IL NUOVO CIMENTO   Vol. L B, N. 1   11 Luglio 1967

The Determination of the Sign of the Spin-Hamiltonian Parameters.

M. E. Foglio

Centro Atómico Bariloche (C.N.E.A.)
Instituto de Física « Dr. José Antonio Balseiro » (U.N. de C. and C.N.E.A.)
San Carlos de Bariloche, Rio Negro

(ricevuto il 3 Aprile 1967)

1. – Introduction.

It has been already shown (1) that the signs of g_x, g_y and g_z are somewhat arbitrary, and in particular that it is possible to change the sign of a pair of them by a canonical transformation. Some results needed later will be briefly reformulated.

The spin Hamiltonian (S.H.) is a linear operator on a vector space (S.H.V.S.) and it is expressed as a polynomial in the operators S_i and I_i (with $i=x, y, z$). The vectors of the S.H.V.S. represent states of a physical system; a convenient orthogonal basis in this space is given by the vectors $|M, m\rangle$, where $M = S, S-1, \dots, -S$ and $m = I, I-1, \dots, -I$ (with S and I integers or half-integers); the dimension of the S.H.V.S. is therefore $(2S+1)(2I+1)$. The matrix elements of S_i and I_i between pairs of vectors of this basis are the standard ones of the corresponding components of angular momenta in units of $\hbar$ (with maximum projections along z equal to S and I respectively).

A canonical transformation is defined by a unitary operator T, and in the new representation the vector $|M, m\rangle^t = T|M, m\rangle$ corresponds to the state described by $|M, m\rangle$ in the old representation; the operator $A^t = TAT^{-1}$ corresponds in the new representation to the magnitude described by A in the old representation.

We introduce four canonical transformations through the linear operators T_a ($a = 1, 2, 3, 4$) defined by their matrix elements

$$\langle M', m'|T_1|M, m\rangle = \delta_{M',-M}\,\delta_{m',m}\,, \tag{1.1}$$

$$\langle M', m'|T_2|M, m\rangle = (-1)^{S-M}\,\delta_{M',M}\,\delta_{m',m}\,. \tag{1.2}$$

By exchanging M', M and S with m', m and I in the second members of (1.1) and (1.2), the operators T_3, T_4 are respectively obtained.

The usual S.H. for axial symmetry is given by

$$\mathscr{H} = \sum g_i H_i S_i + \sum_i A_i I_i S_i + \sum_i \mu_i H_i S_i + D(S_z^2 - S(S+1)/3) + P(I_z^2 - I(I+1)/3)\,, \tag{1.3}$$

---

(1) M. H. L. Pryce: *Phys. Rev. Lett.*, 3, 375 (1959).

where the summations run over x, y, z. Using T_1, the corresponding operator in the new representation is $\mathscr{H}^t = T_1 \mathscr{H} T_1^{-1}$, and since

$$S_x^t = S_x, \quad S_y^t = -S_y, \quad S_z^t = -S_z, \quad I_i^t = I_i,$$

we find that the formal expression of $\mathscr{H}^t$ is the same as that of $\mathscr{H}$, if we change the signs of g_z, g_y, A_y and A_z. Similar results are obtained using the other T_a: with T_2 we have to change the signs of g_x, g_y, A_x and A_y; the parameters μ_y, μ_z, A_y and A_z change sign with T_3, and μ_x, μ_y, A_x, A_y change sign with T_4. In all these cases D and P do not change sign.

Most of the determinations of sign found in the literature will be discussed using the results summarized above.

i) When the sign of the product $g_x g_y g_z$ is measured (1,2), the sign of g_z is determined by the convention $g_x = g_y$ for axial symmetry (or $g_x = g_y = g_z$ for cubic symmetry). Similar results hold for μ_z.

ii) The sign of D is measured by the anysotropy of the magnetic susceptibility (3); it is independent of any convention about the relative signs of other parameters. A similar result holds for P (1).

iii) The relative sign of D and g_z is determined by E.P.R. using the convention $g_x = g_y = g_\perp$; but there is not a reasonable convention to determine the relative sign of D and $g_\perp$. Similar results (3,4) hold for the relative signs of D and A_i or P and A_i: it is possible to change the sign of $A_x = A_y = A_\perp$ using the canonical transformation defined by T_4. Only when the Zeeman nuclear term is considered (5), it is possible to give some meaning to the relative signs of A_z and $A_\perp$ because it is then possible to measure the signs of the two products $P g_z A_z \mu_z$ and $P g_\perp A_\perp \mu_\perp$.

Using other canonical transformations more involved than the T_a defined above, we have been able to show that it is possible to find the sign of $g_x g_y g_z$ for the S.H. defined in (1.1) (axial symmetry), with a resonant experiment that uses only one oscillating magnetic field of a fixed direction. In the derivation (6) we have used a first-order time-dependent calculation, and we have disregarded the interaction of the nuclear Zeeman term with the oscillating field.

2. – The case of resonance in a liquid solution.

The E.P.R. of a complex dissolved in a liquid of low viscosity is described by the following S.H.:

$$\mathscr{H}_{is} = g_{is} H S_z + A_{is} \boldsymbol{S} \cdot \boldsymbol{I} \,. \tag{2.1}$$

When the complex has axial symmetry, it has been shown (7,8) that

$$g_{is} = \bar{g} \qquad \text{and} \qquad A_{is} = \bar{A} \,,$$

where

$$\left\{ \begin{aligned} \bar{g} &= (g_\parallel + 2\, g_\perp)/3 \,, \\ \bar{A} &= (A_\parallel + 2A_\perp)/3 \,. \end{aligned} \right. \tag{2.2}$$

Using these results, the relative signs of $g_\parallel$, $g_\perp$ and of $A_\parallel$, $A_\perp$ are sometime

---

(2) C. A. HUTCHINSON and B. WEINSTOCK: *Journ. Chem. Phys.*, **32**, 56 (1960).

(3) B. BLEANEY and D. J. E. INGRAM: *Proc. Roy. Soc.*, A **205**, 336 (1951).

(4) B. BLEANEY, P. M. LLEWELLYN, M. H. L. PRYCE and G. R. HALL: *Phil. Mag.*, **45**, 992 (1954).

(5) B. BLEANEY: *Phil. Mag.*, **42**, 441 (1951).

(6) M. E. FOGLIO: *Determinación de signos de los parámetros del hamiltoniano de spin*, Publicación C.N.E.A., 1967.

(7) H. M. McCONNELL: *Journ. Chem. Phys.*, **25**, 709 (1956).

(8) N. KIVELSON: *Journ. Chem. Phys.*, **33**, 1094 (1960).

deduced in the literature (9,10) from E.P.R. measurements in liquids. These determinations contradict the results summarized above, and we shall now show that g_{is} and A_{is} are not given by $\bar{g}$ and $\bar{A}$ respectively, when the signs of $g_\parallel$ and $g_\perp$ or of $A_\parallel$ and $A_\perp$ are opposite, but they are given by

$$\text{(2.3)}\quad \begin{cases} g_{is} = \pm\,(|g_\parallel| + 2|g_\perp|)/3\,, \\ A_{is} = \pm\,(|A_\parallel| + 2|A_\perp|)/3\,. \end{cases}$$

In the deduction of (2.2), the S.H. of each molecule of the complex is referred to a co-ordinate system (C.S.) fixed to the molecule. The components of the magnetic field in this C.S. are then expressed as a function of those in another C.S. common to all the molecules and fixed to the laboratory. A canonical transformation defined by a given linear operator $T(R)$ for each molecule is then made (R is the rotation that transforms the molecular C.S. into the laboratory C.S.), and the following S.H. is obtained:

$$\text{(2.4)}\qquad \mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1\,.$$

The operator $\mathscr{H}_0$ is given by (2.1) (with $g_{is} = \bar{g}$ and $A_{is} = \bar{A}$); it is time-independent and it is the same for all the molecules. The operator $\mathscr{H}_1$ has coefficients that depend on the orientation of the molecules and, therefore, it varies with time; it consists of several terms, and each of them contains $g_\parallel - g_\perp$ or $A_\parallel - A_\perp$ as a factor. The next step in the derivation is a perturbation calculation, where $\mathscr{H}_1$ is the perturbation term; the final result is that $\mathscr{H}_0$ determines the position of the lines, and $\mathscr{H}_1$ determines their shape. This derivation requires that $|g_\parallel - g_\perp| \ll |\bar{g}|$ and $|A_\parallel - A_\perp| \ll |\bar{A}|$. When the moduli of $g_\parallel$ and $g_\perp$ are not very different, this condition requires that $g_\parallel \cdot g_\perp$ is positive and the same situation arises with $A_\parallel$ and $A_\perp$. When any of these requirements does not hold, *i.e.* when $g_\parallel \cdot g_\perp$ or $A_\parallel \cdot A_\perp$ are negative, the perturbation calculation breaks down. We shall now extend the previous results to the case when either $g_\parallel \cdot g_\perp$ or $A_\parallel \cdot A_\perp$ or both are negative.

When $g_\parallel \cdot g_\perp > 0$ and $A_\parallel \cdot A_\perp < 0$, instead of the canonical transformation defined by $T(R)$, we perform the one defined by $T(R)T_4$. As we saw before, we have $-A_\perp$ instead of $A_\perp$ in all the formulae given in the representation included by T_4, and proceeding as before we have the same formal expression (2.1) for $\mathscr{H}_0$ but with

$$A_{is} = (A_\parallel - 2A_\perp)/3 = \pm\,(|A_\parallel| + 2|A_\perp|)/3$$

(the + or − sign is given by the sign of $A_\parallel$). The condition for the validity of the perturbation calculation is now $|A_\parallel + A_\perp| \ll |A_\parallel - 2A_\perp|/3$ and in this case it holds when the moduli of $A_\parallel$ and $A_\perp$ are not very different.

In the other two cases, the procedure to follow is obvious: when $g_\parallel \cdot g_\perp < 0$ and $A_\parallel \cdot A_\perp > 0$, we define the canonical transformation by $T(R)T_4T_2$; when $g_\parallel \cdot g_\perp$ and $A_\parallel \cdot A_\perp$ are both negative, the canonical transformation is defined by $T(R)T_2$. In all three cases, the position of the E.P.R. lines is given by $\mathscr{H}_{is}$, but with g_{is} and A_{is} as defined in (2.3).

We have, therefore, shown that it is not possible to determine the relative signs of $g_\parallel$ and $g_\perp$ or $A_\parallel$ and $A_\perp$ by the usual E.P.R. measurements in liquid solutions.

---

(9) N. S. GARIF'YANOV and V. N. FEDOTOV: *Žurn. Structurnei Himii,* 3, M 711 (1962).

(10) A. H. MAKI and B. R. MCGARVEY: *Journ. Chem. Phys.*, 29, 31 (1958).