COMITATO NAZIONALE PER L'ENERGIA NUCLEARE
Laboratori Nazionali di Frascati

LNF-63/15
21. 3. 1963.

V. Montelatici: NUCLEAR DYNAMIC POLARIZATION.

Nota interna: n° 187

Servizio Documentazione
dei Laboratori Nazionali di Frascati del CNEN
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SUMMARY:

The nuclear dynamic polarization steady state is described from thermodynamical and statistical view point. It is shown how the nuclear population in some cases is inverted giving rise to a radio frequency amplification by stimulated emission.

INTRODUCTION.

In this paper some effects, named nuclear dynamic polarization, shall be described and results 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 $S = I = 1/2$ 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, 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.

THE FOUR LEVELS SYSTEM.

A nucleus with spin I in a magnetic field has 21 + 1 different energy states corresponding to an integer or a half integer values 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:

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

which becomes for I = 1/2

$$P = \frac{\frac{n_+}{n_-} - 1}{\frac{n_+}{n_-} + 1}$$

Where n_+ and n_- are the level population with m_I = + 1/2 and -1/2 respectively. In thermodynamic equilibrium, at temperature T, the static polarization is:

$$P_o = \text{tangh} \frac{\gamma_n \hbar H}{2 K T}$$

where γ_n is the nuclear gyromagnetic ratio, K and $\hbar$ are the Boltzmann and Planck costant, and H the magnetic field.

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

The non interacting nuclear and electronic spins under the action of a magnetic field H has the Hamiltonian:

$$\mathcal{H} = |\gamma_e| \hbar \vec{H} x \vec{S} - \gamma_n \hbar \vec{H} x \vec{I}$$

where γ_e, the electronic gyromagnetic ratio, is negative.

In this conditions the (2S + 1) (21 + 1) possible states of the system are those shown in fig. 1.

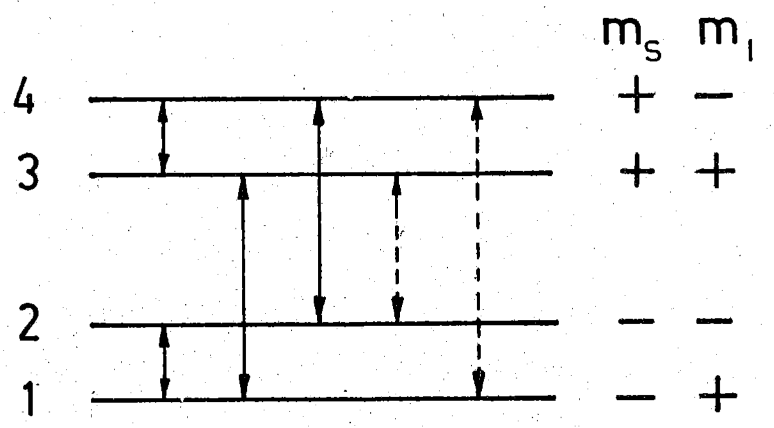

FIG. 1

The allowed transitions are:

$$(1 \rightleftarrows 2);\ (3 \rightleftarrows 4) \text{ and } (1 \rightleftarrows 3);\ (2 \rightleftarrows 4)$$

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 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 relation 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 transitions which are a simultaneous flip of the two types of spins with frequency $\nu = \nu_S \pm \nu_I$.

We will calculate, using thermodinamical 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[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 partion function of the system. This shall be considered a set of ideal particles obeying Boltzmann statistics with the following transitions among the levels:

$$(1)\qquad \begin{array}{ll} \mathcal{N}_1 \rightleftarrows \mathcal{N}_3 & \mathcal{N}_2 \rightleftarrows \mathcal{N}_4 \\ \mathcal{N}_1 \rightleftarrows \mathcal{N}_4 & \mathcal{N}_2 \rightleftarrows \mathcal{N}_3 \\ \mathcal{N}_1 \rightleftarrows \mathcal{N}_2 & \mathcal{N}_3 \rightleftarrows \mathcal{N}_4 \end{array}$$

these correspond to the four relaxation mechanisms listed above, where $\mathcal{N}_i$ stands for the total population of the i^{th} levels.

If $E_i + E_i^{(e)}$ stands for the energy of the i^{th} level, (the suffix (e) denotes the electrons physical quantities, while those of nuclei remain with ut suffix), the partition function is[4]:

$$Z_i = \frac{1}{n_i\,!}\left[\exp\left(-\frac{E_i}{KT}\right)\right]^{n_i} \cdot \frac{1}{N_i\,!}\left[\exp\left(-\frac{E_i(e)}{KT}\right)\right]^{N_i}$$

with the corresponding free energy:

$$F_i = -KT\log Z_i = KTn_i\log n_i - KTn_i + n_iE_i +$$

$$+ KTN_i\log N_i - KTN_i + N_iE_i \quad ,$$

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

$$(2)\qquad \begin{aligned} \mu_i &= \frac{\partial F_i}{\partial n_i} = E_i + KT\log n_i \\ \mu_i^{(e)} &= \frac{\partial F_i}{\partial N_i} = E_i^{(e)} + KT\log N_i \end{aligned}$$

The Gibbs relation is applicable to the system[5]

$$TdS = dU + dW - \sum_r (\mu .\, d\mathcal{N})_r$$

where dW is zero because the magnetic field is constant; and the summation gives the internal entropy production due to the particles transitions from a level to another. The term $\mu d\mathcal{N}$ stands for the summation of two terms. Each one is the product of the particles variation by the corresponding chemical potential for the level one think of.
We will write:

$$\mu d\mathcal{N} = \sum_i \mu_i \, d\mathcal{N}_i$$

where the index i takes values in each transition. The i^{th} level population rate in the transition between the i^{th} and j^{th} levels is given by the equation:

$$\frac{d\mathcal{N}_i}{dt} = \mathcal{N}_j \, w_{ji} - \mathcal{N}_i \, w_{ij}$$

in which $w_{ij} = w_{ji}$ by the detailed balance principle[6]. By writing the summation explicitly one obtains for the entropy production rate:

$$T \frac{dS}{dt})_{int} = \sum_r (\mu d\mathcal{N})_r = \sum_r \left[\sum_i \mu_i \, d\mathcal{N}_i \right]_r =$$

(3) $$= - \Big[2 \, \Delta\mu . \, \Delta n w_n + 2 \, \Delta\mu^{(e)} . \, \Delta N . \, w_e + (\Delta\mu^{(e)} - \Delta\mu) \cdot$$

$$\cdot \, (\Delta N - \Delta n) w_x + (\Delta\mu^{(e)} + \Delta\mu)(\Delta N + \Delta n) \, w_y \Big] .$$

where the differences stand for:

$$\Delta N \equiv N_+ - N_- \quad ; \quad \Delta n \equiv n_+ - n_-$$

$$\Delta\mu^{(e)} \equiv \mu_+^{(e)} - \mu_-^{(e)} \quad ; \quad \Delta\mu \equiv \mu_+ - \mu_- .$$

When the system is in thermal equilibrium at temperature T, the entropy production must be zero.

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[7], Underhauser[8] and double effects[9]. Anticipating the results, the nuclear population ratio n_+/n_- is governed by the electron Boltzmann factor when some levels are equal in population (in the jargon one speaks of "pumping").

Consequently the nuclear polarization is enhanced by about a factor $\frac{|\gamma_e|}{\gamma_n}$ over to static one.

Furthermore it shall be seen how in some cases the pumping permits the radio frequencies amplification by stimulated emission, giving rise to a nuclear maser effect due to a population inversion.

THE OVERHAUSER EFFECT.

In this effect pumping makes the electron populations equal that is $\Delta N = 0$, and $w_y = 0$ must be zero.

From general equation (3) we have:

$$\Delta \mu = \Delta \mu^{(e)} \frac{w_x}{2w_n + w_x} \qquad (4)$$

and with the saturation condition (pumping) applied to relation (2) another expression for the difference of the chemical potentials is obtained:

$$\Delta \mu^{(e)} = \Delta E^{(e)} = |\gamma_e| \hbar H$$

With the value of $\Delta \mu$, obtained by substitution of the precedent equation in the equation (4), the population ratio $\frac{n_+}{n_-}$ is found to be:

$$\frac{n_+}{n_-} = \exp \left(\frac{(\alpha |\gamma_e| + \gamma_n) \hbar H}{KT} \right) .$$

The nuclear polarization takes the form:

$$P = \text{tangh} \frac{(\alpha |\gamma_e| + \gamma_n)}{2KT} \hbar H$$

where

$$\alpha = \frac{w_x}{2w_n + w_x} .$$

If there is not direct relaxation among nuclear magnetic moments, or if $w_n \ll w_x$, $\alpha = 1$, and

$$P = \tanh \frac{|\gamma_e| + \gamma_n}{2KT} \hbar H.$$

THE UNDERHAUSER EFFECT.

With the same pumping and with $w_y = 3\, w_x$ (if $w_x = w_y$ no effects observable) the general equation gives:

$$\Delta\mu = - \Delta\mu^{(e)} \frac{w_y - w_x}{w_x + w_y + 2w_n}$$

The new condition on the probability and the saturation condition applied to relation (2) gives for the differences of the nuclear chemical potentials:

$$\Delta\mu = - |\gamma_e| \hbar H \frac{w_x}{w_n + 2\, w_x}$$

so

$$\frac{n_+}{n_-} = \exp\left(\frac{-(\beta |\gamma_e| - \gamma_n) \hbar H}{KT} \right)$$

with

$$\beta = \frac{w_x}{w_n + 2\, w_x}$$

The nuclear polarization is now:

$$P = - \tanh \frac{(\beta |\gamma_e| - \gamma_n)}{2KT} \cdot \hbar H$$

which can take the form, when $w_x \gg w_n$

$$P = - \tanh \frac{(|\gamma_e| - 2\gamma_n)}{4KT} \hbar H$$

The result is one half of, and inverted with respect to the Overhauser effect. In this case the higher energy level is more populated, that is a maser action is possible. Since the emitted power is proportional to the population difference between the inverted population levels, there is amplification by a factor ν_s given approximatively by:

$$P_{out} \simeq (n_4 - n_3)\, \hbar\, \nu_{43}\, W_{43} \propto (\nu_{42} - \nu_{43})\, \nu_{43}$$

Where W_{43} is the probability for transitions induced by radiation of frequency ν_{43} from the levels 4 to 3. The same argument is valid for levels 2 and 1.

THE DOUBLE EFFECT.

In this effect pumping makes the total population of the levels with energy difference $h(\nu_s - \nu_I)$ equal; that is $\Delta N - \Delta n = 0$.

With a sufficently high steady magnetic field all the three probability transitions w_x, w_y, w_n are different from zero and their values much below than of w_e.

The general equation gives:

$$\Delta\mu^{(e)} = -\Delta\mu \frac{w_n + w_y}{w_e + w_y}.$$

From the saturation condition applied to relation (2), and substituting the value of $\Delta\mu^{(e)}$ from the proceeding equation, one obtains:

$$\Delta\mu = -\hbar H(|\gamma_e| + \gamma_n) \cdot \frac{1}{\delta}$$

with

$$\delta = 1 + \frac{\frac{w_n}{w_e} + \frac{w_y}{w_e}}{1 + \frac{w_y}{w_e}}$$

For $w_e \gg w_n, w_x, w_y$ the population ratio is

$$\frac{n_+}{n_-} = \exp\left(-\frac{\hbar H |\gamma_e|}{KT}\right)$$

consequently the nuclear polarization is:

$$P = - \text{tangh} \frac{\hbar H |\gamma_e|}{2KT} .$$

The nuclear population is again inverted giving rise to amplification with a factor ν_e, given by:

$$P_{out} \simeq (n_4 - n_3) \hbar \nu_{43} W_{43} \propto \nu_{42.} \nu_{43}$$

When the pumping makes the total population of the other two levels with energy difference $h(\nu_S - \nu_I)$ equal, that is $\Delta N + \Delta n = 0$, the general equation gives:

$$\Delta\mu^{(e)} = + \Delta\mu \frac{w_n + w_x}{w_e + w_x} .$$

The saturation condition applied to relation (2), and expressing the difference of the chemical potential $\Delta\mu$, one obtains

$$\Delta\mu = \hbar H(|\gamma_e| - \gamma_n) \frac{1}{\delta}$$

using the same approximation for the transition probabilities the population ratio is given by:

$$\frac{n_+}{n_-} = \exp \frac{\hbar H |\gamma_e|}{KT} .$$

The expression for the nuclear polarization takes the form:

$$P = \text{tangh} \frac{\hbar H |\gamma_e|}{2KT} .$$

It is interesting to note that the electron population ratio is not perturbed. Indeed all the three probabilies is far less than w_e really $\Delta\mu^{(e)} = 0$. Therefore such a ratio is that of a system at equilibrium temperature T in the steady H magnetic field.

NUCLEAR DYNAMIC POLARIZATION CONSEQUENCE.

High polarization of nuclear magnetic moments have been obtained in some Laboratories[10]. It is obsious 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 application 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.

Another application is in building of polarized proton targets which are useful in the study of high energy particles physics.[11]

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