

Springer Series in Solid-State Sciences

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Principles of Magnetic Resonance

Second Revised and Expanded Edition

With 115 Figures

Springer-Verlag Berlin Heidelberg New York 1978

QC 72.555

Since the magnetization element involves coordinates of only one electron, the various values of l now appear as the values of β that are occupied. In a substance such as iron, we may think of some values of β as corresponding to closed shells, some to the $3d$ band, and some to the $4s$ band. We shall discuss these contributions shortly.

The contribution of the term \mathcal{H}_d is somewhat different for a ferromagnet than for a paramagnet. For the latter, the magnetization is uniform in both magnitude and direction for ellipsoidal samples, and the simple demagnetizing arguments follow. For a ferromagnet the magnetization within a domain is uniform, but the various domains have differing magnetization vectors. Thus, for a soft ferromagnet in zero applied field, the magnetization averaged over a volume large compared with the domain size is zero. The density of magnetic poles on the outer surface therefore vanishes. Within the body of the ferromagnet, $\text{div } \mathbf{M} = 0$ even at domain boundaries. If, then, we calculate the dipolar contribution to the magnetic field at a nucleus, we may proceed as follows.

We draw a small sphere about the nucleus, of radius small enough to lie within one domain. We compute the field due to magnetization on atoms within the sphere by a direct sum. The atoms outside the sphere are treated in the continuum approximation. For cubic symmetry, the atoms within the sphere give zero total contribution. The atoms outside the sphere contribute as a result of the surface pole density on the inner sphere and the outer sample surface. The former is the contribution $4\pi\mathbf{M}/3$, where \mathbf{M} is the magnetization within the domain containing the nucleus. The latter contributes $-\alpha \cdot \mathbf{M}'$, where \mathbf{M}' is the magnetization averaged over a volume large compared with a domain size. The total field seen by the j th nucleus H_{Tj} is therefore given by

$$H_{Tj} = H_0 + \frac{4\pi}{3} \mathbf{M} - \alpha \cdot \mathbf{M}' + H_{Sj} \quad (4.172)$$

where H_0 is an externally applied field. Although H_0 and \mathbf{M}' vanish in zero-applied field, H_{Tj} does not. Therefore we have a "zero field" resonance. Such a resonance was first observed by Gossard and Portis [4.11] in the face-centered cubic form of cobalt. Using the Co^{59} resonance, the measured $H_{Sj} = 213,400$ Gauss. In iron, H_{Sj} is 330,000 Gauss. H_{Sj} has also been observed by means of the Mössbauer effect. It was discovered there that application of a static field H_0 lowered the resonance frequency, showing the H_{Sj} points opposed to the magnetization \mathbf{M} .

The contribution from the $3d$ and $4s$ shells in iron is expected by Marshall [4.12] to give a field of 100,000 to 200,000 gauss parallel to the local magnetization. Therefore the inner electrons must give a field of about 400,000 Gauss opposed to the local magnetization [4.13].

This phenomenon, called *core polarization*, was actually already known from electron magnetic resonance of paramagnetic ions for which the $4s$ electrons are missing. In principle the $3d$ electrons are incapable of giving an isotropic hyperfine coupling, since d -states vanish at the nucleus. However, the d -electrons are

coupled to inner shell electrons electrostatically, the coupling of an inner electron of spin parallel to the d -electron spin being different from that of an electron whose spin is opposed to that of the d -electron. Consequently the spatial part of two wave functions such as the $3s$ are different for the two spin states. The spin magnetization of the two electrons does not add to zero at all points of the electron cloud. We can see from (4.171) that if the $3s$ electron densities at the nucleus differ, there will be a nonzero contribution from the $3s$ electrons to H_{Sj} , even though their spins are opposed.

4.8 Second-Order Spin Effects—Indirect Nuclear Coupling

We have discussed the role of electron spin coupling to nuclei in paramagnetic or ferromagnetic materials. Since, in a diamagnetic substance, the total spin of the electrons vanishes, the nuclei experience zero coupling to the electron spins in first order. Effects are found if one considers the coupling in second order, however. The coupling is manifested through an apparent coupling of nuclei among themselves, the so-called indirect coupling.

The indirect coupling was discovered independently by Hahn and Maxwell [4.14] and by Gutowsky and McCall [4.15]. The phenomena they observed are illustrated by the case of PF_3 , a molecule in which all nuclei have spin $\frac{1}{2}$. In liquid PF_3 , the rapid tumbling narrows the line. It is found that both the P^{31} or F^{19} resonances consist of several lines, as illustrated in Fig. 4.11. Since all the

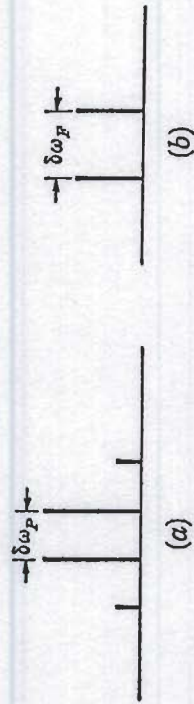


Fig. 4.11. (a) The P^{31} resonance in PF_3 . The lines are equally spaced an amount $\delta\omega_p$, and the intensities are 1:3:3:1. (b) The F^{19} resonance in PF_3 .

fluorine nuclei are chemically equivalent, the splittings cannot be due to chemical shifts. (Furthermore there is only one phosphorus atom per molecule but four phosphorus frequencies). The fact that the individual lines themselves are narrow shows that the motion is sufficiently rapid to narrow the direct dipolar coupling. Moreover, the splittings are found to be independent both of tem-

⁶ See references to " $I_1 \cdot I_2$ Coupling" in the Bibliography.

perature and static field. The number and relative intensity of lines are as though each nuclear species experienced a magnetic field proportional to the z-component of the total spin of the other species. It was found that $\delta\omega_F = \delta\omega_P \gamma_F / \gamma_P$ (see Fig. 4.11), where $\delta\omega_P$ and $\delta\omega_F$ are the frequency separations of adjacent lines in the phosphorus and fluorine spectra, respectively. These facts indicated the coupling was somehow related to the nuclear magnetic moments.

The original explanation proposed was that one nucleus induced currents in the electron cloud, which then coupled to the other nucleus. In a simple picture, the induced currents are represented by an induced electron magnetic moment. If this moment were *isotropic* (as one changes the orientation of the molecule with respect to the nuclear moment), the coupling to a second nucleus would average to zero in a liquid, owing to the rapid random tumbling of the molecules. However, as we observed in connection with the chemical shifts, the induced moment is in general not isotropic. We can estimate the size of the coupling between the two nuclei from second-order perturbation theory. The first nucleus exerts a magnetic field $\gamma_1 \hbar (1/r^3)$ where $(1/r^3)$ is the average of the inverse cube of the distance between the electron and the first nucleus that partially unquenches the orbital angular momentum, producing a fractional admixture of excited state of $\gamma_1 \gamma_2 \hbar^2 (1/r^3) / \Delta E$, where ΔE is the energy to the excited state. A complete unquenching would produce a magnetic field at the second nucleus of $\gamma_2 \hbar / R^3$, where R is the distance between the nuclei (we treat the electron orbital magnetization as equivalent to a magnetic dipole). Therefore the order of magnitude of the nuclear-nuclear interaction energy E_{12} on this model is

$$E_{12} \cong \frac{\gamma_1 \gamma_2 \hbar^2 (1/r^3)}{\Delta E} \frac{\gamma_2 \hbar}{R^3} \gamma_2 \hbar. \quad (4.173)$$

This formula fails by an order of magnitude or more in accounting for the facts. However, it has the virtue of making it seem reasonable that the splittings in PF_3 were an order of magnitude larger than those in PH_3 , since clearly this mechanism is closely related to chemical shifts that are always smaller for hydrogen than for fluorine.

As was pointed out by *Hahn* and *Maxwell*, and *Gutowsky* and *McCall*, any mechanism such as we have described, and which will lead to a result that is bilinear in the two nuclear moments, must take a very simple form. Since the interaction is averaged over all molecular orientations, it can depend only on the relative orientation of the nuclei; hence it must be of the form

$$A_{12} \mu_1 \cdot \mu_2 \quad (4.174)$$

where A_{12} is independent of temperature and field. These workers also pointed out that this particular form would also explain the puzzling fact that, for example, there were apparently no splittings of fluorines by fluorines in PF_3 . We

shall not give the proof here but physically the explanation is based on the idea that the interaction energy, (4.174), which depends on the relative orientation of spins, is unchanged if *both* spins are rotated through the same angle. For equivalent nuclei such as the three fluorines in PF_3 , one cannot rotate one fluorine spin without rotating the others by an equal amount, since the alternating and static fields are identical at all three fluorines. Therefore the coupling between equivalent nuclei does not affect the resonance frequency.

Ramsey and *Purcell* [4.16] proposed another mechanism utilizing the electron spins, which was substantially larger because, as we shall explain, it allowed the two nuclei to interact with nearby electrons, in contrast with the orbital mechanism where only one nucleus is on the same as the electron that is polarized. We may schematize their mechanism as shown in Fig. 4.12.

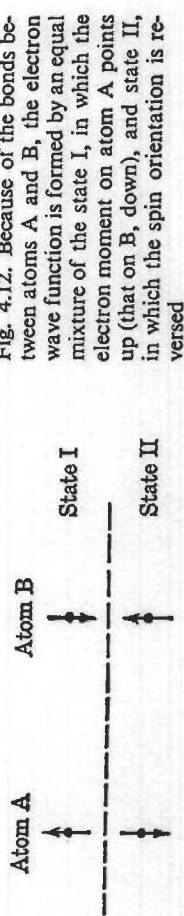


Fig. 4.12. Because of the bonds between atoms A and B, the electron wave function is formed by an equal mixture of the state I, in which the electron moment on atom A points up (that on B, down), and state II, in which the spin orientation is reversed.

In the absence of a nuclear moment the electron bond will consist of an equal mixture of the states I and II, shown in Fig. 4.12. If now we put a nucleus on atom A with its magnetic moment pointing up, state I will be slightly favored over state II. The electronic spin magnetic moment of atom A will have a slight polarization up; that on atom B, down. Therefore a nucleus on atom B will find a nonzero field owing to its own electron. Since this field would reverse if the nucleus on atom A were reversed, an effective nuclear-nuclear coupling results. We can easily estimate the size of the coupling. The fractional excess of state I over state II will be

$$\frac{\frac{8\pi}{3} \gamma_1 \gamma_2 \hbar^2 |\mu(0)|^2}{\Delta E} = \frac{\text{hyperfine energy}}{\text{electrostatic energy}} \quad (4.175)$$

where $|\mu(0)|^2$ is the wave-function density of the electron at atom A, and ΔE is the energy to an appropriate excited state. The coupling of the electrons on atom B to nucleus 2 are thus given by the product of the electron spin coupling if the electron spin is in one orientation only, $(8\pi/3) \gamma_2 \gamma_2 \hbar^2 |\mu(0)|^2$, times the excess fraction of the time the electron is in the favored orientation. Thus the coupling is

$$\left(\frac{8\pi}{3} \gamma_1 \gamma_2 \hbar^2 |\mu(0)|^2 \right) \left(\frac{8\pi}{3} \gamma_2 \gamma_2 \hbar^2 |\mu(0)|^2 \right) \frac{1}{\Delta E} \quad (4.176)$$

This coupling turns out to have the correct order of magnitude. If the electron functions do not contain an s -part, we should instead use the ordinary dipolar coupling between the electron and nuclear spins.

The extension of these ideas to solids was made independently by Bloembergen and Rowland [4.17] and by Ruderman and Kittel [4.18]. We shall discuss the situation for metals, confining our attention to the coupling via the s -state hyperfine coupling. Since the metal is not diamagnetic, we should concern ourselves with the possibility of a first-order effect—related, therefore, to the Knight shift. This mechanism of coupling was originally proposed by Fröhlich and Nabarro [4.19]. As Yosida [4.20] has explained, however, the Fröhlich-Nabarro effect is actually included in the second-order calculation. We shall discuss the physical reason shortly, but for the present, we shall simply ignore any first-order effect [4.21].

The effect of the magnetic moment of a nucleus at any lattice site is to make that site a region favorable for an electron of parallel magnetic moment but unfavorable for an electron of antiparallel moment. In order to take advantage of the magnetic interaction, an electron of parallel moment will distort its wave function to be larger in the vicinity of the nucleus. The distortion is brought about by mixing in other states k of the same spin orientation. As we shall see, the result is as though only states above the Fermi surface were added. The wave functions of the Bloch states are added so as to be in phase with the unperturbed function (Fig. 4.13) at the nucleus in order to interfere constructively at that point, but because of the spread in wavelengths, they rapidly get out of step as one moves away from the nucleus.

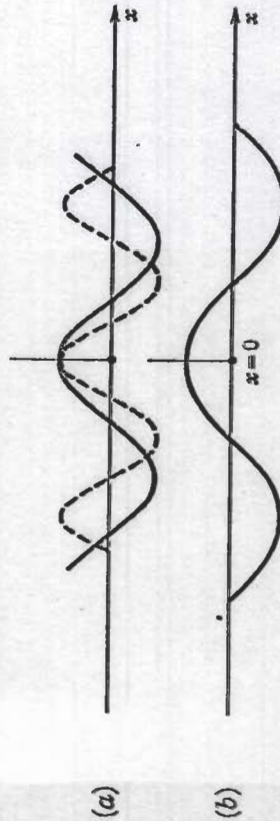


Fig. 4.13. The unperturbed function and two of the higher states mixed in. The nucleus is at $x = 0$, which guarantees that the waves be in phase at $x = 0$. Note that the admixed waves beat with one another. (a) Two of the waves mixed in by the perturbation. (b) Unperturbed function

As a result of the beats between the unperturbed and perturbed functions, the original uniform distribution of spin-up charge density (we neglect the variations due to the lattice charge) is changed to have an oscillatory behavior,

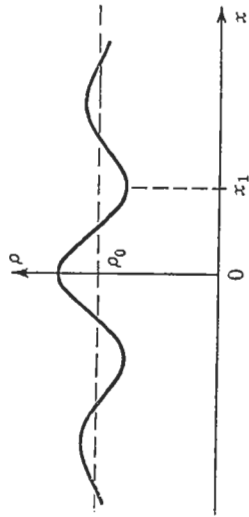


Fig. 4.14. The charge density of electrons whose magnetic moments are parallel to the nuclear moment. The nucleus is located at $x = 0$. ρ_0 is the charge density in the absence of a nuclear moment. At $x = x_1$, the electron charge is deficient, so that the net electron moment there is opposed to the nuclear moment

which dies out as one goes away from the nucleus. The characteristic length describing the attenuation is the wavelength of electrons at the Fermi surface. The resulting charge density of electrons whose moment is parallel to the nucleus is shown in Fig. 4.14.

We now turn to the actual calculation of these effects. For simplicity we shall calculate the interaction between the two nuclei directly rather than compute the changes in the spatial distribution of electron spin. However, the oscillatory nature of the charge will be apparent from the answer.

We consider, therefore, an electron-nuclear coupling \mathcal{H}_{en} involving only two nuclei of spins I_1 and I_2 and for simplicity, treat only the effect of the s -state coupling. We have, then,

$$\begin{aligned} \mathcal{H}_{en} &= \gamma_1 \gamma \hbar^2 I_1 \cdot \sum_l S_l \delta(r_l - R_1) + \gamma_2 \gamma \hbar^2 I_2 \cdot \sum_l S_l \delta(r_l - R_2) \\ &= \mathcal{H}_1 + \mathcal{H}_2 \end{aligned} \quad (4.177)$$

where we have allowed the nuclei to be different by using two values of gyromagnetic ratio γ_1 and γ_2 and spins I_1 and I_2 .

We must take into account the exclusion principle for the electrons. Two methods are available. We could use (4.177) to find perturbed one-electron functions and then fill these functions in accordance with the exclusion principle. Or, we could do perturbation theory in which we used the many electron functions as the unperturbed states. It is this latter procedure that we shall utilize, since it emphasizes that basically we are dealing with a many-electron problem and that the states we use are but one approximation.

Let us therefore consider a many-electron state $|0\rangle$ with energy E_0 and excited states $|n\rangle$ with energy E_n , and compute the second-order energy shift due to \mathcal{H}_{en} . We shall as usual assume the total wave function of the system to be a product of the electron and nuclear functions. Denoting the latter by ψ_α with energy E_α , where α represents the nuclear spin quantum numbers, we shall with to compute the second-order energy shift of states $|0\rangle\psi_\alpha$.

Therefore, for the second-order shift, we have $\Delta E_{0\alpha}^{(2)}$ of the state $|0\rangle\psi_\alpha$:

$$\Delta E_{0\alpha}^{(2)} = \sum_{n,\alpha'} \frac{\langle 0\alpha | \mathcal{H}_{en} | n\alpha' \rangle \langle n\alpha' | \mathcal{H}_{en} | 0\alpha \rangle}{(E_0 + E_\alpha) - (E_n + E_{\alpha'})} \quad (4.178)$$