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An analysis of the magnetic ground state in C_N molecules

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Abstract. We analyse the antiferromagnetic ground state of various fullerenes, namely C_N cluster isomers, in the classical limit of the effective Heisenberg Hamiltonian. The valley structures of the frustrated (semi-spin glass) ground state were determined and the probability distributions of the spin-correlation functions were calculated. Also the energy barriers between minima were estimated and these turned out to be relatively small. We use Monte Carlo relaxation and simulated-annealing methods in the calculations.

1. Introduction

In this paper we provide a detailed analysis of the magnetic ground states of a series of C_N molecules, commonly known as fullerenes [1]. We found differences between the magnetic ground-state properties of the various fullerenes. In our calculations we follow a semi-classical Heisenberg model approach for finding the ground states and use the Ritz variational method. The actual Monte Carlo relaxation procedure is based on the idea of fast cooling and seems to be the most appropriate for the explanation of the experimental observations. We also use the simulated-annealing technique. The results presented in this work can be used as a starting point for further variational calculations for systems with Hamiltonians where the kinetic electron correlations are included [2], and also furnish some contribution to the understanding of the magnetic correlations observed experimentally in fullerenes [1] and fullerides [3].

A group of experiments recently carried out concentrated on investigating the magnetic susceptibility in the fullerides A_xC_{60}, where A is an alkali metal atom (K, Rb, Cs). They show that these systems have short-range antiferromagnetic correlations [4, 5]; this can be significant as regards the understanding of superconductivity in these systems. Similar conclusions are suggested by the time dependence of the electron spin-resonance signal (ESR) at the temperature of the transition [6] (to the superconducting state).

Another group of studies is constituted by papers describing experiments investigating magnetic correlations in non-doped fullerenes. Buntar *et al* [7] (see also references therein) have found that powders of C_{60} and C_{70} in the process of cooling and heating attain irreversible magnetization at temperatures $T = 50$–60 K, i.e. these systems behave like spin glasses with frozen disorder. A singularity of the magnetic susceptibility at the temperature $T = 260$ K in an order–disorder orientation phase transition of C_{60} crystal was reported by Luo *et al* [8].

A third group of papers is devoted to magnetic correlations in the molecular crystal TDAE–C_{60}, in which antiferromagnetic correlations were revealed in an ESR experiment.

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Also, weak ferromagnetism [9] was found below $T = 16$ K. An analogous phase for TDAE–C_{70} does not occur [10].

Although the mechanisms of the antiferromagnetic correlations in the above-mentioned groups seem to be different, their common feature is the presence of C_N molecules which are placed in the systems at relatively large distances (∼10 Å) from each other. Because of this, correlations between shared electrons in external atomic shells in the systems can be expected to possess properties similar to those occurring between correlated π-electrons in isolated molecules.

The simplest Hamiltonian, which is commonly believed to be sufficient for explanation of the basic physical properties of π-electrons in fullerenes, is the Hubbard model, in which the microscopic parameters are the hopping integral t and the Coulomb repulsion energy U acting on the carbon atom. Simple estimations [11–13] indicate that

$$U/t \approx 3\text{–}5.$$

The latter means that the π-electrons are in a state in which single-site repulsion slightly dominates over kinetic correlations. Therefore, in fourth order of perturbation calculus the Hubbard model (with its t/U ratio) effectively becomes a t–J model. Because we consider here the half-filled-band case, we can neglect the kinetic part of the model. The remaining part, which is the quantum Heisenberg model, we solve in the quasi-classical approximation numerically (and, at that level, exactly). So, our Hamiltonian is

$$\hat{H} = -\frac{1}{2}\sum_{i,j} J_{ij}\hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j \tag{1}$$

where the non-zero values of the exchange integrals J_{ij} are proportional to t/U (we assume that $J_{ij} \neq 0$ for nearest neighbours only). That is why the results presented here can be compared directly to the experimental results of Buntar *et al* [7], which suggest that pure powdered C_{60} and C_{70} are spin glasses. The applicability of this Hamiltonian to fullerenes was discussed by Coffey and Trugman [14] and Bergomi *et al* [16].

The frustrations of spin–spin interactions in C_N molecules occur due to the presence of pentagons and thus the specific spherical geometry. We also consider a hypothetical example of a C_N molecule—the truncated tetrahedron C_{12} (with four separated triangles and four hexagons in the structure), which displays similar properties within this model. The triangle bonds are highly frustrated [14, 15]. In real situations the frustrations can result in a metastability (a semi-spin glass) of the ground state [17, 18].

In the classical limit of the Hamiltonian (1) it was found that the magnetic ground states [14, 15] of C_{60} and C_{12} are exotic with non-trivial topology. However, this is not the only result of frustrations caused by pentagons (or, respectively, triangles) with the negative exchange couplings per bond in the systems. Within the framework of the classical approximation we investigated the magnetic ground states of the molecules mentioned here. We considered at first the valley structure of their magnetic ground states. It has been revealed that the character of the ground state is either degenerate or metastable.

This paper is organized as follows. The next section describes two methods which we used in the calculation of the minima—the metastable states and the energy barriers between those minima. Both of these methods are based on the concept of cooling, which seems to be the method of choice for Monte Carlo calculations of ground-state energy minima. In the third section we present our results. The last section contains conclusions and a discussion of our results.

2. Methods of calculation

2.1. The ground state

The basic concept assumed in this investigation is that of treating the magnetic ground states as a probabilistic space in which elementary events are single magnetic metastable states with comparable energies E_l, which should satisfy $E_0 \leqslant E_1 \leqslant \cdots \leqslant E_m$ where the $|E_i - E_j|$ are small, or degenerate ones [20]. As a result of cooling, a C_N molecule can be in a metastable state, taking a spin configuration with a probability p_l ($\sum_l p_l = 1$). Disordered metastable states are characterized by Shanon information entropy:

$$K = -\sum_l p_l \log(p_l). \tag{2}$$

K is bounded by $K \leqslant K_{max} = \log(m)$, where K_{max} is the hypothetical entropy of the system with all metastable states having equal probability. Our aim is to calculate the probabilities p_l of the spins configuration being in metastable states, and their energies E_l for a C_N molecule.

The approach is based on a computer procedure which simulates what one can expect in a real experiment when a system that is at high temperature is rapidly cooled to a near-zero temperature. The cooling process is expressed mathematically by a mapping F on a subset Ω of trial states $|\varphi\rangle$ of the Hilbert space $\mathcal{H}$ of the Hamiltonian $\hat{H}$, equation (1). The mapping should lead to a decrease of the system's energy.

Basically our approach is a slightly modified Ritz variational method. We look for a map F: $\Omega \longrightarrow \Omega$ having the property that its successive iterations $\varphi_n = F_n(\varphi)$, $F_n = F(F(\cdots F)\cdots)$, minimize the functional $R(\varphi) = \langle\varphi|\hat{H}|\varphi\rangle/\langle\varphi|\varphi\rangle$ for every $|\varphi\rangle \in \Omega$. The stable points of F, i.e. the solutions of the equation $\varphi = F(\varphi)$, constitute the required local minima in Ω where the φ-parameters describe the trial state.

Within the framework presented, we define the mapping F on the set Ω of the coherent spin states [21] $|\boldsymbol{s}\rangle$ of the spin operator $\hat{S}$: $\hat{S}|\boldsymbol{s}\rangle = \mathbf{S}|\boldsymbol{s}\rangle$. The spins $\boldsymbol{s}$ are unit vectors. Moreover, $\langle\boldsymbol{s}|\boldsymbol{s}\rangle = \boldsymbol{s}\cdot\boldsymbol{s} = 1$. Thus, in such a case, the proposed description of fullerenes is essentially equivalent to the consideration of the classical limit of the Hamiltonian (1). A C_N molecule is now described by a system of N spins $\boldsymbol{S} = (\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N)$ and the appropriate coherent state is a tensor product $|\boldsymbol{S}\rangle = |\boldsymbol{s}_1\rangle|\boldsymbol{s}_2\rangle\cdots|\boldsymbol{s}_N\rangle$, i.e. $\varphi = |\boldsymbol{S}\rangle$. Then

$$R(|\boldsymbol{S}\rangle) = -\frac{1}{2}\sum_{i,j}\tilde{J}_{ij}\boldsymbol{s}_i\cdot\boldsymbol{s}_j$$

where $\tilde{J}_{ij} = J_{ij}S_iS_j$.

Finally, the procedure yields the set of equations

$$\boldsymbol{s}_i = F_i(\boldsymbol{S}) = \left(\sum_j \tilde{J}_{ij}\boldsymbol{s}_j\right)\Bigg/\left\|\sum_j \tilde{J}_{ij}\boldsymbol{s}_j\right\| \tag{3}$$

($i = 1, 2, \ldots, N$), where $||\boldsymbol{u}||$ is the length of the vector $\boldsymbol{u}$. It is well known [17, 18] that the iterations $F_n(\boldsymbol{S})$ are (for any $\boldsymbol{S}$) convergent to stable points $\boldsymbol{S}_{0l}$ of the mapping F. The mapping rotates the vectors $\boldsymbol{s}_i$, readjusting them to the direction of the local molecular field $\sum_j \tilde{J}_{ij}\boldsymbol{s}_j$ at every site i. Therefore $R(|F_{n+l}(\boldsymbol{S})\rangle) \leqslant R(|F_n(\boldsymbol{S})\rangle)$, and $\boldsymbol{S}_{0l}$ are the local minima of the functional R.

We assumed (as a first approximation) that the parameters $J_{ij} = |J|$ for the nearest-neighbour sites, otherwise being equal to zero. This seems to be a safe assumption, since the bond lengths in the hexagon and pentagon differ by 0.005 nm in C_N molecules. Our calculations show that these differences, which influence the exchange integral values, are not significant and have no actual impact on the number and structure of the metastable states. In the first step of the numerical procedure we randomly chose a considerable number $\mathcal{N}$ ($\mathcal{N} = 10^4$ in our case) of points $\boldsymbol{S}'_k$ ($k = 1, \ldots, \mathcal{N}$) distributed uniformly in the space Ω, i.e. this was the 'high-temperature' starting point of the simulation. Then for every $\boldsymbol{S}'_k$ we found

$$\boldsymbol{S}_{0l} = \lim_{n \to \infty} F_n(\boldsymbol{S}'_k)$$

(k labels the spin configurations and l the metastable states), i.e. the iteration was stopped when the differences between the successive values of the functional R reached a set accuracy (e.g. 10^{-8}). The $\boldsymbol{S}_{0l}$ thus obtained are all local minima of the functional R. This is what we call the Monte Carlo relaxation method [19, 20]. The procedure reflects a fast-cooling process. In practice, the low-energy metastable spin configurations $\boldsymbol{S}_{0l}$ obtained in this way can be regarded as the ground state [22]. The probabilities p_l can be calculated using

$$p_l \cong \mathcal{N}_l / \mathcal{N} \tag{4}$$

where $\mathcal{N}_l$ denotes the number of spin configurations which converge to the lth metastable state, and obviously $\mathcal{N}$ is the total number of spin configurations.

The method described above is different to that used by Coffey and Trugman [14], in which the authors found ground-state spin configurations by direct numerical minimization of the energy over the spin variables. For technical reasons [17], so simple a procedure was not able to reveal all possible local minima of the energy.

2.2. Energy barriers

An important, although difficult to calculate, characteristic of a metastable state φ_k of energy E_k is its lifetime τ_k which, because of quantum tunnelling, is finite. As is common knowledge, the higher the quasi-classical energy barriers E_{kl} between the states φ_k and other metastable states φ_l with lower energies E_l, the longer the lifetime.

We shall focus now on quasi-classical calculations of E_{kl} for two arbitrary magnetic metastable states φ_k and φ_l of a C$_N$ molecule.

Let us consider the set $\mathcal{P}_{kl}$, in the coherent-state phase space Ω, of all continuous paths $\wp$: $[0, 1] \to \Omega$, such that $\wp(0) = \varphi_k$ and $\wp(1) = \varphi_l$. We can easily notice that the equality

$$E_{kl} = \inf_{\wp \in \mathcal{P}_{kl}} \left(\max_{0 \leqslant \tau \leqslant 1} H(\wp(\tau)) \right) \tag{5}$$

holds, where $H(\wp(\tau))$ denotes the value of the Hamiltonian (1) for the classical spin system $\wp(\tau) = \boldsymbol{S}(\tau) = (\boldsymbol{s}_1(\tau), \boldsymbol{s}_2(\tau), \ldots, \boldsymbol{s}_N(\tau))$. The only difficulty which arises as regards formula (5) is that of the determination of the lower limit in the space $\mathcal{P}_{kl}$. We calculate the limit using the simulated-annealing algorithm [23]. We define the following classical Hamiltonian for this purpose:

$$\bar{H}[\wp] = \max_{0 \leqslant \tau \leqslant 1} H(\wp(\tau)) \tag{6}$$

where the set $\mathcal{P}_{kl}$ is the phase space. Obviously E_{kl} is the energy of the classical—generally not unique—ground state $\wp_0(\tau)$ of this Hamiltonian. The simulated-annealing technique used for determination of the Hamiltonian $\bar{H}[\wp]$ ground state consists in Monte Carlo simulation of the equilibrium cooling process, with the thermodynamics of the system described by the Gibbs probability density function

$$\rho[\wp] = \frac{1}{Z} \mathrm{e}^{-\beta \bar{H}[\wp]} \tag{7}$$

Table 1. Local energy minima (the valley structure of the ground states) of the series of fullerenes in effective-coupling units, $|J|$ per C atom. Asterisks indicate degeneracy of the energy valley. (The geometrical structures of the fullerenes were taken as follows: for C_{32}, C_{44}, and C_{58} from Curl and Smalley [25], for C_{60} isomers from Goodwin [26], for C_{70} and C_{78} from Saito and Oshiyama [27], Diederich and Whetten [28], and Colt and Scuseria [30], for C_{76} isomers from Colt and Scuseria [29], and for C_{84} isomers from Saito *et al* [31]. This applies to all of the tables in this paper.)

	Isomer	E_0	E_1	E_2	E_3	E_4
C_{12}		-1				
C_{20}		-1.1180	-1.0884^*			
C_{32}		-1.2345	-1.2162			
C_{44}		-1.2751	-1.2681^*	-1.2645		
C_{50}		-1.3106				
C_{58}		-1.3086^*	-1.3073^*			
C_{60}	D_{2h} or T_h	-1.3090	-1.3009^*			
	D_{3d}	-1.3090	-1.3009^*	-1.3007		
	D_{5d}	-1.3090	-1.3009^*			
C_{70}	D_{5h}	-1.3335	-1.3278^*	-1.3277		
C_{76}	D_2	-1.3440	-1.3366			
	D_{2d}	-1.3337^*	-1.3335^*			
C_{78}	C_{2v}(I)	-1.3463				
	C_{2v}(II)	-1.3482	-1.3453			
	D_3	-1.3422	-1.3414	-1.3391^*		
	D_{3h}(I)	-1.3410^*	-1.3377			
	D_{3h}(II)	-1.3435^*	-1.3428	-1.3424^*	-1.3423	-1.3415^*
C_{84}	D_{6h}	-1.3636	-1.3496	-1.3398		
	D_2(flat)	-1.3569	-1.3559	-1.3512		
	D_2(round)	-1.3584	-1.3527			
	T_d	-1.3559^*	-1.3554^*	-1.3552	-1.3519	

where β is the inverse temperature and Z is the partition function:

$$Z = \int_{\mathcal{P}_{kl}} \mathrm{d}\mu[\wp]\, \mathrm{e}^{-\beta \bar{H}[\wp]}. \tag{8}$$

μ is a uniform measure on the path space $\mathcal{P}_{kl}$. In the Monte Carlo calculation of the barriers, we search all contorted lines consisting of $\mathcal{M}$-'segments'.

Since the state space of the Hamiltonian H for a C_N molecule is an N-fold Cartesian product of two-dimensional spheres (with unit radius), the 'segments' are N-fold Cartesian products of great-circle cross sections. We can easily notice that with sufficiently large $\mathcal{M}$ ($\geqslant 100$) such discretization of the Hamiltonian configuration space $\bar{H}[\wp]$ should not lead to significant errors in the estimation of the energy barriers E_{kl}. The remaining details of the technique that we used are the same as in the work of Kirkpatrick *et al* [24].

The results of the simulation are shown in table 4—see later.

3. Results

We found that C_{12}, C_{50} and C_{78} (C_{2v}(I) isomer) molecules are the only exceptions which have one ground-state spin configuration. The ground states of the other C_N molecules consist of two (C_{32}, C_{58}, C_{60}) or three or even more (C_{44}, C_{70}, C_{76}, C_{78}, C_{84}) spin-configuration space valleys corresponding to slightly different energy values E_l (table 1) and separated by energy barriers. Moreover, some of them exhibit non-trivial degeneracy, i.e. several non-equivalent spin configurations correspond to the given energy, and as indicated in table 2, the net magnetic moments $M = ||\sum_{i=1}^{N} \boldsymbol{s}_i||$, computed in terms of states of every valley, are not always equal to zero.

The metastable states that we obtained are similar for each C_N molecule, i.e. the local spins $\boldsymbol{s}_i$ are almost tangents to the sphere or ellipsoid into which the appropriate molecule can be inscribed.

Table 2. The net magnetic moments in the ground states of the respective fullerenes.

	Isomer	M_0	M_1	M_2	M_3	M_4
C_{12}		0				
C_{20}		0	0.0330			
C_{32}		0	0.0458			
C_{44}		0	0.1001	0		
C_{50}		0.2708				
C_{58}		0.2380	0.2105			
C_{60}	D_{2h} or T_h	0	0			
	D_{3d}	0	0	0		
	D_{5d}	0	0			
C_{70}	D_{5h}	0	0.0099	0		
C_{76}	D_2	0	0			
	D_{2d}	0	0			
C_{78}	C_{2v}(I)	0				
	C_{2v}(II)	0	0.0054			
	D_3	0	0.0169	0.2117		
	D_{3h}(I)	0	0.0415			
	D_{3h}(II)	0	0	0	0	0
C_{84}	D_{6h}	0	0	0		
	D_2(flat)	0	0	0.0036		
	D_2(round)	0	0			
	T_d	0	0	0	0	

As we have mentioned, the applied relaxation procedure is a reasonable characterization of the effective freezing observed in a very fast experiment. The cooling process of a C_N molecule is equivalent to a relaxation of its spins to local equilibrium positions. From the estimates of the relative frequencies of appearances of the configurations $\boldsymbol{S}_{0l}$ we could obtain the probabilities p_l of finding the system in the given spin-energy valley (table 3). Thus the method also enabled us to determine the probabilities of finding molecules in a possible metastable ground-state spin configuration in a powder sample of given molecules C_N after rapid cooling.

Moreover, within this approach, we are able to calculate a probability distribution density $\langle \delta(x-A) \rangle$ of a physical quantity A in the ground state ($\delta(x)$ is the Dirac δ-function). That is, the distribution can be obtained after differentiation of the appropriate Heaviside θ-functions:

$$\langle \theta(x - A) \rangle = \frac{1}{\mathcal{N}} \sum_l p_l \theta(x - A(\boldsymbol{S}_{0l})). \tag{9}$$

Table 3. Probabilities of finding the fullerenes in their respective energy valleys.

	Isomer	p_0	p_1	p_2	p_3	p_4	Entropy[a]
C_{12}		1					0
C_{20}		0.6461	0.3539				0.6498
C_{32}		0.9770	0.0230				0.1095
C_{44}		04614	0.5382	0.0004			0.6935
C_{50}		1					0
C_{58}		0.8758	0.1242				0.3752
C_{60}	D_{2h} or T_h	0.5716	0.4284				0.6829
	D_{3d}	0.5758	0.4240	0.0002			0.6833
	D_{5d}	0.5830	0.4170				0.6793
C_{70}	D_{5h}	0.6752	0.3244	0.0004			0.6335
C_{76}	D_2	0.8866	0.1134				0.3536
	D_{2d}	0.7094	0.2906				0.6027
C_{78}	C_{2v}(I)	1					0
	C_{2v}(II)	0.9998	0.0002				0.0019
	D_3	0.5996	0.1936	0.2068			0.9505
	D_{3h}(I)	0.9998	0.0002				0.0019
	D_{3h}(II)	0.2370	0.1754	0.3196	0.0002	0.2678	1.3656
C_{84}	D_{6h}	0.9230	0.0548	0.0222			0.3176
	D_2(flat)	0.4884	0.3894	0.1222			0.9741
	D_2(round)	0.8364	0.1636				0.4456
	T_d	0.5893	0.2966	0.0001	0.1140		0.9206

[a] The entropy was calculated using formula (2). The maximal entropies K_{max} for two, three, four, and five metastable states are equal respectively to 0.6931, 1.0986, 1.3863, and 1.6094.

As an example, we considered the angle operator

$$\hat{\phi}_{ij} = \arccos(S^{-2}\hat{\boldsymbol{S}}_i \cdot \hat{\boldsymbol{S}}_j) \tag{10}$$

defined by electron spins at sites i and j. The results of Monte Carlo calculations of the probability distribution $\hat{\phi}_{ij}$ of the correlations with respect to a nearest-neighbour pair of spins on a pentagon are displayed in figure 1.

The magnetic ground states of C_N molecule isomers are frustrated because there are pentagons with negative exchange couplings per bond in the systems. The C_{60} molecule has three isomers, denoted as D_{2h} (T_h), D_{3d} and D_{5d}. In all cases the pentagons are separated. The D_{2h} form, the soccer ball, is observed in solids. The D_{3d} and D_{5d} forms are observed in solutions. This variety is caused by Jahn–Teller distortion. Since the separation of the frustrated pentagons is observed in C_{60} or larger molecules, i.e. when every pentagon of the molecular structure is surrounded by hexagons only, the spin frustrations of the respective pentagons in this case affect each other only slightly. This leads to differences in the magnetic ground-state properties between the C_{60}, C_{70}, and C_{84} molecules and the others. This is particularly apparent when comparing the results gathered together in table 2 and the information about the distributions of angles between neighbouring spins on pentagons of the molecules (figure 1). Only in the case of the C_{60}, C_{70}, and C_{84} molecules are the distributions peaked around the angle 144° (i.e. $4\pi/5$) as should be expected when different pentagons do not frustrate each other any more [14]). For some isomers of C_{76} and C_{78} molecules, the angle does not follow this pattern. Evidently, the C_{58} molecule constitutes an intermediate case. Its two local energy minima (valleys) are degenerate, the angles between

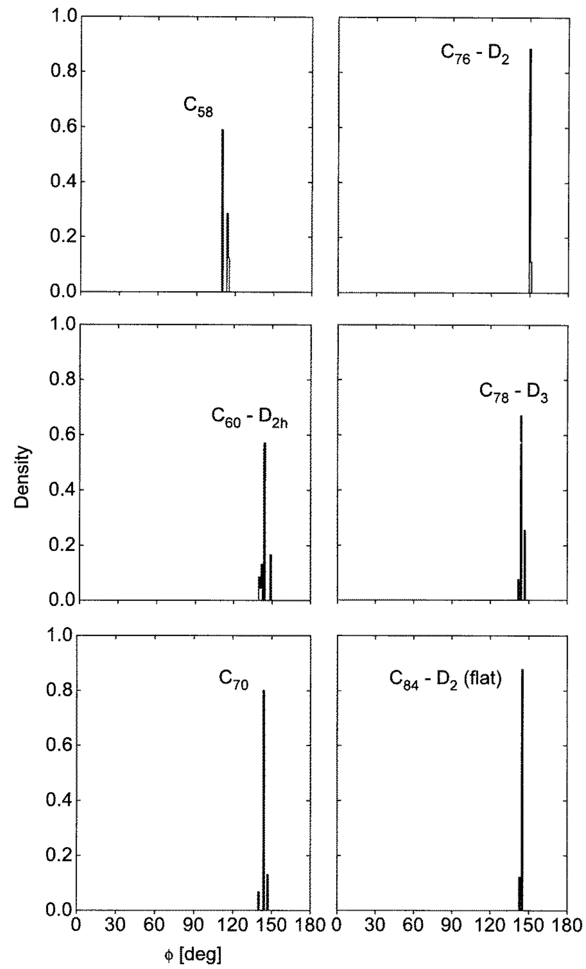

Figure 1. The probability distribution (density) of the angle made by a nearest-neighbour pair of spins on a pentagon of a C_N free molecule.

neighbouring spins on pentagons are quite different to those in any other case, and each ground-state spin-configuration net magnetic moment is non-zero. This molecule is just the last one with non-separated pentagons.

From the comparison of our results with those presented by Coffey and Trugman [14], we obtained the valley structure of the ground states of the fullerenes (local minima of the energy were found). We obtained exactly the same lowest-energy spin configuration for all isomers of C_{60}. This configuration corresponds to the situation in which there is no frustration beyond that of an elementary pentagon, and spins on a non-pentagon bond are antiparallel. The energy obtained is the natural lower bound in this case [14]. Any other frustrations would increase the energy. However, we found that the system has another local energy minimum, close to the first one (table 1). Moreover, the probabilities of finding the molecule after its rapid cooling in the two minima are comparable (see table 3). Thus we cannot be sure whether one of them is distinguished. In particular the metastable states in solids (isomer D_{2h} or T_h) and solutions (isomers D_{3d} and D_{5d}) are virtually the same.

Table 4. The estimates of the energy barriers, calculated in the units $|J|$ per site, obtained by the simulated-annealing Monte Carlo method. The hooked arrows indicate barriers between values in neighbouring columns from the first line. (Asterisks indicate degeneracy of the energy valley.)

	Isomer	E_0	E_1	E_2
C_{58}		-1.3086^*	-1.3073^*	
		$\hookrightarrow$	~ -1.3071	
C_{60}	D_{2h} or T_h	-1.3090	-1.3009^*	
		$\hookrightarrow$	~ -1.2788	
	D_{3d}	-1.3090	-1.3009^*	-1.3007
		$\hookrightarrow$	~ -1.2793	~ -1.2824
			$\hookrightarrow$	~ -1.2999
	D_{5d}	-1.3090	-1.3009^*	
		$\hookrightarrow$	~ -1.2788	
C_{70}	D_{5h}	-1.3335	-1.3278^*	-1.3277
		$\hookrightarrow$	~ -1.3156	~ -1.3107
			$\hookrightarrow$	~ -1.2987
C_{76}	D_2	-1.3440	-1.3366	
		$\hookrightarrow$	~ -1.3107	
	D_{2d}	-1.3337^*	-1.3335^*	
		$\hookrightarrow$	~ -1.2291	

Unlike those carried out by Coffey and Trugman [14], our investigations show that the C_{84} molecule does reach the above-mentioned lower bound for the energy in this case, as well. Moreover, as can be seen in table 3, the lowest-energy spin arrangement is the most probable, and thus is distinguished. This seems reasonable, because this molecule has the most hexagons preventing its pentagons from interference with each other. In our opinion, the calculations presented imply that in principle some magnetic properties of C_{60} and C_{84} are similar. Therefore, we do not confirm the conclusion of Coffey and Trugman [14] that the C_{60} molecule is unique. Notice that these are the only cases with zero net magnetic moment among all of the ground states (table 2). In the case of the C_{70} system our conclusions in general agree with those of Coffey and Trugman [14]. The molecule does not reach its lower bound energy, although our lowest energy is about 0.1% lower than that obtained by Coffey and Trugman [14].

The energy barriers for some molecules are presented in table 4. Because the energy barriers heights are of order $|J|$ in the quantum approach, the tunnelling effect will occur, and thus there will be a common quantum spin state which can be treated as an instanton.

4. Conclusions

In this work we have presented a calculation of the magnetic ground states of different isomers of fullerenes, C_N, in the quasi-classical approximation. We found that the ground states of these systems generally (i) have several valleys, (ii) are frustrated (with comparable energy order) and that (iii) many of them have net magnetic moment $M = 0$. The properties of the informational entropy suggest that effectively we have two-valley systems, but with growing number of carbon atoms the number of valleys effectively tends to three (cf. table 3).

The heights of the energy barrier between the valleys are of order $|J|$. Because of this, we can expect that in the quantum picture the tunnelling effect will occur, and thus they will merge into a single quantum (mixed) state—an instanton. These results can explain the properties exhibited by C_{60} and C_{70} powders in the process of cooling and heating, where they attain irreversible magnetization at temperatures $T = 50$–60 K and behave like spin glasses with frozen disorder [7].

The question of a metastable character of the ground states of fullerenes that were found needs a more refined treatment. Obviously, either quantum spin fluctuations or thermal activation as well as interactions with molecule vibrations and/or rotations should be taken into account to describe a mechanism for a possible decay and mixing of the states [22]. Recently it was found that in C_{60} single crystal there is a discontinuity of the magnetic susceptibility in the temperature range in which the cooperative orientation ordering phase transition occurs [8].

Because in the Hubbard model the hopping integrals and Coulomb repulsion are of the same order of magnitude [14], the kinetic energy contribution might be significant. That is why we expect electron motion to cause the fullerene ground state to be of spin-liquid type with clearly marked antiferromagnetic correlations rather than instanton-like (frustrated with quantum tunnelling). Indeed, the calculations for the Gutzwiller state carried out by us, where as the starting point for the variational calculations we used the results presented here, confirm that this is the case for C_{60} molecules [2]. This also agrees with the experimental results presented by Kiefl *et al* [34] in their muon study, in which no intrinsic magnetic moments were found. Our calculations also indicate that the ground state of spin-density-wave type is unstable. This result is the opposite of what was described by Bergomi *et al* [16] but the authors carried out their calculations using the Hartree–Fock approximation.

It seems to us that non-doped nanotubes with half-filled bands [32, 33] should exhibit magnetic properties similar to those of fullerenes. In open nanotubes the ground state should be non-frustrated with net magnetic moment $M = 0$, because they are 'wrapped' fragments of graphite layers (they just bear the properties of the layers). The ends of closed nanotubes have pentagons which incur frustrations. Thus, we can expect them to have frustrated magnetic ground states, like fullerenes.

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