Fermi-Dirac statistics: Pauli paramagnetism

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Wolfgang Ernst Pauli (25 April 1900 – 15 December 1958) was an Austrian-born Swiss and American theoretical physicist and one of the pioneers of quantum physics. In 1945, after having been nominated by Albert Einstein, Pauli received the Nobel Prize in Physics for his "decisive contribution through his discovery of a new law of Nature, the exclusion principle or Pauli principle". The discovery involved spin theory, which is the basis of a theory of the structure of matter.

https://en.wikipedia.org/wiki/Wolfgang_Pauli

The magnetic susceptibility of conduction electrons in metal consists of two contributions; Pauli paramagnetism due to the spin magnetic moment under the magnetic field, ans the Landau diamagnetism due to the orbital motion of conduction electrons. The susceptibility of the conduction electron is given by

$$\chi = \chi_P + \chi_L = \chi_P - \chi_P/3 = 2\chi_P/3 ,$$

where χ_L is the Landau diamagnetic susceptibility due to the orbital motion of conduction electrons. The Pauli paramagnetism can be explained using the Fermi Dirac statistics and quantum mechanics. Using the Sommerfeld formula, we discuss the temperature dependence of the Pauli paramagnetism. The degeneracy between the electrons of opposite spins is resolved by a magnetic field. In a metal this causes a redistribution of electrons between the two spin orientations, and hence gives rise to a magnetic moment.

1. Pauli paramagnetism

The magnetic moment of spin is given by

$$\hat{\mu}_z = -\frac{2\mu_B \hat{S}_z}{\hbar} = -\mu_B \hat{\sigma}_z \qquad \text{(quantum mechanical operator).}$$

Then the spin Hamiltonian (Zeeman energy) is described by

$$\hat{H} = -\hat{\mu}_z B = -(-\frac{2\mu_B \hat{S}_z}{\hbar})B = \mu_B \hat{\sigma}_z B,$$

in the presence of a magnetic field, where the Bohr magneton μ_B is given by

$$\mu_B = \frac{e\hbar}{2mc}. \qquad (e>0)$$

with

$\mu_B = 9.27400915(23) \times 10^{-24}$ J/T (S.I. unit)

$\mu_B = 9.27400915(23) \times 10^{-21}$ erg/Oe (cgs unit)

erg/Oe = emu

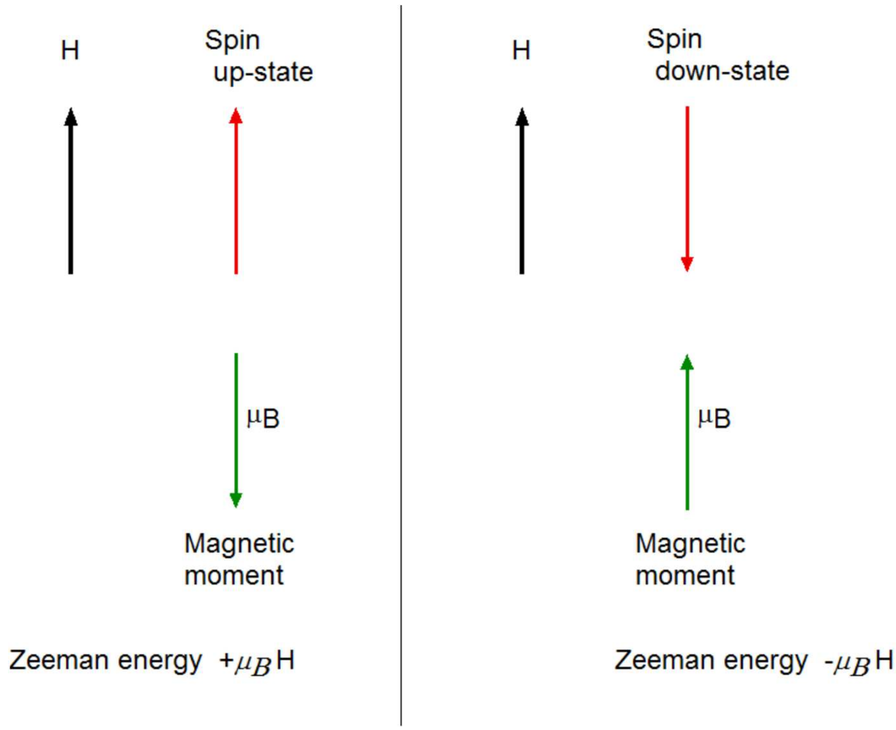

Fig. The magnetic field is applied along the z axis. (a) Spin–up state $|\sigma_z\rangle = |+\rangle$. The spin magnetic moment is antiparallel to the magnetic field. The Zeeman energy is +$\mu_B B$. (b) Spin-down state $|\sigma_z\rangle = |-\rangle$. The spin magnetic moment is parallel to the magnetic field. The Zeeman energy is -$\mu_B B$.

(i) **The magnetic moment antiparallel to *B***. Note that the spin state is given by an up-state,

$$|\sigma_z\rangle = |+\rangle .$$

The energy of electron is given by

$$\varepsilon = \varepsilon_k + \mu_B B ,$$

with $\varepsilon_k = (\hbar^2 / 2m)k^2$. The density of state for the spin-up state (the down-state of the magnetic moment) is

$$D_-(\varepsilon)d\varepsilon = \frac{L^3}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{\varepsilon - \mu_B B} d\varepsilon ,$$

or

$$D_-(\varepsilon) = \frac{1}{2} D(\varepsilon - \mu_B B) .$$

The factor 1/2 comes from the fact that $D_-(\varepsilon)$ is the density of states per spin. Then we have

$$N_- = \int_{\mu_B B}^{\infty} \frac{1}{2} D(\varepsilon - \mu_B B) f(\varepsilon) d\varepsilon \,.$$

(ii) The magnetic moment parallel to *B*. Note that the spin state is given by

$$\left|\sigma_z\right\rangle = \left|-\right\rangle .$$

The energy of electron is given by

$$\varepsilon = \varepsilon_k - \mu_B B \,,$$

The density of state for the spin down-state (the up-sate of the magnetic moment) is

$$D_+(\varepsilon) d\varepsilon = \frac{L^3}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{4\pi^2} (\frac{2m}{\hbar^2})^{3/2} \sqrt{\varepsilon + \mu_B B} d\varepsilon \,,$$

or

$$D_+(\varepsilon) = \frac{1}{2} D(\varepsilon + \mu_B B) .$$

Then we have

$$N_+ = \int_{-\mu_B B}^{\infty} \frac{1}{2} D(\varepsilon + \mu_B B) f(\varepsilon) d\varepsilon \,.$$

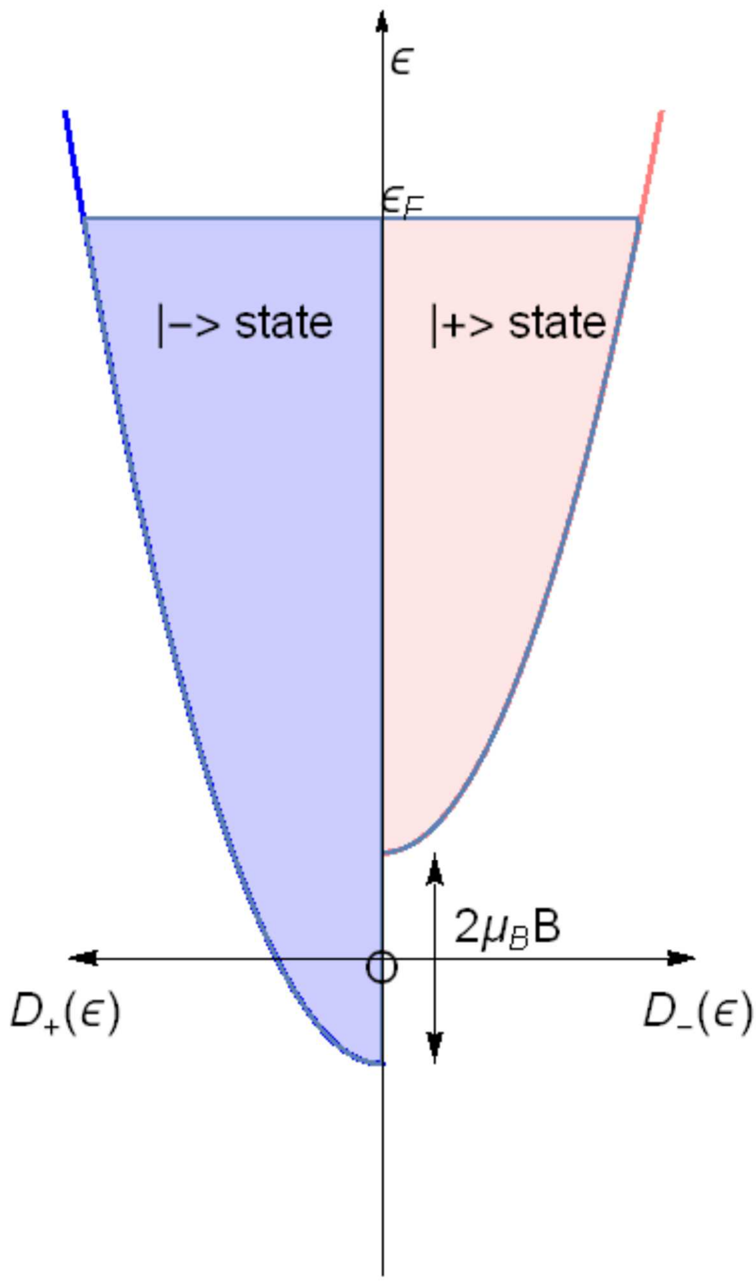

Fig. Density of states for the Pauli paramagnetism of free electron. Left: ($D_+(\varepsilon)$ for the $\left|\sigma_z\right\rangle = \left|-\right\rangle$, the direction of the spin magnetic moment is parallel to that of magnetic field). Right: ($D_-(\varepsilon)$ for $\left|\sigma_z\right\rangle = \left|+\right\rangle$; the direction of the spin magnetic moment is antiparallel to that of magnetic field).

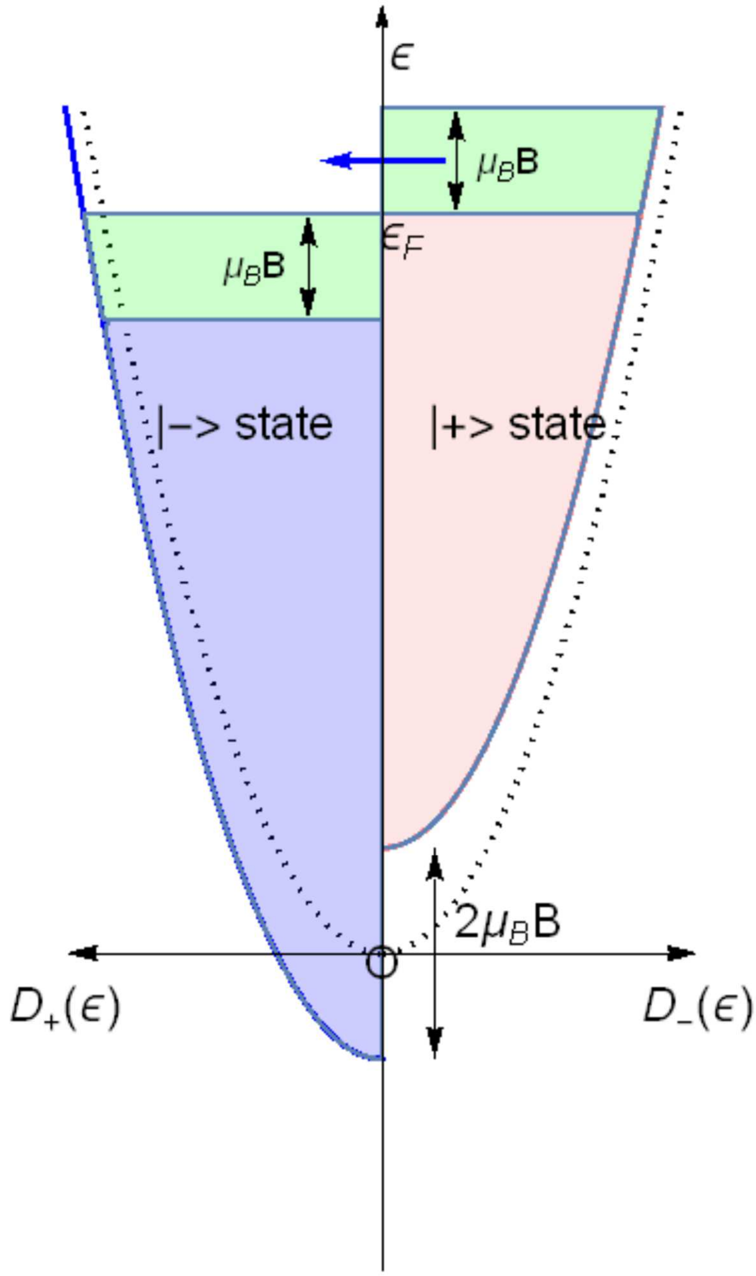

Fig. Spin 1/2 Fermi-Dirac gas at $T = 0$ K. The right-hand half of the figure gives the density of states for the spin up state (magnetic moment down state), whereas the right-hand half is for spin down state (magnetic moment up state). The dotted curve shows the density of states at $B = 0$, and the blue full curve when the field B is applied. Only a small number of the spins close to the Fermi energy (indicated by the green region) are able to realign when B is applied. So that the Fermi energy of the right side region becomes equal to that of the left-side region. Most of the spins are unable to align because there are no available empty states. The only spins which realign in the field are those in the green shaded states, $\mu_B B \frac{1}{2} D(\varepsilon_F)$, the factor 1/2 arising since only half the states are in the spin down state.

Each of these electrons has its spin reversed (i.e., changed by $2\mu_B$), giving a total magnetization of $M = 2\mu_B \mu_B B \frac{1}{2} D(\varepsilon_F) = \mu_B{}^2 BD(\varepsilon_F)$. This is independent of T in the degenerate region.

The magnetic moment *M* is expressed by

$$M = \mu_B (N_+ - N_-) = \frac{\mu_B}{2} [\int_{-\mu_B B}^{\infty} D(\varepsilon + \mu_B B) f(\varepsilon) d\varepsilon - \int_{\mu_B B}^{\infty} D(\varepsilon - \mu_B B) f(\varepsilon) d\varepsilon],$$

or

$$\begin{aligned} M &= \frac{\mu_B}{2} \int_0^{\infty} D(\varepsilon)[f(\varepsilon - \mu_B B) - f(\varepsilon + \mu_B B)] d\varepsilon \\ &= \mu_B{}^2 B \int_0^{\infty} D(\varepsilon)(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}) d\varepsilon \\ &= \mu_B{}^2 BD(\varepsilon_F) \end{aligned}$$

Here we use the relation;

$$(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}) = \delta(\varepsilon - \varepsilon_F)$$

The susceptibility (*M*/*B*) thus obtained is called the Pauli paramagnetism.

$$\chi_p = \mu_B{}^2 D(\varepsilon_F).$$

((**Sommerfeld formula**))

$$\int_0^\infty D(\varepsilon)(-\frac{\partial f(\varepsilon)}{\partial \varepsilon})d\varepsilon = \int_0^\infty D'(\varepsilon)f(\varepsilon)d\varepsilon$$

$$= \int_0^\mu D'(\varepsilon)d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 D''(\varepsilon_F)$$

$$= \int_0^{\varepsilon_F} D'(\varepsilon)d\varepsilon + (\mu - \varepsilon_F)D'(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 D''(\varepsilon_F)$$

$$= D(\varepsilon_F) - \frac{\pi^2}{6}(k_B T)^2 \frac{[D'(\varepsilon_F)]^2}{D(\varepsilon_F)} + \frac{\pi^2}{6}(k_B T)^2 D''(\varepsilon_F)$$

$$= D(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F)[\frac{\partial}{\partial \varepsilon}\frac{D'(\varepsilon)}{D(\varepsilon)}]_{\varepsilon=\varepsilon_F}$$

$$= D(\varepsilon_F) + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F)[\frac{\partial^2}{\partial \varepsilon^2}\ln D(\varepsilon)]_{\varepsilon=\varepsilon_F}$$

where

$$\mu - \varepsilon_F = -\frac{\pi^2}{6}(k_B T)^2 \frac{D'(\varepsilon_F)}{D(\varepsilon_F)}$$

The magnetization is

$$M = \frac{\mu_B}{2}\int_0^\infty D(\varepsilon)[f(\varepsilon - \mu_B B) - f(\varepsilon + \mu_B B)]d\varepsilon$$

$$= \mu_B{}^2 B D(\varepsilon_F)[1 + \frac{\pi^2}{6}(k_B T)^2 \frac{\partial^2}{\partial \varepsilon^2}\ln D(\varepsilon)|_{\varepsilon=\varepsilon_F}]$$

The Pauli susceptibility is

$$\chi_{Pauli} = \frac{M}{B} = \mu_B{}^2 D(\varepsilon_F)[1 + \frac{\pi^2}{6}(k_B T)^2 \frac{\partial^2}{\partial \varepsilon^2}\ln D(\varepsilon)|_{\varepsilon=\varepsilon_F}]$$

For the free electron Fermi gas model, we have

$$\frac{\partial^2}{\partial \varepsilon^2}\ln D(\varepsilon)|_{\varepsilon=\varepsilon_F} = -\frac{1}{2\varepsilon_F{}^2}$$

and

$$\chi_{Pauli} = \mu_B{}^2 D(\varepsilon_F)[1 - \frac{\pi^2}{12}(\frac{k_B T}{\varepsilon_F})^2]$$

Experimentally we measure the susceptibility per mol, χ_P (emu/mol)

$$\chi_P = \mu_B{}^2 \frac{D(\varepsilon_F)}{N} N_A = \mu_B{}^2 N_A D^A(\varepsilon_F)\,,$$

where $\mu_B{}^2 N_A = 3.23278\times10^{-5}$ (emu eV/mol) and $D_A(\varepsilon_F)$ [1/(eV atom)] is the density of states per unit energy per atom. Since

$$\gamma = \frac{1}{3}\pi^2 N_A k_B{}^2 D^A(\varepsilon_F)\,,$$

we have the following relation between χ_P (emu/mol) and γ (mJ/mol K^2),

$$\chi_P = 1.37148\times10^{-5}\gamma\,.$$

((**Exampl-1**)) Rb atom has one conduction electron.

$\gamma = 2.41$ mJ/mol K^2,
$\chi_P = (1.37\text{x}10^{-5})\times 2.41$ (emu/mol)
1 mol = 85.468 g
$\chi_P = 0.386\times10^{-6}$ emu/g (calculation)

((**Exampl-2**)) K atom has one conduction electron.

$\gamma = 2.08$ mJ/mol K^2,
$\chi_P = (1.37\text{x}10^{-5})\times 2.08$ (emu/mol)
1 mol = 39.098 g
$\chi_P = 0.72\text{x}10^{-6}$ emu/g (calculation)

((**Exampl-3**)) Na atom has one conduction electron.

$\gamma = 1.38$ mJ/mol K^2,
$\chi_P = (1.37\text{x}10^{-5})\times 1.38$ (emu/mol)
1 mol = 29.98977 g
$\chi_P = 0.8224\text{x}10^{-6}$ emu/g (calculation)

The susceptibility of the conduction electron is given by

$$\chi = \chi_P + \chi_L = \chi_P - \chi_P/3 = 2\chi_P/3\,,$$

where χ_L is the Landau diamagnetic susceptibility due to the orbital motion of conduction electrons.

Using the calculated Pauli susceptibility we can calculate the total susceptibility:

Rb: $\chi = 0.386\times(2/3)\times10^{-6} = 0.26\times10^{-6}$ emu/g
K: $\chi = 0.72\times(2/3)\times10^{-6} = 0.48\times10^{-6}$ emu/g
Na: $\chi = 0.822\times(2/3)\times10^{-6} = 0.55\times10^{-6}$ emu/g

These values of χ are in good agreement with the experimental results.[6]

REFERENCES

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