operators

- Unlike in the case of the helium atom the electron-electron interaction can typically not be treated as a perturbation.
- However, a simplifying assumption that is made for heavier atoms is that each electron experiences an average potential, which is generated by all other electrons.
- This allows to formulate a single-body Schrödinger equation for each electron, which however contains a potential that depends on the wave functions of all the other electrons.

- This system of coupled equations can then be solved in an iterative fashion.
- A first ansatz of this kind is the so-called Hartree approximation (developed in 1927).
- Here, the many-body electron wave function is written in terms of single-electron states u_i :

$$\Psi(1, \dots, N) = u_1(1) u_2(2) \dots u_N(N).$$

- In order to respect the Pauli principle one assumes that all u_i are different.
- However, no antisymmetrisation is performed.
- With the above ansatz one can formulate a charge density $\rho_j(\vec{r})$ which is associated with the j -th atom:

$$\rho_j(\vec{r}) = -e |u_j(\vec{r})|^2$$

↑ probability density
 electron charge of j -th electron

From electrostatics we know that the associated electric potential is given by

$$\int d^3\vec{r}' \frac{\rho_j(\vec{r}')}{| \vec{r} - \vec{r}' |} = -e \int d^3\vec{r}' \frac{|u_j(\vec{r}')|^2}{| \vec{r} - \vec{r}' |}.$$

- Therefore, the interaction of the i -th electron with all remaining electrons and the nucleus is described by the potential

$$V_i(\vec{r}) = \int d^3\vec{r}' \frac{e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|} \sum_{j \neq i} |u_j(\vec{r}')|^2 - \frac{ze^2}{4\pi\epsilon_0 |\vec{r}|},$$

and the associated single-electron Schrödinger equation - also referred to as Hartree equation - is

$$\left(-\frac{\hbar^2}{2m} \Delta + V_i(\vec{r}) \right) u_i(\vec{r}) = E_i u_i(\vec{r}).$$

- One now proceeds as follows:

- Select a set of orthonormal start functions $u_i^{(0)}$, e.g. eigenstates of hydrogen (with spin).
- Calculate the potentials V_i using the $u_i^{(0)}$.
- Solve the associated Hartree equations and determine from them the new u_i and the eigenenergies E_i .
- Calculate the potentials with the new u_i and restart until convergence (u_i and E_i no longer change).

- We now calculate the energy of the many-electron system with the Hartree approximation.

- Calculating the expectation value $\langle H \rangle$ within the Hartree ansatz yields

$$\begin{aligned}\langle H \rangle &= \int d^3\vec{r}_1 \dots d^3\vec{r}_N u_i^*(\vec{r}_1) \dots u_N(\vec{r}_N) H u_1(\vec{r}_1) \dots u_N(\vec{r}_N) \\ &= \sum_{i=1}^{N=2} \int d^3\vec{r}_i u_i^*(\vec{r}_i) \left(-\frac{\hbar^2}{2m} \Delta_i - \frac{ze^2}{4\pi\epsilon_0 |\vec{r}_i|} \right) u_i(\vec{r}_i) \\ &\quad + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N=2} \int d^3\vec{r}_i d^3\vec{r}_j \frac{e^2 |u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}\end{aligned}$$

- This expression can be simplified by multiplying the Hartree equation from the left by $u_i^*(\vec{r})$ and integrating over \vec{r} , which yields

$$\epsilon_i = \int d^3\vec{r} u_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m} \Delta - \frac{ze^2}{4\pi\epsilon_0 |\vec{r}|} \right) u_i(\vec{r}) + \sum_{j \neq i} \int d^3\vec{r} d^3\vec{r}' \frac{e^2 |u_j(\vec{r}')|^2 |u_i(\vec{r})|^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}'|}.$$

- Using this expression to replace the first term on the right hand side of $\langle H \rangle$ yields:

$$\langle H \rangle = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \int d^3\vec{r}_i d^3\vec{r}_j \frac{e^2 |u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

corrects the double counting when summing over Hartree energies (electron i interacts with j and vice versa)

- The energies ϵ_i can be interpreted as single electron ionisation energies, assuming that the wave functions of the other electrons do not change after the removal of this electron.
- An improvement over the Hartree method can be achieved via the so-called Hartree-Fock ansatz, which was developed in 1935.
- Here the electronic wave function is chosen to have the form of a Slater determinant

$$\Psi(1, \dots, N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_1(1) & \dots & u_1(N) \\ \vdots & \ddots & \vdots \\ u_N(1) & \dots & u_N(N) \end{pmatrix}, \quad \text{the } u_i \text{ contain spatial and spin parts}$$

which is a far more accurate description of the electronic many-body state.

Using this ansatz, the energy expectation value evaluates to:

$$\langle H \rangle = \sum_{i=1}^{N=2} \int d^3 \vec{r}_i u_i^*(\vec{r}_i) \left(-\frac{\hbar^2}{2m} \Delta_i - \frac{Z e^2}{4\pi\epsilon_0 |\vec{r}_i|} \right) u_i(\vec{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N=2} \int d^3 \vec{r}_i d^3 \vec{r}_j \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} \underbrace{\left(|u_j(\vec{r}_j)|^2 |u_i(\vec{r}_i)|^2 - \delta_{s_i s_j} u_i^*(\vec{r}_i) u_j^*(\vec{r}_j) u_i(\vec{r}_i) u_j(\vec{r}_j) \right)}_{\text{exchange term}}$$

exchange term, which only contributes when electron i and j are in the same spin state

- The appearance of the exchange term is new, compared to the Hartree approximation, and a consequence of the antisymmetrisation of the electronic wave function. (99)
- The exchange term is "non-local", i.e. it necessitates the evaluation of an electronic wave functions at two distinct spatial points.
- The wave functions u_i , which are still unknown, can be derived using the variational principle due to Ritz, i.e. one finds the set that minimises $\langle H \rangle$ under the constraint, that all u_i shall be normalised.
- This leads to the Hartree-Fock equation.

$$\epsilon_i u_i(\vec{r}) = \left(-\frac{\hbar^2}{2\mu} \Delta - \frac{ze^2}{4\pi\epsilon_0 |\vec{r}|} \right) u_i(\vec{r}) + \int d^3 p' \frac{e^2}{4\pi\epsilon_0 |\vec{r}-\vec{r}'|} \sum_{j=1}^{N=7} u_j^*(\vec{r}') [u_j(\vec{r}') u_i(\vec{r}) - \delta_{s_i, s_j} u_j(\vec{r}) u_i(\vec{r}')] .$$

- Here, the ϵ_i are Lagrangian parameters (due to the constrained minimisation), which again can be interpreted as ionisation energies.
- From the Hartree-Fock equation one sees that the effective single electron potential depends on the anti-symmetrised spatial wave function, when the i -th and j -th atom are in the same spin state.
- This is yet another manifestation of the Pauli principle.

- The Hartree - Fock approach allows to develop (100) a systematic picture of the atomic structure and the periodic table of elements.
- The effective potential emerging in the Hartree - Fock equation is to a good degree of approximation spherically symmetric.
- The single electron wave functions ψ_i can therefore be chosen as eigenfunctions of the angular momentum operators L^2 and L_z .
- We can thus write the single electron states in the form

$$|n, l, m, s_z\rangle$$

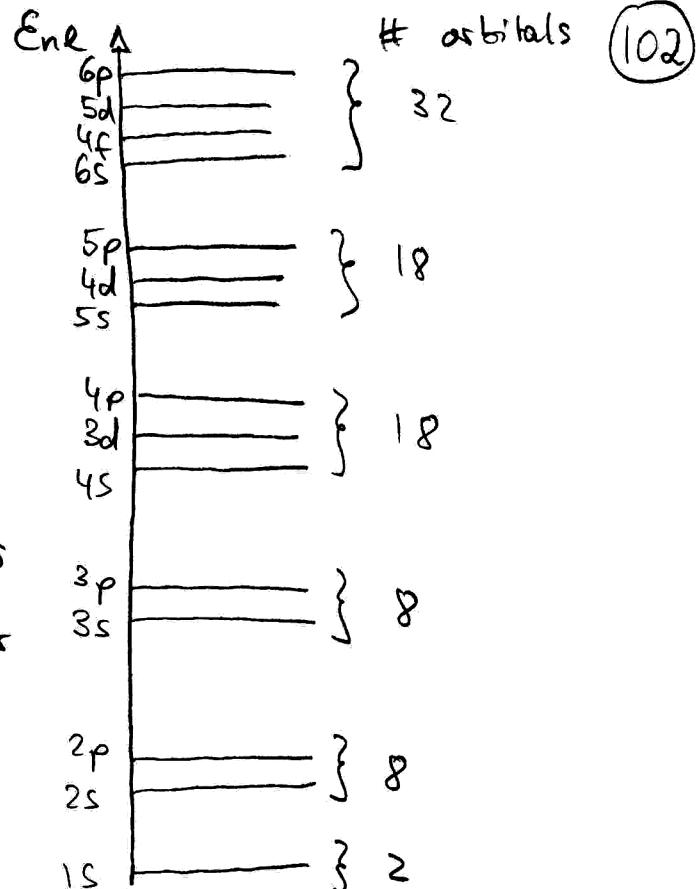
↑ ↑ ↑
 principal quantum number angular momentum projection q_m spin projection q_m
 angular momentum q_m

- Since the Hartree - Fock potential is not a pure Coulomb potential, the energy eigenvalues of the Hartree - Fock equation will depend on the principal quantum number n and the angular momentum quantum number l
- ↳ End.

- Each of the energy levels has a degeneracy of $2(2l+1)$.
 - ↑ number of possible m -values
number of possible s_z -values
- These $2(2l+1)$ electronic states, which one also calls orbitals, form a shell.
- Each orbital can contain one electron.
 - ↳ S-shell ($l=0$) - 2 electrons
 - P-shell ($l=1$) - 6 electrons
 - d-shell ($l=2$) - 10 electrons
 - f-shell ($l=3$) - 14 electrons
- To construct the ground state configuration of a given element with Z electrons, one fills the orbitals one by one (no orbital can be populated by more than one electron).
- In which order the orbitals are filled depends on a number of factors.
- One important aspect is the energy E_{nl} of the orbitals, and one always populates the orbital with lowest available energy.
- In general, for given n , the energy increases with increasing l :

$$\epsilon_{1s} < \underbrace{\epsilon_{2s}}_{\text{# orbitals } 2} < \underbrace{\epsilon_{2p}}_{\text{# orbitals } 6} < \underbrace{\epsilon_{3s}}_{\text{# orbitals } 2} < \underbrace{\epsilon_{3p}}_{\text{# orbitals } 6} < \underbrace{\epsilon_{3d}}_{\text{# orbitals } 10}$$

- However, due to screening effects (higher l electrons are further away from the nucleus), s-states with principle quantum number $n+1$ can be lower in energy than, e.g., d-states with principle quantum number n (see 3d vs. 4s).
- Considering this, one can construct the entire periodic table:



- Hydrogen has one electron in 1s orbital and helium has the 1s orbital fully occupied.
- Filling the 2s-shell yields Li and Be, and the 2p-shell is filled from B to Ne.
- Ne has fully filled 1s, 2s, 2p-shells.
- The systematics of the $n=2$ shells is repeated for $n=3$: Na to Ar.
- For $n=4$ first the s-shell is filled (K, Ca), but this is followed by 3d (Sc to Zn) and only then by 4p (Ga to Kr).
- This systematics is repeated for (5s, 4d, 5p).
- Next, one fills the shells in the order 6s, 4f, 5d, 6p).

- The position of the elements in the periodic table also determines their chemical properties.
- Noble gases have fully occupied shells and are chemically inert.
- Elements of the first group (except H) possess only one weakly bound valence electron (Li , Na , ...) and are therefore chemically very reactive.
- The halogenides (7. group) are also very reactive since only one p-electron is missing for completing the noble gas configuration.
- Let us finally consider atoms whose shells are neither fully nor nearly closed.
- Their electronic configuration is given by Hund's rules:
 - i) The electrons fill the orbitals such that their total spin S is maximised. This leads to a spin wave function, that is as symmetric as possible. In turn this means that the spatial wave function is anti-symmetric which reduces the probability for two electrons to be at the same position and therefore lowers their electrostatic interaction.

- iii) Is there more than one possibility to maximize the total electron spin, then the state with maximum orbital angular momentum is chosen.
- iii) If a shell is less than half-filled, the total angular momentum of the electronic ground state is $J = |L-S|$. Conversely, for a filling greater than half, the electronic ground state has $J = L+S$.

Periodic table of elements

| Periodic table | | | | | | | | | | | | | | | | | | | |
|----------------|--------------------------|--------------------|-----------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------------|--------------------|
| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | |
| Period | Hydrogen & alkali metals | | Alkaline earth metals | | | | | | | | | | | | | | | | |
| 1 | 1 H 1.008 | | | | | | | | | | | | | | | | | He 2 He 4.0028 | |
| 2 | 3 Li 6.94 | 4 Be 9.0122 | | | | | | | | | | | | | | | | Ne 10 Ne 20.180 | |
| 3 | 11 Na 22.990 | 12 Mg 24.305 | | | | | | | | | | | | | | | | Ar 18 Ar 39.95 | |
| 4 | 19 K 39.098 | 20 Ca 40.078 | | | | | | | | | | | | | | | | Kr 36 Kr 83.798 | |
| 5 | 37 Rb 85.488 | 38 Sr 87.62 | | | | | | | | | | | | | | | | Xe 54 Xe 131.29 | |
| 6 | 55 Cs 132.91 | 56 Ba 137.33 | * | 71 Lu 174.97 | 72 Hf 178.49 | 73 Ta 180.05 | 74 W 183.84 | 75 Re 186.21 | 76 Os 190.23 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.97 | 80 Hg 200.59 | 81 Tl 204.38 | 82 Pb 207.2 | 83 Po 208.98 | 84 At [210] | 85 Rn [222] | |
| 7 | 87 Fr [223] | 88 Ra [226] | * | 103 Lr [266] | 104 Rf [267] | 105 Db [268] | 106 Sg [269] | 107 Bh [270] | 108 Hs [269] | 109 Mt [278] | 110 Ds [281] | 111 Rg [282] | 112 Cn [285] | 113 Nh [286] | 114 Fl [286] | 115 Mc [290] | 116 Lv [293] | 117 Ts [294] | 118 Og [294] |
| | | | * | 57 La 138.91 | 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | 61 Pm [145] | 62 Sm 150.36 | 63 Eu 151.96 | 64 Gd 157.25 | 65 Tb 158.93 | 66 Dy 162.50 | 67 Ho 164.93 | 68 Er 167.26 | 69 Tm 168.93 | 70 Yb 173.05 | | |
| | | | * | 89 Ac [227] | 90 Th 232.04 | 91 Pa 231.04 | 92 U 238.03 | 93 Np [237] | 94 Pu [244] | 95 Am [243] | 96 Cm [247] | 97 Bk [247] | 98 Cf [251] | 99 Es [252] | 100 Fm [257] | 101 Md [258] | 102 No [259] | Nobelium | |

Ionization-Energy

