Concept of Temperature and the Overhauser Nuclear Polarization Effect

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The polarization of nuclei by the Overhauser method is examined for the case of metals. It is shown that the concept of temperature is valid for the conduction electrons if they are viewed form a coordinate system rotating at the electron Larmor frequency ω. Relative to this system, the nuclei precess at nearly $-\omega$, a result equivalent to an enormous nuclear magnetic coupling. The Overhauser result then follows immediately.

OVERHAUSER[1] has proposed a method for polarizing nuclear spins. It has been verified experimentally both in metals[2] and in nonmetals.[3,4] Prior to the experimental verification, which actually preceded the publication of Overhauser's detailed account, there was some skepticism expressed, one argument running as follows.

The nuclei become polarized by interaction with an electron system which is held saturated by a strong alternating magnetic field. By saturation we mean equal numbers of electron spins in the two spin orientations. Since a saturated magnetic resonance corresponds to an infinite spin temperature, the electron spin system has an infinite temperature. Therefore, the nuclei must arrive at infinite spin temperature since their contact with their surroundings is via the electrons. Hence, the nuclear polarization is *zero*.

The above argument, though plausible, is incorrect. As we shall discuss, the electrons cannot be said to have infinite temperature, because their distribution function is not *describable* by a temperature. If we could describe the electrons by a temperature, we could readily derive the nuclear polarization as the thermal equilibrium value. The purpose of this paper is to show that the temperature concept applies to the electrons in a properly chosen rotating coordinate system, relative to which the apparent nuclear Zeeman splitting is very much larger than usual. The resulting thermal equilibrium nuclear polarization is just that predicted by Overhauser. Let us turn to the details.

The Hamiltonian describing the conduction electron and nuclear system may be written as

$$\mathcal{H}=\mathcal{H}_T+\mathcal{H}_{SL}+\gamma_e\hbar H_0\sum_i S_{zi}+\gamma_n\hbar H_0\sum_j I_{zj}+\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\sum_{i,j}\delta(r_i-r_j)\mathbf{S}_i\cdot\mathbf{I}_j+\mathcal{H}_{\text{sat}},$$

where $\mathcal{H}_T$ represents the electron kinetic and potential energies, $\mathcal{H}_{SL}$ is the electron spin-lattice interaction, γ_e and γ_n the electron and nuclear gyromagnetic ratios, H_0 the applied static magnetic field (in the z-direction), $\mathbf{S}$ and $\mathbf{I}$ the electron and nuclear spin angular momenta, and $\mathcal{H}_{\text{sat}}$ the interaction which saturates the electron spin system.

The terms $\mathcal{H}_{SL}$ and $\mathcal{H}_{\text{sat}}$ determine the relative population of electron spins up or down. We consider the case of complete saturation, in which case there are equal numbers of electrons spins up or down. We will then neglect the presence of the terms $\mathcal{H}_{SL}$ and $\mathcal{H}_{\text{sat}}$, and simply consider that the electron spin population is maintained saturated despite the electron-nuclear couplings.

If we think of the electrons as described by two Fermi distributions, one for each spin orientation, we can see readily why the concept of electron temperature fails. The bottoms of the distributions, representing zero electron kinetic energy, are displaced by the electron magnetic energy. Since there are equal numbers of electrons in both distributions the tops are also displaced by the same amount. Clearly, there is *no* temperature which corresponds to a displacement of the tops. If the tops were in coincidence, the temperature concept would apply, and the temperature would be simply the "lattice" temperature T, which describes the shape of the tail.

If we now transform to a reference system rotating at the electron Larmor frequency, we cancel off the electron magnetic energy. That is, speaking classically, in the rotating reference system the electron's precessional motion has been "stopped." Mathematically we produce the transformation by the operator $\exp(-i\gamma_e\hbar H_0\sum_j S_{zj})$, which removes the electron magnetic energy from $\mathcal{H}$. However, this transformation would introduce explicit time dependence into the $\mathbf{I}\cdot\mathbf{S}$ coupling term, since $\sum_j S_{zj}$ does not commute with this operator. Explicit time dependence in a Hamiltonian corresponds to a "driven" system, so that energy conservation no longer applies within the nuclear plus electron system. To avoid considering a nonconservative system, therefore, we use instead the operator $\exp[-i\gamma_e\hbar H_0\sum_j(S_{zj}+I_{zj})]$ which rotates *both* electrons and nuclei at the same rate, $\gamma_e\hbar H_0$, and leaves the coupling term invariant.

[1] A. W. Overhauser, Phys. Rev. **91**, 476 (1953); **92**, 411 (1953). For further discussions see, for example, F. Bloch, Phys. Rev. **93**, 944(A) (1954); C. Kittel, Phys. Rev. **95**, 589 (1954); J. Korringa, Phys. Rev. **94**, 1388 (1954); A. Abragam, Phys. Rev. **98**, 1729 (1955).

[2] T. R. Carver and C. P. Slichter, Phys. Rev. **92**, 212 (1953).

[3] T. R. Carver, thesis, University of Illinois, 1954 (unpublished).

[4] Beljers, Van der Kint, and Van Wieringen, Phys. Rev. **95**, 1683 (1954).

The transformed Hamiltonian is then

$$\mathcal{H}=\mathcal{H}_T+(\gamma_e\hbar H_0-\gamma_e\hbar H_0)\sum_i S_{zi}+(\gamma_n\hbar H_0-\gamma_e\hbar H_0)\sum_j I_{zj}+\frac{8\pi}{3}\gamma_e\gamma_n\hbar^2\sum_{i,j}\mathbf{S}_i\cdot\mathbf{I}_j.$$

We note that the electron Zeeman energy is now zero. The electrons are now describable by a temperature since the tops of the Fermi surfaces coincide, but the nuclei have acquired a different splitting, equivalent to their having a gyromagnetic ratio nearly that of the electron. Since the temperature concept applies to the electrons, we can say the nuclei will come to thermal equilibrium at temperature T, among levels of spacing $(\gamma_n-\gamma_e)\hbar H_0$. Thus the Overhauser polarization is produced.

We can summarize, then, by saying that to apply the concept of temperature we must view the nuclei and electrons from a system rotating with the electrons. Relative to this system, the nuclei are precessing at nearly the electron Larmor frequency. Such a rapid precession is equivalent to the production of an enormous nuclear magnetic interaction.

As a subsidiary consideration, we might point out that in many ways the Overhauser effect has been with us a long time, although unnoticed. Let us think of the magnetization of a paramagnetic sample in a static field. The spin polarization is determined by the Boltzmann exponent $\gamma\hbar H_0/kT$. If we now transform to a rotating reference system to cancel off the magnetic energy, we realize there is a seeming contradiction since the full polarization must still be produced although the magnetic interaction is zero. The explanation of our difficulty is clearly that the lattice (which we must rotate to avoid explicit time dependence in the spin-lattice coupling) is no longer described by the temperature T. That is, the spacing of lattice energy levels has collapsed, giving a much greater population difference for the (zero) energy gap than we would get if we used the energy gap in the rotating system and the temperature T.

Our considerations should not be confused with the interesting discussion by Redfield[5] of the use of the temperature concept with rotating reference frames to discuss saturation. He is concerned with the coherent transverse magnetization of a saturated spin system with strong spin-spin interactions. We are concerned with the longitudinal magnetization of the nuclear spin system produced by coupling to a saturated spin system (that of the electron) of greatly different Lamor frequency, and possessing additional (translational) degrees of freedom. We have neglected effects of the sort described by Redfield.

[5] A. G. Redfield, Phys. Rev. 98, 1787 (1955).