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Elena V. Orlenko, Elena F. Sheka and Fedor E. Orlenko

**THE EUROPEAN
PHYSICAL JOURNAL D**

Regular Article

Influence of spin-orbit interaction on magnetic properties of fullerenes[⋆]

Elena V. Orlenko[1,a], Elena F. Sheka[2], and Fedor E. Orlenko[1]

[1] Peter the Great St.Petersburg Polytechnic University, Polytechnicheskaya, 29, 194021 St.Petersburg, Russian Federation
[2] Peoples Friendship University of the Russia, Miklukho-Maklaya str. 6, 117198 Moscow, Russian Federation

Abstract. The current paper is devoted to the consideration of sp^2-carbonaceous fullerenes molecules in a homogeneous magnetic field. Due to a reduction system symmetry in the magnetic field, the energy splitting gives rise dominant atomic structures in fullerene molecules with local symmetries. Spin-orbit interaction plays a crucial role in this phenomenon. The current paper is aimed at determine spin-orbit coupling parameters, as an energy E_{SO} and a constant a_{SO} as well as a Lande g-factor for the C_{60}-based compounds in the magnetic field.

1 Introduction

C_{60}-based compounds in the magnetic field for a wide temperature range demonstrate, such as reduced Lande' g-factor values, as $g < 1$ [1,2]. Shown fullerene C_{60} g-factor pulsed magnetic field up to 32 T in the frequency range $\nu = 60$–90 GHz at $T = 1{:}8$ K has three g-factor: namely, $g_1 = 0.43 \pm 0.03$; $g_2 = 0.27 \pm 0.02$ and $g_3 = 0.19 \pm 0.01$. It gives rise to (1) the existence of three different independent configurations of local spins in the molecule; (2) the influence of the spin-orbit coupling forming the eigenstates with determined total angular momentum.

Commonly, spin-orbit coupling in light atoms (as a carbon) is a small second order relativistic correction. However, a well-known Rashba effect in solids, discovered in 1959 [3–5], a theoretical grounds for fundamental research and applications, as spintronic. It gives a basis for investigations of the influence spin-orbit interaction on the spectrum of 2-D electrons in the magnetic field in heterostructures [6–8]. The importance of spin-orbit coupling (SOC) for the electronic systems [9–12]. It is reported the spin-orbit interaction increasing in graphene [10,11], where the changes in electronic properties of graphene were fixed using photoelectron spectrometers.

From a Group Theory point of view, fullerenes are cage-like, hollow molecules of pseudospherical symmetry consisting of pentagons and hexagons only, with exactly three edges joining every vertex occupied by sp^2 hy-

bridised carbon atoms [13]. Icosahedron C_{60} belongs to the class of Archimedean solids. C_{60}-I_h is the minimal arrangement such that no two pentagons share an edge (isolated pentagons): the edges of each pentagon join only hexagons, and the edges of each hexagon alternately join pentagons and hexagons. A symmetric group I_h consist of 6 axes of order 5, 10 axes of 3rd order, 15 axes of 2nd order; 15 mirror planes, the number of hexagonal faces $F_6 = 20$ etc. 120 elements in total, including E (identity transformation) (see Tab. A.1 in the Appendix), altogether, 28 points groups. Symmetry of fullerenes in magnetic field is reduced to the low axial symmetry of magnetic field perturbation. Instead of 28 point groups of C_{60}-fullerenes, in magnetic fields one has a 9 chiral point groups (I, T, D_6, D_5, D_3, D_2, C_3, C_2, C_1) and 6 polar point groups (C_{3v}, C_3, C_{2v}, C_2, C_s, C_1). A point group with an inversion center or a mirror plane perpendicular to the axis of rotation cannot be polar. That means an irreducible representation of the wave function of the unperturbed system becomes reducible in the magnetic fields and should be represented as an expansion the irreducible representations of low-symmetry polar point groups. There is an energy splitting in magnetic fields. The energy states remain degenerate only with respect to the symmetry of polar point groups. The fraction of low-symmetry to high-symmetry grows rapidly, and the polar point groups increasingly dominate. Only 6 polar point groups are responsible for the behaviour of fullerenes in magnetic field and could determine its magnetic susceptibility.

The current paper is devoted to the consideration of the magnetic properties of fullerenes and determination of parameters such as SOC energy E_{SO} and constant a_{SO} as well as Lande' g-factors.

[⋆] Contribution to the Topical Issue "Atomic Cluster Collisions (7th International Symposium)", edited by Gerardo Delgado Barrio, Andrey Solov'Yov, Pablo Villarreal, Rita Prosmiti.

[a] e-mail: eorlenko@mail.ru

2 A general consideration of spin-orbit coupling in fullerenes

Commonly, spin-orbit interaction from Dirac Hamiltonian for a system in the magnetic field by reducing the relativistic four-component Dirac-Coulomb-Breit operator to two components developed and separating spin-independent and spin-dependent terms [14]:

$$\hat{\mathcal{H}} = \left[mc^2 + \frac{1}{2m} \left(\mathbf{p} - \frac{e}{c}\mathbf{A} \right)^2 - \frac{p^4}{8m^3c^2} \right] + e\varphi - \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \mathbf{H}$$
$$+ \left\{ -i\frac{e\hbar^2}{8m^2c^2}\boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \mathbf{E} - \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot \mathbf{E} \times \mathbf{p} \right\}$$
$$- \frac{e\hbar^2}{8m^2c^2}\boldsymbol{\nabla} \cdot \mathbf{E}. \tag{1}$$

Terms in figure brackets corresponds to spin-orbit interaction. In a special case of spherical electric fields, we have $\boldsymbol{\nabla} \times \mathbf{E} = 0$. Then a Hamiltonian of the spin-orbit interaction for a many-electronic system with spherical symmetry could be written in Breit-Pauli form:

$$\hat{H}_{\mathrm{SO}}^{BP} = \frac{e^2\hbar}{2m^2c^2} \sum_i \left(\boldsymbol{\nabla}_i \left(\sum_I \left\{ \frac{Z_I}{r_{iI}} - \sum_{j \neq i} \frac{1}{r_{ij}} \right\} \right) \mathbf{p}_i \right) \cdot \hat{\mathbf{s}}_i, \tag{2}$$

Here I labels nuclei while i and j do the same for electrons, Z_I is the charge of nucleus I, $\hat{\mathbf{s}}_i$ is the spin operator of ith electron.

A self-consistent potential for the ith electron of atomic center

$$I \ U_I(r_i) = \frac{Z_I e^2}{r_{iI}} - \sum_{(I)j \neq i} \frac{e^2}{r_{ij}}$$

is spherically symmetric, due to

$$\boldsymbol{\nabla}_i U_I(r_i) = \left(\frac{d}{dr_i} U_I(r_i) \right) \cdot \frac{\mathbf{r}_i}{r_i}$$

and the spin-orbit Hamiltonian has the form:

$$\hat{H}_{\mathrm{SO}}^{BP} = \frac{\hbar}{2m^2c^2} \sum_I \sum_i (\boldsymbol{\nabla}_i U_I(r_i)) \times \hat{\mathbf{p}}_i \cdot \hat{\mathbf{s}}_i$$
$$= \frac{\hbar^2}{2m^2c^2} \sum_I \sum_i \left(\left(\frac{d}{dr_i} U_I(r_i) \right) \cdot \frac{1}{r_i} \right) \hat{\mathbf{l}}_i \cdot \hat{\mathbf{s}}_i. \tag{3}$$

Averaging over the value of the total orbital momentum $\hat{\mathbf{L}}_I = \sum_i \hat{\mathbf{l}}_i$ gives us

$$\hat{H}_{\mathrm{SO}}^{av} \approx \frac{\hbar^2}{2m^2c^2} \sum_I \overline{\left\{ \frac{1}{r_i} \left(\frac{d}{dr_i} U_I(r_i) \right) \right\}} \cdot \hat{\mathbf{L}}_I \cdot \sum_i \hat{\mathbf{s}}_i$$
$$= \frac{\hbar^2}{2m^2c^2} \sum_I \overline{\left\{ \frac{1}{r_i} \left(\frac{d}{dd} U_I(r_i) \right) \right\}} \cdot \hat{\mathbf{L}}_I \cdot \hat{\mathbf{S}}_I. \tag{4}$$

The eigenvalues of the Hamiltonian, once rewritten as:

$$\hat{H}_{\mathrm{SO}}^{av} = \sum_I a_{\mathrm{SO}} \left(\hat{\boldsymbol{L}}_I \cdot \hat{\mathbf{S}}_I \right), \tag{5}$$

where

$$a_{\mathrm{SO}} = \frac{\hbar^2}{2m^2c^2} \left\{ \frac{1}{r_i} \left(\frac{d}{dr_i} U_I(r_i) \right) \right\} \tag{6}$$

has the form

$$E_{\mathrm{SO}} = a_{\mathrm{SO}} \frac{1}{2} \sum_I (J_I(J_I+1) - L_I(L_I+1) - S_I(S_I+1)), \tag{7}$$

according to which the constant a_{SO} is an spin-orbit coupling.

3 Spin-orbit coupling parameters of sp² nanocarbons

The constant a_{SO} of spin-obit interaction could be found using an unrestricted Hartree-Fock approximation. According to the Pople and Nesbet algorithm [15], we write the molecular orbitals in LCAO form

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i},$$

where χ_r are any general set of specified single electron functions, then self-consistent values of C_{ri} are determined by the condition that the first variation of the energy of the system should vanish, subject to the orthonormality conditions. Following the method and notation of reference [15], it is easily to show that the effective potential U_{eff} has a form:

$$U_{\mathrm{eff}} = \langle U_I \rangle_i + \frac{1}{2} \sum_j^{\alpha+\beta} \langle Q \rangle_{jj} - \frac{1}{2} \left(\sum_{i,j}^{\alpha} \langle J \rangle_{ij} + \sum_{i,j}^{\beta} \langle J \rangle_{ij} \right), \tag{8}$$

where α, β, $(\alpha+\beta)$-indicate summation over α, β, and all orbitals, respectively. Direct Coulomb $\langle Q \rangle_{jj}$ and exchange $\langle J \rangle_{ij}$ matrix elements, defined by:

$$\langle U_I \rangle_i = \sum_I^{\alpha+\beta} \left\langle \phi_i \left| \frac{Z_I}{r_{iI}} \right| \phi_i \right\rangle;$$
$$\langle Q \rangle_{jj} = \left\langle \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_j(2) \right\rangle;$$
$$\langle J \rangle_{ji} = \left\langle \phi_j(2) \left| \frac{1}{r_{12}} \right| \phi_i(2) \right\rangle. \tag{9}$$

In general case such effective potentials are not symmetrical spherically, nevertheless we assume, for spherical fullerene molecules that functions $U_{\mathrm{eff}}(r)$ symmetric. Open-shell molecules, we approximate equation (6) as

$$a_{\mathrm{SO}} = \frac{\hbar^2}{2m^2c^2} \left\{ \frac{1}{r_i} \left(\frac{d}{dr_i} U_I(r_i) \right) \right\}$$
$$\approx \frac{\hbar^2}{2m^2c^2} \left(\frac{1}{R} \left(\frac{d}{dR} E_{\mathrm{SO}}(R) \right) \right), \tag{10}$$
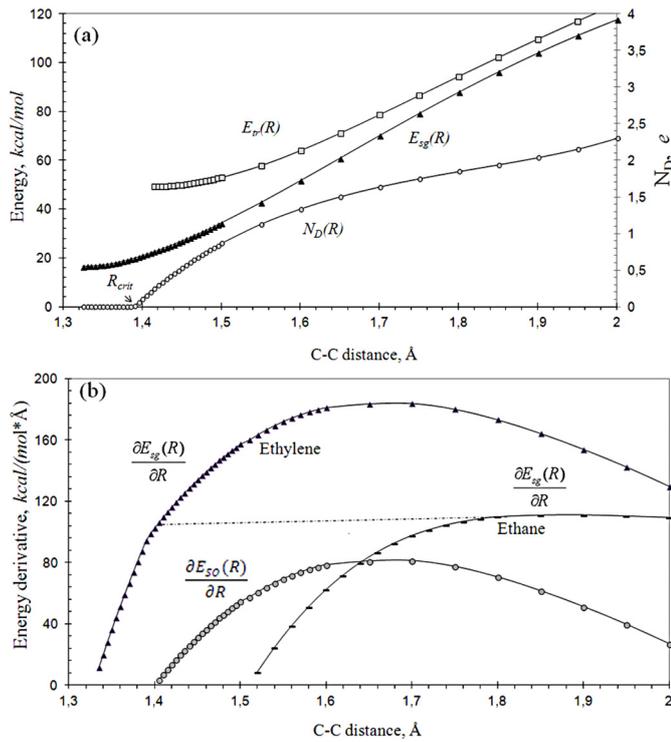
Fig. 1. Spin-orbit coupling in stretched ethylene molecule (UHF calculations).

where $E_{SO}(R)$ is the part of the molecule total energy is dependent on the covalent bond length promoting the closed-open shell transformation and responsible for SOC. UHF CI- approach can be applied to determine both of the energy $E_{SO}(R)$ and constant a_{SO}, which will be demonstrated for the ethylene molecule as an example.

Characteristics, stretching the ethylene C-C bond up to 2 Å, are shown in Figure 1a. Equilibrium C-C distances constitute 1.326 Å and 1.415 Å in singlet and triplet states of the molecule, respectively. As seen in the figure, as stretching of the bond increases, energies $E_{sg}(R)$ and $E_{tr}(R)$ approach each other up to quasidegeneracy, which is characteristic for bi-radicals and which is necessary for an effective SOC [16]. Simultaneously, the number of effectively unpaired electrons N_D, which is zero until C-C distance reaches R_{crit}, starts to grow a gradual radicalisation of the molecule as the bond is stretched, as well as exhibiting the transformation of the behaviour, from a closed-shell to an open-shell one when R_{crit}, is overstepped.

The force applied to the ethylene C-C bond stretching is presented in Figure 1b. At the beginning it proceeds linearly slow down when R is approaching R_{crit}. A kink, for comparison, the curve with horizontal bars presents the force caused by stretching a single C-C bond of ethane, R_{crit} for which 2.11 Å, that is why the molecule remains closed-shell one within the interval of C-C distances presented in the figure. As seen the force is saturated at the level of 110 kcal/(mol×Å) that is close to the kink position on the ethylene curve. It is quite reasonable to suggest that the excessing force over this value in the latter case, is caused by the closed-open shell transformation

of the ethylene molecule over 1.4 Å. Consequently, this excess can be as $dE_{SO}(R)/dR$ that is by the gray-ball curve in the figure. Using the curve values in the C-C distance interval from 1.40 Å to 1.47 Å, which is typical for the C-C bond dispersion in fullerenes, carbon nanotubes and graphene, and substituting them into equation (10), one can obtain the a_{SO} constant. This constant in the interval from 15 meV to 350 meV, which is typically expected for molecules of light elements [16] and which was predicted [17] and experimentally determined [18] for graphene. This value is not a small correction to the exchange interaction, but approximately same order. It is necessary to point out that the $dE_{SO}(R)/dR$ force maximum amplitude for ethylene molecule is consistent with those determined under uniaxial deformation of benzene molecule and graphene [18,19] which the a_{SO} constant values can be considered as typical for the whole family of sp^2 nanocarbons.

Last results were obtained by using semi-empirical AM1 UHF implemented in the CLUSTER-Z1 cod [20]. Spin-orbit coupling determines total angular momentum J. The eigenvalue (7) of the Hamiltonian (5) that the normal term corresponds to the minimal value of total angular momentum $J = |L - S|$, because of positive value of spin-orbit coupling constant $a_{SO} > 0$.

4 Local point groups for fullerenes in magnetic field

Generally, a total Hamiltonian $\hat{H}$ for the fullerene-molecule in magnetic field can be written in the form of a sum an unperturbed part $\hat{H}_0$ (without magnetic field) and a perturbation operator $\hat{V}$, the interaction of C_{60}-fullerene with magnetic field:

$$\hat{H} = \hat{H}_0 + \hat{V}.$$

A symmetry unperturbed Hamiltonian $\hat{H}_0$ corresponds to I_h point group and have 28 subgroup in total (see Tab. A.1 in the Appendix); a symmetry of the perturbation $\hat{V}$ corresponds to the point group $C_{\infty v}$ (corresponding to axial symmetry of field) and I_h point groups. An irreducible representation of the wave function of the unperturbed system becomes reducible in the magnetic fields and should be represented as an expansion of the irreducible representations of the low-symmetry group. For the dimension f_Y of I_h point group we have:

$$f_Y = \sum_{\beta}^{r} a^{(\beta)} f_\beta,$$

where f_β is the irreducible representations dimension, $a^{(\beta)}$ is a coefficient, how many times a representation β is contained in the reducible representation of the wave function. For characters we have the same expansion:

$$\chi(Y_h) = \sum_{\beta}^{r} a^{(\beta)} \chi^{(\beta)}(Y_h).$$

That is why, all degenerate energy levels of unperturbed fullerenes an energy splitting in magnetic fields.

In the magnetic fields – C_{60}-I_h fullerenes point groups lacking an inversion center are further divided into polar and chiral point groups. A polar point group allows the fullerene to have a dipole moment. A point group with an inversion center or a mirror plane perpendicular to the axis of rotation cannot be polar. As above, there are three dominant symmetric atomic groups of C_{60}-I_h, corresponding to the polar point groups (C_{3v}, C_3, C_{2v}, C_2, C_s, C_1), which are:

(1) hexagon-faces;
(2) edges (double bonds, lying on the circle about the direction of magnetic field);
(3) vertices (of pentagons, transited about magnetic field direction).

Such a conclusion from the group theory is in agreement with results of computations, performing by Sheka using the unrestricted Hartree-Fock (UHF) approach presented in reference [21].

Figure 2 presents a distribution related to fullerene C_{60} in the absence (panel (a)) and presence (panel (b)) of magnetic field. The total spin density in panel (a) is equal to zero while α and β spins are antiferromagnetically and space-symmetrically distributed according to the C_i point-group symmetry of the molecule (see detailed discussion of the C_{60} symmetry in Ref. [22]). As seen in the figure three different types of configurations of local spins (in terms of [23]), namely: hexagons (cyan); three couples (green, rose, and red), and singles (blue). Application of a magnetic field disturbs the antiferromagnetic regularity of spins towards ferromagnetic one (see panel b) that corresponds to the maximum of magnetic ordering.

Taking into account the above-mentioned dominant symmetric complexes, it is convenient to write a SO Hamiltonian (5) and its eigenvalue (7), respectively, in the form:

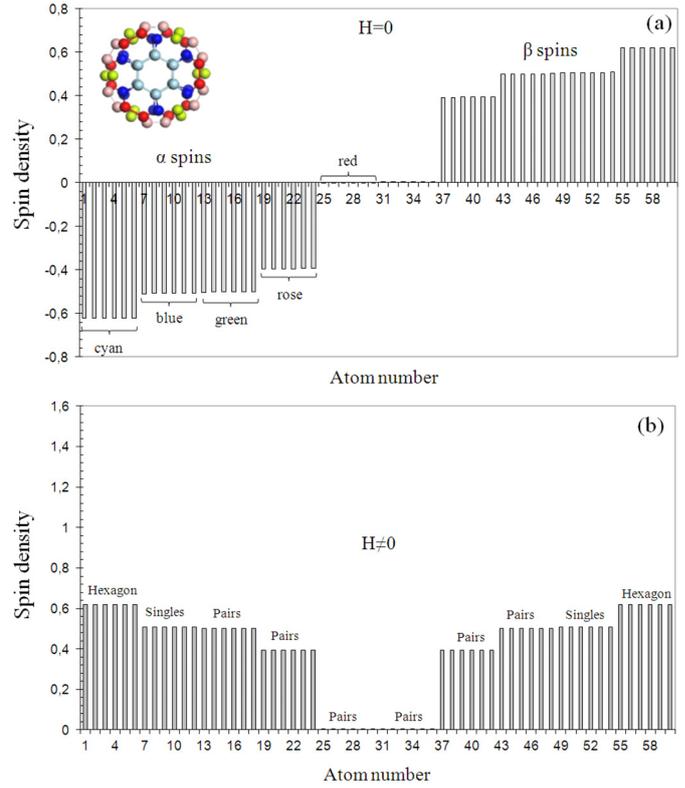$$\hat{H}_{\text{SO}}^{av} = \frac{1}{2}\sum_c a_{\text{SO}c}\hat{\mathfrak{L}}_c \cdot \hat{\mathfrak{S}}_c \qquad (11)$$

$$E_{\text{SO}} = \frac{1}{2}\sum_c a_{\text{SO}c}\big(\mathfrak{I}_c\,(\mathfrak{I}_c+1) - \mathfrak{L}_c\,(\mathfrak{L}_c+1)$$
$$- \mathfrak{S}_c\,(\mathfrak{S}_c+1)\big). \qquad (12)$$

Here $\hat{\mathfrak{L}}_c$ and $\hat{\mathfrak{S}}_c$ are an orbital angular momentum and spin operators of the complex, respectively.

5 Lande' g-Factor for fullerenes in the magnetic field

The Hamiltonian (1) for a system of non-interactive atoms, in the homogenous magnetic field **H**, has been transformed to the Hamiltonian [24]

$$\hat{H} = \sum_I \left(\hat{H}_{0I} + \hat{\boldsymbol{\mu}}_I \cdot \mathbf{H} + \frac{e^2}{8mc^2}\sum_i[\mathbf{H}\cdot\mathbf{r}_{I,i}]^2\right),$$

Fig. 2. Spin density distribution over C_{60} atoms in the absence (a) and presence (b) of the magnetic field. Insert the color image of the local spin distribution over the molecule atoms (UHF calculation).

where $\hat{\boldsymbol{\mu}}_I$ magnetic momentum operator for atom I, $\hat{\boldsymbol{\mu}}_I = -\mu_B(\hat{\mathbf{L}}_I + \hat{\mathbf{S}}_I)$.

For the case of symmetric atomic complexes, as planes and edges of fullerene, we can assume the formation of a total orbital angular momentum $\mathfrak{L}$ and a total spin $\mathfrak{S}$ of the complex. Then the Hamiltonian will have a form:

$$\hat{H} = \hat{H}_0 + \hat{\mathfrak{M}} \cdot \mathbf{H} + \frac{e^2}{8mc^2}\sum_{I,i}[\mathbf{H}\cdot\mathbf{r}_{I,i}]^2, \qquad (13)$$

where $\hat{\mathfrak{M}}$ is an magnetic momentum operator of the symmetric complex and equals to $\hat{\mathfrak{M}} = -\mu_B(\hat{\mathfrak{L}} + 2\hat{\mathfrak{S}})$.

The unperturbed part of Hamiltonian $\hat{H}_0$ can be written in the spin representation as

$$\hat{H}_0 = -\sum_c\sum_{i<j}J_{ij}\hat{\mathbf{s}}_i\cdot\hat{\mathbf{s}}_j \approx -\sum_c\overline{J}_c\sum_{i<j}\hat{\mathbf{s}}_i\cdot\hat{\mathbf{s}}_j$$
$$= -\sum_c\frac{1}{2}\overline{J}_c\left\{\hat{\mathfrak{S}}_c^2 - N_c\hat{\mathbf{s}}^2\right\}, \qquad (14)$$

where, J_{ij} is a Heisenberg parameter, and $\overline{J}$ is related to exchange (or superexchange) coupling constant of electron-electron Coulomb interaction i-j, and its average value in the symmetric complex, respectively.

In the case of weak magnetic field, the $|\mu_B H|$ is small to the spin-orbit coupling constant a_{LS}, fine structure

intervals. Then the second and the third terms of equation (13) can be regarded as a perturbation, the unperturbed levels being the separate components of the symmetric complexes multiplets. In the first approximation, we omitted the third term, which is quadratic with respect to the fields, in with the second linear term. Finally, we have a total Hamiltonian in spin representation with spin-orbit interaction:

$$\hat{H}_{tot} = -\sum_c \frac{1}{2}\overline{J}_c \left\{ \hat{\mathfrak{S}}_c^2 - N_c \hat{\mathbf{s}}^2 \right\} + \sum_c \hat{\mathfrak{M}}_c \cdot \mathbf{H}$$
$$+ \frac{1}{2}\sum_c a_{\mathrm{SO}c} \hat{\mathfrak{L}}_c \cdot \hat{\mathfrak{S}}_c. \tag{15}$$

Then the eigenvalue of the energy of symmetric complexes in magnetic field with a SOC term is determined by the mean values of the perturbation in the unperturbed states:

$$E_c = -\frac{1}{2}\overline{J}_c \left\{ \mathfrak{S}_c(\mathfrak{S}_c + 1) - N_c \frac{1}{2}\left(\frac{1}{2}+1\right) \right\} + \mu_B g_c \mathfrak{M}_c H$$
$$+ a_{\mathrm{SO}c}\left(\mathfrak{I}_c\left(\mathfrak{I}_c + 1\right) - \mathfrak{L}_c\left(\mathfrak{L}_c + 1\right) - \mathfrak{S}_c\left(\mathfrak{S}_c + 1\right)\right) \tag{16}$$

where g is g-factor:

$$g_c = 1 + \frac{\mathfrak{I}\left(\mathfrak{I}+1\right) - \mathfrak{L}\left(\mathfrak{L}+1\right) + \mathfrak{S}(\mathfrak{S}+1)}{2\mathfrak{I}(\mathfrak{I}+1)}. \tag{17}$$

Here $\mathfrak{I}_c \mathfrak{L}_c$ and $\mathfrak{S}_c$ are the values of the total angular momentum, the total orbital angular momentum and the total spin momentum of the symmetric complex, respectively.

6 Lande' g-factor for the local symmetric C-complexes in fullerenes

Dominant symmetric groups responding a magnetic field: (1) a hexagon-faces; (2) edges (double bonds); (3) vertexes.

6.1 Hexagon Face group of πp_z local spins

Using Exchange Perturbation theory for evaluation of the Heisenberg parameter [25,26], the main contribution to the binding energy of the hexagon complex is given by the term with the superexchange interaction. An effective Hamiltonian for πp_z electrons forming cyclic π-bonds has the form [25]:

$$H_{\mathrm{eff}6} = \sum_{I,K,L=1}^{6}\sum_{i,j=1}^{6} a_{Ii\sigma}^+ a_{Kj\sigma'}^+ V_{ij} a_{Ij\sigma'} a_{Li\sigma},$$
$$V_{ij} = \langle \phi_{I,i}\phi_{K,j}| \left(\frac{1}{r_{i,j}} - \frac{1}{r_{i,I}} - \frac{1}{r_{j,L}} + \frac{1}{R_{L,I}} \right)|\phi_{I,j}\phi_{L,i}\rangle. \tag{18}$$

Hereinafter $a_{I\sigma}^+$ and $a_{I\sigma}$ are creation and annihilation operators for the spin projection σ OT atom I, respectively.

The main contribution in the hexagon's energy is given by the interactions among neighbouring atoms. Effective Hamiltonian of the hexagon in such an approximation of nearest neighbours, could be written in the matrix form as

$$H_{\mathrm{eff}6} = \begin{pmatrix} 0 & V & A & 0 & A & V \\ V & 0 & V & A & 0 & A \\ A & V & 0 & V & A & 0 \\ 0 & A & V & 0 & V & A \\ A & 0 & A & V & 0 & V \\ C & A & 0 & A & C & 0 \end{pmatrix}, \tag{19}$$

where C and Q are direct Coulomb and exchange interaction neighbouring, respectively; A is a superexchange term.

$$V = \langle \phi_{I,i+1}\phi_{I-1,i}| \left(\frac{1}{r_{i,i+1}} - \frac{1}{r_{iI}} - \frac{1}{r_{i+1,I-1}} + \frac{1}{R_{I,I-1}} \right)$$
$$\times |\phi_{I-1,i}\phi_{I,i+1}\rangle + (-1)^{(\sigma+\sigma')}\langle\phi_{I-1,i+1}\phi_{I,i}| \left(\frac{1}{r_{i,i+1}} \right)$$
$$- \frac{1}{r_{iI}} - \frac{1}{r_{i+1,I-1}} + \frac{1}{R_{I,I-1}} |\phi_{I-1,i}\phi_{I,i+1}\rangle$$
$$= C + (-1)^{(\sigma+\sigma')}Q;$$
$$A = (-1)^{(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)}\langle\phi_{I+1,i+1}\phi_{I,i}|$$
$$\times \left(\frac{1}{r_{i,i+1}} - \frac{1}{r_{iI}} - \frac{1}{r_{i+1,I-1}} + \frac{1}{R_{I,I-1}} \right)$$
$$\times |\phi_{I-1,i}\phi_{I,i+1}\rangle \langle\phi_{I,i}|\phi_{I-1,i}\rangle^4$$
$$= (-1)^{(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)} \cdot \mathfrak{R} \cdot S_{I,I-1}^4. \tag{20}$$

Eigenvalues of energy x are found from the equation

$$\det \begin{bmatrix} -x & V & A & 0 & A & C \\ V & -x & V & A & 0 & A \\ A & V & -x & V & A & 0 \\ 0 & A & V & -x & V & A \\ A & 0 & A & V & -x & V \\ C & A & 0 & A & V & -x \end{bmatrix} = 0 \tag{21}$$

or

$$4A^6 - 12A^4V^2 + 12A^2V^4 - 4V^6$$
$$+ (12A^5 - 24A^3V^2 + 12AV^4)x$$
$$+ (9A^4 - 18A^2V^2 + 9V^4)x^2$$
$$- (4A^3 + 12AV^2)x^3 - (6A^2 + 6V^2)x^4 + x^6 = 0.$$

There are six solutions:

$$\{\{x \to -A - V\}, \quad \{x \to -A - V\},$$
$$\{x \to 2(A - V)\}, \quad \{x \to -A + V\},$$
$$\{x \to -A + V\}, \quad \{x \to 2(A + V)\}\}. \tag{22}$$

The normal term of such a system is determined by the value and sign of all these C, Q and A contributions and

by the value of total spin $S_{i,i+1}$ for each electron couple. That is the reason, why the same atomic configuration could have a different value of total spin. For the distances R from 1.40 Å to 1.47 Å, which is typical for the C-C bond dispersion in fullerenes, the lowest energy state of normal term is $\{x \to 2(A+V)\}$, due to $C \to +0$, $Q > 0$, then the convenient value of total spin is $S = 1$, and its projection $S_z = \sigma + \sigma' = 1$. Then $V < 0$, $\mathfrak{R} > 0$, hence, an average value of coupling constant $J_{\text{eff6}}(R) > 0$ in equations (13) and (14), and the convenient value of the total spin $\mathfrak{S}$ of hexagon is $\mathfrak{S} = 3$, and its projection $\mathfrak{S}_z = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 = 3$. The total orbital momentum of the hexagon p_z electrons, $\mathfrak{L} = 6$. Consequently, the total angular momentum J of the hexagon may have seven components: $(6+3)$, 8, 7, 6, 5, 4, $(6-3)$. According to equation (14), the lowest energy state corresponds to the minimum value of the total angular momentum $\mathfrak{J} = 3$. Following equation (17), the relevant Lande factor $g_6 = 0.25$.

6.2 Edge group of local spin pairs

The main contribution in the Hamiltonian for this case is given by the term

$$H_{\text{eff2}} = \sum_{\substack{I=1 \\ i \neq j=1}}^{2} a^+_{(I+1)\sigma} a^+_{I\sigma'} V_{ij} a_{(I+1)\sigma'} a_{I\sigma},$$

$$V_{ij} = \langle \phi_{I,j} \phi_{I+1,i} | \left(\frac{1}{r_{i,j}} - \frac{1}{r_{i,I+1}} - \frac{1}{r_{j,I+1}} + \frac{1}{R_{I,I+1}} \right) \\ \times | \phi_{I,i} \phi_{I+1,j} \rangle . \tag{23}$$

The normal term corresponds to the lowest energy state $x = C + (-1)^{(\sigma+\sigma')}Q$, where the direct Coulomb C and exchange Q were determined by equation (17). Because of $Q > 0$, the spin state is $\mathfrak{S} = 1$ with its projection $\mathfrak{S}_z = \sigma + \sigma' = 1$, the total orbital momentum of two p_z-electrons is $\mathfrak{L} = 2$ and the total angular momentum $\mathfrak{S}$ has three components: $(1+2)$, 2, $(2-1)$. Taking the least value component, with respect to equations (16) and (17) one to obtain the relevant Lande' g-factor, $g_2 = 0.5$.

6.3 Local spin singles

For a single p_z electron, the total spin $\mathfrak{S} = 1/2$, the orbital angular momentum $\mathfrak{L} = 1$, while the total angular momentum $\mathfrak{J}$ has two components: $3/2$ and $1/2$. According to equation (14), the lowest energy term corresponds to $\mathfrak{J} = 1/2$ so that the Lande' factor, $g_1 = 0.66$.

6.4 σ-Bonds electrons

The total spin S_{at}, total orbital L_{at} and total angular momentum J_{at} of each sp^2-atom, forming the σ-bonds with respect to the internal atomic fine structures. Here for three sp^2-hybridised electrons of C-atom: $S_{at} = 3 \times \frac{1}{2}$,

Table 1. g-Factors of fullerene C_{60}.

Calculated		Experimental [2,3]	
Attribution	Value	Attribution	Value
Hexagons	0.125	g_6	0.19 ± 0.01
Pairs	0.250	g_2	0.27 ± 0.02
Singles	0.330	g_1	0.43 ± 0.03

$L_{at} = 2$, the minimal value of the total angular momentum, corresponding to the normal term is $J_{at} = |L_{at} - S_{at}| = 1/2$. Then from equation (14) we have the factor Lande' $g_{at} = 0$. Taking into account g_{at}, we have the average values of g-factor for three type of complexes g_1, g_2, g_6,

$$\overline{g}_6 = \frac{1}{2}(g_6 + g_{tot}) = 0.125$$

$$\overline{g}_2 = \frac{1}{2}(g_2 + g_{tot}) = 0.25$$

$$\overline{g}_1 = \frac{1}{2}(g_1 + g_{tot}) = 0.33. \tag{24}$$

It is reported in reference [1], that the magneto-optical study of the mosaic sample prepared (ET)2C60 single crystals was carried out in pulsed magnetic field up to 32 T in the frequency range $\nu = 60$–90 GHz at $T = 1$–8 K. The obtained transmission curves show three broad absorption lines corresponding to $g_1 = 0.43 \pm 0.03$, $g_2 = 0.27 \pm 0.02$ and $g_3 = 0.19 \pm 0.01$. The calculated in equations (15) and (20) and the experimental g values are in good agreement and presented in Table 1. At the same time, no ESR absorption in the sample was found around $g = 2$ [1,2].

7 Conclusions

Considering a C_{60} molecule in the magnetic field taking into account the internal spin-orbit interaction, one can come to the following conclusions:

(1) According to the C_{60} molecule in magnetic field consists of identical C-10 compositions formed by thee type of atomic groups: 6-C-cycle (hexagon faces), two-centered 2-C-bonds (two-bond edges), and single atomic 1-C-type.

(2) An angular momentum ordering in the above mentioned C-atom groups is determined by the collective exchange and superexchange interaction, which forms the total spin state for the symmetric group and is dependent of the electron-overlapping configuration. From other hand, the ground state of the group is dependent of the internal spin-orbit interaction forming the definite value of a total angular momentum for the symmetric complex. For such a system, the spin-orbit coupling constant is not a small relativistic correction to the normal term, but it is compared to the value of the super-exchange interaction for couples C-atoms.

(3) The estimated Lande' g-factor for each atomic group is qualitatively and quantitively in good agreement with the experimental results.

Table A.1. Point Groups for Fullerenes.

Order	Point groups	Order	Point groups	Order	Point groups
120	I_h	60	I	24	T_d, T_h, D_{6h}, D_{6d}
20	D_{5h}, D_{5d}	12	T, D_6, D_{3h}, D_{3d}	10	D_5
8	D_{2h}, D_{2d}	6	D_3, S_6, C_{3h}, C_{3v}	4	D_2, S_4, C_{2h}, C_{2v}
3	C_3	2	C_3, C_s, C_i	1	C_1

Table A.2. Local symmetry point groups.

Symmetry Points	Symmetries (order)
Vertices	$C_{3v}(4), C_3(3), C_s(2), C_1(1)$
Edge Centers	$C_{2v}(4), C_2(2), C_s(2), C_1(1)$
Pentagon Centers	$C_{5v}(8), C_5(3), C_s(2), C_1(1)$
Hexagon Centers	$C_{6v}(12), C_6(6), C_{3v}(6), C_3(3),$
	$C_{2v}(4), C_2(2)C_s(2), C_1(1)$
Cage Center	Full Point Group

Author contribution statement

All authors contributed equally to the paper.

Appendix

The full isometry group $\mathcal{G}$, which correspond to the rotations, reflections, roto-inversions, and inversions that leave the ideal polyhedron invariant [13], is collected in Table A.1.

The symmetry points of interest in a fullerene are the vertices, midpoints of edges, the barycenter of the polygons and the whole cage, the latter having the full symmetry of the point group. They have certain site symmetries according to the rotational axes or mirror planes going through these symmetry points, which are collected [13] in Table A.2.

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