



Editors' Note

This paper draws attention to the advantages that would be obtained by adopting a new convention for the sign of g factors that would make the g factor for electron spin a negative quantity ($g \approx -2$), rather than a positive quantity as generally adopted at present. The editors are aware that the proposal made in this paper concerning the conventional sign of the g factor for electron spin will be seen by some readers as controversial. We have nonetheless agreed to publish this paper in the hope that it will stimulate discussion. The editors would welcome comments on this proposal in the form of short papers, which they will then be happy to consider for publication together at a later date.

Remarks on the signs of g factors in atomic and molecular Zeeman spectroscopy

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Various magnetic moments, associated with rotational, vibrational, nuclear spin, electron orbital and electron spin angular momenta, can contribute to the Zeeman effect in atoms and molecules. They are considered in this paper in the context of the effective Hamiltonian where relativistic and other corrections as well as the effects of mixing with other electronic states are absorbed in appropriate g factors. In spherically symmetric systems, the magnetic dipole moment arising from a specific angular momentum can be written as the product of three factors: the nuclear or Bohr magneton (which is positive), the g factor (which may be positive or negative), and the corresponding angular momentum (which is a vector). A convention is discussed, in which the sign of the g factor is positive when the dipole moment is parallel to its angular momentum and negative when it is antiparallel. This would have the advantage that it could be applied consistently in any situation. Such a choice would require the g factors for the electron orbital and electron spin angular momenta to be negative. This concept can easily be extended to the case of a general molecule where the relation between the dipole and angular momentum vectors has tensorial character.

1. Introduction

The g factor, first introduced by Landé [1] to explain anomalous Zeeman effects in atomic spectra, now has a more wide-ranging significance. It is generally utilized to represent the linear relationship between magnetic moments and angular momenta. For nuclei, g factors are usually positive but are occasionally negative, e.g. ^3He , ^{17}O . The underlying convention is that for positive g factors the magnetic moment of the nucleus is oriented parallel to its angular momentum but for negative g factors the reverse is true. Such is the usage in particle physics and in nuclear magnetic resonance (NMR). In electron spin resonance spectroscopy (ESR) the opposite convention is used by most authors, that is the g factor, g_S^e , is chosen to be positive even though the electron spin and magnetic moment vectors are antiparallel, as first shown by Dirac [2]. The results of many magnetic field experiments do not depend on the relative orientations of the two vectors. For example, the theory of magnetic oscillations in metals (de Haas–van Alphen effect, used for probing Fermi surfaces) shows that the ‘sign of g_S^e is indeterminate and it is natural to assume that it is positive’ [3]. In this paper, we wish to discuss the situation where several different kinds of moment are present, and where their relative orientations are of great importance. In particular, we explore the implications of the sign of g_S^e (and of g_L^e , the orbital electronic g factor) on terms in the molecular Hamiltonian, for high resolution Zeeman studies of molecular species.

2. The effective Zeeman Hamiltonian

The basic Hamiltonian for the magnetic field interaction is

$$H = -\mathbf{m} \cdot \mathbf{B}, \quad (1)$$

where \mathbf{m} is the magnetic dipole moment operator and \mathbf{B} the magnetic flux density. Various contributions to \mathbf{m} are considered below. The minus sign in equation (1)

implies that the direction of the moment is chosen such that the torque imposed by the field acts to align \mathbf{m} in the direction of \mathbf{B} . The same sign is used in classical electrodynamics, and therefore is in agreement with the direction of macroscopic moments induced by any electric current distribution. A common example is the permanent magnetic dipole moment of a small planar conducting loop, which can be expressed as

$$\mathbf{m} = iA\mathbf{n}_\perp \quad (2)$$

where i is the current in the wire, A is the area enclosed by the loop, and \mathbf{n}_\perp its normal vector defined by the right hand rule [4]. The direction of i is defined in accordance with the transport of positive charges.

Zeeman effects in diamagnetic species observed at high resolution are caused by rotational, vibrational, and nuclear magnetic moments (neglecting magnetizability contributions). They all have in common that a linear relation holds between the magnetic moment and the angular momentum. Thus, a rotational moment \mathbf{m}^{rot} can be formulated [5]:

$$m_i^{\text{rot}} = \mu_N g_{ij}^{\text{rot}} J_j, \quad (3)$$

where \mathbf{J} is the rotational angular momentum in units of \hbar , \mathbf{g}^{rot} is the rotational g tensor, i and j refer to the molecule-fixed axes, and summation is implied over $j = x, y, z$. The nuclear magneton, $\mu_N = e\hbar/2m_p$ [6], is a positive scaling factor (e and m_p are the charge and mass of the proton, \hbar is the Planck constant divided by 2π). The other angular momenta considered below are, like \mathbf{J} , all understood to be given in units of \hbar .

Linear and symmetric-top molecules in degenerate vibrational states can exhibit a vibrational angular momentum p_z about the figure axis which gives rise to a magnetic moment [7]

$$m_z^{\text{vib}} = \mu_N g^{\text{vib}} p_z, \quad (4)$$

where the vibrational g factor, g^{vib} , is a scalar.

Experiments have shown [8] that g_{ii}^{rot} and g^{vib} can be positive or negative depending on the details of the nuclear–electron couplings in different molecules. Classically speaking, the sum of all nuclear currents induced in a rovibrating molecule may or may not be outweighed by that of the electronic ones in forming the total \mathbf{m} , according to equation (2).

Atomic nuclei also show measurable magnetic dipole moments of either sign when their nuclear spin angular momenta, \mathbf{I} , do not vanish:

$$\mathbf{m}^{\text{nuc}} = \mu_{\text{N}} g^{\text{nuc}} \mathbf{I}, \quad (5)$$

where g^{nuc} , a scalar, means the nuclear g factor. The magnetogyric ratio, $\gamma = \mu_{\text{N}} g^{\text{nuc}} / \hbar$, is frequently used as an alternative description in NMR spectroscopy because $\omega = \gamma B$ gives the angular transition frequency between neighbouring states directly [9].

In equations (3), (4) and (5), we note the common principle that the g factors determine the orientations of the magnetic dipole moments relative to those of the angular momenta.

Paramagnetic species contain unpaired electrons so that electron spin magnetic moments contribute to the total magnetic moment. In cases of sufficient symmetry (e.g. cylindrical symmetry in linear molecules), conserved orbital angular momenta may also occur. An orbiting electron is equivalent to a current $i = -(e/T)$ where T is the time needed for one orbit. The corresponding magnetic moment is

$$\mathbf{m}_L^e = -\mu_{\text{B}} \mathbf{L} \quad (6)$$

where $\mu_{\text{B}} = e\hbar/2m_e$ is the Bohr magneton, defined as a positive quantity [6] (m_e is the mass of the electron and \mathbf{L} is the angular momentum of the electron). Following the lead of equations (3–5) it is tempting to write this as

$$\mathbf{m}_L^e = \mu_{\text{B}} g_L^e \mathbf{L}, \quad (7)$$

with $g_L^e = -1$ for the g factor of the unperturbed (classical) orbiting electron. In order to meet the precision achievable in high resolution experiments, relativistic corrections [10], nuclear motion corrections [11] and non-adiabatic corrections must be applied, which cause $|g_L^e|$ to deviate from unity in the effective Hamiltonian of an atomic or molecular paramagnetic species. Many authors prefer, therefore, to use an orbital g factor instead of writing the operator in the form of equation (6). Note that equation (6) is the basic operator which also gives rise to the electronic contribution of \mathbf{m}^{rot} and which appears as an additive Van Vleck perturbation term in the tensor components g_{ij}^{rot} which is always negative in the electronic ground state [5]. It seems appropriate to ascribe the same sign to g_L^e because the two phenomena, electronic molecular rotational and

orbital magnetism, are both caused by circulating negative charges (a similar remark applies to m_z^{vib} , equation (4)).

The situation with the electron spin magnetic moment is at first sight more difficult since the particle can be considered point-like, without spatial extension [12]. Thus, the classical picture of a spinning charged sphere does not apply. However, Dirac has shown that the relativistic version of the Schrödinger equation gives a half-odd spin angular momentum component S_z , and a magnetic moment [2]

$$\mathbf{m}_S^e = -\frac{e\hbar}{m_e} \mathbf{S}, \quad (8)$$

which shows that the spin magnetic moment points *anti-parallel* to the spin. This again can be written

$$\mathbf{m}_S^e = \mu_{\text{B}} g_S^e \mathbf{S}, \quad (9)$$

where $g_S^e = -2$. Later it was found that quantum electrodynamic corrections have to be applied [13, 14], and that small amounts of directional dependence must be taken into account in a molecule [15], but this does not affect our considerations (g_S^e of a bound electron needs also, in principle, a relativistic correction, and the radiative corrections might differ from those of the free electron). The various small corrections to g_L^e (equation (7)) and g_S^e (equation (9)) frequently have been discussed in the literature in terms of effective Zeeman Hamiltonians. For example, extensive calculations have been carried out in atomic and molecular open-shell systems in [16] and [17].

Summarizing this part, we see that, if we follow the line that the sign of a g factor should determine the direction of its associated magnetic moment, we end up with negative electronic g factors for both the orbital and spin magnetism of the electron. Landé [1] introduced a formula for the g factor of a many-electron atom in the adiabatic approximation which usually yields positive values. This formula was developed before studies of molecular Zeeman effects. If one wishes to keep consistency between atomic and molecular studies, the signs of Landé g factors would need to be reversed.

3. Discussion

It is perhaps helpful to put the proposals in equations (7) and (9) into historical perspective and to review usage in the literature. The basic form of equation (6), as obtained from electrodynamic theory, is

$$\mathbf{m}_L^e = -\left(\frac{e\hbar}{2m_e}\right) \mathbf{L}. \quad (10)$$

The important characteristic of this relation in the present discussion is that the magnetic dipole moment

is oriented in the opposite direction to the angular momentum because the motion involved is that of a negatively charged particle. Three different approaches to the implementation of this property have been used in the literature.

(i) *Negative Bohr magneton*

Here the Bohr magneton is defined to be negative, reflecting the negative charge $-e$ on the electron:

$$\mu_B' = -\frac{e\hbar}{2m_e}$$

This approach is used by Messiah [18] and by Cohen-Tanoudji *et al.* [19] in their texts on quantum mechanics. However, it does not conform to the IUPAC [6] and IUPAP [20] definition of the Bohr magneton, and is not widely used.

(ii) *Positive electronic g factor*

In this approach, equation (7) is rewritten as

$$\mathbf{m}_L^e = -\mu_B g_L^e \mathbf{L}$$

with g_L^e now equal to $+1$. There is a similar equation corresponding to equation (9) with g_S^e written as $+2$. This has been used widely by atomic physicists [21–23] and by workers in the field of open-shell molecules, where the electronic contribution to the magnetic moment dominates the smaller nuclear contributions (see, e.g. [24–26]). This convention is appealing in the following respect. It attempts to define all g factors as positive by the introduction of an explicit positive or negative sign in the relationship between the magnetic dipole moment and the associated angular momentum, depending on whether the particle which generates the magnetic field carries a positive or negative charge (see equation (5) for a proton and equation (10) for an electron). Its weakness is that it is not possible to apply it consistently in all situations. There are, for example, many nuclei which have negative g factors [6] despite carrying a positive charge. In addition, it gives no indication of the sign of the g factor of a neutral particle such as the neutron.

(iii) *Negative electronic g factors*

This is the convention given above in equations (7) and (9). This approach has also been used before, for example by Townes and Schawlow [27], Frauenfelder and Henley [28] and Sard [29], and has also recently been endorsed by the Committee on Data for Science and Technology (CODATA) [30]. It has the merit of being consistent with the accepted description of nuclear and rovibrationally induced magnetic moments, and gives the orientation of the magnetic moment relative to its associated angular momentum directly.

It is now becoming commonplace to measure magnetic effects in molecules where there are several different contributions to the experimental magnetic dipole moment; these are incorporated in an effective Hamiltonian. For example, laser resonance studies have recently been carried out (in zero field) on a helium atom in which one electron was replaced by an antiproton, $\bar{p}^4\text{He}^+$ [31]. It might soon be possible for similar exotic molecular systems to be formed containing a positron. In this situation, it is desirable to establish a universal convention for the sign of a magnetic dipole moment relative to its associated angular momentum.

It has already been mentioned in the introduction that magnetic resonance results often do not depend on the orientations of the relevant magnetic moments. Workers in such fields will not see the need for a general g factor convention. However, there are a number of situations where the sign is indeed observable. One such example is the hyperfine interaction in an atom which, in a spherically averaged environment, is proportional to the term $\mu_B g_S^e \mu_N g^{\text{nuc}} |\psi_A(0)|^2$. The product of the electron (g_S^e) and the nuclear (g^{nuc}) g factors determines the sign of the hyperfine interaction. Moreover, in a multi-electron system and in particular in molecules the expectation value of the wavefunction at the nuclear site, $|\psi_A(0)|^2$, is replaced by the spin density which may be either positive or negative depending on the electronic state. It is of considerable importance for an understanding of the electronic state to determine the sign of the spin density. A common consensus of the sign of the g factors would immediately give a clue about the sign of the spin density without any theory. The sign of the hyperfine interaction can be determined experimentally from NMR Knight shifts in metals [32] or from triple ENDOR measurements [33] in organic radicals or other paramagnetic materials.

4. Conclusion

In conclusion, any of the three possible conventions given above can be used to describe Zeeman effects in atoms and molecules correctly. They need only to be used consistently within a given piece of work in which the convention followed is made explicit so that others can correctly use the results. In the present communication, we wish to point out that approach (iii), in which the sign of the g factor depends on the relative orientation of the magnetic dipole moment and the angular momentum which produces it, has the merits of consistency and simplicity.

Finally, we wish to add that in any application in which the results are sensitive to the sign of g factors it is imperative that the convention followed should be

made clear and explicit, whether or not the one proposed here is adopted.

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