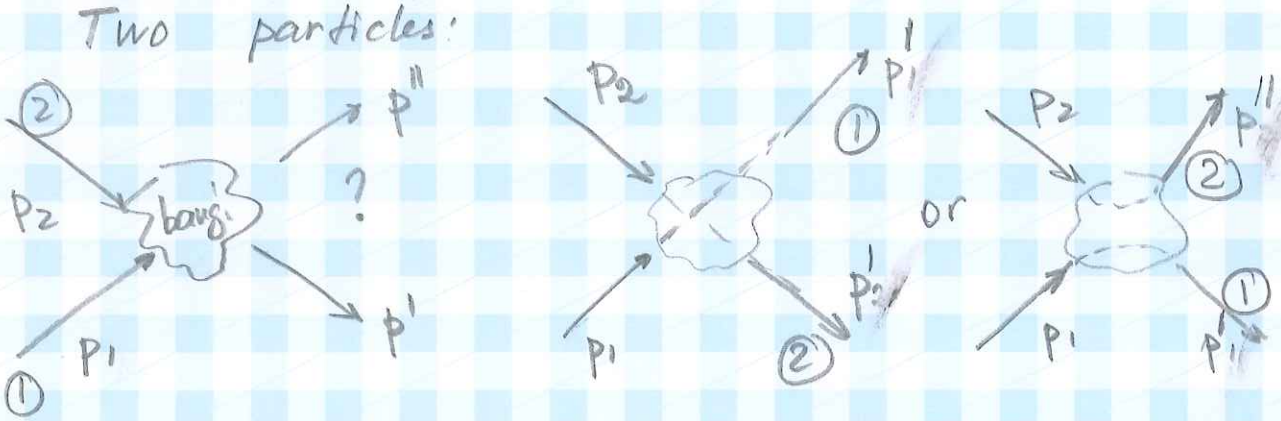
Identical particle.

Often we can distinguish particles, even if they are alike

this is built in the classical statistics

However, in quantum physics the particle that are indistinguishable, must be described by the wave function that respects the permutation symmetry

Two particles:



Two – particle wave function – notation

$|①\rangle\,|②\rangle$

Final state $c_1|\vec{p}'\rangle|\vec{p}''\rangle + c_2|\vec{p}''\rangle|\vec{p}'\rangle$

Let's define the permutation operator

$$P_{12}\,|\vec{p}'\rangle_{①}|\vec{p}''\rangle_{②} = |\vec{p}''\rangle_{①}|\vec{p}'\rangle_{②} \qquad P_{12}^2 = \hat{1}$$

or $P_{12}\,\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_2,\vec{r}_1) = e^{i\delta}\,\psi(\vec{r}_1,\vec{r}_2)$

$P_{12}^2\,\psi(\vec{r}_1,\vec{r}_2) = e^{2i\delta}\,\psi(r_1,r_2) = \psi(\vec{r}_1,\vec{r}_2)$

$e^{2i\delta} = 1 \qquad e^{i\delta} = \pm 1$

Two distinct options

$P_{12}\,\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_1,\vec{r}_2)$ symmetric, bosons

$P_{12}\,\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_1,\vec{r}_2)$ anti-symmetric, fermions

Bosons are particles whose wavefunction is symmetric under exchange of any two particles

2 particles: $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) = \frac{1}{\sqrt{2}}\left[\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) + \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)\right]$

N particles

$\psi_B(\vec{r}_1, \ldots \vec{r}_i \ldots \vec{r}_j \ldots \vec{r}_N) = + \psi(\vec{r}_1, \ldots \vec{r}_j \ldots \vec{r}_i \ldots \vec{r}_N)$

Special case: if only one state available

$\psi_B(\vec{r}_1 \ldots \vec{r}_N) = \psi_0(\vec{r}_1)\psi_0(\vec{r}_2) \ldots \psi_0(\vec{r}_N)$ BEC

Fermions are particle whose wavefunction is anti- symmetric under exchange of any two particles

$\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1) = \frac{1}{\sqrt{2}}\left[\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)\right]$

$\psi_F(\vec{r}_1 \ldots \vec{r}_i \ldots \vec{r}_j \ldots \vec{r}_N) = -\psi_F(\vec{r}_1 \ldots \vec{r}_j \ldots \vec{r}_i \ldots r_N)$

No two particle can be in the same state

Pauli exclusion principle

Particle statistics is defined by its spin

All half-integer particles are fermions

($e^-, e^+, p, n, \ldots {}^2H, {}^{40}K, {}^6Li$)

All integer-spin particles are bosons

(γ, Z^0, Higgs, ${}^{87}Rb$, ${}^{39}K$, ${}^7Li$, ${}^1H, {}^3H$)

Two-electron system

Total spin is conserved $[\vec{S}_{tot}, \hat{H}] = 0$,

$\vec{S}_{tot}$ is a good quantum number

$$\Psi(\vec{r}_1, \vec{r}_2, m_{s_1}, m_{s_2}) = \varphi(\vec{r}_1, \vec{r}_2)\,\chi(m_{s_1}, m_{s_2})$$

must have opposite symmetry

Possible total spin value

$S=1$ (triplet) $\quad \varphi(\vec{r}_1, \vec{r}_2) = -\varphi(\vec{r}_2, \vec{r}_1)$

$$\begin{cases} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}\left(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle\right) \end{cases} \Big\} \text{ Symmetric}$$

$S=0$ (singlet) $\quad \frac{1}{\sqrt{2}}\left(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\right)$ anti-symmetric

$$\varphi(\vec{r}_1, \vec{r}_2) = \varphi(\vec{r}_2, \vec{r}_1)$$

For a distinct single-particle state

$$\varphi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) \pm \varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)\right)$$

Probability density of finding electron 1 in $\vec{r}_1$, and of finding electron 2 in $\vec{r}_2$

$$dP_{12} = \rho_{exch}\, d\tau_1 d\tau_2 = |\varphi(\vec{r}_1, \vec{r}_2)|^2 d\tau_1 d\tau_2 =$$

$$= \frac{1}{2}\left\{|\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)|^2 + |\varphi_1(\vec{r}_2)\varphi_2(\vec{r}_1)|^2 \pm 2\,\mathrm{Re}\left[\varphi_1(r_1)\varphi_2(r_2)\varphi_1^*(r_2)\varphi_2^*(r_1)\right]\right\} \times d\tau_1 d\tau_2$$

exchange density

Probability of finding two electrons at the same place is zero.

Also, even if $\vec{r}_1 \approx \vec{r}_2$ (close locations), the last term reduces the probability of joint detection

Excited state of He

Singlet spin state

$$\psi_{\underset{\text{para}}{}}(r_1, r_2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(\vec{r}_1)\psi_{2s}(\vec{r}_2) + \psi_{1s}(\vec{r}_2)\psi_{1s}(\vec{r}_1)\right]\left[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right]$$

para-helium → He in a singlet spin-state

ground state is parahelium by definition

triplet state

$$\psi_{\text{ortho}}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_{1s}(\vec{r}_1)\psi_{2s}(\vec{r}_2) - \psi_{1s}(\vec{r}_2)\psi_{2s}(\vec{r}_1)\right]\begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle \end{cases}$$

ortho-helium

For parahelium the electrons are closer to each other (on average), thus the energy of this state is higher

$$E_{\text{para}} > E_{\text{orto}}$$

We can now treat the e-e repulsion term perturbatively

$$\hat{V} = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$\Delta E_{\substack{\text{para}\\\text{orto}}} = \langle \psi_{\substack{\text{para}\\\text{orto}}} | \hat{V} | \psi_{\substack{\text{para}\\\text{orto}}} \rangle =$$

$$= \frac{1}{2}\iint d^3\vec{r}_1 d^3\vec{r}_2 \left(\psi^*_{1s}(\vec{r}_1)\psi^*_{2s}(\vec{r}_2) \pm \psi^*_{1s}(\vec{r}_2)\psi^*_{2s}(\vec{r}_1)\right)\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\left(\psi_{1s}(\vec{r}_1)\psi_{2s}(\vec{r}_2) \pm \psi_{1s}(\vec{r}_2)\psi_{2s}(\vec{r}_1)\right)$$

equal contributions

$$= \frac{1}{2}\iint d^3\vec{r}_1 d^3\vec{r}_2 \left\{|\psi_{1s}(\vec{r}_1)|^2|\psi_{2s}(\vec{r}_2)|^2 + |\psi_{1s}(\vec{r}_2)|^2|\psi_{2s}(\vec{r}_1)|^2\right\}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \pm$$

$$\pm \frac{1}{2}\iint d^3\vec{r}_1 d^3\vec{r}_2 \left[\psi^*_{1s}(\vec{r}_2)\psi^*_{2s}(\vec{r}_1)\psi_{1s}(\vec{r}_1)\psi_{2s}(\vec{r}_2) + \psi^*_{1s}(\vec{r}_1)\psi^*_{2s}(\vec{r}_2)\psi_{1s}(\vec{r}_2)\psi_{2s}(\vec{r}_1)\right]\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

equal contributions

$= I > 0$ coulomb repulsion

$$= \left(\iint d^3\vec{r}_1 d^3\vec{r}_2 \, |\psi_{1s}(r_1)|^2 |\psi_{2s}(r_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right) \pm \left(\iint d^3\vec{r}_1 d^3\vec{r}_2 \, \psi^*_{1s}(r_1)\psi_{1s}(r_2)\psi^*_{2s}(r_2)\psi_{2s}(r_1) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right)$$

$J > 0$ exchange interaction

$1s\,2s$: $I + J$ (singlet, para helium); $I - J$ (doublet, ortho helium)

$E_{1s} + E_{2s}$

$(1s)^2$ para helium

$2E_{1s}$

Spin-dependent energy, even though no spin-spin interaction in the Hamiltonian!

Structure of Larger atoms

Hartree's self-consistent field

The multi-electron wavefunction has terms

$\psi = u_1(\vec{r}_1)\, u_2(\vec{r}_2) \ldots u_n(\vec{r}_n)$ with $\int |u_i(\vec{r})|^2 d^3\vec{r} = 1$

Hamiltonian $\hat{H} = \sum_i \frac{p_i^2}{2m} + \left(\sum_i \frac{Ze^2}{r_i} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \right)$

instead of calculating the exactly, replace the interaction terms in $\square$ with a central force effective potential $V_{eff}(r_i)$ (field created by all other electrons in the location of the i^{th} one)

Solve for energy using variational method

Choose $\psi(r_1 \ldots r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(\vec{r}_1) & u_2(\vec{r}_1) & \cdots & u_n(\vec{r}_1) \\ u_1(\vec{r}_2) & u_2(\vec{r}_2) & \cdots & u_n(\vec{r}_2) \\ \vdots & & & \\ u_1(\vec{r}_n) & & \cdots & u_n(\vec{r}_n) \end{vmatrix}$

↓

Calculate $\bar{H} = \int \psi^* \sum_{i=1}^{n} \left(-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(r_i) \right) \psi \, d^3\vec{r}_1 d^3\vec{r}_2 \ldots$

↓

vary $u_1, u_2 \ldots u_n$ such that $\delta \bar{H} = 0$

repeat until satisfied with accuracy

Very computationally-intense for large systems.