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V. Montelatici: THERMODYNAMICAL APPROACH TO THE NUCLEAR
DYNAMIC POLARIZATION.

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Thermodynamical Approach to the Nuclear Dynamic Polarization.

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Summary. — If a system of particles with spin is divided into groups according to spin state, a chemical potential can be assigned to each group. The entropy production rate is written as function of chemical potentials and transition probabilities. At thermodynamic equilibrium the entropy production must be zero and the nuclear dynamic polarization is derived for a system of electron and nuclear magnetic moments with spin $\frac{1}{2}$. The results are consistent in first-order approximation with those obtained by solving the rate equations.

1. — Introduction.

In this paper some effects, named nuclear dynamic polarization, shall be described and results are obtained employing the thermodynamical and statistical approach.

The dynamic polarization is produced in a system that includes two types of interacting ^(1,2) magnetic moments: namely those associated with the spin angular momentum of the electron and those of the nuclei.

Only systems with spin angular momentum $S = I = \frac{1}{2}$ shall be considered (S for electron, I for nucleus).

A nuclear dynamic polarization experiment is characterized by the simultaneous application of two electromagnetic fields to the spins system, which also is subjected to a strong steady magnetic field. While the magnetic field is used to separate the energy levels with different magnetic quantum numbers,

(¹) A. ABRAGAM: *Phys. Rev.*, **98**, 1729 (1955).

(²) A. ABRAGAM: *The Principles of Nuclear Magnetism* (Oxford, 1961).

the higher frequency and intensity field induces electronic or quasi-electronic transitions, the lower one is used to detect the nuclear resonance transitions.

In the following only double-resonance phenomena involving electronic or quasi-electronic transitions shall be considered, and nuclear transitions shall be observed.

2. - The four-level system.

A nucleus with spin I in a magnetic field has $2I+1$ different energy states corresponding to an integer or a half-integer value that the magnetic quantum number m_I takes from $-I$ to $+I$ according to the integer or half-integer I values.

If n_m stands for the number of nuclei with quantum number m_I , the polarization of n nuclei is defined by the expression

$$P = \frac{\sum_{-I}^{+I} m \cdot n_m}{I \sum_{-I}^{+I} n_m},$$

which becomes for $I = \frac{1}{2}$

$$(1) \quad P = \frac{(n_+/n_-) - 1}{(n_+/n_-) + 1},$$

where n_+ and n_- are the level population with $m_I = +\frac{1}{2}$ and $-\frac{1}{2}$, respectively. In thermodynamic equilibrium, at temperature T , the static polarization is

$$P_0 = \operatorname{tgh} \frac{\hbar H \gamma_N}{2KT},$$

where γ_N is the nuclear gyromagnetic ratio, K and \hbar are the Boltzmann and Planck constant, and H the magnetic field.

Generally, the double-resonance phenomena occur when interactions between the electronic and nuclear spins are present which induce transitions that normally are forbidden.

The noninteracting nuclear and electronic spins under the action of a magnetic field H have the Hamiltonian

$$\mathcal{H} = |\gamma_e| \hbar \mathbf{H} \cdot \mathbf{S} - \gamma_N \hbar \mathbf{H} \cdot \mathbf{I},$$

where γ_e , the electronic gyromagnetic ratio, is negative.

In this conditions the $(2S+1)(2I+1)$ possible states of the system are those shown in Fig. 1.

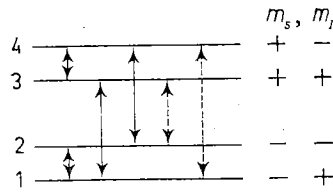


Fig. 1.

The allowed transitions are

$$(1 \rightleftharpoons 3), \quad (2 \rightleftharpoons 4) \quad \text{and} \quad (1 \rightleftharpoons 2), \quad (3 \rightleftharpoons 4)$$

with frequencies

$$\nu_e = \frac{|\gamma_e| H}{2\pi} \quad \text{and} \quad \nu_n = \frac{\gamma_N H}{2\pi}$$

for the electronic and nuclear transitions respectively.

The presence of the nuclear and electronic spin interaction (*) allows further transitions giving rise to four relaxation mechanisms:

1) Electronic relaxation with transition probability w_e and selection rule $\Delta m_s = \pm 1, \Delta m_I = 0$.

2) Simultaneous electronic and nuclear relaxation with transition probability w_x and selection rule $\Delta m_s = \pm 1, \Delta m_I = \mp 1$.

3) Simultaneous electronic and nuclear relaxation, with transition probability w_y and selection rule $\Delta m_s = \pm 1, \Delta m_I = \pm 1$.

4) Nuclear relaxation probability w_N and selection rule $\Delta m_I \pm 1, \Delta m_s = 0$.

Case 2) and 3) show a quasi-electronic transition which are a simultaneous flip of the two types of spins with frequency $\nu = \nu_s \pm \nu_I$.

We will calculate, using thermodynamical and statistical arguments, values for the polarization P assuming particular values for the four transition probabilities w . Justification for these assumption is beyond the scope of this article but is found both theoretically and experimentally (2), however we remember that it is

$$w_e \gg w_x \simeq w_y \gg w_N \quad \text{with } w_x, w_y \neq 0.$$

(*) We assume: electron Zeeman energy \gg nuclear Zeeman energy \gg spin-spin interaction energy.

3. - System statistics and thermodynamics.

The electrons and nuclei in the system are distributed in four energy levels in such a way that their number is obtained from the partition function of the system. This shall be considered a set of ideal particles obeying Boltzmann statistics.

If E_i stands for the energy of the i -th level, the partition function is ⁽³⁾

$$(2) \quad Z_i = \frac{1}{n_i!} \left[\exp \left[-\frac{E_i}{KT} \right] \right]^{n_i}$$

with the corresponding free energy

$$F_i = -KT \log Z_i = KT n_i \log n_i - KT n_i + n_i E_i$$

when the relation $\log n! \simeq n \log n/e$ is used. The number of electrons and nuclei in the i -th level is obtained from the expression for chemical potentials:

$$(3) \quad \frac{\partial F_i}{\partial n_i} \equiv \mu_i = E_i + KT \log n_i.$$

The Gibbs relation is applicable to the system ⁽³⁾

$$T dS = dU + dW - \sum_{i=1}^4 \mu_i dn_i,$$

where dW is zero because the magnetic field is constant; and the summation gives the internal entropy production due to the particle transitions from a level to another and each term is the product of the particle variation of the i -th level by the corresponding chemical potential for the level one thinks of.

The rate of the i -th level due to « thermal » relaxation and to transition induced by external radiation is

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij}) + \sum_j W_{ji} (n_j - n_i),$$

where

$$w_{ji} \exp \left[-\frac{E_j}{KT} \right] = w_{ij} \exp \left[-\frac{E_i}{KT} \right]$$

⁽³⁾ L. D. LANDAU and E. M. LIFSHITZ: *Statistical Physics* (London, 1959).

is the probability of the «thermal» relaxation. They carry the system in a Boltzmann equilibrium when the external radiation is off.

$W_{ji} = W_{ij}$ is the probability of induced transition by the field of the external radiation with frequency $\nu_{ji} = (1/h) \cdot (E_j - E_i)$ which tends to equalize the populations.

By writing the summation explicitly one obtains for the entropy production rate:

$$\begin{aligned}
 (4) \quad \left(\frac{dS}{dt}\right)_{\text{int}} = & \frac{1}{T} \left\{ (\mu_2 - \mu_1) [(n_1 + n_3) - (n_2 + n_4)] w_N + \right. \\
 & + (\mu_3 - \mu_1) [(n_1 + n_2) - (n_3 + n_4)] (w_e + W_e) + \\
 & + (\mu_4 - \mu_1) (n_1 - n_4) (w_x + W_x) + (\mu_3 - \mu_2) (n_2 - n_3) (w_y + W_y) \left. \right\} - \\
 & - \frac{1}{T} \left\{ (\mu_2 - \mu_1) \frac{\beta \delta}{2} (n_1 + n_2 + n_3 + n_4) w_N + (\mu_3 - \mu_1) \frac{\beta \Delta}{2} (n_1 + n_2 + n_3 + n_4) w_e + \right. \\
 & \left. + (\mu_4 - \mu_1) \beta \frac{\Delta + \delta}{2} (n_1 + n_4) w_x + (\mu_3 - \mu_2) \beta \frac{\Delta - \delta}{2} (n_2 + n_3) w_y \right\},
 \end{aligned}$$

where

$$\beta = \frac{1}{KT}, \quad \delta = \gamma_N \hbar H, \quad \Delta = |\gamma_e| \hbar H,$$

when the system is in thermal equilibrium at temperature T , the entropy production must be zero:

$$\left(\frac{dS}{dt}\right)_{\text{int}} = 0.$$

If N_+ and N_- stands for the population of the electronic spins with quantum number $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ one obtains

$$(5) \quad \begin{cases} N_+ = n_3 + n_4, & n_+ = n_1 + n_3, \\ N_- = n_1 + n_2, & n_- = n_2 + n_4. \end{cases}$$

The chemical potentials of the levels are not independent among them, but one obtains

$$(6) \quad \mu_4 - \mu_2 = \mu_3 - \mu_1,$$

since the chemical potential of each level is the sum of the chemical potentials of the electrons and of the nuclei.

The ratio n_+/n_- shall be obtained by imposing different conditions on the

population differences, in order to obtain the expressions for the polarization. In this way it shall be possible to obtain the Overhauser ⁽⁴⁾, Underhauser ⁽⁵⁾ and double effects ⁽⁶⁾

4. - The Overhauser effect (direct and reversed).

In this effect pumping makes the electron populations equal, that is,

$$(7) \quad N_+ - N_- = n_3 + n_4 - (n_1 + n_2) = 0 .$$

Simultaneously we put

$$W_x = W_y = 0 , \quad W_e \rightarrow \infty .$$

The first term of (4) is zero for

$$\mu_2 - \mu_1 = -(\mu_3 - \mu_1) \frac{w_x - w_y}{2w_N + w_x + w_y} .$$

The saturation condition (7) is equivalent to write

$$\frac{N_+}{N_-} = \frac{n_3}{n_1} = \frac{n_4}{n_2} = 1 ,$$

which, with relations (3), gives

$$\mu_3 - \mu_1 = |\gamma_e| \hbar H .$$

We obtain from relation (8), with $w_y = 0$ or if $w = 3w_x$,

$$(9) \quad \mu_2 - \mu_1 \left\{ \begin{array}{l} = -\hbar H |\gamma_e| \frac{1}{2w_N/w_x + 1} \simeq -\hbar H |\gamma_e| , \\ = \hbar H |\gamma_e| \frac{1}{w_N/w_x + 2} \simeq \frac{1}{2} \hbar H |\gamma_e| , \end{array} \right.$$

when the approximation $w_x \gg w_N$ is made.

The second term in (4) is zero in the same order of approximation if one resolves for $\mu_2 - \mu_1$.

(4) A. OVERHAUSER: *Phys. Rev.*, **89**, 689 (1953).

(5) A. ABRAGAM, J. COMBRISSE and J. SOLOMON: *Compt. Rend.*, **245**, 157 (1957).

(6) E. ERB, J.-L. MOCCHANE and J. UEBERSFELD: *Compt. Rend.*, **246**, 2121 (1958).

The polarization (1) with the aid of (9) and (3), is found to be in both cases:

$$P \begin{cases} = \operatorname{tgh} \frac{|\gamma_e| + \gamma_N}{2KT} \hbar H & \text{Overhauser effect} \\ = \operatorname{tgh} \frac{|\gamma_e| - 2\gamma_N}{2KT} \hbar H & \text{Underhauser effect.} \end{cases}$$

5. - The double effect.

In this effect pumping makes the total populations between levels equal. The population of levels 4 and 1 are equalized, that is,

$$(10) \quad 2(n_4 - n_1) = N_+ - N_- - (n_+ - n_-) = 0,$$

and we put

$$W_x \rightarrow \infty, \quad W_y = W_e = 0.$$

When populations of levels 2 and 3 are equalized one obtains

$$(11) \quad 2(n_3 - n_2) = N_+ - N_- + n_+ - n_- = 0,$$

and we put

$$W_y \rightarrow \infty, \quad W_x = W_e = 0,$$

The first term of (4) is zero for

$$(12) \quad \mu - \mu \begin{cases} = -(\mu_3 - \mu_1) \frac{w_e + w_y}{w_N + w_y}, \\ = (\mu_3 - \mu_1) \frac{w_e + w_x}{w_N + w_x}. \end{cases}$$

From (12) we note that the electron population ratio is not perturbed in the approximation $w_e \gg w_x, w_y \gg w_N$.

Really $\mu_3 - \mu_1$ is zero, therefore it is that of an electronic system at equilibrium temperature T in the steady H magnetic field.

The second term of the sum (4) is zero in the same order of approximation if one resolves for $\mu_3 - \mu_1$.

The relations (10) and (11) are equivalent to write the saturation condition:

$$(13) \quad \frac{N_+ n_-}{N_- n_+} = \frac{n_3 n_2}{n_1 n_1} = 1, \quad \frac{N_+ n_+}{N_- n_-} = \frac{n_3 n_1}{n_1 n_2} = 1.$$

From (13) with the aid of (3), one obtains

$$(14) \quad \mu \begin{matrix} \rightarrow \\ \mu \\ \begin{matrix} 1 & 2 \end{matrix} \end{matrix} \left\{ \begin{array}{l} = -\hbar H(|\gamma_e| + \gamma_N) \frac{1}{(w_N + w_y)/(w_e + w_y) + 1} \simeq -\hbar H(|\gamma_e| + \gamma_N), \\ = \hbar H(|\gamma_e| - \gamma_N) \frac{1}{(w_N + w_x)/(w_e + w_x) + 1} \simeq \hbar H(|\gamma_e| - \gamma_N). \end{array} \right.$$

Using the relation (3) one obtains the nuclear polarization (1):

$$P = \mp \operatorname{tgh} \frac{\hbar H |\gamma_e|}{2KT}.$$

6. - Conclusions.

Defining the fractional change in the polarization P from its thermal equilibrium value P_0 , as function of the transition probabilities we obtain the first-order polarization enhancement in double effect:

$$\eta = \frac{P - P_0}{P_0} \simeq \pm \frac{|\gamma_e|}{\gamma_N} \frac{1 + f}{1 + 2f + b}$$

where $f = w/w_e$, $b = w_N/w_e$, and $w = w_x$ with the upper sign and $w = w_y$ with the lower one.

In the direct and inverse Overhauser effect:

$$\eta \simeq - \frac{|\gamma_e|}{\gamma_N} \frac{f_1 - f_2}{f_1 + f_2 + 2b},$$

where $f_1 = w_y/w_e = 0$ for direct and $f_1 = 3f_2 = 3w_x/w_e$ for inverse Overhauser effect.

High polarization of nuclear magnetic moments have been obtained in some laboratories (7). It is obvious that the possible study of the relaxation phenomena and electron-nucleus interactions are greatly enhanced and give rise to much interest.

One of the possible practical applications of such phenomena would be the building of quantum oscillators and amplifiers in the radio-frequency range. Furthermore by a nuclear adiabatic demagnetization there is the possibility of dropping the temperature from 10^{-3} °K to 10^{-6} °K. This is due to a greater heat capacity (a factor $|\gamma_e/\gamma_N|$) of the dynamically polarized nuclear magnetic moments.

(7) T. J. SCHMUGGE and C. D. JEFFRIERS: *Phys. Rev. Lett.*, **9**, 268 (1962).

Another application is in building of polarized proton targets which are useful in the study of high-energy particle physics ⁽⁸⁾.

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⁽⁸⁾ C. HWANG and T. M. SANDERS: *Proc. VII Int. Conf. on Low Temp. Phys.* (Toronto, 1960).

RIASSUNTO

Se un sistema di particelle dotate di spin è diviso in gruppi a seconda dello stato di energia, può essere assegnato a ciascun gruppo un potenziale chimico. La variazione temporale della produzione di entropia è scritta in funzione dei potenziali chimici e delle probabilità di transizione. All'equilibrio termodinamico la produzione di entropia deve essere zero e la polarizzazione dinamica nucleare è ricavata per un sistema di elettroni e di nuclei il cui momento magnetico di spin vale $\frac{1}{2}$. I risultati sono concordi al primo ordine di approssimazione con quelli che si ricavano dalle equazioni cinetiche.