

BULLETIN OF THE POLISH ACADEMY OF SCIENCES TECHNICAL SCIENCES, Vol. 71(1), 2023, Article number: e144575 DOI: 10.24425/bpasts.2022.144575

Quantum magnetostriction effect resulting from the asymmetric structure of matter measured with EPR spectrometer

Marek SIKON¹⁰* and Ewa BIDZINSKA²

¹ Cracow University of Technology, Kraków, Poland ² Jagiellonian University, Kraków, Poland

Abstract. This paper explains the rotation and displacement as well as the couple and force stress in material with unpaired electrons/nucleons subjected to a magnetic field. This phenomenon is described in terms of quantum mechanics for nanoparticle and quantum statistical mechanics for loose nanomaterial. Quantitative calculations are carried out based on experimental data collected under the magnetic field of an EPR spectrometer from a set of nanocrystallites of hydrated copper sulfate.

Key words: atomic arm of action; non-paired electron/nucleon; polar rotation; Cosserat mechanics; EPR.

1. INTRODUCTION

The formation of asymmetric matter is favored by nature at the stage of filling electron/nucleon shells, when the most energetically favorable number of unpaired electrons/nucleons is as large as possible (the Hund rule) [1]. However, the common occurrence of symmetrization in nature (electronic, for the formation of chemical compounds, and nucleonic, for the formation of elements) removes the asymmetry. A magnetostriction [2, 3] is created in the case of incomplete symmetrization. Mechanically, incomplete symmetrization results in the polar continuum [4]. The asymmetric matter is revealed by the angular momentum of the atom. This state comes from both spinons, which are carriers of electron/nucleon spin, and orbitons, which are associated with the orbital motion of the electron/nucleon.

2. ASYMMETRIC ATOM IN MAGNETIC FIELD

2.1. Classical description

The interaction between an external magnetic field $B(B_x, B_y, B_z)$ and an asymmetric atom k (shown in Fig. 1) generates a mechanical moment:

$$\boldsymbol{M}_{\mathbf{k}} = -\gamma_{J} \boldsymbol{J}_{\mathbf{k}} \times \boldsymbol{B},\tag{1}$$

where γ_J is the magneto-mechanical ratio, and J_k is the angular momentum of the atom k (Fig. 1).

The Fig.1 shows formation of the moment M_k , force P_k and polar rotation φ_k in a magnetic field $B(B_x, B_y, B_z)$ for an atom



Fig. 1. Asymmetric atom in a magnetic field

k containing one electron e_k and one proton p_k . C_k is the center of mass of the atom k.

We define the arm of action ρ_k of an asymmetrical atom k as:

$$\boldsymbol{\rho}_{\mathbf{k}} = \boldsymbol{\rho}_o \boldsymbol{I}^2, \qquad (2)$$

where ρ_o is the reduced Bohr radius of the atom k, and I is the principal quantum number. Based on equations (1) and (2), we can write the action force $P_k(B)$ of the moment $M_k(B)$ in the form, APPENDIX I:

$$P_{\rm k} = -\frac{\gamma_J}{\rho_{\rm k}} J_{\rm k} B, \qquad (3)$$

where P_k , J_k and B are modules of the vectors P_k , J_k , B.

The moment $M_k(B)$ induces additional motion of the atom in the form of precession, as shown in Fig. 1, and the force $P_k(B)$ displaces the atom. We define the polar rotation of an atom *k* under the action of a magnetic field *B* as the precession angle $\varphi_k \stackrel{\text{df}}{=} \triangleleft (J_k, B)$.

^{*}e-mail: sikon@autograf.pl

Manuscript submitted 2022-05-08, revised 2022-09-16, initially accepted for publication 2022-12-30, published in February 2023.



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The energy of an atom k in a magnetic field B can be expressed as:

$$U_{\mathbf{k}} = \gamma_J \boldsymbol{J}_{\mathbf{k}} \cdot \boldsymbol{B}. \tag{4}$$

The precession angle $\boldsymbol{\varphi}_k$ can be also shown to have components:

$$\varphi_{k}^{(i)} = \arccos \frac{J_{k}^{(i)}}{J_{k}}, \qquad (5)$$

where (i) = (x), (y), (z) is the selected component of the polar rotation vector $\boldsymbol{\varphi}_k \left(\boldsymbol{\varphi}_k^{(i)} \right)$ and the angular momentum vector $\boldsymbol{J}_k \left(J_k^{(i)} \right)$ of the atom *k*, in relation to the axes of the Cartesian coordinate system (x, y, z), Fig. 1.

2.2. Quantum description

Taking into account the solutions of quantum mechanics, where the quantum angular "vector" does not have a direction in the sense of classical mechanics, and only one of the angular momentum projections $J_k^{(i)}$ has values that are simultaneously defined with the square of the angular momentum J_k^2 , we can rewrite the classical equation (5) as an operator in the form:

$$\hat{\cos \varphi_k^{(i)}} = \frac{\hat{J}_k^{(i)}}{J_k},\tag{6}$$

where $\hat{J}_{k}^{(i)}$ is the operator of $J_{k}^{(i)}$. Similarly, we can write the operators:

$$\hat{\boldsymbol{M}}_{\mathbf{k}}^{(i)} = \frac{\boldsymbol{g}_{\mathbf{k}}^{(i)} \boldsymbol{\mu}_{\mathbf{B}}}{\hbar} \boldsymbol{\Omega}_{\mathbf{k}}^{(i)} \hat{J}_{\mathbf{k}}^{(i)}, \qquad (7)$$

$$\hat{\boldsymbol{P}}_{k}^{(i)} = \frac{g_{k}^{(i)} \mu_{\mathrm{B}} \boldsymbol{\Omega}_{k}^{(i)}}{\hbar \rho_{k}} \hat{J}_{k}^{(i)}, \qquad (8)$$

$$\hat{U}_{k}^{(i)} = -\frac{g_{k}^{(i)}\mu_{B}}{\hbar}B_{(i)}\hat{J}_{k}^{(i)},$$
(9)

where $g_k^{(i)} \mu_B / \hbar = \gamma_J$, $g_k^{(i)}$ is the so-called g-ratio, μ_B is the reduced Bohr magneton, $\mathbf{\Omega}_k^{(i)} = \mathbf{j}\mathbf{B}_k - \mathbf{k}\mathbf{B}_j$, $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are unit vectors parallel to the *x*, *y* and *z* directions, *i*, *j*, *k* change cyclically.

We can formulate operator equations for the parameters of Cosserat magnetostriction on the atomic scale in the form:

$$\frac{\hat{J}_{k}^{(i)}}{J_{k}}\Phi = \cos\varphi_{k}^{(i)}\Phi, \qquad (10)$$

$$\frac{g_k^{(i)}\mu_{\rm B}}{\hbar}\Omega_k^{(i)}\hat{J}_k^{(i)}\Phi = M_k^{(i)}\Phi, \qquad (11)$$

$$\frac{g_k^{(i)}\mu_{\rm B}}{\hbar\rho_k}\Omega_k^{(i)}\hat{J}_k^{(i)}\Phi = P_k^{(i)}\Phi, \qquad (12)$$

$$-\frac{g_{k}^{(i)}\mu_{\rm B}}{\hbar}B_{(i)}\hat{J}_{k}^{(i)}\Phi = U_{k}^{(i)}\Phi, \qquad (13)$$

where Φ is the wave function, and $\cos(\hat{p}_{k}^{(i)}, M_{k}^{(i)}, P_{k}^{(i)}, U_{k}^{(i)})$ are the eigenvalues of the operators $\cos(\hat{p}_{k}^{(i)}, \hat{M}_{k}^{(i)}, \hat{P}_{k}^{(i)})$, and $\hat{U}_{k}^{(i)}$ respectively, $\Omega_{k}^{(i)}$ is modules of the vector $\Omega_{k}^{(i)}$. We can write the operator $\hat{J}_{k}^{(i)}$, APPENDIX II, for the direction (*i*) as:

$$\hat{J}_{k}^{\uparrow\downarrow} = \hbar \begin{pmatrix} \dots, J-1, J & 0\\ 0 & -J, -J+1, \dots \end{pmatrix}, \quad (14)$$

where J = l + l is the quantum number of the resultant angular momentum of atom k, l is the orbital quantum number, and lis the spin quantum number. We write the wave function Φ in the form:

$$\Phi = \begin{cases} \Phi^{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, & \text{for } m = \dots, J - 1, J, \\ \Phi^{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, & \text{for } m = -J, -J + 1, \dots, \end{cases}$$
(15)

where m is the magnetic quantum number and takes the values:

$$M = -J, -J+1, \dots, J-1, J.$$
 (16)

By solving equations (10)–(13), we can write a whole spectrum of solutions depending on the magnetic quantum number II as:

$$\cos \varphi_k^{(i)} = \frac{1}{\sqrt{J(J+1)}} \, \mathbb{I}, \tag{17}$$

$$\mathbf{M}_{\mathbf{k}}^{(i)} = g_{\mathbf{k}}^{(i)} \boldsymbol{\mu}_{\mathbf{B}} \boldsymbol{\Omega}_{\mathbf{k}}^{(i)} \boldsymbol{I} , \qquad (18)$$

$$\mathbf{P}_{k}^{(i)} = \frac{g_{k}^{(i)}\,\boldsymbol{\mu}_{B}}{\boldsymbol{\rho}_{k}}\,\boldsymbol{\Omega}_{k}^{(i)}\,\boldsymbol{m}\,,\tag{19}$$

$$\mathbf{U}_{\mathbf{k}}^{(i)} = -g_{\mathbf{k}}^{(i)} \mu_{\mathbf{B}} B^{(i)} \mathbf{I} , \qquad (20)$$

where formula $J_k = \hbar \sqrt{J(J+1)}$ is related to equation (17).

3. STATISTICAL DESCRIPTION

We consider a probabilistic space in a Cosserat material in the form of an elementary surface $\Delta F^{(i)}$ (analogous to the Saint-Venant infinitesimal interaction area), which is connected with a material exposed to a magnetic field $B_{(i)}$, as shown in Fig. 2. In the analysis we take into account the asymmetric atoms $k^{(i)} = 1, 2, 3, ..., \Delta N^{(i)}$ filling the surface $\Delta F^{(i)}$. The surface $\Delta F^{(i)}$ is small enough that the action of the magnetic field $B_{(i)}$ is almost constant, but large enough for the set of asymmetric atoms $k^{(i)} = 1, 2, 3, ..., \Delta N^{(i)}$ to be subjected to statistical analysis.



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Fig. 2. Definition of the magneto-mechanical state of the Cosserat magnetostriction

We can write the canonical distribution for the asymmetric atoms $k^{(i)} = 1, 2, 3, ..., \Delta N^{(i)}$:

$$\chi^{(i)} = 1, 2, 3, \dots, \Delta N^{(i)} \exp\left[-\frac{U_{k}^{(i)}(m)}{kT}\right] \\ \prod(m) = \frac{m=J}{\sum_{m=-J}^{m=J} \exp\left[-\frac{U_{k}^{(i)}(m)}{kT}\right]}, \quad (21)$$

where k is the Boltzmann constant and T is the absolute temperature.

Based on the above, we can write the average values of the random variables of the atoms $k^{(i)} = 1, 2, 3, ..., \Delta N^{(i)}$ on the elementary surface $\Delta F^{(i)}$ as:

$$\left\langle \text{COS} \varphi_{\mathbf{k}}^{(i)} \right\rangle = \sum_{m=-J}^{m=J} \text{COS} \varphi_{\mathbf{k}}^{(i)} \Pi,$$
 (22)

$$\left\langle M_{k}^{(i)} \right\rangle = \sum_{m=-J}^{m=J} M_{k}^{(i)} \Pi,$$
 (23)

$$\left\langle P_{\mathbf{k}}^{(i)} \right\rangle = \sum_{m=-J}^{m=J} P_{\mathbf{k}}^{(i)} \Pi,$$
 (24)

$$\left\langle U_{\mathbf{k}}^{(i)}\right\rangle = \sum_{m=-J}^{m=J} U_{\mathbf{k}}^{(i)} \Pi, \qquad (25)$$

Components of the couple stress $\mathbf{m}^{(i)}$, force stress $\mathbf{p}^{(i)}$ and polar rotation $\boldsymbol{\varphi}^{(i)}$, related to a surface element $\Delta F^{(i)}$, (i) = x, y, z. We introduce the concentration coefficients:

$$N_F^{(i)} = \lim_{\Delta F^{(i)} \to 0} \frac{\Delta N_F^{(i)}}{\Delta F^{(i)}} = \frac{dN_F^{(i)}}{dF^{(i)}}, \qquad (26)$$

and finally, obtain:

$$\cos \varphi^{(i)} = \frac{J}{\sqrt{J(J+1)}} \mathbf{B}_{\mathrm{Br}},\tag{27}$$

$$\mathbf{m}^{(i)} = \mathbf{N}_F^{(i)} g^{(i)} \mu_B J \mathbf{\Omega}^{(i)} \mathbf{B}_{Br},$$
(28)

$$\mathbf{p}^{(i)} = \mathbf{N}_F^{(i)} \frac{g^{(i)} \mu_{\mathrm{B}} J}{\rho} \mathbf{\Omega}^{(i)} \mathbf{B}_{\mathrm{Br}}, \tag{29}$$

$$\mathbf{u}^{(i)} = \mathbf{N}_F^{(i)} g^{(i)} \mu_{\rm B} / B_{(i)} \mathbf{B}_{\rm Br},$$
(30)

where:

$$B_{Br} = \left[\frac{2J+1}{2J} \operatorname{ctgh}\left(\frac{2J+1}{2}\frac{g^{(i)}\mu_{B}B_{(i)}}{kT}\right) -\frac{1}{2J}\operatorname{ctgh}\left(\frac{1}{2}\frac{g^{(i)}\mu_{B}B_{(i)}}{kT}\right)\right], \quad (31)$$

is the Brillouin function. At room temperature, when:

$$\frac{g^{(i)}\mu_{\rm B}B_{(i)}}{\mathsf{k}T} \ll 1,\tag{32}$$

we can write the hyperbolic cotangent in equation (31) in the form of a power series. Using only the first two terms, we write:

$$\varphi^{(i)} = \arccos \frac{g^{(i)} \mu_{\rm B} \sqrt{J(J+1)}}{3kT} B_{(i)}, \qquad (33)$$

$$\mathbf{n}^{(i)} = \mathbf{N}_F^{(i)} \, \Omega^{(i)} \left(g^{(i)} \right)^2 \frac{\mu_{\mathbf{B}}^2 J(J+1)}{3 \mathbf{k} T} \, \boldsymbol{B}_{(i)}, \tag{34}$$

$$\mathbf{p}^{(i)} = \mathbf{N}_{F}^{(i)} \mathbf{\Omega}^{(i)} \left(g^{(i)} \right)^{2} \frac{\mu_{\mathrm{B}}^{2} J (J+1)}{3 \rho \mathsf{k} T} \mathbf{B}_{(i)}, \tag{35}$$

$$\mathbf{u}^{(i)} = \mathbf{N}_F^{(i)} \left(g^{(i)} \right)^2 \frac{\mu_{\rm B}^2 J (J+1)}{3 \mathbf{k} T} B_{(i)}^2.$$
(36)

4. EXPERIMENTAL STUDY

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In the first stage, our experimental analysis was limited to the electron level, $\rho_k \approx \rho_k^e = \overline{e_k C_k}$, Fig. 1. The sample tested was a powder of mass 0.005 g, which was obtained from a hydrated copper sulfate crystal, CuSO₄ · 5H₂O, by grinding in a mortar. This material contained asymmetric copper ions Cu²⁺ with an unpaired electron in the configuration 3d⁹. The sample was subjected to the magnetic field:

$$\boldsymbol{B}_{\text{EPR}}^{(i)} = B_I (i \cos \omega t - k \sin \omega t) + B_o \boldsymbol{j}, \qquad (37)$$

of an EPR spectrometer as shown in Fig. 3, where B_I is a variable magnetic field rotating in a vertical plane with angular velocity $\boldsymbol{\omega}$, B_o is a constant magnetic field operating in the horizontal direction, and t is time.

Measurements were carried out for two sample positions: the first when the magnetic induction B_o was parallel to the y axis (i) = (y), and the second after rotating the sample around the z axis by 90°, when B_o was parallel to the x axes, (i) = (x), (Fig. 3).

The magneto-mechanical parameters were determined for the magnetic field $\boldsymbol{B}_{\text{EPR}}$ acting on the sample under resonance conditions: $\hbar \omega^{(i)} = g^{(i)} \mu_{\text{B}} B_o^{(i)}$.





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Fig. 3. Nanoparticle in the magnetic field of the EPR spectrometer

EPR measurements were carried out at the Chemistry Department of the Jagiellonian University, using an X-band (9.2 GHz) Bruker ELEXSYS 500 (Karlsruhe) with 100 kHz field modulation. Spectra were recorded at 293 K with a modulation amplitude of 5 mT, a microwave power of 10 mW and a receiver gain of 30. The EPR parameters were determined by simulation, using the software program EPR Sim 32.

5. RESULTS

The results are shown in Fig. 4 as the first derivative of the absorption curve. The spectra for (i) = (x), (y) are almost the same. Tables 1 and 2 show the results of quantitative measurements. The arm of action of the Cu²⁺ ion was taken as





 $\rho = \rho_{Cu^{2+}}^e = 0.73 \cdot 10^{-10}$ $\rho = \rho_{Cu^{2+}}^e = 0.73 \cdot 10^{-10}$ m (Period

 $\rho = \rho_{Cu^{2+}}^e = 0.73 \cdot 10^{-10}$ m (Periodic Table of Elements). The amount of Cu²⁺ measured in the volume of the sample by the comparative method (EPR Sim 32 program) was converted into a unit area, $N_F^{(i)}$.

6. DISCUSSION AND CONCLUSION

Disturbance of symmetry of the atom, where the center of mass and center of action of the Coulomb forces do not coincide, creates an arm of action, which together with the angular momentum of the atom generates the torque, couple stress and rotation of the material in a magnetic field. This gives rise to displacement, force, and force stress. Also in [5] it is noticed that the basic variable of magnetostriction is not the elastic strain tensor. The authors of [5] associate local rotation with positiondependent magnetization.

Based on quantum statistical mechanics and experimental results, it was found that magnetic induction $B_o = 0.328(4)$ T using an EPR spectrometer at a temperature of 293 K generates a rotation in loose nanomaterial of hydrated copper sulfate of $|\Delta \phi| = |\phi - \phi_o| \approx 5'2(8)''$, with couple stress of $1.12(2) \times 10^{-7} \frac{\text{Nm}}{\text{m}^2}$ and force stress of $1537.16(4) \frac{\text{N}}{\text{m}^2}$. The magnetostriction energy per unit volume of material was calculated as $u_V = 179.73(1) \frac{\text{J}}{\text{m}^3}$.

The asymmetric structure of the atom was not taken into account in initial studies of atomic interactions with the use of quantum mechanics (Schrödinger, Feynman, etc.) [2], and has not been considered in contemporary attempts to represent mechanical stress through the application of quantum mechanics (Kugler, Nielsen, Martin, Gosfrey, Folland, Rogers, Rappe, etc.) [6].

The quantum-classical model of the polar continuum is proposed, as one of the first, in work [7]. The enclose numerical example demonstrates the possible applicability of the theory.

 Table 1

 Results of EPR measurements

<i>(i)</i>	$\mathrm{N}_{F}^{(i)}=rac{\mathrm{amount\ of\ Cu}^{2+}}{\mathrm{m}^{2}}$	<i>g</i> ^(<i>i</i>)	$B_o^{(i)}$ [T]	$\omega^{(i)}$ [Hz]
(<i>x</i>)	$2.57(8) imes 10^{18}$	2.143	0.328(4)	$61.88029(6) imes 10^9$
(y)	$2.58(9) imes 10^{18}$	2.143	0.328(4)	$61.88487(0) imes 10^9$

Table 2 Results of quantum statistical computing

(i)	$\left \left \frac{\Delta \varphi^{(i)}}{\varphi_o^{(i)}} \right = \left \frac{\Delta \arccos \frac{g^{(i)} \mu_{\rm B} \sqrt{J(J+1)} B^{(i)}}{3 \text{k} T}}{\varphi_o^{(i)}} \right $ [%e]	$\mathbf{m}^{(i)} = \mathbf{N}_{F}^{(i)} \frac{\mathbf{\Omega}^{(i)} \left(g^{(i)}\right)^{2} \mu_{\mathrm{B}}^{2} J(J+1) B^{(i)}}{3 \mathrm{k} T}$ $\begin{bmatrix} \mathbf{N} \mathbf{m} \\ \mathbf{m}^{2} \end{bmatrix}$	$\mathbf{p}^{(i)} = \mathbf{N}_{F}^{(i)} \frac{\mathbf{\Omega}^{(i)} \left(g^{(i)}\right)^{2} \mu_{\mathrm{B}}^{2} J(J+1) B^{(i)}}{3 \rho_{\mathrm{Cu}^{2+}} \mathbf{k} T} \\ \left[\frac{\mathbf{N}}{\mathbf{m}^{2}}\right]$
(<i>x</i>)	1.01(3)	$1.11(9) imes 10^{-7}$	1533.89(1)
(y)	1.01(3)	$1.12(5) imes 10^{-7}$	1540.43(6)



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$m_{\rm k}$

APPENDIX I. REFERENCE TO LORENTZ FORCE

We introduce the reduced mass m_k of the asymmetrical atom k and the velocity of this mass v_k into equation (3), and we write:

$$P_{\rm k} = \frac{g_{\rm k}\,\mu_{\rm B}}{\hbar}m_{\rm k}v_{\rm k}B. \tag{AI.1}$$

In general, we present the force P_k acting on the atom k in the magnetic field **B** in the form:

$$\boldsymbol{P}_{k} = \frac{g_{k}q}{2} \left(\boldsymbol{v}_{k} \times \boldsymbol{B} \right), \qquad (AI.2)$$

where *q* is an elementary charge. Based on the above we will write for an electron *e* when l = 0, J = J = 1/2:

$$\boldsymbol{P} = q\left(\boldsymbol{v}_e \times \boldsymbol{B}\right), \tag{AI.3}$$

which corresponds to the Lorentz force.

APPENDIX II. REFERENCE TO PAULI MATRIX

We can describe the angular momentum of an atom in a magnetic field with a magnetic quantum number m, equation (16).

Positive values of m:

$$\mathfrak{m}^{\uparrow} = \dots, J - 1, J, \qquad (AII.1)$$

refer to atoms with precession momentum J_k^{\uparrow} in the direction of the magnetic field **B**, whereas negative values of m:

$$\mathbf{I} = -J, -J+1, \dots, \qquad (AII.2)$$

refer to the opposite direction J_k^{\downarrow} . We introduce to the states \mathbb{M}^{\uparrow} , \mathbb{M}^{\downarrow} the wave functions:

$$\Phi^{\uparrow} = \begin{pmatrix} 1\\ 0 \end{pmatrix} \quad \text{for } \mathbb{I}^{\uparrow}, \qquad (\text{AII.3})$$

$$\Phi^{\downarrow} = \begin{pmatrix} 0\\ 1 \end{pmatrix} \quad \text{for } m^{\downarrow}. \tag{AII.4}$$

According to quantum formalism, the measured values of J_k^{\uparrow} , J_k^{\downarrow} correspond to the operators \hat{J}_k^{\uparrow} , \hat{J}_k^{\downarrow} . We expect operator equations for J_k^{\uparrow} and J_k^{\downarrow} , in the form:

$$\hat{J}_{k}^{\uparrow} \Phi^{\uparrow} = \hbar \mathbf{I} \Phi^{\uparrow}, \qquad (AII.5)$$

$$\hat{J}_{k}^{\downarrow} \Phi^{\downarrow} = \hbar m^{\downarrow} \Phi^{\downarrow}. \qquad (AII.6)$$

Based on equations (AII.3), (AII.4), (AII.5), and (AII.6), we can write the formula:

$$\hat{J}_{\mathbf{k}}^{\uparrow\downarrow} = \hbar \left(\begin{array}{cc} \mathbf{I} & \uparrow & \mathbf{0} \\ \mathbf{0} & \mathbf{I} & \downarrow \end{array} \right), \qquad (AII.7)$$

that defines the operator of quantum magnetostriction. When $l = 0, J = \delta = 1/2$, we get:

$$\hat{J}_{k}^{\uparrow\downarrow} = \hbar \, \mathscr{I} \left(egin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}
ight),$$
 (AII.8)

where expression:

 $\left(\begin{array}{cc} 1 & 0\\ 0 & -1 \end{array}\right), \tag{AII.9}$

refers to a Pauli matrix for the "up-down" direction.

APPENDIX III. REFERENCE TO JOULE'S MAGNETOSTRICTION

From equation (36), we can write the linear magnetostriction coefficient as:

$$C_l = \frac{N_F g^2 \mu_B^2 J(J+1)}{3E\rho \mathbf{k}T}, \qquad (AIII.1)$$

and Joule's magnetostriction can be written in the form:

$$\Delta l/l = C_l B^2, \qquad (AIII.2)$$

which corresponds to the current state of knowledge, where: E is Young's modulus, l is the linear dimension.

APPENDIX IV. REFERENCE TO THE PRINCIPLE OF CORRESPONDENCE

Using classical mechanics, the direction of angular momentum J_k for an atom k is unknown, and hence the rotation $\varphi_k \stackrel{df}{=} (J_k, B)$ of an atom k in a magnetic field B cannot be known. However, we know the range of the changes in the direction of J_k with respect to the direction of the magnetic field B, i.e., $\varphi_k \in (0, \pi)$, and we can determine the average value of the sine for this range as:

$$\langle \sin \varphi_k \rangle = \frac{1}{\pi} \int_0^{\pi} \sin \varphi_k,$$
 (AIV.1)

corresponding to the average value of the moment $\langle M_k \rangle = -\gamma_J J_k B \langle \sin \varphi_k \rangle$, equation (1). By transforming equation (AIV.1) we get: $\langle \sin \varphi_k \rangle = 2/\pi$. The angle associated with $\langle M_k \rangle$ takes the values: $\varphi_k^{\langle M_k \rangle} \cong 39.5(4)^\circ$.

Using quantum statistical mechanics, at very low temperatures, when the following conditions are met:

$$T < 1 \text{ K}, \quad \frac{g^{(i)} \mu_{\text{B}} B_{(i)}}{\mathbf{k} T} \gg 1$$
 (AIV.2)

and counting the limits of the hyperbolic cotangents:

$$\lim_{T<1 \text{ K}, \frac{g^{(i)}\mu_{\text{B}}B_{(i)}}{kT} \gg 1} \operatorname{ctgh}\left(\frac{2J+1}{2}\frac{g^{(i)}\mu_{\text{B}}B_{(i)}}{kT}\right) = 1, \quad \text{(AIV.3)}$$

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$$\lim_{T<1\text{ K},\frac{g^{(i)}\mu_{B}B_{(i)}}{kT}\gg1}\operatorname{ctgh}\left(\frac{1}{2}\frac{g^{(i)}\mu_{B}B_{(i)}}{kT}\right)=1,\qquad(\text{AIV.4})$$

we can write equation (27) as:

$$\varphi^{(i)} = \arccos\left(\frac{J}{\sqrt{J(J+1)}}\right),$$
 (AIV.5)

which corresponds to the average quantum value of the moment $\langle M_k\rangle$. For orbital quantum number $\ell=1$ and spin $\mathscr{S}=1/2$, we can write $\phi_k^{\langle M_k\rangle}\cong 39.2(3)^\circ$ which fulfils the Bohr correspondence minimize with an error of 0.79%.

ACKNOWLEDGEMENTS

Many thanks to my two daughters Alicja Sikoń and Agata Wierzbicka for the inspiration to write this work.

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