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SYMBOLS FOR FINE AND HYPERFINE STRUCTURE PARAMETERS

(IUPAC Recommendations 1994)

Prepared for publication by

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Symbols for fine and hyperfine structure parameters (IUPAC Recommendations 1994)

Abstract - The symbols for fine and hyperfine structure parameters are standardized in order to eliminate confusion and misunderstanding caused by various uses of expressions for these parameters. Only those parameters for which the symbols are quite well established and widely accepted are considered. Because the parameters appear with the associated operators in the Hamiltonian, the symbols are listed with the operators. Although much of the discussion is appropriate for molecules in the gas phase only, reference is also made to the symbols used in electron spin or electron paramagnetic resonance spectroscopy in the condensed phase, where possible. Two types of molecules are considered separately: linear and nonlinear molecules. The parameters listed include the spin-orbit interaction, the spin-rotation coupling, the spin-spin coupling, the Λ-type doubling, the electron orbital/nuclear spin coupling, the Fermi contact interaction, the electron spin/nuclear spin dipole-dipole coupling, the nuclear electric quadrupole coupling, and the nuclear spin-rotation coupling parameters and also their centrifugal correction terms, wherever appropriate.

Molecules with unquenched electron orbital and/or electron spin angular momenta give spectra which, when observed with high resolution, are split into fine and hyperfine structure components. The splittings may be expressed in terms of parameters which are referred to as fine and hyperfine structure parameters. The coupling between the electronic, nuclear spin, and vibrational and rotational angular momenta is quite complicated enough in many cases, but the situation can be further confused by the use of different nomenclature and even definition of the coupling parameters from one research group to another. The present note aims at standardizing the symbols for the coupling parameters to eliminate confusion and misunderstanding caused by these various uses. Only those parameters for which the symbols are quite well established and widely accepted are considered. In some cases we need to discriminate between slightly different variants of the same parameter, for example for different vibrational states, but such higher-order contributions are disregarded in the present note. Experimentally the coupling parameters are determined as the coefficients of operators which correspond to physical quantities, i.e. the observed spectra are analyzed by the least-square method using a Hamiltonian which consists of such operators with their coefficients as parameters. The present note lists the symbols of coupling constants together with the associated operators. Although much of the discussion is appropriate for molecules in the gas phase only, reference is also made to the symbols used in electron spin (or electron paramagnetic) resonance spectroscopy in condensed phases, where possible. Two types of molecules are considered separately: linear and nonlinear molecules.

The notation of physical quantities involved is as follows:

- $\boldsymbol{L}$ electron orbital angular momentum
- $\boldsymbol{S}$ electron spin angular momentum
- $\boldsymbol{J}$ total angular momentum apart from the nuclear spin angular momentum
- $\boldsymbol{N}$ rotational angular momentum including $\boldsymbol{L}$
- $\boldsymbol{R}$ rotational angular momentum
- $\boldsymbol{I}$ nuclear spin angular momentum

$$\boldsymbol{N} = \boldsymbol{R} + \boldsymbol{L}, \quad \boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}$$

- ϕ azimuthal angle for the unpaired electron (applicable to a linear molecule)

The components of the angular momentum on the molecule-fixed axes are expressed as either J_x, J_y, J_z or J_a, J_b, and so on, and the ladder operators are defined as $J_\pm = J_x \pm iJ_y$, z being reserved for the molecular axis in the case of a linear molecule.

The anticommutator of two operators A and B is defined as

$$[A,B]_+ = AB + BA.$$

1. FINE STRUCTURE CONSTANTS

(i) Spin–orbit interaction constant

A, A_{SO} operator $\boldsymbol{L}\cdot\boldsymbol{S}$

Comment 1: It is rare to use a tensorial form.

Comment 2: A may be used for linear molecules, but for nonlinear molecules A_{SO} must be used to avoid confusion with the A rotational constant.

The centrifugal correction term

A_D operator $(1/2)[(\boldsymbol{J}-\boldsymbol{S})^2,\boldsymbol{L}\cdot\boldsymbol{S}]_+$

Comment: A_J is also used but it is defined as $A_J = A_D/2$ in some cases and as $A_J = A_D$ in others, and thus A_D is the recommended parameter.

(ii) Spin–rotation coupling constants

a) linear molecule

γ operator $(\boldsymbol{J}-\boldsymbol{S})\cdot\boldsymbol{S}$

The centrifugal correction term

γ_D operator $(1/2)[(\boldsymbol{J}-\boldsymbol{S})\cdot\boldsymbol{S},\boldsymbol{N}^2]_+$

b) nonlinear molecule

$\epsilon_{\alpha\beta}$ operator $(1/2)[N_\alpha,S_\beta]_+$

($\alpha,\beta = a, b, c$: principal axes of inertia)

(iii) Spin–spin coupling constants

a) linear molecule

λ operator $(2/3)(3S_z^2-\boldsymbol{S}^2)$

(z: molecular axis)

Comment: The symbol ϵ is sometimes used as the coefficient of $(3S_z^2-\boldsymbol{S}^2)$, i.e., $\epsilon = (2/3)\lambda$. Because of confusion with the spin-rotation parameter, λ is to be preferred.

The centrifugal correction term

λ_D operator $(1/2)[(2/3)(3S_z^2-\boldsymbol{S}^2),\boldsymbol{N}^2]_+$

b) nonlinear molecule

diagonal term α operator $3S_z^2-S^2$

off-diagonal term β operator $S_x^2-S_y^2$

(z, x, y: inertial axes of the molecule)

Comment: For molecules of symmetry lower than orthorhombic, some or all of the following off-diagonal terms are added [see J. H. Van Vleck, *Rev. Mod. Phys.* **23**, 213-227 (1951)]:

γ operator $[S_x,S_y]_+$

δ operator $[S_z,S_x]_+$

ϵ operator $[S_y,S_z]_+$

For a gas-phase study, the axes x, y, z refer to the principal axes of inertia.

c) condensed phase

diagonal term D operator $S_z^2-(1/3)S^2$

off-diagonal term E operator $S_x^2-S_y^2$

(z, x, y: principal axes of the coupling tensor)

$\lambda = (1/2)D$ and $\beta = E$

(iv) Λ-type doubling constants for linear molecules with a non-zero electron orbital angular momentum component along the molecular axis, $\Lambda \neq 0$

$\Lambda = 1$, Π state

o operator $(S_x^2-S_y^2)$ or $(1/2)(S_+^2e^{-2i\phi}+S_-^2e^{+2i\phi})$

p operator $-(N_xS_x-N_yS_y)$ or $-(1/2)(N_+S_+e^{-2i\phi}+N_-S_-e^{+2i\phi})$

q operator $(N_x^2-N_y^2)$ or $(1/2)(N_+^2e^{-2i\phi}+N_-^2e^{+2i\phi})$

Comment 1: The terms in $e^{\pm 2i\phi}$ force the matrix elements to link states with $\Lambda = +1$ and $\Lambda = -1$. The recommended phase convention is $<\Lambda = \pm 1|e^{\pm 2i\phi}|\Lambda = \mp 1> = +1$.

Comment 2: $\bar{p} = p + 2q$ and q, rather than p and q, are determined directly from most observed spectra.

Comment 3: For a $\Lambda = 2$, Δ state, see J. M. Brown, A. S.-C. Cheung, and A. J. Merer, *J. Mol. Spectrosc.*, **124**, 464-475 (1987).

The centrifugal correction terms for p and q

p_D and q_D operator $(1/2)[Op, \boldsymbol{N}^2]_+$

(Op denotes the operators for the p and q terms.)

2. HYPERFINE STRUCTURE PARAMETERS

(i) Electron orbital/nuclear spin coupling constant in a linear molecule

a operator $\boldsymbol{I}\cdot\boldsymbol{L}$

(ii) Fermi contact interaction constant

a) linear molecule

b_F, b_η operator $\boldsymbol{I}\cdot\boldsymbol{S}$

Comment: Both b_F and b_η are used, but b_F is recommended. The parameter b defined by $b_F - c/3$ is often reported because it is the quantity determined by the observed splittings.

b) nonlinear molecule

a_F, $(0)_I$ operator $\boldsymbol{I}\cdot\boldsymbol{S}$

Comment: Both symbols are used.

c) condensed phase

a, A_f operator $\boldsymbol{I}\cdot\boldsymbol{S}$

Comment: Both symbols are used.

(iii) Electron spin/nuclear spin dipole–dipole coupling constants

$\boldsymbol{T}$ (tensor) appears as $\boldsymbol{S}\cdot\boldsymbol{T}\cdot\boldsymbol{I}$ in the Hamiltonian

a) linear molecule

diagonal term $c\ [= (2/2)T_{zz}]$ operator $(1/3)(3I_zS_z - \boldsymbol{I}\cdot\boldsymbol{S})$

(z: molecular axis)

Comment: Some authors use $t = (1/3)c$ as the parameter, but c is preferred.

off-diagonal term $d\ [= -(1/2)(T_{xx} - T_{yy})]$ operator $-(S_xI_x - S_yI_y)$

or $-(1/2)(S_+I_+e^{-2i\phi} + S_-I_-e^{+2i\phi})$

(x, y: two axes perpendicular to the molecular axis)

b) nonlinear molecule

$T_{\alpha\beta}$ operator $(1/2)[S_\alpha, I_\beta]_+$

(α, β are usually the inertial axes of the molecule)

c) condensed phase

$T_{\alpha\beta}$, $T_{\alpha\beta}'$, A_d operator $(1/2)[S_\alpha, I_\beta]_+$

(α, β: any convenient molecule-fixed axes)

Comment: All of these symbols are employed.

(iv) Nuclear electric quadruple coupling constants

a) linear molecule

diagonal term eQq_0 operator $[1/4I(2I-1)](3I_z^2-I^2)$

off-diagonal term eQq_2 ($\Lambda = 1$, Π) operator $[1/4I(2I-1)](I_x^2-I_y^2)$

or $[1/8I(2I-1)](I_+^2e^{-2i\phi}+I_-^2e^{+2i\phi})$

(z: molecular axis; x, y: any two axes perpendicular to z)

(I denotes the nuclear spin quantum number)

Comment: It is important to realize that, with the definition for the electric quadrupole recommended here, q_0 for example is the *negative* of the electric field gradient along the z axis. This point is not always appreciated and suggests that it would be more logical to change the sign of the operator terms given above. However, the convention endorsed here is firmly established (see, for example, C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York, 1955, Chapters 6 and 9); to change it at this stage would lead to considerable confusion. Some workers also use e^2Qq_0 and e^2Qq_2 for the parameters rather than eQq_0 and eQq_2. In this case, the electric field gradient is $-eq_0$ and so on.

b) nonlinear molecule

$eQq_{\alpha\beta}$, $\chi_{\alpha\beta}$ operator $[1/2I(2I-1)][I_\alpha,I_\beta]_+$

(α, β: inertial axes of the molecule)

Comment: Some workers use $(\alpha\beta)_Q$ as the coefficient of $I_\alpha I_\beta$. This parameter therefore equals $eQq_{\alpha\beta}/[2I(2I-1)]$.

(v) Nuclear spin-rotation coupling constants

a) linear molecule

diagonal term C_I operator $\boldsymbol{I}\cdot\boldsymbol{J}$

off-diagonal term C_I' operator $-(I_xJ_x-I_yJ_y)$

or $-(1/2)(I_+J_+e^{-2i\phi}+I_-J_-e^{+2i\phi})$

(x, y: two axes perpendicular to the molecular axis)

b) nonlinear molecule

$C_{\alpha\beta}$ operator $(1/2)[N_\alpha,I_\beta]_+$

(α, β: inertial axes of the molecule)

(vi) Nuclear spin/nuclear spin dipole–dipole coupling constants

(The notation has not been well established.)