Lecture: 11
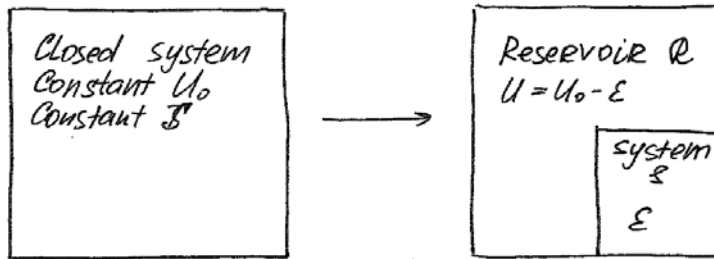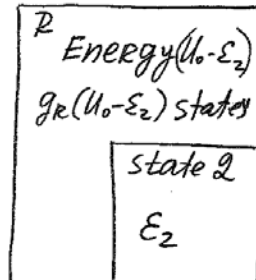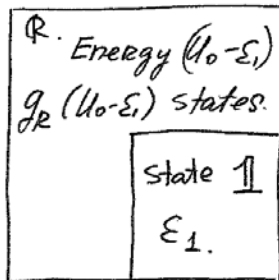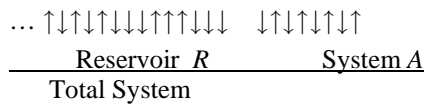**Boltzmann Statistics. Boltzmann statistics in magnetic systems**

Let us consider a closed system decomposed into a reservoir R in thermal contact with a system A.
Example

$$\dots \uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow \quad \downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow$$

| Reservoir R | System A |

Total System

A central problem of thermal physics is to find the probability that the system A will be in a specific quantum state S of energy E_S. When we specify that A should be in the state S, the number of accessible state of the total system is reduced to the number of accessible states of the reservoir at the appropriate energy

(1) $g_{R+A} = g_R \times 1 = g_R$

(Just a reminder what is specific quantum state for spin system.)

a) $\uparrow\uparrow\downarrow\downarrow\uparrow$

b) $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$ ---Examples of specific quantum states

c) $\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow$

Multiplicity of each (a) (b) (c) is 1 (each state is a quantum state and each is specific)
Quantum state is a *microstate*. The direction of each spin is defined.
For *macrostate* we only specify total spin excess and total number of spins.

$$g = \frac{N!}{N_\uparrow ! N_\downarrow !} - \text{Multiplicity of macro state.}$$

If the energy of the system A is E_S, the reservoir energy is $(U_o - E_S)$ and the multiplicity of reservoir is
$g_R(U_0 - E_s)$
If P (E_1), P (E_2) are probabilities to find the system in quantum states 1 and 2 then,

(2) $$\frac{P(E_1)}{P(E_2)} = \frac{g_R(U_0 - E_1)}{g_R(U_0 - E_2)}$$

1

$S_R = k \ln g_R (U - E)$ - Entropy of the reservoir

$g_R = \exp\left[\dfrac{1}{k} S_R (U - E)\right]$ - multiplicity of the reservoir expressed through entropy.

We can now re-write (2) as

(3) $\dfrac{P(E_1)}{P(E_2)} = \dfrac{\exp\left(\dfrac{1}{k} S_R (U - E_1)\right)}{\exp\left(\dfrac{1}{k} S_R (U - E_2)\right)} = \exp\left(\dfrac{1}{k}\left(S_R(U_0 - E_1) - S_R(U_0 - E_2)\right)\right) = \exp\left(\dfrac{1}{k}\Delta S_R\right),$

where $\Delta S_R = S_R(U_0 - E_1) - S_R(U_0 - E_2)$

Let us expand the entropies in (3) in a Taylor series expansion about $S_R(U_0)$. The Taylor series expansion

of $f(x)$ and $f(x_o)$ is $f(x_0 + a) = f(x_0) + a\left(\dfrac{df}{dx}\right)_{x=x_0} + \dfrac{1}{2!}a^2\left(\dfrac{d^2 f}{dx^2}\right)_{x=x_o}$

We have then

$S_R(U_0 - E) = S_R(U_0) - E\left(\dfrac{\partial S}{\partial U}\right)_{V,N} + \ldots\ldots = S_R(U_0) - E\dfrac{1}{T}$

Therefore

$\Delta S_R = S_R(U_0 - E_1) - S_R(U_0 - E_2) = -(E_1 - E_2)/T$

and

(4) $\dfrac{P(E_1)}{P(E_2)} = \dfrac{\exp\left(-E_1\big/kT\right)}{\exp\left(-E_2\big/kT\right)}$

Most important and most known result of statistical mechanics

Equation (4) gives the ratio of probabilities of finding a system in a quantum state 1 to the probability of finding a system in a quantum state 2.

<u>**Partition Function**</u>

It is helpful to consider the function

$Z(T) = \sum_i \exp\left(E_i\big/kT\right)$ – Partition function

The sum is over the Boltmann factors exp (E_i/kT) of all states. Then the probability of finding system in a particular q.state j is

(5) $P(E_j) = \dfrac{\exp\left(-E_j\big/kT\right)}{Z}$ - (One of the most useful results of statistical physics)

This can be seen from following.

(6) $\dfrac{1}{P(E_j)} \cdot \sum_i P(E_i) = \dfrac{1}{\exp\left(E_j\big/kT\right)} \cdot \sum_i \exp\left(E_i\big/kT\right)$

In (6) j – index of a particular state, i is acounter over all states

$$\sum_i P(E_i)=1 \qquad \sum_i \exp\left(\frac{E_i}{kT}\right)=Z$$

As a result we have (5). With eq (7-5) average energy of a system can be computed as

(7) $\quad U_S=\langle E\rangle=\sum E_i . P(E_i)=\dfrac{\sum_i E_i \exp\left(-E_i\middle/ kT\right)}{Z}$

Remember that E is energy of a system in a thermal contact with a reservoir so it can fluctuate.

Helmholt free Energy

$F = U - TS$

This is the total energy you need to create the system minus heat you can get for free from environment with temperature *T*. The Helmholtz free energy plays the part in thermal physics at constant temperature that the energy *U* plays in ordinary mechanical processes. The free energy tells us how to balance the conflicting demands of a system for minimum energy and maximum entropy. The free energy will be a minimum for a system *A* in thermal contact with a reservoir *R*, if the volume of the system is constant.

Calculation of F from Z (the partition function)

Because $F=U–TS$ and $dF=-SdT-PdV$

$$S=-\left(\frac{\partial F}{\partial T}\right)_V \quad \text{and} \quad F=U+T\left(\frac{\partial F}{\partial T}\right)_V$$

We can rewrite the later equation in the following way

(8) $U=-T^2\dfrac{\partial}{\partial T}\left(\dfrac{F}{T}\right)_V$

This can be easily verified by taking derivative with respect to *T*.

We now show that the equation (8) is correct if we choose $F=-kT\ln Z$ (Z is the partition function).

(9) $U=T^2\dfrac{\partial}{\partial T}\left(k\ln Z\right)$.

Using the relation $\dfrac{\partial}{\partial x}\ln\left(f(x)\right)=\dfrac{1}{f(x)}\dfrac{\partial}{\partial x}f(x)$ we have from (9)

(10) $\dfrac{U}{T^2}=\dfrac{k}{Z}\dfrac{\partial Z}{\partial T}$

The partition function by definition is $Z=\sum_i\exp\left(-E_i\middle/ kT\right)$. We then have

(11) $\dfrac{\partial}{\partial T}Z=\sum_i\dfrac{\partial}{\partial T}\exp\left(-\dfrac{E_i}{kT}\right)=\sum_i\exp\left(-\dfrac{E_i}{kT}\right)\cdot\left(-\dfrac{E_i}{k}\right)\cdot\left(-\dfrac{1}{T^2}\right)=\dfrac{1}{kT^2}\cdot\sum_i E_i\exp\left(-\dfrac{E_i}{kT}\right)$

After substitution (11) in (10) we have

(12) $U=\dfrac{\sum_i E_i\exp\left(-E_i\middle/ kT\right)}{z}$.

But that is exactly how we fined the internal energy of a system. Therefore the definition $F=-kT\ln Z$ is correct.

Boltzmann factor. Effect of degeneracy.

(13)
$$\frac{P(E_1)}{P(E_2)} = \frac{\exp\left(-E_1/kT\right)}{\exp\left(-E_2/kT\right)}$$

1 and 2 are indexed assigned to specific quantum states. But we know that energy E might correspond to many different arrangements (many different quantum states) for example in spin system in magnetic field certain spin excess number S (that determines the energy of the system) is the same for many different quantum states.

↑↑↑↓↓↓↓↓ -- Different quantum states, same energy, same excess number.

↑↓↑↑↓↓↓↓

To emphasize this fact we may re-write (18) in more accurate form.

(14)
$$\frac{P(E_1, A_i)}{p(E_2, A_k)} = \frac{\exp\left(-E_1/kT\right)}{\exp\left(-E_2/kT\right)}$$

Here $P(E_1, Ai)$ means probability of specific quantum state A_i that has energy E_1.
Another example is a Hydrogen atom
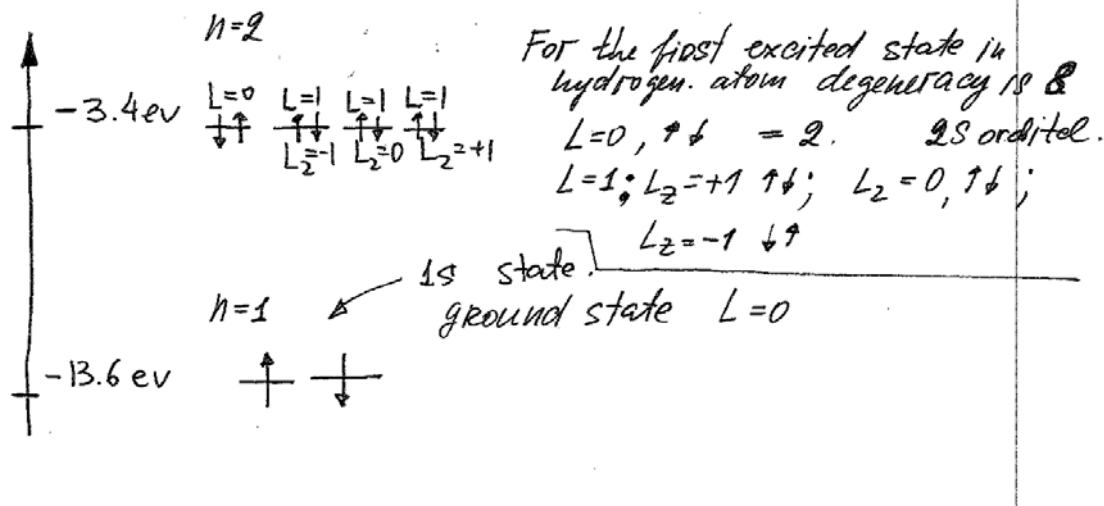
P_X, P_Y P_Z are not the same orbital as $L_Z = -1$, $L_Z = 0$, and $L_Z = +1$, they are some linear combination of $(L_Z = 0, L_Z \pm 1)$

Degeneracy – number of distinct quantum states with the same energy

We say that degeneracy of the ground state 2 (two distinct quantum states with different direction of the spin have same energy). The degeneracy of 1st excited state is 8. (eight distinct quantum states have the same energy: one 2S, three 2P orbitals and each of these orbital can carry an electron with two direction of the spin). In this example we assume that external magnetic field is zero. If external field is not zero, we level splits and the degeneracy is lifted.

What if we are interested in following question what is the ratio of the probability to find an *H* atom in 1st excited state to the probability to find an *H* atom in ground state.

(15)
$$\frac{P(E_1)}{P(E_2)} = \frac{g_1 \exp\left(-\dfrac{E_1}{kT}\right)}{g_2 \exp\left(-\dfrac{E_2}{kT}\right)}$$

$g_1 = 8$ – degeneracy of the 1st excited state.
$g_g = 2$ – degeneracy of the ground state.

Why we have (15) is easy to see if consider particular terms, as for example

$$\frac{P(L=1, L_z=+1, \uparrow)}{P(L=0, \uparrow)} = \frac{\exp\left(-E_1/kT\right)}{\exp\left(-E_g/kT\right)}$$

The degeneracy factors g_1 and g_g just indicate the fact that we sum up all terms to get (15).
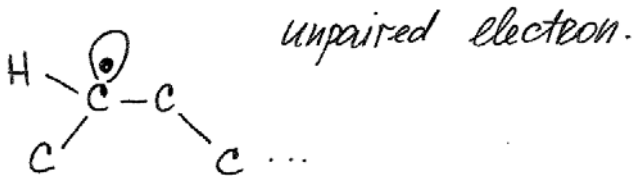
Boltzmann distribution in systems of spins

We have collection of spins in magnetic field B in thermal contact with reservoir at temperature T. Spins do not interact with each other.
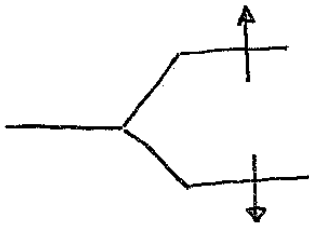
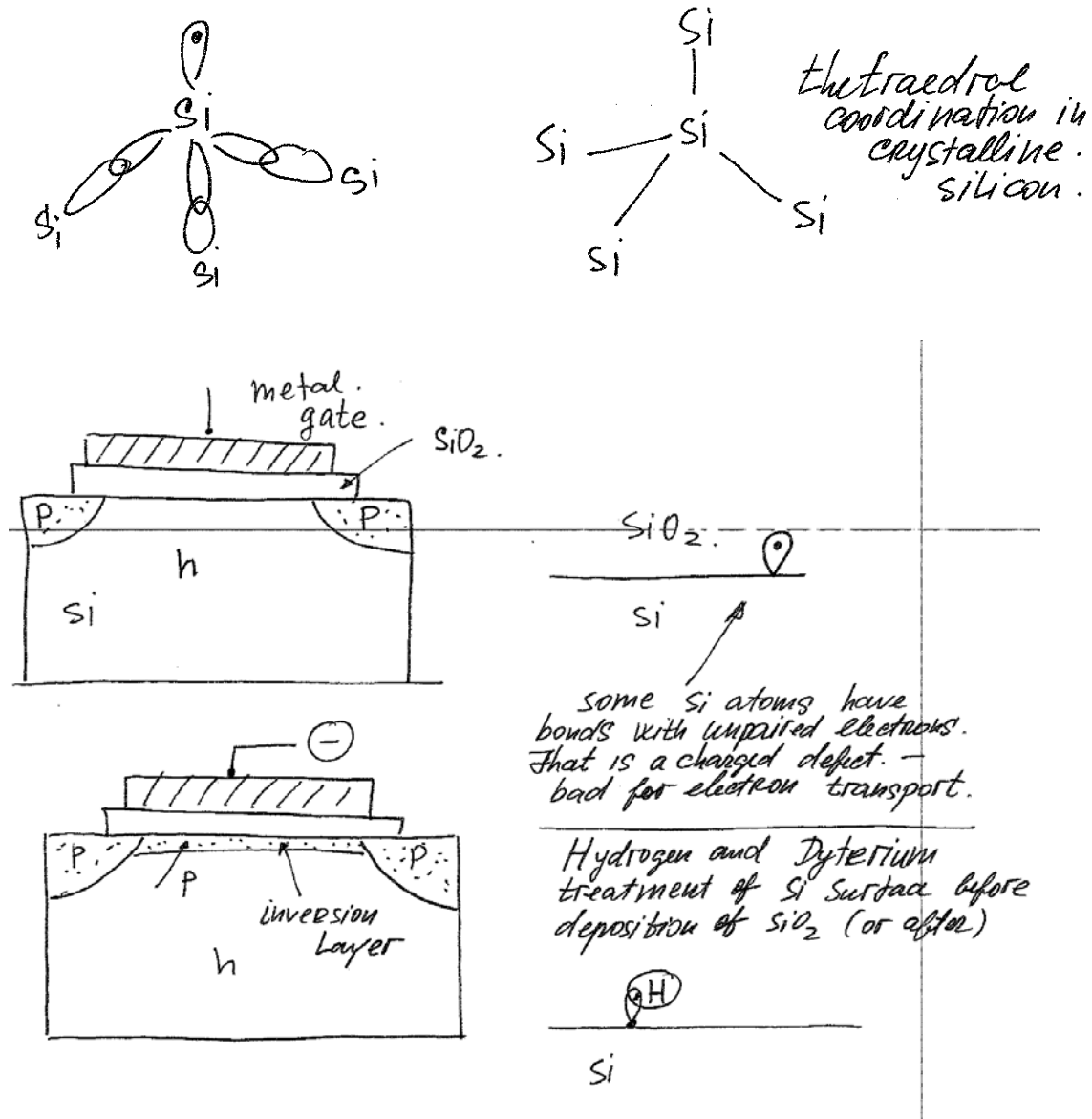Questions: what is magnetization of the spins, their total energy, entropy, and specific heat.

Real examples of system with non-interacting spins.

Organic free radicals

Dangling bond in amorphous Si (backing layer in LCD displays is made of amorphous Si L-Si)

Dangling bond in crystalline Si at the interface with SiO$_2$ in field effect transistors

tlutraedrol coordination in crystalline silicon.

some Si atoms have bonds with unpaired electrons. That is a charged defect. — bad for electron transport.

Hydrogen and Dyterium treatment of Si surface before deposition of SiO$_2$ (or after)

Nuclear spins in H$_2$O molecules (MRI)

Magnetic moment of electron spin

Statistical approach based on partition function and Boltzmann factors gives us an easy way to solve this problem. Magnetic moments in our magnet do not interact. Therefore if we know an average property of a single magnetic moment we may just multiply the average value of a quantity in question by number of spins in the system to obtain say *M, S, U*.

.

$$M = g\mu_B . S_z$$

g- so called g-factor, do not confuse with multiplicity function. For electron g = 2.

$$\mu_B = \frac{eh}{4\pi m_e} = \frac{e\hbar}{2m_e} \approx 9.3 \times 10^{-24} \, J/T \,.$$ **The μ_B is called Bohr magnetron**

S_Z – projection of electron spin on z-axis.

Energy of magnetic moment in magnetic field is $U = -MB$

Figure

$$u = +\mu_B B$$

$$u = -g\mu_B S_z B = -\mu_B B \quad (g = 2, \, S_z = \tfrac{1}{2})$$

Partition function for magnetic moment in magnetic field

$$Z = \sum_S \exp\left(-\frac{E_S}{kT}\right) = \exp(\beta\mu B) + \exp(-\beta\mu B), \text{ where}$$

$$\beta = \frac{1}{kT}, \quad \mu = \mu_B \text{ just to shorten the notations}$$

$$Z = 2\cosh(\beta\mu B)$$

$$P(\uparrow) = \frac{\exp(-\beta\mu B)}{2\cosh(\mu\beta B)} \quad \text{Probability to find a spin in spin-up configuration}$$

$$P(\downarrow) = \frac{\exp(-\beta\mu B)}{2\cosh(\beta\mu B)} \quad \text{Probability to find a spin in spin-down configuration.}$$

The average energy of a spin magnetic moment is

$$\langle E \rangle = -\mu B P_\uparrow + \mu B P_\downarrow = \frac{-\mu B\left(\exp(\beta\mu B) - \exp(-\beta\mu B)\right)}{\exp(\beta\mu B) + \exp(\beta\mu B)} = -\mu B \tanh(\beta\mu B)$$

$$U = N\langle E \rangle = -N\mu B \tanh(\beta\mu B)$$

The same result can be obtained from the equation $\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$

The average value of a spin magnetic moment can be found as

$$\langle m \rangle = +\mu P_\uparrow + (-\mu)P_\downarrow = \mu \tanh(\beta\mu B)$$
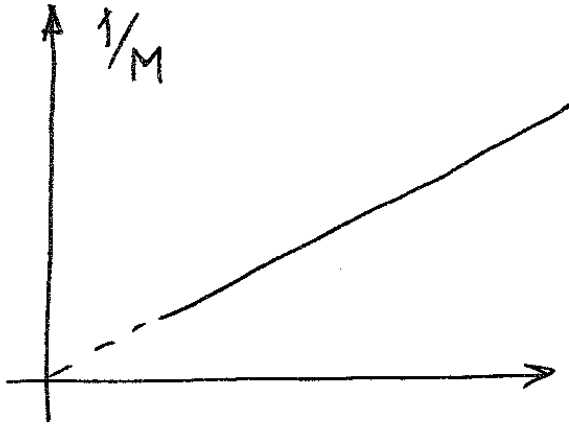
Then the total magnetic moment of the sample is

$$M = N\langle m \rangle = N\mu \tanh(\beta\mu B)$$

High temperature, low field expansion of magnetization

$$e^x \cong 1 + x, \quad e^{-x} \cong 1 - x$$

$$M = \mu N \tanh(\beta\mu B) = \mu N \frac{\exp(\beta\mu B) - \exp(-\beta\mu B)}{\exp(\beta\mu B) + \exp(-\beta\mu B)} = \mu N . \frac{\mu B}{kT}$$

Curie's Law.

Heat Capacity

By definition heat capacity is $C_V = \dfrac{dQ}{dT}$. We assume that we have reversible exchange of energy, therefore dQ is well defined. From the first law $dU = dQ - PdV$ at constant volume we have $dQ=dU$ and therefore

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

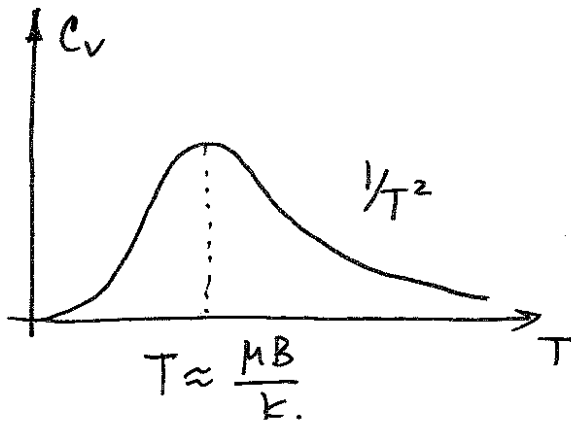$$C_V = \frac{\partial}{\partial T}\left(-\mu BN \tanh\left(\beta \mu B\right)\right), \text{ where } \beta = \frac{1}{kT}$$

$$C_V = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}\left(-\mu BN.\tanh\left(\mu B\beta\right)\right) = -\frac{1}{kT^2}\left(-\mu BN\right).\frac{\partial}{\partial \beta}\frac{\exp\left(\beta \mu B\right)-\exp\left(\beta \mu B\right)}{\exp\left(\beta \mu B\right)+\exp\left(\beta \mu B\right)} =$$

$$= \frac{\mu BN}{kT^2}\times \mu B \times \left[\frac{\exp\left(\beta \mu B\right)+\exp\left(-\mu B\beta\right)}{\exp\left(\mu \beta B\right)+\exp\left(-\beta \mu B\right)} - \frac{\exp\left(\beta \mu B\right)-\exp\left(-\beta \mu B\right)}{(\exp\left(\beta \mu B\right)+\exp\left(-\beta \mu B\right))^2}\times\exp\left(\beta \mu B\right)-\exp\left(-\beta \mu B\right)\right]$$

and

$$C_V = kN\left(\frac{\mu B}{kT}\right)^2 \frac{1}{\cosh^2\left(\mu B/kT\right)}$$
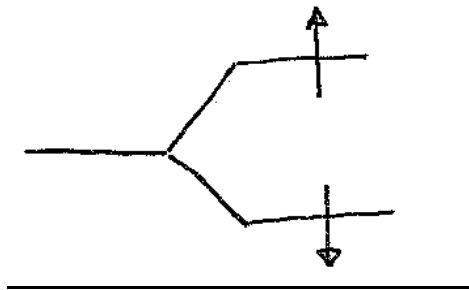
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$$T \approx \frac{\mu B}{k}$$

Nuclear spin MRI

Problem related to the MRI

A system of nuclear spins is placed in magnetic in field 2 Tesla at room temperature. Find probabilities of nuclear to be found in "spin up" and "spin down" state. Find splitting energy between the states.

Similarly to electron, magnetic moment of nuclear can be expressed as

$m = g.\mu_P.S_z$

g – nuclear g-factor, . For proton $g = 5.85$,

μ_P - Nuclear magneton. $\mu_p = \frac{e\hbar}{2m_p} = 5.05 \times 10^{-27} J / T$

$E_\downarrow = g.\mu_p .\frac{1}{2}.B = +3.10^{-26} J$

$E_\uparrow = -g \cdot \mu_p \cdot \frac{1}{2}.B = -3.10^{-26} J$

Energy splitting between levels $2|E| = 6.10^{-26} J$

When we deal with magnetic resonance phenomena the splitting energy is often expressed in frequency units

$E_v = \frac{E}{h} = \frac{6 \times 0^{-26} J}{6.6 \times 10^{-34} J \cdot s} = 0.9.10^8 Hz = 90 MHz$

Let' compute the Boltzmann factors

Spin up (along the field)

$\exp\left(-\frac{E_\uparrow}{kT}\right) = \exp\left(\frac{3.10^{-26} J}{300k.1.38.10^{-23} J / k}\right) = \exp\left(2.425 \times 10^{-6}\right) = 1.0000024.$

spin down (anti parallel to magnetic field)

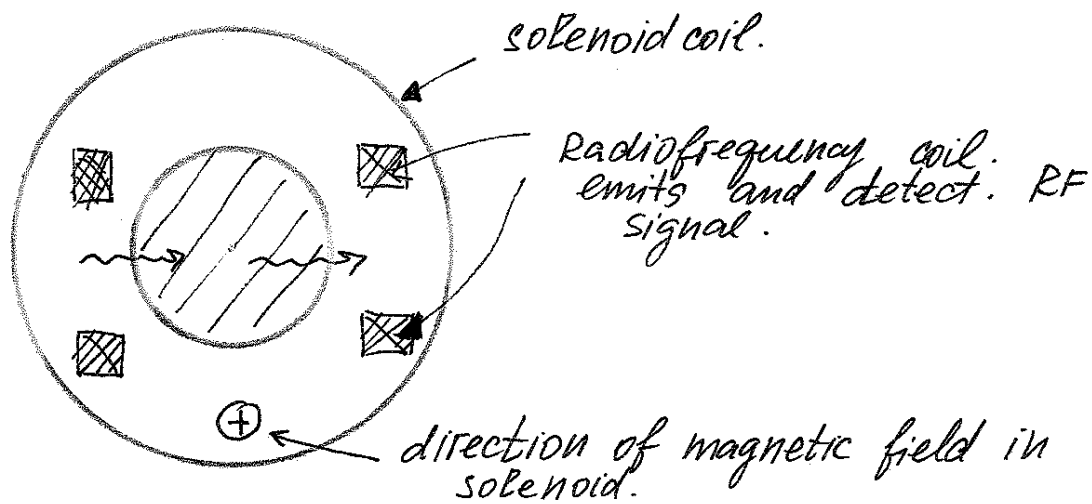$$\exp\left(-E_\downarrow\big/kT\right)=0.9999976.$$

Probabilities

$$P(\uparrow)=\frac{\exp\left(-E_\uparrow\big/kT\right)}{Z}=0.5000012 \qquad P(\downarrow)=0.4999988$$

The difference in population between spins down and spin up population is incredibly small , but it is precisely the quantity that is measures in MRI. MRI stands for magnetic resonance imaging. The method should be called nuclear MRI but "Nuclear" scared public so business people decided to drop it. NMR (Nuclear magnetic resonance) is surely most "Noble" phenomenon in nature. It is connected to 4 Noble prizes: 2 in physics 1 is chemistry and 1 in medicine. So, how does it work?
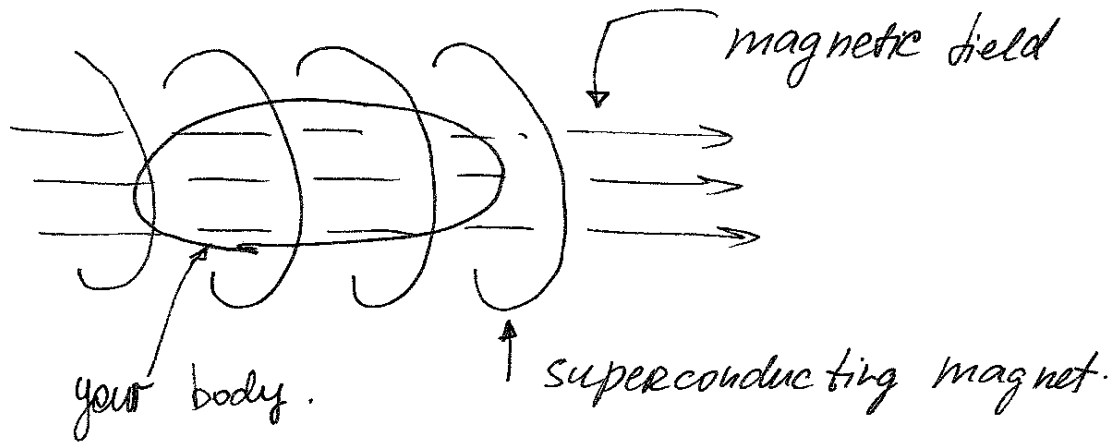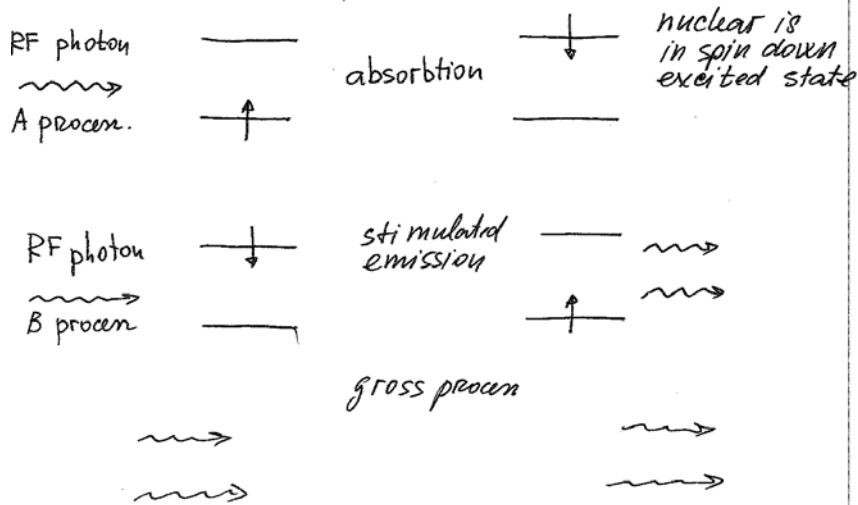

Superconductor so it can carry huge current. Electrical current creates huge magnetic field in the coil (Solenoid) that penetrates the body of patient. The most common MRI's check the content of water, more accurately content of protons.

solenoid coil.

Radiofrequency coil.
emits and detect. RF
signal.

direction of magnetic field in
solenoid.

Microscopic picture.

RF photon — — — absorbtion — ⊥ — nuclear is
in spin down
excited state

A process. — ↑ — — — —

RF photon — ⊥ — stimulated — — — ⌇⌇⟶
emission

B process — — — — ↑ — ⌇⌇⟶

gross process

⌇⌇⟶ ⌇⌇⟶

⌇⌇⟶ ⌇⌇⟶

two photon in, two photon out. There is no net
absorbtion if consentration of nucleons with spin
up and spin down states is the same.

We should not see any attention at all. The net absorption of RF photons occurs only because we have this tiny difference $\sim 10^{-5}$ in population members of spin up and spin down state. MRI is practical because the tiny difference is multiplied by huge number (10^{22}/ccm) (10^{22}/cm^3) of protons.

How do we get spatial resolution in proton concentration?
Only proton that has frequency in resonance with spin splitting can be absorbed or can case stimulated emission. Spatial variation of magnetic field is created by additional "gradient" set of magnetic coils.

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