

Advanced computational method for studying molecular vibrations and spectra for symmetrical systems with many degrees of freedom, and its application to fullerene

Igor Bogush, Victor Ciobu, and Florentin Paladi^a

Department of Theoretical Physics, Moldova State University, A. Mateevici Str. 60, Chisinau 2009, Republic of Moldova

Received 16 May 2017 / Received in final form 23 July 2017

Published online 16 October 2017 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2017

Abstract. A computational method for studying molecular vibrations and spectra for symmetrical systems with many degrees of freedom was developed. The algorithm allows overcoming difficulties on the automation of calculus related to the symmetry determination of such oscillations in complex systems with many degrees of freedom. One can find symmetrized displacements and, consequently, obtain and classify normal oscillations and their frequencies. The problem is therefore reduced to the determination of eigenvectors by common numerical methods, and the algorithm simplifies the procedure of symmetry determination for normal oscillations. The proposed method was applied to studying molecular vibrations and spectra of the fullerene molecule C_{60} , and the comparison of theoretical results with experimental data is drawn. The computational method can be further extended to other problems of group theory in physics with applications in clusters and nanostructured materials.

1 Introduction

The vibration frequency and the frequency degeneracy are important characteristics in the study of molecular vibrations and spectra. Each frequency corresponds to normal oscillation in classical mechanics or certain phonon eigenfunction in quantum mechanics. When one needs to investigate not only such phenomenological characteristics, but also it is important to study the vibration process itself, it becomes useful to consider compliance of the normal oscillation with certain irreducible representation of the point group symmetry. This allows us to consider, for example, the vibration symmetry or the parity of oscillation with respect to the action of reflection operator regarding a specific plane. This problem becomes laborious for molecules with many degrees of freedom, like fullerene. In the classical approach to the problem described in [1–3], the numerical algorithm is difficult to automate for its computer implementation, because the intermediate calculations do not deal with a particular vector, but with a subspace or chains of subspaces, i.e. linear combinations of the vectors and their chains. If the matrix operators in the space of a certain irreducible representation are unknown, it is necessary to solve the problem of finding the basis of irreducible representation. These problems can be overcome by a computational method described in this article.

The method is applied to the molecule of fullerene C_{60} . In such a way, the performance and reliability of the developed computational algorithm for finding the normal coordinates with the use of group theory are proved by results for the fullerene molecule. Meanwhile, the accuracy of these results would depend on the used assumption for the potential function of the interaction between carbon atoms, and it does not depend on the group classification method.

2 Theoretical model

Let us consider a molecule of N atoms, and locate the center of the Cartesian coordinate system in the center of mass of the molecule. The position of the i atom is described by the radius vector:

$$\vec{r}_i(t) = \vec{r}_i^0 + \vec{s}_i(t), \quad i = 1, 2, \dots, N,$$

where \vec{r}_i^0 is the position of the i atom in the unexcited molecule, \vec{s}_i is the displacement vector of the i atom from the initial position. Then the energy of the system is

$$\begin{aligned} H(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_N, \dot{\vec{s}}_1, \dot{\vec{s}}_2, \dots, \dot{\vec{s}}_N) \\ = T(\dot{\vec{s}}_1, \dot{\vec{s}}_2, \dots, \dot{\vec{s}}_N) + U(\vec{s}_1, \vec{s}_2, \dots, \vec{s}_N). \end{aligned}$$

^a e-mail: fpaladi@usm.md

It is well known that the kinetic energy depends on the square velocity, and the potential energy function is considered to be a quadratic form of s_i , as normal molecular vibrations are harmonious. A local orthonormal basis $\{\vec{e}_1^{(i)}, \vec{e}_2^{(i)}, \vec{e}_3^{(i)}\}$ is provided for each i atom. System state is completely described by $3N$ values $s_\alpha^{(i)}$ in the configuration space \mathbb{R}^{3N} , where $s_\alpha^{(i)}$ is the i atom movement projection on α axis of the local basis. The displacement vector in this space is defined by the following expression, that is, mechanical representation

$$\vec{x} = (s_1^{(1)}, s_2^{(1)}, s_3^{(1)}, s_1^{(2)}, s_2^{(2)}, s_3^{(2)}, \dots, s_1^{(N)}, s_2^{(N)}, s_3^{(N)}).$$

There are totally $3N - 6$ normal vibrations in the molecule (or $3N - 5$ for the linear molecules). Vector \vec{x} can be decomposed on $3N$ normal coordinates, three of which correspond to translation and three – to rotation. If the total momentum of the molecule is zero, then \vec{x} can be represented in the form

$$\vec{x} = \sum_{j=1}^{3N-6} Q_j \vec{e}_j \sin(\omega_j t + \alpha_j),$$

where Q_j is the normal coordinate j , ω_j corresponds to the angular frequency of the vibration j , and $\{\vec{e}_j\}$ forms a new orthonormal basis for the normal coordinates. If the frequencies $\omega_i \neq \omega_j$ for $i \neq j$, then the vectors are orthogonal, i.e. $\vec{e}_i \perp \vec{e}_j$. If different vibrations have the same frequencies, it is impossible to determine the specific basis vectors, because normal coordinates with the same frequency are determined with accuracy up to their linear combination. Therefore, one can always request that the condition for orthonormality of vectors $\{\vec{e}_j\}$ is respected in this vibrational representation.

The problem of determining normal vibration frequencies and the symmetry classification of normal vibrations, i.e. \vec{e}_j vectors, using the group theory approach is further studied. Let us consider a point group symmetry of the molecule $G, g \in G, |G| = m$. We denote vibrational representation of the point group in $3N - 6$ dimensions by Γ_{vib} , and Γ_{mec} is the mechanical representation of the group, which includes also translation and rotation of the molecule as a whole. Γ_{mec} and Γ_{vib} are reducible and can be decomposed into irreducible representations Γ'_i . Decomposition of reducible representation into irreducible ones shall follow the standard procedure described, for example, in [2]. For nonlinear molecules in a tridimensional space the irreducible representation, a basis of which is translation of the molecule along the axes, is the tridimensional antisymmetric representation T_u , and the irreducible representation with rotational basis is the tridimensional symmetric representation T_g (or it is bidimensional symmetric one for the linear molecules B_g). Let us denote by $\hat{T}(g)$ the operator of g element in the mechanical representation; $D_{\alpha\beta}^{(i)}(g)$ is the matrix element in the irreducible representation i , and $Tr D_{\alpha\beta}^{(i)}(g) \equiv \chi_i(g)$ is the character of g element in the representation i . Projectors on the invariant subspace of irreducible representation are

defined as follows [2]:

$$\hat{P}_{\alpha\beta}^{(i)} = \sqrt{\frac{l_i}{m}} \sum_{g \in G} \overline{D_{\alpha\beta}^{(i)}(g)} \hat{T}(g), \quad (1)$$

where $\overline{D_{\alpha\beta}^{(i)}(g)}$ is the complex conjugate element to $D_{\alpha\beta}^{(i)}(g)$, and l_i denotes the representation dimension.

2.1 The classic algorithm

Let us consider the classic algorithm for obtaining the normal coordinates, as described in [2]:

- decompose mechanical representation on the irreducible representation;
- create symmetric and antisymmetric displacements;
- get the chain vectors by applying the operators of mechanical representation to the displacement vectors;
- compose the projector operators of the irreducible representations by using the matrix elements of the operators in this representation;
- get the set of basis vectors by applying projector operators on one of the vectors of each chain;
- find the linear combination of basis vectors obtained for projectors of a certain irreducible representation, which will be the normal mode vector.

Representation decomposition on the irreducible representations is optional. Knowing how many times the irreducible representation is included in the mechanical one allows to exclude from the calculation those operator actions on the various displacements which do not bring new information about the invariant subspace. Also, drawing symmetric and antisymmetric displacements is not necessary, but it allows us to consider only a rotation group without inversion (mirror image) instead of the whole symmetry group. Therefore, finding the chains of vectors is optional, but makes it possible not to perform unnecessary additional calculations. Projections are further obtained according to equation (1), and act on any vector of each chain. Finding all projectors is not required since the total number of independent vectors is equal to the product of dimension of the irreducible representation and the number of occurrences of this representation into the mechanical one. Acting with a set of operators for a particular type of the irreducible representation, one obtains the invariant basis of the space of the aggregate of all irreducible representations of this type. Then we find another basis of this subspace, so that every basis vector corresponds to a normal vibration of the system of atoms. This step is either done intuitively for trivial cases of subspaces with small dimensions or diagonalizing the Hamiltonian formed by coordinates of one of the spaces. The method in which some of the above-mentioned steps are excluded is described in [3]. This method has been developed to reduce the number of laborious calculations for researchers. With the development of computer technology, it has become possible to exclude the step of

creating symmetric and antisymmetric displacement vectors in order to reduce the number of elements in the group used in these calculations. To obtain the projector, characters are used instead of the matrix elements in irreducible representations, which allow the method proposed below to be used when the matrix form of the irreducible representations are not known [4–6].

2.2 The new algorithm

The algorithm of the modified calculation method has the following steps:

- build one projector for each type of the irreducible representation according to equation (1);
- find eigenvectors with nonzero eigenvalues, which will be the basis of the projector invariant subspace;
- find a linear combination of basis vectors obtained for the projector of a certain irreducible representation, which will be the normal mode vector.

Let us consider N number of atoms, n_e is the number of elements in the group, and n_p is the number of projectors. The computational complexity for one projector operator is $O(n_e N^2)$, and the first step takes $O(n_p n_e N^2)$. The second step resolves the eigenvector problem for each projector. The complexity of the problem for determining the eigenvector has the form $O(N^\xi)$, where constant ξ is equal approximately to 3, depending on the method of diagonalization of matrices. Therefore, the complexity of the entire second step of the algorithm is $O(n_p N^3)$. The complexity of the third step is proportional to the complexity of the potential function of the interaction between atoms, and the complexity of the algorithm for determination of the eigenvectors.

Let us build the projector $\hat{P}^{(i)}$, at step 1, by summing projectors $\hat{P}_{\alpha\alpha}^{(i)}$ after all α [6]:

$$\begin{aligned} \hat{P}^{(i)} &= \sum_{\alpha} \hat{P}_{\alpha\alpha}^{(i)} = \sum_{\alpha} \sqrt{\frac{l_i}{m}} \sum_{g \in G} \overline{D}_{\alpha\alpha}^{(i)}(g) \hat{T}(g) \\ &= \sqrt{\frac{l_i}{m}} \sum_{g \in G} \left(\sum_{\alpha} \overline{D}_{\alpha\alpha}^{(i)}(g) \right) \hat{T}(g) \\ &= \sqrt{\frac{l_i}{m}} \sum_{g \in G} \overline{\chi}_i(g) \hat{T}(g). \end{aligned}$$

One can choose such a basis in space L , that some of the vectors form the basis of the projector’s subspace $\hat{P}^{(i)}$. Then any vector in the space can be decomposed in the next vector sum:

$$\overline{x} = \sum_j x_j \overline{e}_j^{(x)} + \sum_k y_k \overline{e}_k^{(y)},$$

where $\overline{e}_k^{(y)}$ is the basis vector in the subspace, and $\overline{e}_j^{(x)}$ is the complementary orthogonal basis vector. Index k takes all projections in the invariant subspace, and index j takes all projections outside the invariant subspace. Let us act on the vector by projector, taking

into account that the element must be in an invariant subspace:

$$\begin{aligned} \hat{P}^{(i)} \overline{x} &= \sum_j x_j \hat{P}^{(i)} \overline{e}_j^{(x)} + \sum_k y_k \hat{P}^{(i)} \overline{e}_k^{(y)} \\ &= \sum_k y_k \hat{P}^{(i)} \overline{e}_k^{(y)} = \sum_k y'_k \overline{e}_k^{(y)}. \end{aligned} \tag{2}$$

We replace \overline{x} with any projector’s eigenvector with eigenvalues λ , and compare it to equation (2):

$$\hat{P}^{(i)} \overline{x} = \lambda \overline{x} = \sum_k y'_k \overline{e}_k^{(y)}. \tag{3}$$

If the eigenvector lies outside the subspace, then it cannot be represented as a linear combination of the basis vectors in the subspace, so its eigenvalue is zero. Since the eigenvectors should form a basis of the space, the number of eigenvectors lying in the subspace matches the subspace dimension. It follows for any \overline{x} from the subspace that the eigenvalues of the eigenvectors, lying in the subspace, must be equal to 1, because of the properties of the projector $\hat{P}^{(i)} \overline{x} = \overline{x}$. Therefore, in order to obtain a basis for the irreducible representation of this type, it is sufficient to choose the eigenvectors with their eigenvalues equal to 1. The normal vibrations of the system, which belong to a given irreducible representation, are obtained by reducing the potential energy to the sum of the squared components of the invariant subspace vector. Vibration frequency degeneration is equal to the dimension of the irreducible representation. Since the normal vibrations are orthogonal, they can be used to build an orthonormal basis of the irreducible representation in order to obtain matrices of the group elements.

3 Results and discussion

It is well known that the fullerene molecule C_{60} has the symmetry of icosahedron (Fig. 1a), and the fullerene itself represents an icosahedron with truncated vertices (Fig. 1b). There are 60 different rotation operators, the action of which transforms the icosahedron into itself. One can associate a reflection operator to each rotation operator, which keeps the icosahedron symmetry. It is possible to obtain a tridimensional representation of the rotation group, the basis of which coincides with the basis of the Cartesian coordinate system (x, y, z) , implying coordinates of the icosahedron vertices. This process consists of two stages. The first stage is to find 12 rotations of the icosahedron, which translate one of the 12 vertices of the icosahedron to a certain pre-selected node (e.g. to the point 2 in Fig. 1a), in which the icosahedron goes into itself without changing orientation in the coordinate system. These rotations are found in a simple way from geometrical considerations. The second step is to apply the rotation operator around an axis that runs through the vertex, which was selected at the first stage (in our example, the axis goes through vertices 1 and 2 in Fig. 1a), for each operator used at this stage. Thus, applying five rotation

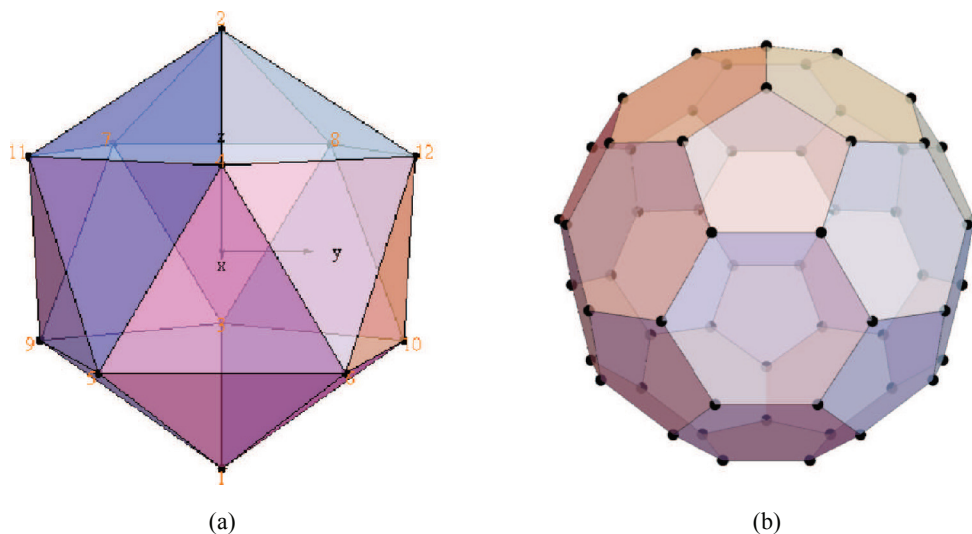


Fig. 1. The icosahedron (a) and truncated icosahedron (b).

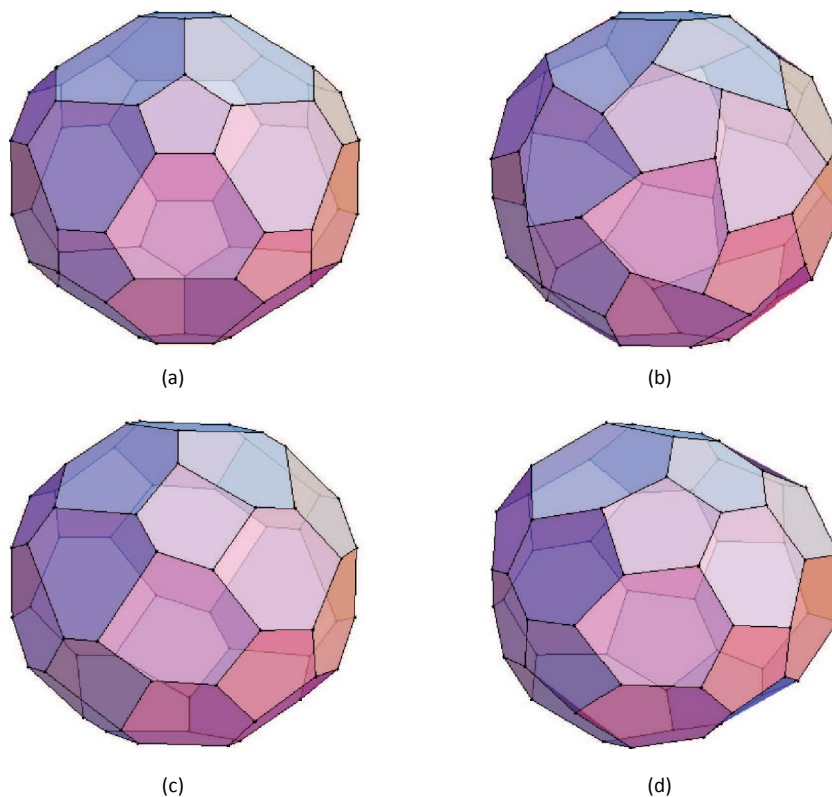


Fig. 2. Examples of the vibrational modes for the following representations: A_g (a), A_u (b), H_g (c), and G_u (d).

operators around the axis at $\frac{2\pi}{5}i$, where $i = 0, 1, 2, 3, 4$, for each of the first 12 vertices, one can obtain all 60 rotation operators. Then, in order to get the complete group, which would also contain reflection, each of the 60 rotation operators is multiplied by the reflection (inversion) operator with respect to one of the reflection planes (e.g. in Fig. 1a the plane (x, z) can be chosen, which is equivalent to the operator $y \rightarrow -y$).

In order to find the mechanical group representation, each atom of the fullerene (i.e. the vertex of truncated icosahedron) needs to be associated with a local basis, in which the displacement vector can be decomposed. One can choose any orthonormal basis, for example, which coincides with the axes x, y, z . For convenience, the following basis has been assigned to one of the atoms: the first vector coincides with the radius vector of the atom; the

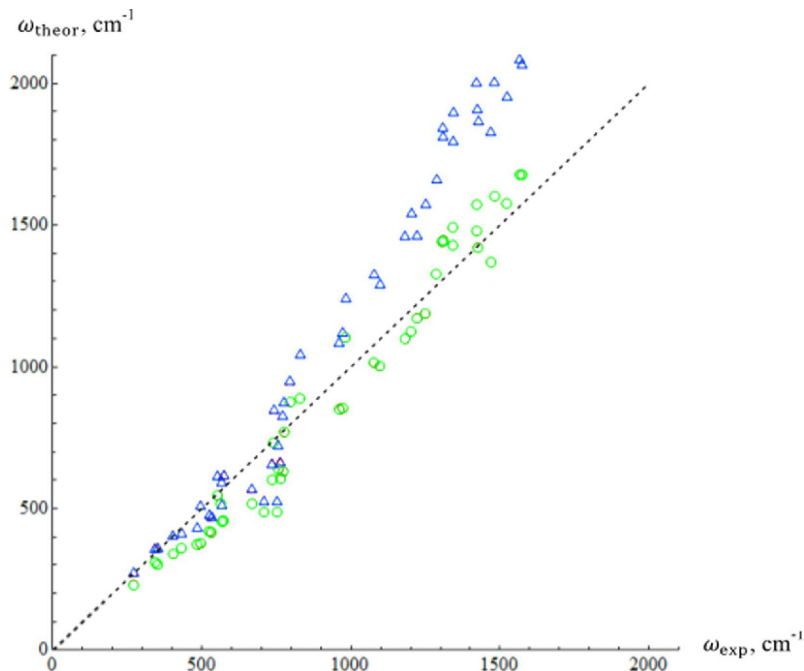


Fig. 3. Deviation of theoretical frequencies from the experimental data: “o” – theoretical results obtained based on the developed algorithm, “Δ” – theoretical result obtained for the elastic interaction model [8].

second vector is chosen perpendicular to the first one, so that it is coplanar with the edge formed by two hexagonal faces; the third vector is determined as a cross product of the first and second vectors, and this automatically ensures its orthogonality to the first two vectors. Such an ordered triplet of vectors forms the right basis, that is, the mixed product of these vectors is greater than zero. By rotating this atom with the rotation operators, one can get the local basis for every other atom.

Figure 2 shows examples of fullerene deformation for the normal oscillations. Figures 2a and 2b correspond to the symmetric and antisymmetric one-dimensional representations, respectively, and Figure 2b being the case where the oscillation frequency is zero. One may notice that this oscillation is the rotation of the pentagon, in which the pentagon bonds are not changed and the motion of atoms in hexagons is perpendicular to the bonds. Figure 2c is an example of oscillations in the five-dimensional symmetric representation, and Figure 2d represents an example of oscillations in the four-dimensional antisymmetric representation.

In order to obtain the mechanical representation of operators, the operator of g_i element is represented by $A^{(i)}$ matrix formed by $60 \times 60 = 3600$ blocks $B_{lm}^{(i)}$, where each block is a 3×3 matrix. Thus, the matrix dimension for the operator of g_i element coincides with the number of degrees of freedom of fullerene, i.e. 180, and it contains a total of 32 400 elements. If the operator i translates the m atom into the l atom, then the matrix $B_{lm}^{(i)}$ is a unitary matrix, which transforms the basis of m atom into the basis of l atom. Otherwise, if the operator does not translate the m atom into the l atom, then the matrix $B_{lm}^{(i)}$ is zero. Obviously, there is only one non-zero block in

each column and each row of the matrix $A^{(i)}$, because each atom is translated into another atom only. Mechanical representation of the fullerene molecule can be decomposed into irreducible representations as follows [2]:

$$\Gamma_{mec} = 2A_g + 3T_{1g} + 4T_{3g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{3u} + 6G_u + 7H_u.$$

Oscillator representation contains all irreducible representations, excluding tridimensional representations corresponding to translation (T_{1u}) and rotation (T_{1g}). Knowing the mechanical representation, it is not difficult to obtain the projectors according to equation (3), and to find their eigenvectors, which are the basis of its invariant subspace. Forming the potential energy function of coordinates in this subspace basis, it is easy to determine such linear combinations of these vectors, which would be normal coordinates. Let us decompose the potential energy function into the Taylor series approximation around the undisturbed state up to the second-derivative terms. One can choose the potential energy so that the zero-degree term is null, and the sum of first-derivative terms is also zero, because the potential energy is minimal in the undisturbed state. Then the potential energy function takes the form $U = \sum_{i,j} a_{ij}x_i x_j$. One can obtain the eigenvectors, which are identical with the vectors of normal vibrations, by diagonalization of the matrix $|a_{ij}|$, that is, it follows from the meaning of the procedure for the matrix diagonalization, because the obtained matrix has non-zero values on the diagonal only, which corresponds to the term $a_{ii}x_i'^2$. By substituting the obtained vectors of normal vibrations into the potential energy function, one can write according to the Lagrange equation $m\ddot{x}'_i + a'_{ii}x'_i = 0$,

Table 1. Comparison of the theoretical and experimental frequencies of normal vibrations for the fullerene molecule.

	Degeneration degree	$\omega_{\text{theor, cm}^{-1}}$	$\omega_{\text{theor, cm}^{-1}}$ [8]	$\omega_{\text{theor, cm}^{-1}}$ [9]	$\omega_{\text{exp, cm}^{-1}}$ [9,10]	$\omega_{\text{exp, cm}^{-1}}$ [11]
A_g	1	374	510	494	496	497
		1369	1830	1607	1470	1469
T_{1g}	3	450	513	565	568	567
		885	1045	813	831	875
		1327	1662	1309	1289	1282
T_{3g}	3	542	615	547	553	536
		638	724	717	756	–
		874	951	757	796	800
		1491	1900	1385	1345	1333
G_g	4	369	433	484	485	487
		513	593	554	567	569
		599	657	745	736	756
		1012	1327	1123	1079	–
		1443	1813	1332	1310	1307
		1600	2006	1578	1482	1501
H_g	5	229	274	259	272	271
		357	413	427	433	434
		485	526	694	709	711
		627	828	760	772	774
		999	1292	1103	1099	1101
		1187	1575	1328	1252	1248
		1479	1910	1535	1425	1422
		1675	2068	1628	1575	1573
A_u	1	1101	1243	929	984	946
T_{1u}	3	419	478	522	526	–
		457	618	570	575	574
		1098	1462	1227	1182	1182
		1416	1868	1560	1429	1427
T_{3u}	3	307	358	330	343	–
		483	526	696	753	–
		851	1122	954	973	1044
		1123	1543	1239	1205	1200
		1574	1954	1598	1525	1536
G_u	4	300	360	353	353	–
		604	663	708	764	–
		769	876	753	776	–
		849	1086	970	961	960
		1440	1845	1369	1309	1313
		1571	2004	1525	1422	–
H_u	5	339	405	399	403	–
		414	470	533	534	–
		514	569	654	668	667
		731	849	727	743	682
		1167	1464	1243	1223	1219
		1426	1797	1387	1344	1375
		1676	2086	1622	1567	–

where $\frac{a'_{ii}}{m} = \omega_i^2$ is the square of the angular frequency of normal vibrations.

The ω_{theor} values of the angular frequency of normal vibrations are obtained for the molecule of fullerene C_{60} according to the model described in [7] by using the proposed in this paper computational method. The results are shown in Table 1. In the papers [12–16] the theoretical frequencies are obtained by using the Density Function Theory (DFT) in the local density

approximation (LDA). Depending on the choice of the set of basis functions, i.e. the expansion of 24 000 planar waves [14], the following relative standard deviation values from the experimental data were reported: 0.019 [14,15], 0.022 [16], 0.039 [13], 0.1 [12]. One can mention that the results for the elastic interaction model [8] are improved, while DFT can lead to the more accurate results, which would require larger computational resources.

Theoretical values calculated based on the developed algorithm and the experimental data [9,10] are drawn in Figure 3. The dotted line represents the first quadrant bisector. One can see that the oscillations with lower frequencies gave greater contribution to the deviation from the experimental values. At the same time, we can conclude that the theoretical model lowers the low frequencies and increases the higher frequencies. The detailed description of the experimental works, including the magnitude of the experimental errors, is given in [11]. In order to describe fullerene oscillations more precisely, one can use modifications of the Tersoff or Brenner potential functions [17], Density Function Theory (DFT) or Density Function Perturbation Theory (DFPT) [11,18,19]. One shall mention that the vibrational spectrum of the crystalline structure (T_h symmetry group) formed from the hydrated single fullerene C_{60} molecules in aqueous solutions was calculated using the molecular dynamics (MD) approach [20], as well as the equation of state for C_{60} fullerene aqueous solutions was proposed [21]. An analogous problem for the fullerene ionization energy calculations based on an efficient Gaussian-basis implementation of ab initio GW with explicit treatment of the dynamical screening through contour deformation techniques was studied [22]. The suggested group classification algorithm can be also applied to the solutions obtained with different approaches, including above-mentioned ones. Investigation of the contribution of different bonds and long-range non-bond interactions between atoms in the fullerene molecule could be the tasks for following works on this topic.

4 Conclusions

The modified computational approach proposed in this article allows us to automate the decomposition process of the mechanical representation of the system into the irreducible ones, which is crucial to consider, in general, complex symmetric system by using the group theory approach. The application of this algorithm allows us to consider any symmetric structures with a large number of interacting particles. In order to obtain the invariant subspaces corresponding to the irreducible representations, it is not necessary to define the potential function a priori.

This approach allows decomposing mechanical representation of the fullerene molecule C_{60} resolving eigenvector problem. The first order approximation is not fully suitable to describe the complete set of vibrations, which leads to the appearance of zero frequencies and unrelated movements of the individual subsystems. Undoubtedly, such oscillations would have lower frequency and energy when taking into account the higher orders. After the functional minimization by using the gradient method [23], the relative standard deviation decreased to 14.7%. The result obtained in the simulations is based on the experimental data presented in [9,10]. The relative standard deviation of theoretical frequencies constitutes 18.4% compared to the experimental ones. More advanced potential functions, such as Brenner or Tersoff, describe the interatomic interaction and molecule oscillations more accurate, and their parameters can be obtained by fitting

theoretical results to the experimental data. As a further progress of the work on fullerene molecules [24,25], a computational method for multi-parameter fitting of potential constants could be developed, in particular, for the simulations of nanoscale systems based on the fullerene.

This work was supported by the Moldova State University project no. 15.817.02.29F. Authors are grateful to Professor Ion I. Geru for his constant help, many valuable remarks and stimulating suggestions.

Author contribution statement

F.P. conceived the study, led the data analysis, proposed theoretical interpretation and wrote the manuscript; I.B. and V.C. assisted with computational method development and theoretical interpretation, and carried out computer simulations.

References

1. S. Sternberg, *Group Theory and Physics* (Cambridge University Press, 1995)
2. M.I. Petrashen, E.D. Trifonov, *Applications of Group Theory in Quantum Mechanics* (Dover Publications, 2009)
3. N.A. Poklonski, *Point Symmetry Groups* (BSU, Minsk, 2003)
4. R.S. Drago, *Physical Methods in Chemistry* (Saunders, Philadelphia, 1977)
5. F.A. Cotton, *Chemical Applications of Group Theory*, 3rd edn. (Wiley-Interscience, 1990)
6. G.L. Bir, G.E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Nauka, Moscow, 1972; English translation: Wiley, New York, 1974)
7. V. Ciobu, Ph.D. thesis, MSU, 2016, p. 172, <http://www.cnaa.md/en/thesis/50909/>, accessed on: 2017/23/07
8. D.E. Weeks, W.G. Harter, *Chem. Phys. Lett.* **144**, 366 (1988)
9. J. Menéndez, J.B. Page, in *Light Scattering in Solids VIII*, edited by M. Cardona, G. Guntherodt (Springer-Verlag, Berlin, Heidelberg, 2000), p. 27
10. J.G. Hou, A.D. Zhao, T. Huang, S. Lu, in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H.S. Nalwa (American Scientific Publishers, 2004), p. 409
11. S.F. Parker, S.M. Bennington, J.W. Taylor, H. Herman, I. Silverwood, P. Albers, K. Refson, *Phys. Chem. Chem. Phys.* **13**, 7789 (2011)
12. G.B. Adams, J.B. Page, O.F. Sankey, K. Sinha, J. Menendez, D.R. Huffmanet, *Phys. Rev. B* **44**, 4052 (1991)
13. G.B. Adams, J.B. Page, O.F. Sankey, M. O'Keeffe, *Phys. Rev. B* **50**, 17471 (1994)
14. P. Giannozzi, S. Baroni, *J. Chem. Phys.* **100**, 8537 (1994)
15. A.A. Quong, M.R. Pederson, J.L. Feldman, *Solid State Commun.* **87**, 535 (1993)
16. X.Q. Wang, C.Z. Wang, K.M. Ho, *Phys. Rev. B* **48**, 1993 (1984)
17. J. Che, T. Çagin, W.A. Goddard III, *Nanotechnology* **10**, 263 (1999)
18. V. Schettino, M. Pagliai, L. Ciabini, G. Cardini, *J. Phys. Chem. A* **105**, 11192 (2001)

19. K. Refson, P.R. Tulip, S.J. Clark, Phys. Rev. B **73**, **155114** (2006)
20. Yu.I. Prylutsky, S.S. Durov, L.A. Bulavin, I.I. Adamenko, K.O. Moroz, I.I. Geru, I.N. Dihor, P. Scharff, P.C. Eklund, L. Grigorian, Int. J. Thermophys. **22**, 943 (2001)
21. I.I. Adamenko, K.O. Moroz, Yu.I. Prylutsky, P.C. Eklund, P. Scharff, T. Braun, Int. J. Thermophys. **26**, 795 (2005)
22. X. Blase, C. Attacalite, V. Olevano, Phys. Rev. B **83**, 115103 (2011)
23. J.A. Snyman, *Practical Mathematical Optimization: An Introduction to Basic Optimization Theory and Classical and New Gradient-Based Algorithms* (Springer US, 2005)
24. V. Ciobu, F. Paladi, Gh. Căpățână, Studia Universitatis Moldaviae **2**, 10 (2015)
25. I. Boguş, V. Ciobu, F. Paladi, Studia Universitatis Moldaviae **7**, 3 (2015)