SIGN OF g IN MAGNETIC RESONANCE, AND THE SIGN OF THE QUADRUPOLE MOMENT OF Np^{237}

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When the Hamiltonian for an electronic spin system is written in the form

$$\mathcal{H}=\beta(g_{xx}H_xS_x+g_{yy}H_yS_y+g_{zz}H_zS_z),$$

there is in general some ambiguity about the signs of the principal values of the g tensor. Except in very simple systems the components S_x, S_y, S_z do not refer to the true spin, but to some "fictitious" spin operator which may be quite different from it, and their definition in terms of physically observable quantities is to some extent arbitrary.

The product $g_{xx}g_{yy}g_{zz}$, however, is quite unambiguous and is directly related to physically observable quantities. Its sign, in particular, determines whether the precession of the magnetic moment in a magnetic field is left-handed or right-handed, and this sense can be directly observed in a resonance type of measurement, as has recently been demonstrated for NpF_6.[1]

One way of seeing this simply is to consider the quantum equations of motion for the components of magnetic moment, $\mu_x=-g_{xx}\beta S_x$, etc. They are

$$\dot{\mu}_x=(\mu_x\mathcal{H}-\mathcal{H}\mu_x)/i\hbar$$

$$=\frac{e}{2mc}\left(\frac{g_{xx}g_{yy}}{g_{zz}}H_y\mu_z-\frac{g_{xx}g_{zz}}{g_{yy}}H_z\mu_y\right),\ \text{etc.}$$

For a system of many independent spins the macroscopic moment $\vec{M}=\sum\vec{\mu}$ satisfies the same equations, which may then be regarded as classical equations determining the precession of the moment. The quantities $g_{xx}g_{yy}/g_{zz}$, etc., thus have a direct observational significance, which implies that the magnitudes $|g_{xx}|$, etc., and the magnitude and sign of $g_{xx}g_{yy}g_{zz}$ are observables. A more general form for the latter, of course, not limited to principal axes of the g tensor, is $\det|g|$.

When the system has an axis of symmetry, $g_{xx}=g_{yy}=g_\perp$ so that the sign as well as the magnitude of $g_{zz}=g_\parallel$ has meaning. In general, however, the sign of $g_\perp$ is conventional and can be reversed by a trivial transformation. Consider a system with two states ($S=\frac{1}{2}$). The basic states $|a\rangle$, $|b\rangle$ are chosen as the eigenstates for $S_z=\pm\frac{1}{2}$, thereby in part defining the fictitious spin if this differs from the true spin. Changing the sign of one of these states results in reversing the definition of S_x and S_y, and thereby of g_{xx} and g_{yy}, but not of g_{zz}. Interchanging $|a\rangle$ and $|b\rangle$ changes the sign of S_y and S_z, and so of g_{yy} and g_{zz}, but not g_{xx}. In a system with axial symmetry the latter transformation leads to $g_{yy}=-g_{xx}$, which destroys the symmetry of the formulation, and is therefore inadmissible.

These considerations are relevant to the neptunyl ion, which has been studied by Eisenstein and Pryce.[2] In that paper we paid no attention to the signs of g, and defined the basic states so that $g_\parallel$ was positive, since this seemed convenient. We overlooked, however, that this definition entailed $g_{yy}=-g_{xx}$. To be consistent we should have interchanged our basic states, thereby reversing the sign of $g_\parallel$. Simultaneously, the hfs coefficient A has to change sign. The experiments of Bleaney et al.[3] should therefore be interpreted as leading to the parameters

$$\left.\begin{aligned} g_\parallel &= -3.405\pm0.008,\\ |g_\perp| &= 0.205\pm0.006,\\ A &= -0.16547\pm0.00005\ \text{cm}^{-1}\\ |B| &= 0.01782\pm0.00003\ \text{cm}^{-1}\\ P &= +0.03015\pm0.00005\ \text{cm}^{-1}\end{aligned}\right\}\ Np^{237}.$$

The sign of the quadrupole term P is directly determined as being opposite to A. According to the theory P is of opposite sign to the nuclear quadrupole moment Q.

$Q(Np^{237})$ is therefore deduced from magnetic resonance to be negative. This is in accordance with the deduction from the emission of α particles from oriented Np^{237} nuclei.[4] There has been an apparent discrepancy between the two methods, which is now resolved by the realization that the sign of $g_\parallel$ is not just conventional and has in fact been incorrectly chosen.

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[1] C. A. Hutchison and B. Weinstock, J. Chem. Phys. (to be published).

[2] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. (London) A229, 20 (1955).

[3] Bleaney, Llewellyn, Pryce, and Hall, Phil. Mag. 45, 992 (1954).

[4] Roberts, Dabbs, Parker, and Ellison, Bull. Am. Phys. Soc. 1, 207 (1956).