

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

center of mass

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

separation between the particles

$$\vec{P} = \vec{p}_1 + \vec{p}_2$$

total momentum

$$\vec{p} = \frac{m_2 \vec{p}_1 - m_1 \vec{p}_2}{m_1 + m_2}$$

Kinetic energy =  $\frac{\vec{P}^2}{2(m_1 + m_2)}$  +  $\frac{\vec{p}^2}{2\mu}$

center of mass motion (under  $M = m_1 + m_2$ )

relative motion of two particles (under  $\mu$ , reduced mass)

SE:  $\left[ \frac{\hat{P}^2}{2M} + V(\vec{r}) \right] u(\vec{r}) = \left( E - \frac{\vec{P}^2}{2M} \right) u(\vec{r})$

wave function of the two-particle system

$$\Psi(\vec{r}, \vec{R}) = e^{i\vec{P} \cdot \vec{R} / \hbar} u(\vec{r})$$

plane wave of the free motion of the center of mass

Postulate: quantum particles of the same physical nature (e.g. electrons) are identical  $\rightarrow$  none of the observable properties should depend on exchange of two particles

Two-particle Hamiltonian:  $H(1, 2)$   
 coordinates and spins of two particles

$$H(1, 2) u_E(1, 2) = E u_E(1, 2)$$

Exchange operator:  $P_{12} u_E(1, 2) = u_E(2, 1)$

The fact that observable properties are not affected by  $P_{12}$  formally implies that

$$[H, P_{12}] = 0$$

(similar to the parity operator)

$P_{12}^2 = 1 \rightarrow$  eigenvalues of  $P_{12}$  are  $\pm 1 = \lambda$

$$\underline{\lambda = +1} : \psi^S(1, 2) = \frac{1}{N_{2S}} [\psi(1, 2) + \psi(2, 1)]$$

$$\underline{\lambda = -1} : \psi^A(1, 2) = \frac{1}{N_{2A}} [\psi(1, 2) - \psi(2, 1)]$$

### 13-3. The Pauli principle

- ①. Systems consisting of identical particles with spin  $1/2, 3/2, \dots$  are described by antisymmetric wave functions. These are fermions and they obey Fermi-Dirac statistics.
- ②. Systems consisting of identical particles with spin  $0, 1, 2, \dots \rightarrow$  symmetric wave functions, bosons, Bose-Einstein statistics.

Non-interacting fermions:

$$H = \sum_{i=1}^N H_i, \quad H_i = \frac{p_i^2}{2m} + V(x_i)$$

Hartree product:

$$\psi_E(1, 2, \dots, N) = \psi_{E_1}(1) \dots \psi_{E_N}(N)$$

$$E = E_1 + E_2 + E_3 + \dots + E_N$$

↑ the total energy is the sum of the individual energies

Two electrons:

$$u_E(12) = u_{E_1}(1) u_{E_2}(2)$$

$$P_{12} u_E(12) = u_E(21) = u_{E_1}(2) u_{E_2}(1)$$

Hartree product does not satisfy the requirement that the wave function should be antisymmetric. One can produce an antisymmetric linear combination

$$u^{(A)}(1,2) = \frac{1}{\sqrt{2}} [u_{E_1}(1) u_{E_2}(2) - u_{E_1}(2) u_{E_2}(1)]$$

Now,

$$P_{12} u^{(A)}(12) = -u^{(A)}(12)$$

Let's assume that  $1=2$ , i.e.  $\vec{r}_1 = \vec{r}_2$ ,  $\beta_1 = \beta_2$ , that is two electrons with the same spin are at the same point in space. Then

$$u^{(A)}(1,1) \equiv 0$$

This is another formulation of the Pauli exclusion principle: no two electrons with the same spin can occupy the same position in space.

There's an effective repulsion between equal spins — Fermi hole!

# Slater determinant

One can write  $u^A(1,2)$  in the form

$$u^{(A)}(1,2) = \frac{1}{2^{1/2}} \begin{vmatrix} u_{E_1}(1) & u_{E_1}(2) \\ u_{E_2}(1) & u_{E_2}(2) \end{vmatrix}$$

For  $N$  particles, the antisymmetric wave function is determined by Slater determinant

$$u^{(A)}(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_{E_1}(1) & u_{E_1}(2) & \dots & u_{E_1}(N) \\ u_{E_2}(1) & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ u_{E_N}(1) & u_{E_N}(2) & & u_{E_N}(N) \end{vmatrix}$$

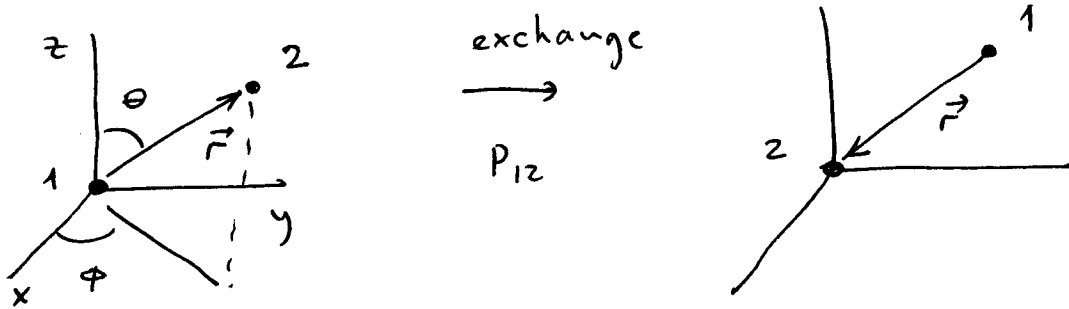
states  $\longrightarrow$  particles

$P_{ij} u^{(A)}(1,2,\dots,N) \equiv$  interchange of two columns  $\rightarrow$   
 $\rightarrow$  according to properties of determinants  
it results in  $-u^{(A)}(\dots i \dots j \dots N)$

A Slater determinant forms the eigenstate of  $N$  non-interacting electrons satisfying the Pauli exclusion principle

# 13-4 Exclusion principle and two-particle problem

Two electrons at the distance  $\vec{r}$ :



$$\begin{aligned} \theta &\rightarrow \pi - \theta \\ \phi &\rightarrow \phi + \pi \end{aligned}$$

$$\begin{aligned} u(\vec{r}) &= R_{nl}(r) Y_{lm}(\theta, \phi) \rightarrow R_{nl}(r) Y_{lm}(\pi - \theta, \phi + \pi) \\ &= (-1)^l Y_{lm}(\theta, \phi) \end{aligned}$$

Two electrons can be either in a singlet state:

$$\frac{1}{\sqrt{2}} (\chi_+^{(1)} \chi_-^{(2)} - \chi_-^{(1)} \chi_+^{(2)}) \leftarrow \text{"A" antisymmetric}$$

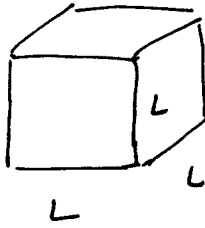
or in a triplet state

$$\begin{aligned} &\chi_+^{(1)} \chi_+^{(2)} \\ &\frac{1}{\sqrt{2}} (\chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)}) \leftarrow \text{"S" symmetric} \\ &\chi_-^{(1)} \chi_-^{(2)} \end{aligned}$$

Since the total wave function is a product of  $u(\vec{r})$  and the spin function,  $l=0, 2, 4, \dots$  in the singlet,  $l=1, 3, 5, \dots$  in the triplet.

13-5 Exclusion principle for a large number of electrons

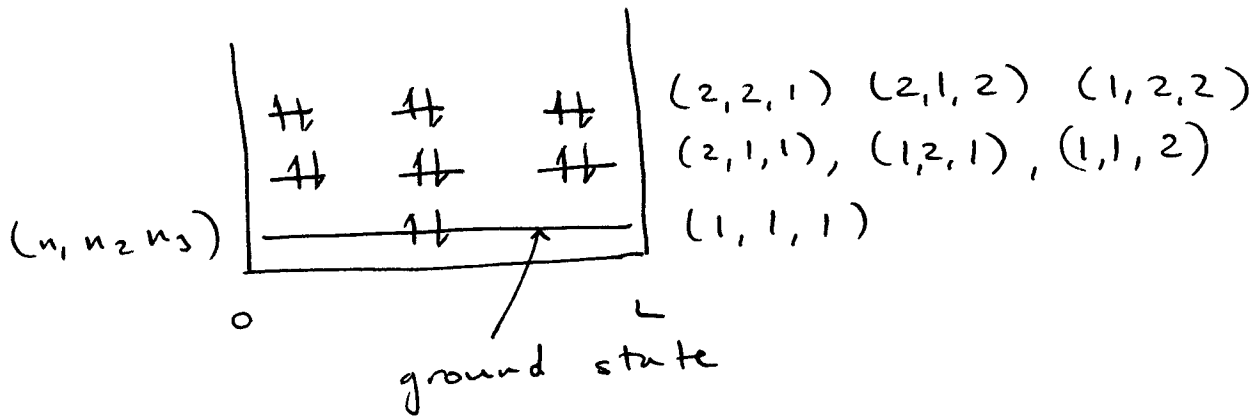
3D Box:



$$E(n_1, n_2, n_3) = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$$

$$u_E(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \sin \frac{n_3 \pi z}{L}$$

Aufbau principle: put electrons in pairs to energy levels of increasing energy



What if you have a macroscopic number of electrons?

Let's limit the energy  $E = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$

by the energy  $E_F$

How many electrons consistent with the Pauli principle will be found with  $E \leq E_F$ ?

$$n_1^2 + n_2^2 + n_3^2 = R^2 = \frac{2mE_F L^2}{\hbar^2 \pi^2}$$

Volume corresponding to  $n_1, n_2, n_3 > 0$  is

$$V = \frac{1}{8} \frac{4\pi}{3} R^3 = \frac{\pi}{6} L^3 \left( \frac{2mE_F}{\hbar^2 \pi^2} \right)^{3/2}$$

The number of electrons (two per each box):

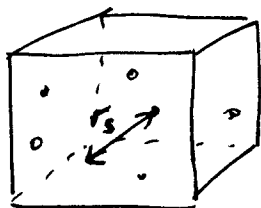
$$N = \frac{\pi}{3} L^3 \left( \frac{2mE_F}{\hbar^2 \pi^2} \right)^{3/2}$$

Density (number) of electrons:  $n = \frac{N}{L^3}$

$$E_F = \frac{\hbar^2 \pi^2}{2m} \left( \frac{3n}{\pi} \right)^{2/3} = \frac{\hbar^2 k_F^2}{2m}$$

$$k_F = \left( 3\pi^2 n \right)^{1/3}, \quad k_F = \frac{2\pi}{\lambda_F}$$

The usual way to represent these results is through the average distance between the electrons  $r_s$



$$\frac{1}{n} = \frac{V}{N} = \frac{4\pi}{3} r_s^3$$

$$k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s} = \frac{3.63 \text{ \AA}^{-1}}{(r_s/a_0)}$$

In typical metals:

$$r_s/a_0 \approx 2 - 6$$

$$v_F = \frac{\hbar}{m} k_F = \frac{4.20}{(r_s/a_0)} \times 10^8 \text{ cm/s} \approx \frac{c}{100}$$

↑  
Bohr  
radius



Let's estimate  $E_F$ :

$$E_F = \frac{\hbar^2}{2m a_0^2} (a_0 k_F)^2 = \frac{e^2}{8\pi\epsilon_0 a_0} (a_0 k_F)^2 = 13.6 \text{ eV} (a_0 k_F)^2$$

$$a_0 k_F = \frac{1.92}{r_s/a_0}$$

$$E_F = \frac{13.6 \times (1.92)^2 \text{ eV}}{(r_s/a_0)^2} = \frac{50.1 \text{ eV}}{(r_s/a_0)^2}$$

For Cu,  $r_s/a_0 = 2.67$ ,  $E_F = 7 \text{ eV}$

$$E_F = 7 \times 8065 \text{ cm}^{-1} = 7 \times 1.1 \times 10^4 \text{ K} \approx \underline{\underline{8 \times 10^4 \text{ K}}}$$

this is the temperature of  
conductance electrons  
in metals

$$T_F = \frac{E_F}{k_B} = \frac{58.2 \times 10^4 \text{ K}}{(r_s/a_0)^2}$$

Total energy:

$$\frac{E}{V} = \frac{1}{4\pi^3} \int_{k < k_F} d\vec{k} \frac{\hbar^2 k^2}{2m} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$$

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} E_F \leftarrow \begin{array}{l} \text{energy per electron} \\ \text{in a metal} \end{array}$$