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Fullerene in a Magnetic Field

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Abstract: The manuscript presents a trajectory method for describing the rotations of surface crystals such as fullerenes, nanotubes, and nanotori. This method does not require the implementation of successive rotations of the considered molecular structures around the axes of the selected basis. Therefore, it is free from the shortcomings of the approaches of Euler and Hamilton. On its basis, an efficient algorithm for calculating the motions of a magneto-susceptible fullerene in an alternating magnetic field has been developed. The nature of rotation of fullerenes in fields of various configurations has been studied.

Keywords: mathematical modeling; molecular dynamics; nanomaterials

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1. Introduction

To date, a whole class of surface crystals closed on themselves, called buckyballs, has been synthesized. Many isomers of fullerenes have been studied. This class will noticeably expand if atoms of metals, nitrogen, hydrogen, etc., are added to carbon structures [1,2]. The resulting molecular systems have different properties. Moreover, these properties can differ greatly even due to minor changes—defects, temperature, chemical factors, and exposure to fields [3–6]. In order to act on a molecular fullerene structure with a magnetic field, it is necessary that it contains iron atoms or other ferromagnetic material. The magnetic fullerene system can practically be obtained both as a result of an exoendral arrangement of the K_3C_{60} type and with an endohedral arrangement of iron, i.e., $Fe@C_{60}$. At the same time, none of the species has yet been prepared, but the work on the synthesis of magnetic materials is quite active [7–10]. In this work, we will proceed from the simplest design of $Fe@C_{60}$. This makes it possible to spin fullerenes by an alternating field. Of particular interest are fullerites created on the basis of magnetically susceptible fullerenes. In these molecular crystals, due to the high degree of symmetry of the location of the crystal lattice sites and the symmetry of the molecule itself, fullerenes can be unwound without changing their vibrational movements around their centers of mass (without changing the crystal temperature). There are potential opportunities for such unwinding since, in an ideal C_{60}-based fullerite, large-amplitude angular vibrations of molecules are realized. According to [11], their frequency is 34 GHz. In this case, we can talk about the independence of rotational and translational motions, and the material will not be destroyed even with an intensive unwinding of the crystal lattice nodes. Moreover, studies [12–17] have shown that C_{60} fullerenes have a gyroscopic effect, which means that the material becomes more resistant to deformation. Thus, it is possible to accumulate energy on rotational degrees of freedom and thereby control the hardness of molecular crystals. The biomedical focus of articles on molecular robots has a very important aspect related to the release of drugs from the carbon container during their targeted delivery to the affected areas. One of the ways of such release is the unwinding of fullerenes or their dimers [18] by an external alternating magnetic field. In this theoretical work, we wanted to answer the question

of the possibility of spinning up a magneto-susceptible fullerene under the action of an alternating magnetic field. By implementing the developed numerical model, we found the answer to this question.

2. Materials and Methods

We will consider the problem of the rotation of a supermolecule that has its own magnetic moment and is in an alternating magnetic field $\boldsymbol{B} = \boldsymbol{B}(t)$:

$$B_x = B_x(t),\ B_y = B_y(t),\ B_z = B_z(t). \tag{1}$$

Here B_x, B_y, B_z are the projections of the magnetic induction vector on the axes of the absolute basis, the center of which we place at the center of mass of the fullerene.

The specific configuration of the magnetic field, i.e., the distribution of its intensity by components, will be presented below in the calculation results section. Now let us consider a scheme for solving the problem in the case of an arbitrary law of changes in the field components with time. We will use the equations of rotational motion written in the absolute basis (theorem on the change in the angular momentum):

$$\frac{d\boldsymbol{K}}{dt} = \boldsymbol{M}. \tag{2}$$

The projections K_x, K_y, K_z of the vector $\boldsymbol{K}$ are defined by the following relationships:

$$\begin{array}{l} K_x = A\omega_x + F\omega_y + E\omega_z, \\ K_y = F\omega_x + B\omega_y + D\omega_z, \\ K_z = E\omega_x + D\omega_y + C\omega_z. \end{array} \tag{3}$$

Here A, B, C are axial, and D, E, F are centrifugal moments of inertia, which are determined by known formulas:

$$A = m\sum\left(y_i^2 + z_i^2\right),\ B = m\sum\left(z_i^2 + x_i^2\right),\ C = m\sum\left(x_i^2 + y_i^2\right). \tag{4}$$

$$D = -m\sum y_i z_i,\ E = -m\sum z_i x_i,\ F = -m\sum x_i y_i. \tag{5}$$

The moment of magnetic action $\boldsymbol{M}$ on the fullerene is the vector product of its own magnetic moment and the magnitude of the magnetic field strength $\boldsymbol{B}$:

$$\begin{array}{c} \boldsymbol{M} = \boldsymbol{\mu} \times \boldsymbol{B} = \mu \begin{vmatrix} \boldsymbol{i} & \boldsymbol{j} & \boldsymbol{k} \\ \alpha & \beta & \gamma \\ B_x & B_y & B_z \end{vmatrix} = \\ = \mu\left(\beta B_z - \gamma B_y\right)\boldsymbol{i} + \mu(\gamma B_x - \alpha B_z)\boldsymbol{j} + \mu\left(\alpha B_y - \beta B_x\right)\boldsymbol{k}. \end{array} \tag{6}$$

Here $\boldsymbol{i}$, $\boldsymbol{j}$, $\boldsymbol{k}$ are absolute basis vectors; α, β, γ coordinates of the unit vector, coinciding in direction with the vector of the intrinsic magnetic moment $\boldsymbol{\mu}$. If the magnetic moment is directed along the radius of the fullerene, then the coordinates of the unit vector can be found from the coordinates of any atom of the supermolecule as follows:

$$\alpha = \frac{x_k}{r_k};\ \beta = \frac{y_k}{r_k};\ \gamma = \frac{z_k}{r_k}, \tag{7}$$

where $r_k = \sqrt{x_k^2 + y_k^2 + z_k^2}$. As can be seen from the written representations in the equation for changing the angular momentum, the differential sign includes the following functions of time: $\omega_x(t)$, $\omega_y(t)$, $\omega_z(t)$, and also $x_i(t)$, $y_i(t)$, $z_i(t)$ $\left(i = \overline{1, N}\right)$. All of these features are currently unknown. However, there are too many of them to solve the problem only on the basis of three scalar Equation (2). Euler's theorem is known that a complex spatial rotation of a body can always be represented as a rotation around some axis with an instantaneous

angular velocity. Using this theorem in the case of rotational motion of fullerene around its center of mass, we can write:

$$\frac{d\boldsymbol{r}_i}{dt} = \boldsymbol{\omega} \times \boldsymbol{r}_i \ \left(i = \overline{1,N}\right). \tag{8}$$

Here $\boldsymbol{r}_i = (x_i, y_i, z_i)$, $\boldsymbol{\omega} = \left(\omega_x, \omega_y, \omega_z\right)$. Moreover, the coordinates of these vectors are presented in an absolute basis. Since we consider the framework structure of the fullerene to be non-deformable, the vector $\boldsymbol{\omega}$ will be the same for all fullerene nodes, i.e., will not depend on the number "i". Thus, the equations for the coordinates of fullerene nodes $x_i(t)$, $y_i(t)$, $z_i(t)$ $\left(i = \overline{1,N}\right)$ are kinematic relations (8). As a result, we have obtained a closed system of scalar equations for finding all unknown time functions that appear under the differential sign on the left side of (2). Differential Equations (2) and (8) are integrated under the following initial conditions:

$$\begin{array}{rl} t = 0, & K_x = A^0\omega_x^0 + F^0\omega_y^0 + E^0\omega_z^0, \\ & K_y = F^0\omega_x^0 + B^0\omega_y^0 + D^0\omega_z^0, \\ & K_z = E^0\omega_x^0 + D^0\omega_y^0 + C^0\omega_z^0, \\ x_i = x_i^0, & y_i = y_i^0,\ z_i = z_i^0 \ \left(i = \overline{1,N}\right). \end{array} \tag{9}$$

Here, the index zero at the top marks the initial values of all considered quantities. Thus, relations (2)–(9) determine the formulation of the problem of fullerene rotations in alternating magnetic fields. One-step methods of a high order of accuracy, to which it belongs, and the standard Runge–Kutta scheme of the fourth order of accuracy use the idea of recalculating the desired values at intermediate positions of a single time step. Therefore, all calculated values are determined both on time layers and at intermediate positions between layers. However, it follows from the above relations that the components of the instantaneous angular velocity vector of a molecular object are found each time from the solution of an algebraic system of equations using new values of the angular momentum projections on the right-hand sides of these algebraic equations.

The presented method for calculating the rotation of bodies does not use the Euler angles connecting the relative positions of the absolute and local bases. Therefore, when implementing it, there is no need to use the kinematic Euler relations, which have a coordinate singularity at nutation angles that are multiples of π. In this regard, studies carried out on the basis of the presented mathematical model have no restrictions on nutation angles. Moreover, we do not use Hamiltonian quaternions. Therefore, in this study, we approve the third method of specifying the rotation of bodies in space, associated with the calculation of the projections of the angular velocity of the body on the axes of the absolute basis and the determination of the instantaneous position of the body by a set of coordinates of representative points of the body. A distinctive feature of calculations of body rotations in the absolute basis is the absence of successive rotations at the level of elementary angles $\omega_x \frac{\Delta t}{2}$, $\omega_y \frac{\Delta t}{2}$, $\omega_z \frac{\Delta t}{2}$. This is achieved by simultaneously finding the projections of angular velocities as a result of solving a system of algebraic equations according to Cramer's rule.

Conservation of Total Energy in the System

Let a fullerene, having its own magnetic moment, be placed in a constant magnetic field B_0 = const. If these vectors do not match, then the object, which has its own magnetic moment, will oscillate endlessly. We will assume that at the initial moment of time, the arrow is deviated from the direction of the magnetic field by an angle $\varphi - \varphi_0$. The total energy balance of a moving magnetic needle (magnetic pendulum) will be determined by the following relationship:

$$\frac{J\omega^2}{2} + E_M^0 - \Delta E_M = E_M^0 = const. \tag{10}$$

Here $\omega = \sqrt{\omega_x^2 + \omega_y^2 + \omega_z^2}$ is the local value of the angular velocity of the fullerene molecule; $J = A{\alpha_1}^2 + B{\beta_1}^2 + C{\gamma_1}^2 + 2D\beta_1\gamma_1 + 2E\gamma_1\alpha_1 + 2F\alpha_1\beta_1$—the magnitude of the moment of inertia of the supermolecule relative to the instantaneous axis of rotation; $\alpha_1, \beta_1, \gamma_1$—direction cosines of this axis with respect to the axes of the absolute basis.

The characteristic energy in the magnetic pendulum problem is E_M^0. This value can be calculated analytically, then the relative error of the fulfillment of relation (10) will be as follows:

$$\varepsilon = \frac{J\frac{\omega^2}{2} - \Delta E_M}{E_M^0}. \tag{11}$$

The magnitude of the magnetic moment is:

$$M = \mu B_0 \sin\varphi. \tag{12}$$

The characteristic potential energy of the magnetic field and the change in this energy when the arrow turns as an angle of $\varphi - \varphi_0$ are determined by the relations:

$$E_M^0 = \mu B_0 \int_0^{\varphi_0} \sin\varphi d\varphi = -\mu_0 B_0 \cos\varphi \Big|_0^{\varphi_0} = \mu B_0(1 - \cos\varphi_0), \tag{13}$$

$$\Delta E_M = \mu B_0(\cos\varphi - \cos\varphi_0). \tag{14}$$

3. Results of Calculations

Two field configurations were considered. One of these configurations:

$$B_x = B_0 \sin(ft),\ B_y = 0,\ B_z = 0. \tag{15}$$

The other is a rotating field:

$$B_x = B_0 \sin(ft),\ B_y = B_0 \cos(ft),\ B_z = 0. \tag{16}$$

It was assumed in the calculations that the value of the intrinsic magnetic moment of the fullerene is equal to the magnetic moment of the iron atom. We consider this atom to be intercalated into the framework structure of fullerene. The oscillation amplitude of the alternating magnetic field was taken equal to B_0 = 1 T.

According to the presented mathematical model, it is possible to determine the projections of the instantaneous angular velocity vector on the axes of the absolute basis, as well as the trajectories of the nodes of the molecular structure. Cases with different frequencies of field change were calculated. Two typical cases f = 100 GHz and f = 1000 GHz, are shown in Figures 1–4. In the case of a unidirectional field, the fullerene moves parallel to the plane, passing through the initial position of the magnetic field vectors and intrinsic magnetic moment.

The Figure 1 refers to the rotation of a magneto-susceptible fullerene in a unidirectional magnetic field with a frequency f = 100 GHz.

The Figure 2 refers to the rotation of a fullerene intercalated with iron in a unidirectional magnetic field with a frequency f = 1000 GHZ.

The Figure 3 refers to the spatial rotations of fullerene in a rotating magnetic field f = 100 GHz.

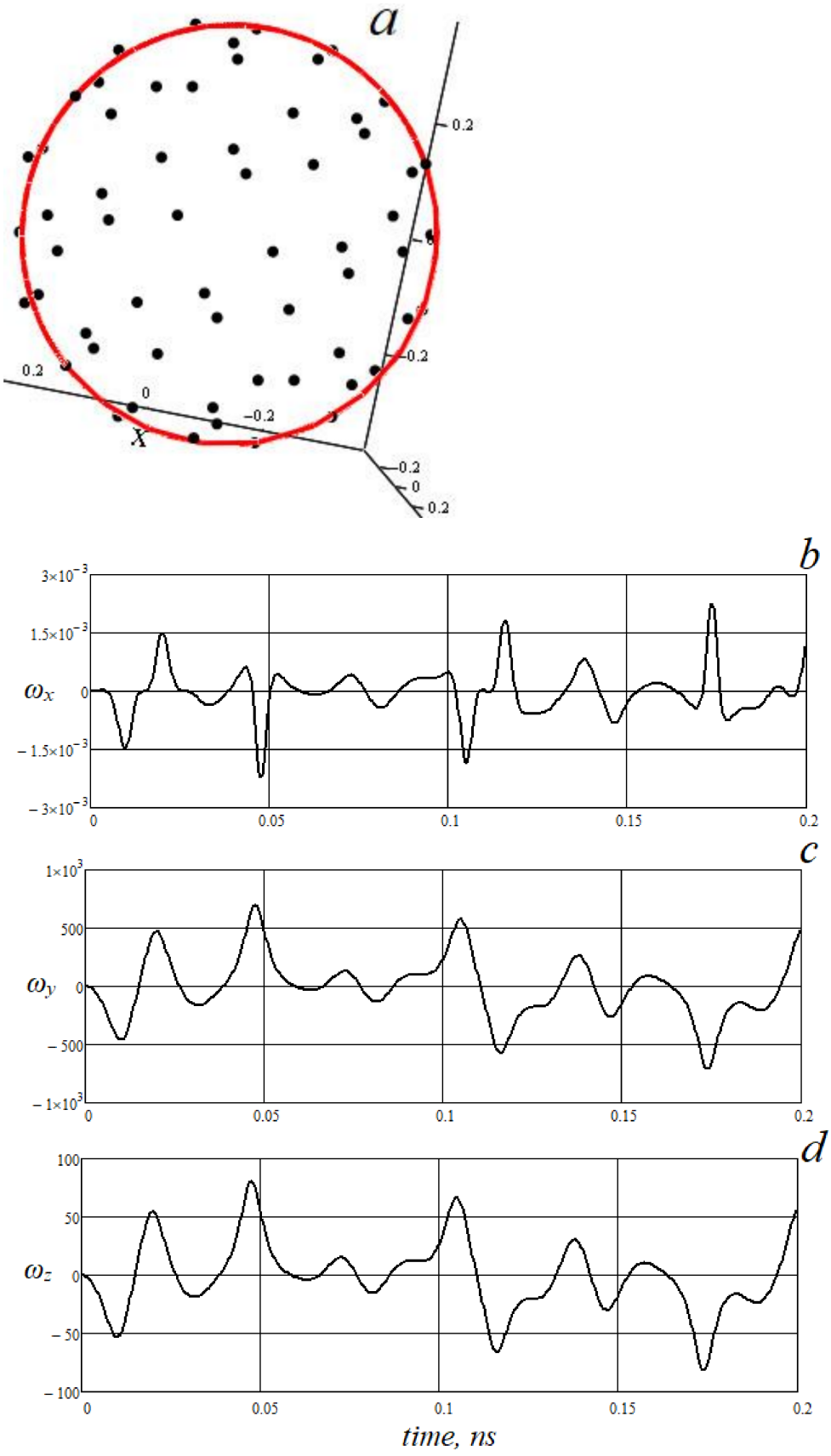

Figure 1. (**a**) Fullerene point trajectory; (**b**) *x*-projection of fullerene rotation frequency; (**c**) *y*-projection of fullerene rotation frequency; (**d**) *z*-projection of fullerene rotation frequency.

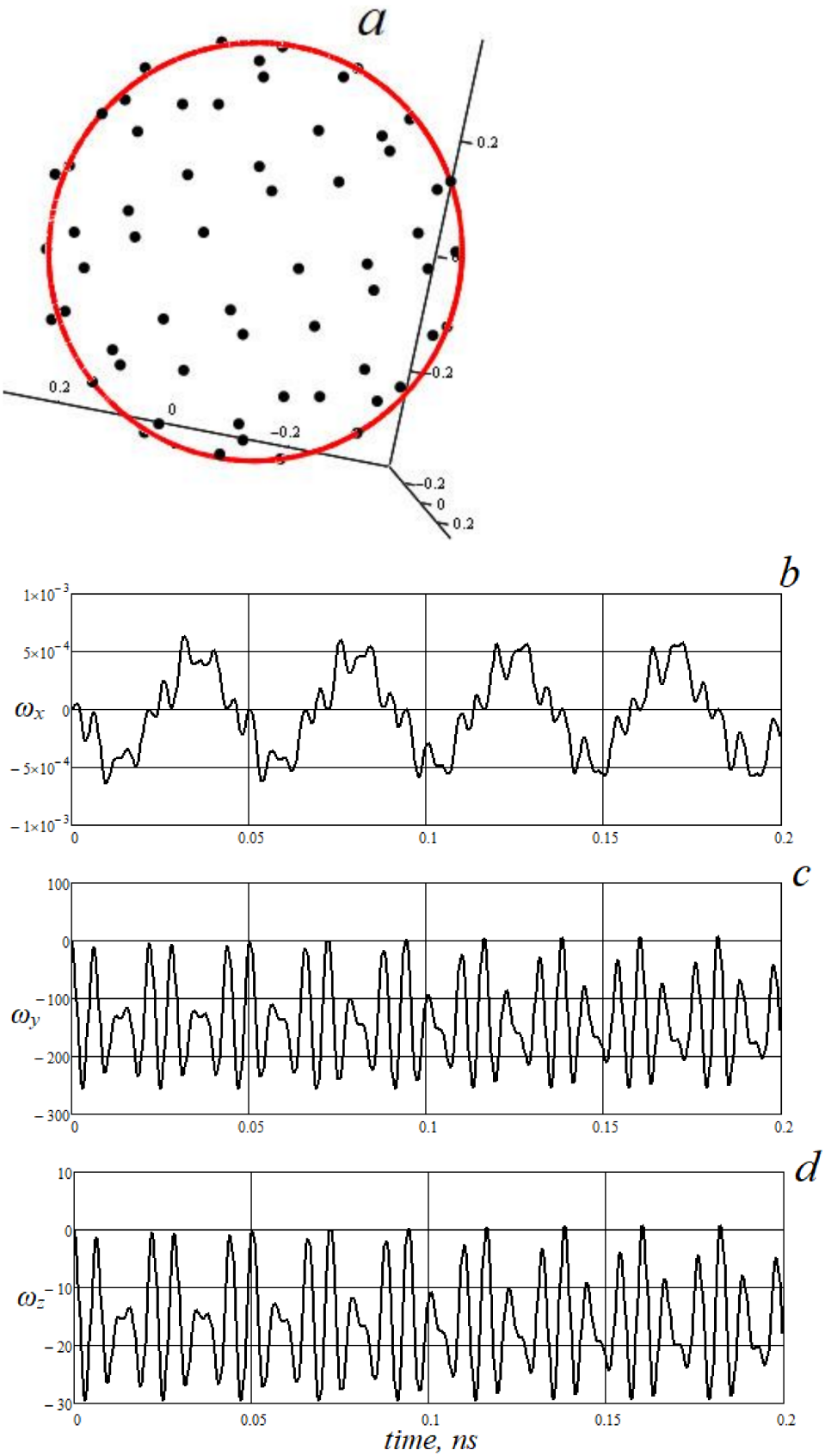

Figure 2. (**a**) Fullerene point trajectory; (**b**) *x*-projection of fullerene rotation frequency; (**c**) *y*-projection of fullerene rotation frequency; (**d**) *z*-projection of fullerene rotation frequency.

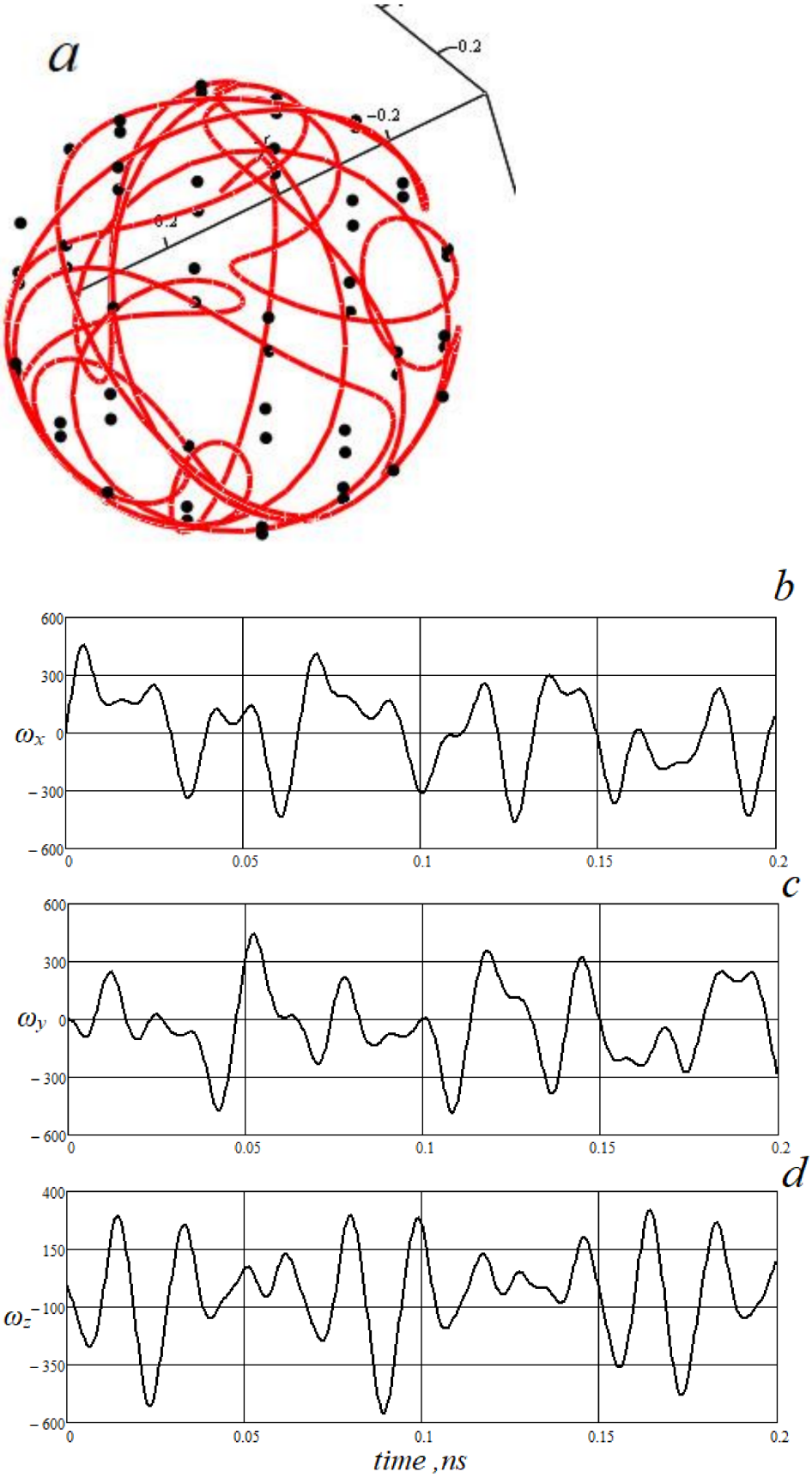

Figure 3. (**a**) Fullerene point trajectory; (**b**) *x*-projection of fullerene rotation frequency; (**c**) *y*-projection of fullerene rotation frequency; (**d**) *z*-projection of fullerene rotation frequency.

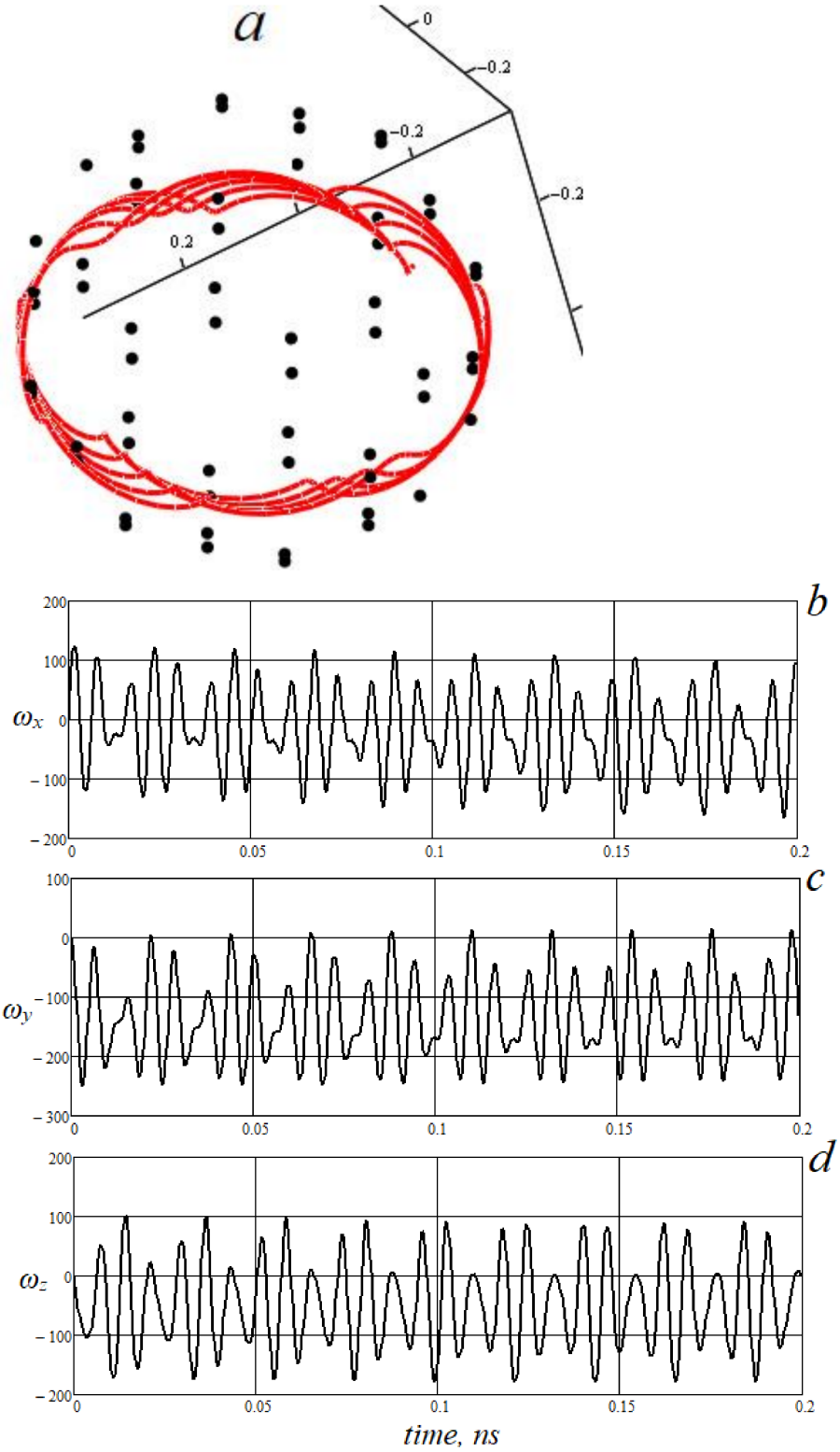

Figure 4. (**a**) Fullerene point trajectory; (**b**) x-projection of fullerene rotation frequency; (**c**) y-projection of fullerene rotation frequency; (**d**) z-projection of fullerene rotation frequency.

Figure 4 refer to the quasi-plane fullerene rotation in a rotating field f = 1000 GHz. The red line shows the trajectory of a representative carbon atom located at the initial time in the plane of vectors $\boldsymbol{B}$ and $\boldsymbol{\mu}$. By integrating the angular velocity over the section of unidirectional rotation, one can determine the amplitude of the resulting quasi-periodic oscillations. It turned out to be close to 2π. Therefore, we called this mode of motion

2π-rotations. It is interesting to note that somersaults that occur during an unstable rotation of a body around an intermediate axis (Louis Poinsot instability) are π rotations of the body around an axis with a minimum value of the moment of inertia. Rice. 2. demonstrates the nature of the movement of a magneto-susceptible fullerene at a magnetic field frequency f = 1000 GHz. As can be seen from the distributions of the components of the instantaneous angular velocity vector at moments close to the initial one, the fullerene motion is quasi-periodic, then it becomes periodic with time. Due to the initial direction of the intrinsic magnetic moment vector, chosen randomly, the plane of motion of the carbon atoms that make up the fullerene has slightly deviated from the x_z plane. This can be seen from the projection ω_z, which is synchronous with the projection ω_y and is slightly more than ten percent of it. In addition, both of these projections have the same sign. This means that the corresponding angular coordinates will change monotonically. Thus, the movement, in this case, will be a rotation (albeit uneven) around an axis that has a constant direction in space. Figure 3 shows the oscillations of a magnetic pendulum in a rotating magnetic field corresponding to the frequency f = 100 GHz. In this case, the components of the vector of the angular velocity of the magnetic fullerene are not synchronized and are equivalent in magnitude. As can be seen from Figure 4, at a frequency f = 1000 GHz in a rotating magnetic field, motions of a molecular object are obtained with the trajectory of an atomic particle on the surface of fullerene close to a certain plane determined by the initial data of magnetic quantities. In this case, the instantaneous angular velocity vector has significant deviations from the normal to the specified surface. However, as can be seen from Figure 4. there is a thickening of the trajectories, and we named this regime quasi-plane rotation.

4. Discussion

The desire to determine the position of a body in space by the angles of its rotation relative to some absolute basis inevitably leads to problems associated with restrictions on nutation angles in Euler's approach or to a complex algebra of hypercomplex numbers in Hamilton's approach. In this paper, we propose to determine the position of a non-deformable body rotating in space by a set of coordinates of its representative points (the trajectories of these points). In this work, we combined the tractor approach with a high-precision scheme for calculating evolutionary equations and obtained a calculation error in the test problem of a spherical magnetic pendulum close to machine accuracy. Based on the computational procedure developed by the authors, the possibility of spinning C_{60} fullerene intercalated by an iron atom by an alternating magnetic field was analyzed. It is found that angular vibrations of fullerene are observed at the field frequency f = 100 GHz. At a frequency above the specified value, the oscillations turn into directed rotations.

The proposed approach can be used to analyze the rotational dynamics of any body. In particular, it has wide applications in molecular dynamics since it can be generalized to the case of deformable molecular structures.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Fowler, P.W.; Manolopoulos, D.E. *An Atlas of Fullerenes*; Clarendon: Oxford, UK, 1995.
2. Guan, J.; Jin, Z.; Zhu, Z.; Chuang, C.; Jin, B.Y.; Tománek, D. Local curvature and stability of two-dimensional systems. *Phys. Rev. B* **2014**, *90*, 245403. [CrossRef]
3. Harris, P.J.F. Fullerene Polymers: A Brief Review. *C—J. Carbon Res.* **2020**, *6*, 71. [CrossRef]
4. Thakral, S.; Mehta, R.M. Fullerenes: Introduction and Overview of Their Biological Properties. *Indian J. Pharm. Sci.* **2006**, *68*, 13. [CrossRef]
5. Wang, L.; Wang, Y.; Hao, J.; Dong, S. Magnetic fullerene-DNA/hyaluronic acid nanovehicles with magnetism/reduction dual-responsive triggered release. *Biomacromolecules* **2017**, *18*, 1029–1038. [CrossRef]
6. Mallik, S.; Mattauch, S.; Dalai, M.K.; Brückel, T.; Bedanta, S. Effect of magnetic fullerene on magnetization reversal created at the Fe/C_{60} interface. *Sci. Rep.* **2018**, *8*, 5515. [CrossRef] [PubMed]
7. Lee, G.H.; Huh, S.H.; Jeong, J.W.; Ri, H.C. Excellent magnetic properties of fullerene encapsulated ferromagnetic nanoclusters. *J. Magn. Magn. Mater.* **2002**, *246*, 404–411. [CrossRef]
8. Takenobu, T.; Chi, D.H.; Margadonna, S.; Prassides, K.; Kubozono, Y.; Fitch, A.N.; Kato, K.; Iwasa, Y. Synthesis, structure, and magnetic properties of the fullerene-based ferromagnets Eu_3C_{70} and Eu_9C_{70}. *J. Am. Chem. Soc.* **2003**, *125*, 7, 1897–1904. [CrossRef]
9. Giacalone, F.; Martin, N. Fullerene polymers: Synthesis and properties. *Chem. Rev.* **2006**, *106*, 12, 5136–5190. [CrossRef]
10. Bhakta, P.; Barthunia, B. Fullerene and its applications: A review. *J. Indian Acad. Oral. Med. Radiol.* **2020**, *32*, 159–163. [CrossRef]
11. Bubenchikov, A.M.; Bubenchikov, M.A.; Mamontov, D.V.; Lun-Fu, A.V. Md-Simulation of Fullerene Rotations in Molecular Crystal Fullerite. *Crystals* **2019**, *9*, 496. [CrossRef]
12. Bubenchikov, A.M.; Bubenchikov, M.A.; Lun-Fu, A.V.; Ovchinnikov, V.A. Gyroscopic effects in fullerite crystal upon deformation. *Eur. Phys. J. Plus* **2021**, *136*, 388. [CrossRef]
13. Bubenchikov, M.A.; Bubenchikov, A.M.; Lun-Fu, A.V.; Ovchinnikov, V.A. Dynamics of Fullerenes in the Molecular Crystal of Fullerite. *Phys. Status Solidi A* **2021**, *218*, 2000174. [CrossRef]
14. Bubenchikov, M.; Ovchinnikov, V.; Mamontov, D. Numerical study of precession characteristics of rotating fullerene-C_{60} in intermolecular interaction. *AIP Conf. Proc.* **2020**, *2212*, 020013. [CrossRef]
15. Bubenchikov, M.A.; Lun-Fu, A.V.; Ovchinnikov, V.A. Precession of fullerite rotating node at simplest deformations of crystal fragment. *AIP Conf. Proc.* **2021**, *2337*, 020005. [CrossRef]
16. Bubenchikov, A.M.; Bubenchikov, M.A.; Ovchinnikov, V.A. Gyroscopic effect in intermolecular collision with the C_{60} fullerene molecule. *J. Phys. Conf. Ser. IOP Publ.* **2020**, *1537*, 012007. [CrossRef]
17. Sepahvand, S.; Farhadi, S. Fullerene-modified magnetic silver phosphate ($Ag_3PO_4/Fe_3O_4/C_{60}$) nanocomposites: Hydrothermal synthesis, characterization and study of photocatalytic, catalytic and antibacterial activities. *RSC Adv.* **2018**, *8*, 10124–10140. [CrossRef]
18. Bubenchikov, A.M.; Bubenchikov, M.A.; Mamontov, D.V.; Chelnokova, A.S.; Chumakova, S.P. Movement of fullerenes and their dimers inside carbon nanotubes. *Fuller Nanotub. Carbon Nanostructures* **2021**, *29*, 803–809. [CrossRef]