

THE PRINCIPLES OF  
NUCLEAR  
MAGNETISM

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disregarding the polarization. Positive as well as negative values of  $R$  may occur. In contrast with  $\gamma$ ,  $|R|$  is less than unity even for heavy atoms.† Unfortunately there is no way at present in which these calculated values of  $R$  can be checked. As a consequence there is a significant uncertainty over the values of most nuclear quadrupole moments.

## II. MAGNETIC INTERACTIONS

### A. The coupling Hamiltonian

A logical procedure would be to develop the theory of the magnetic interactions between the electron and the nucleus along the same lines as for the electrostatic interactions; that is, to assign to the electrons and to the nucleus electric-current densities (rather than charge densities as in the previous section) and to calculate their interactions according to the laws of classical electromagnetism. One would thus define for the nucleus magnetic multipole operators which like the electric ones would be tensor operators of integer order  $l$ .

If one recalls the opposite parity properties of the electric field (a polar vector) and of the magnetic field (an axial vector) it is understandable that even, rather than odd, values of  $l$  are forbidden for permanent magnetic multipoles, by the assumption of a well-defined parity of nuclear-energy states. The first non-vanishing nuclear multipole is thus a magnetic dipole, the next a magnetic octopole, etc.

Although the existence of magnetic octopoles has been established by atomic beam methods (7, 8), they have never been observed by means of magnetic resonance in bulk matter. Furthermore, the description of the magnetic properties of a nucleus as those of a system of currents is more complicated and at the same time, in our present state of knowledge, much less satisfying than the description of its electrostatic properties as those of a system of charges. We shall therefore be content to describe the magnetic properties of the nucleus as those of a magnetic dipole  $\boldsymbol{\mu}_N = \gamma_N \hbar \mathbf{I}$ . The reason why the magnetic dipole is collinear with the spin vector  $\mathbf{I}$  is again that, within the manifold of the substates of a given nuclear state of spin  $I$ , all tensor operators of given  $l$  (vectors in the present case) have the same matrix elements. Magnetic fields of impossibly high values, of the order of  $10^{16}$  gauss or more, would have to be applied to the nucleus before its magnetic energy  $-\boldsymbol{\mu}_N \mathbf{H}$  became comparable to the interval between two different nuclear energy states, invalidating the approximation  $\boldsymbol{\mu}_N = \gamma_N \hbar \mathbf{I}$ .

† See a table of values of  $R$  in reference (3), p. 362.

The interaction of the nuclear dipole  $\boldsymbol{\mu}_N$  with the electronic shell is small even compared with atomic-energy splittings (let alone the nuclear ones) and will be computed by a perturbation method.

The behaviour of an electron in a magnetic field  $\mathbf{H}$  is obtained by replacing the momentum  $\mathbf{p}$  by  $\mathbf{p} + (e/c)\mathbf{A}$  in its Hamiltonian, where  $\mathbf{A}$  is the magnetic vector potential defined by

$$\operatorname{div} \mathbf{A} = 0, \quad \operatorname{curl} \mathbf{A} = \mathbf{H}.$$

According to classical electromagnetic theory a magnetic dipole  $\boldsymbol{\mu}$  produces at a point removed from it by a vector  $\mathbf{r}$ , a magnetic field deriving from a vector potential

$$\mathbf{A} = \frac{\boldsymbol{\mu} \wedge \mathbf{r}}{r^3} = \operatorname{curl} \left( \frac{\boldsymbol{\mu}}{r} \right). \quad (27)$$

Near the dipole the vector potential  $\mathbf{A}$  has a singularity of order  $r^{-2}$  and  $\mathbf{H} = \operatorname{curl} \mathbf{A}$  a singularity of order  $r^{-3}$ , so some care must be exercised in the calculation of its interaction with an electron. In the non-relativistic Pauli description of the electron the Hamiltonian in the presence of  $\mathbf{A}$  is

$$\mathcal{H} = \frac{1}{2m} \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 + 2\beta \mathbf{s} \cdot \operatorname{curl} \mathbf{A}, \quad (28)$$

where  $\beta$  is a Bohr magneton and  $\mathbf{s}$  the electron spin. In a first-order perturbation calculation the only terms of (28) to be retained are those linear in  $\mathbf{A}$ :

$$\mathcal{H}_1 = \frac{e}{2mc} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + 2\beta \mathbf{s} \cdot \operatorname{curl} \mathbf{A}.$$

This can be written by (27) as

$$\mathcal{H}_1 = 2\beta \frac{\mathbf{l} \cdot \boldsymbol{\mu}}{r^3} + 2\beta \mathbf{s} \cdot \operatorname{curl} \operatorname{curl} \left( \frac{\boldsymbol{\mu}}{r} \right), \quad (29)$$

where  $\mathbf{l} = \mathbf{r} \wedge \mathbf{p}$  is the orbital momentum of the electron.

The spin-dependent part of (29) gives

$$\begin{aligned} \mathcal{H}_1^s &= 2\beta \mathbf{s} \cdot \left[ \nabla \wedge \left( \nabla \wedge \frac{\boldsymbol{\mu}}{r} \right) \right] \\ &= 2\beta [(\mathbf{s} \cdot \nabla)(\boldsymbol{\mu} \cdot \nabla) - (\mathbf{s} \cdot \boldsymbol{\mu}) \nabla^2] \frac{1}{r}, \end{aligned} \quad (30)$$

which for reasons to appear presently we rewrite as

$$\mathcal{H}_1^s = 2\beta [(\mathbf{s} \cdot \nabla)(\boldsymbol{\mu} \cdot \nabla) - \frac{1}{3}(\mathbf{s} \cdot \boldsymbol{\mu}) \nabla^2] \left( \frac{1}{r} \right) - \frac{4\beta}{3} (\mathbf{s} \cdot \boldsymbol{\mu}) \nabla^2 \left( \frac{1}{r} \right). \quad (31)$$

The magnetic interaction of the nuclear moment with the electron spin  $W_m^s = \langle \psi_e | \mathcal{H}_1^s | \psi_e \rangle$  is obtained by multiplying (31) by the electronic

density  $\rho = \psi_e^* \psi_e$  and integrating over the electron coordinates. For  $r \neq 0$   $\mathcal{H}_1^s$ , as given by (31), is a regular function where the first term is equal to  $2\beta[3(\mathbf{s} \cdot \mathbf{r})(\boldsymbol{\mu} \cdot \mathbf{r})/r^5 - \mathbf{s} \cdot \boldsymbol{\mu}/r^3]$ , which is the usual dipole-dipole interaction, and the second term vanishes because of Laplace's equation. When  $r$  tends toward zero we may remark that the first term  $\mathcal{H}_1^{s'}$  of (31) behaves under a rotation of the coordinate system as a spherical harmonic of order 2. Hence if  $\psi_e$  is expanded in a sum of spherical harmonics,  $\psi_e = \sum_l a_l \psi^{(l)}$ , the only non vanishing contributions to  $(\psi_e | \mathcal{H}_1^{s'} | \psi_e)$  will come from terms  $(\psi^{(l)} | \mathcal{H}_1^{s'} | \psi^{(l')})$  such that  $l+l' \geq 2$ . It is well known that a wave function  $\psi^{(l)}$  is of order  $r^l$  near the origin so that in the matrix element

$$(\psi^{(l)} | \mathcal{H}_1^{s'} | \psi^{(l')}) = \int \psi^{(l)*} \mathcal{H}_1^{s'} \psi^{(l')} r^2 dr d\Omega$$

the integrand varies as  $r^{(l+l'+2-3)}$  and the corresponding integral always remains finite since  $l+l' \geq 2$ . According to the theory of the Coulomb potential the second term of (31) is equal to  $\frac{16}{3}\pi\beta(\mathbf{s} \cdot \boldsymbol{\mu})\delta(\mathbf{r})$  and by integration gives

$$\frac{16}{3}\pi\beta(\mathbf{s} \cdot \boldsymbol{\mu}) |\psi_e(0)|^2,$$

which is finite for  $s$  electrons and zero for the others. The Hamiltonian for the magnetic interaction of the electron with the nucleus can then be written without ambiguity as

$$\mathcal{H}_1 = 2\beta\gamma\hbar\mathbf{I} \cdot \left[ \frac{\mathbf{1}}{r^3} - \frac{\mathbf{s}}{r^3} + 3\frac{\mathbf{r}(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8}{3}\pi \mathbf{s}\delta(\mathbf{r}) \right]. \quad (32)$$

If several electrons surround the nucleus, the interaction Hamiltonian is the sum of the contributions of the individual electrons. Although the expression (32) has been derived for the purpose of calculating its expectation value  $(\psi_e | \mathcal{H}_1 | \psi_e)$ , it is clear that it also gives unambiguous results for off-diagonal matrix elements  $(\psi_e | \mathcal{H}_1 | \phi_e)$ , between, say, the ground state and an excited state of the electronic system. Use will be made of this to calculate some effects of  $\mathcal{H}_1$ , using second-order perturbation theory.

The vector operator

$$\mathbf{H}_e = -2\beta \left[ \frac{\mathbf{1}}{r^3} - \frac{\mathbf{s}}{r^3} + \frac{3\mathbf{r}(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8}{3}\pi \mathbf{s}\delta(\mathbf{r}) \right] \quad (33)$$

can be called the field produced by the electron at the nucleus. For an atomic electron of orbital momentum  $l$  and total angular momentum  $j = l \pm \frac{1}{2}$  it is possible inside the manifold  $j$  to replace in the Hamiltonian (32),  $\mathcal{H}_1 = -\gamma_n \hbar \mathbf{H}_e \cdot \mathbf{I}$ , the vector  $-\gamma \hbar \mathbf{H}_e$ , by a vector  $a_j \mathbf{j}$  proportional to  $\mathbf{j}$ . The value of  $a_j$  is obtained by writing

that the expectation values  $\langle a_j \mathbf{j} \cdot \mathbf{j} \rangle$  and  $\langle -(\gamma \mathbf{H}_e \cdot \mathbf{j}) \rangle$  are equal. Using (33) and remembering that  $\mathbf{j} = \mathbf{l} + \mathbf{s}$ , that  $\mathbf{r} \cdot \mathbf{l} = (1/\hbar) \mathbf{r} \cdot (\mathbf{r} \wedge \mathbf{p}) = 0$ , and that for a spin  $s = \frac{1}{2}$  relations such as  $s_x^2 = \frac{1}{4}$ ,  $s_x s_y = -s_y s_x$ ,  $s_x s_y = \frac{1}{2} i s_z$  are valid, it is easily found that

$$a_j = \frac{16}{3} \pi \beta \gamma \hbar |\psi(0)|^2 \quad \text{for an } s\text{-electron} \quad (34)$$

and

$$a_j = 2\beta\gamma\hbar \left\langle \frac{1}{r^3} \right\rangle \frac{l(l+1)}{j(j+1)} \quad \text{if } l \neq 0. \quad (35)$$

For a free atom or a paramagnetic molecule with many electrons in a state of total angular momentum  $J$  it is also possible to write  $\mathcal{H}_1 = a_J \mathbf{I} \cdot \mathbf{J}$  for the magnetic coupling of the electrons with the nucleus, where the value of  $a_J$ , to be determined by the same method as for a single electron, will depend on the electronic structure of the atom or the molecule.

In bulk matter the manifestations of the interaction (32) are manifold and greatly dependent on the nature of the substance. They can change the phenomenon of nuclear magnetic resonance in two ways, by introducing changes in the energy levels of the nuclear spin system and also by providing powerful relaxation mechanisms for the coupling of this system to the lattice. Only the first aspect of the electron-nucleus magnetic coupling will be considered in this chapter, the relaxation phenomenon being deferred till Chapters VIII and IX.

## B. The effect of electron-nucleus coupling in diamagnetic substances

### (a) General

The overwhelming majority of nuclear-resonance experiments are performed on diamagnetic samples, that is on substances without either spin or orbital electron paramagnetism. The lack of electron paramagnetism in, for instance, a molecule embedded in a molecular solid, or in an ion belonging to a crystal or a solution, corresponds to vanishing expectation values of  $(\psi_0 | L_q | \psi_0)$  and  $(\psi_0 | S_q | \psi_0)$  for all components of the total orbital and spin angular momentum of the molecule or the ion, of which  $\psi_0$ , a function of both orbital and spin coordinates, describes the ground state.

In spite of an apparent symmetry there is an important difference between the behaviour of the orbital and spin momentum in diamagnetic substances and consequently between the ways in which they affect the resonance of nuclear spins. The forces between electrons, atoms, and molecules are essentially electrostatic forces, and the magnetic spin-dependent forces are negligible compared to them. It follows