New approach to nonlinear dynamics of fullerenes and fullerites

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New type of nonlinear (anharmonic) excitations — bushes of vibrational modes — in physical systems with point or space symmetry are discussed. All infrared active and Raman active bushes for C_{60} fullerene are found by means of special group-theoretical methods.

1. Introduction

Vibrations of many fullerenes and fullerites were investigated by different experimental and theoretical methods (see [1,2] and references in these papers). Although the majority of such studies are based on the harmonic approximation only, some nonlinear (anharmonic) effects also were discussed in a number of papers. For example, combination modes of second order brought about by anharmonicity of interactions in C_{60} fullerene are discussed and the appropriate lines in infrared transmission spectra are reported in [3]. The above effects do not exhaust the influence of anharmonicity on the fullerene and fullerite vibrational spectra, and we want to consider an application for these objects of the consistent group-theoretical approach for studying nonlinear vibrations in arbitrary physical systems with discrete (point or space) symmetry developed in [4–7]. This approach reveals the existence of new nonlinear dynamical objects (or new type of anharmonic excitations) in systems with discrete symmetry which we call bushes of normal modes. The concept of the bush of modes can be explained as follows.

In the frame of the harmonic approximation, the set of normal modes can be introduced which are classified by irreducible representations (irreps) of the symmetry group G of the considered physical system in equilibrium. In this harmonic approximation, normal modes are independent of each other, while interactions between them appear when some anharmonic terms in the Hamiltonian are taken into account. Let us note that a very specific pattern of atomic displacements corresponds to each normal mode. As a consequence, we can ascribe to a given mode a definite symmetry group G_D which is a subgroup of the symmetry group G. The group G_D is a symmetry group of the instantaneous configuration of our system in its vibrational state.

Let us excite at the initial instant t_0 only one, arbitrarily chosen mode which will be called the root mode. We suppose that all other modes at the initial moment have zero amplitude. Let the symmetry group G_D and irrep Γ_0 correspond to this root mode. Then we can pose the following question: to which other modes can this initial excitation spread from the root mode? We will refer to these initially "sleeping" modes, belonging to the different irreps Γ_j $(j \neq 0)$, as secondary modes.

A very simple answer to the above question was found in [4,5]. It turns out that initial excitation can spread from the root mode only to those modes whose symmetry is higher than or equal to the symmetry group G_D of the root mode. We call the complete collection containing the root mode and all secondary modes corresponded to it a bush of modes. Since no other modes are excited, the full energy is trapped in the given bush. As a consequence of the above idea, we can ascribe the symmetry group G_D (remember that this is a group of the root mode) to the whole bush, and in this sense we can consider the bush as a geometrical object.

It was proved in [4–6] that all modes belonging to a given bush B $[G_D]$ are coupled by force interactions. It is very important that the structure of a given bush is independent of the type of interactions between particles of our physical system.

A bush of normal modes can be considered as a dynamical object, as well. Indeed, the set of modes corresponding to a given bush B $[G_D]$ does not change in time, while the amplitudes of these modes do change. We can write exact dynamical equations for the amplitudes of the modes contained in the bush B $[G_D]$, if interactions between particles of our physical system are known. Thus, the bush B $[G_D]$ represents a dynamical system whose dimension can be essentially less than that of the original physical system.

The above properties of bushes of normal modes can be summarized in the following manner. A normal mode represents a specific dynamical regime in a linear physical system which, upon being exciting at the initial instant t_0, continues to exist for any time $t > t_0$. Similarly, a bush of normal modes represents a specific dynamical regime in a nonlinear system which can exist as a certain object for any time $t > t_0$.

2. Some mathematical aspects of bushes of normal modes

Let us examine a nonlinear mechanical system of N mass points (atoms) whose Hamiltonian is described by a point or space group G. Let three-dimensional vectors $\mathbf{x}_i(t)$ $(i = 1, 2, \dots, N)$ determine the displacement of the i-th atom from its equilibrium position at time t. The $3 \times N$-dimensional vector $\mathbf{X}(t) = \{\mathbf{x}_1(t), \mathbf{x}_2(t), \dots, \mathbf{x}_N(t)\}$, describing the full set of atomic displacements, can be decomposed into the basis vectors (symmetry-adapted coordinates) of all irreps Γ_j of the group G contained in the mechanical representation[1] Γ

$$\mathbf{X}(t) = \sum_{ji} \mu_{ji}(t)\boldsymbol{\varphi}_i^{(j)} = \sum_j \boldsymbol{\Delta}_j. \qquad (1)$$

Here $\boldsymbol{\varphi}_i^{(j)}$ is the i-th basis vector of the n_j-dimensional irrep Γ_j. The time dependence of $\mathbf{X}(t)$ is contained only in the coefficients $\mu_{ji}(t)$ while the basis vectors are time independent. Thus, a given nonlinear dynamical regime of the mechanical system described by the concrete vector $\mathbf{X}(t)$ can be written as a sum of the contributions $\boldsymbol{\Delta}_j$ from the individual irreps Γ_j of the group G.

Each vibrational regime $\mathbf{X}(t)$, can be associated with a definite subgroup G_D ($G_D \subseteq G$) which describes the symmetry of the instantaneous configuration of this system. Now the following essential idea is proposed. The subgroup G_D is conserved in time; its elements cannot disappear during time evolution except for the case of spontaneous breaking of symmetry which we will not consider in the present paper. This is the direct consequence of the principle of determinism in classical mechanics.

Introducing the operators $\hat{g} \in \hat{G}$ acting on the $3N$-dimensional vectors $\mathbf{X}(t)$, which correspond to the elements $g \in G$ acting on the three-dimensional vectors $\mathbf{x}_i(t)$, we can write the above condition of conservation of G_D as a condition of invariance of the vector $\mathbf{X}$(t) under the action of the elements of the group G_D

$$\hat{g}\mathbf{X}(t) = \mathbf{X}(t), \quad g \in G_D. \qquad (2)$$

Combining Eqs. (1) and (2) one obtains (for the details see [6]) the following invariance conditions for individual irreps Γ_j

$$(\Gamma_j \downarrow G_D)\mathbf{c}_j = \mathbf{c}_j. \qquad (3)$$

Here $\Gamma_j \downarrow G_D$ is the restriction of the irrep Γ_j of the group G to the subgroup G_D, i.e. the set of matrices of Γ_j which correspond to the elements $g \in G_D$ only. The n_j-dimensional vector $\mathbf{c}_j$ in Eq. (3) is the invariant vector in the carrier space of the irrep Γ_j corresponding to the given subgroup $G_D \subset G$. Note that each invariant vector of a given irrep Γ_j determines a certain subspace of the carrier space of this representation, and the total number of arbitrary constants upon which the vector depends is equal to the dimension of this subspace. If in solving Eq. (3) we find that $\mathbf{c}_j \neq 0$, then the irrep Γ_j does contribute to the dynamical regime $\mathbf{X}(t)$ with the symmetry group G_D. Moreover, the invariant vector $\mathbf{c}_j$ determines the explicit form of the mode of the irrep Γ_j belonging to the bush of modes associated with the given nonlinear dynamical regime.

We shall illustrate the general statements of bush theory with C_{60} fullerene having the buckyball structure and the icosahedral symmetry group $G = I_h$. There are 10 irreducible representations of dimensions 1 (A_g, A_u), 3 (F_{1g}, F_{1u}, F_{2g}, F_{2u}), 4 (G_g, G_u) and 5 (H_g, H_u) associated with the group I_h. The infrared (IR) active modes belong to the irrep F_{1u}, and the modes, which are active in Raman (R) experiments, belong to irreps A_g or H_g. We found all bushes of modes for C_{60} fullerene. There are 22 different bushes for this fullerene. Let us consider the bush B7 corresponding to the symmetry group $G_D = C_{5v} \subset I_h$. Only four irreps A_g, H_g, F_{1u} and F_{2u} contribute to it (the appropriate invariant vectors are zero for all other irreps of the icosahedral group $G = I_h$)[2]

B7: [symmetry C_{5v}]:

$$A_g(a) - I_h,\ H_g(a, 0.577a, 0, 0.516a, -0.258a) - D_{5d}$$

$$F_{1u}(0, 0, a) - C_{5v},\ F_{2u}(a, 0.258a, 0.197a) - C_{5v}. \qquad (4)$$

The arbitrary constants entering into the description of different invariant vectors are not connected with each other. As all invariant vectors listed in Eq. (4) are one-parametric (their arbitrary constants are denoted by the same symbol a only for clarity), it is clear that the bush B7 depends on four arbitrary constants (one constant for each of the four irreps). The structure of the bush B7 (see Eq.(4)) shows that there exist only four contributions $\boldsymbol{\Delta}_j$ to the appropriate dynamical regime $\mathbf{X}(t)$. We denote them[3] as $\boldsymbol{\Delta}[A_g]$, $\boldsymbol{\Delta}[H_g]$, $\boldsymbol{\Delta}[F_{1u}]$, $\boldsymbol{\Delta}[F_{2u}]$. The invariant vectors listed in Eq. (4) permit us immediately to write the explicit form of the dynamical regime $\mathbf{X}(t)$ corresponding to the bush B7 by replacing the arbitrary constants with the four functions of time $\mu(t)$, $\nu(t)$, $\gamma(t)$ and $\xi(t)$

$$\begin{aligned}\mathbf{X}(t) &= \boldsymbol{\Delta}[A_g] + \boldsymbol{\Delta}[H_g] + \boldsymbol{\Delta}[F_{1u}] + \boldsymbol{\Delta}[F_{2u}] \\ &= \mu(t)\boldsymbol{\varphi}[A_g] + \nu(t)\{\boldsymbol{\varphi}_1[H_g] + 0.577\boldsymbol{\varphi}_2[H_g] \\ &+ 0.516\boldsymbol{\varphi}_4[H_g] - 0.258\boldsymbol{\varphi}_5[H_g]\} + \gamma(t)\boldsymbol{\varphi}_3[F_{1u}] \\ &+ \xi(t)\{\boldsymbol{\varphi}_1[F_{2u}] + 0.258\boldsymbol{\varphi}_2[F_{2u}] + 0.197\boldsymbol{\varphi}_3[F_{2u}]\}. \qquad (5)\end{aligned}$$

Eq. (5) is a consequence of the relation of the group G and its subgroup G_D only, and now we should take into account the concrete structure of our physical system to find the explicit form of the basis vectors $\boldsymbol{\varphi}_i^{(j)}$ of the irreps entering into Eq. (5). They can be obtained by conventional group-theoretical methods, for example, by the projection operation method. The basis vectors of the irreps determine the specific patterns of the displacements of all 60 atoms of the C_{60} fullerene structure.

It is important to note that each of the irreps A_g, H_g, F_{1u} and F_{2u} is contained in the vibrational representation of C_{60} fullerene several times, namely, 2, 8, 4 and 5 times, respectively. (These numbers are equal to the numbers of fundamental frequencies of normal modes associated with

[1] Considering vibrational regimes only, we can treat Γ as a $3N - 6$ vibrational representation of the group G.

[2] Since some elements of the matrices of multidimensional irreps of the group $G = I_h$ are irrational numbers, we keep only three digits after the decimal point when we write the invariant vectors.

[3] Hereafter we write the symbol j of the irrep Γ_j generating the contribution $\boldsymbol{\Delta}_j$ in square brackets next to symbol $\boldsymbol{\Delta}$.

the considered irreps). As a consequence, we must treat the time-dependent coefficients in Eq. (5) as vectors of the appropriate dimensions. Because of this we ascribe a new index (k) to the basis vectors determining the number of times (m_j) the irrep Γ_j enters into the vibrational representation. Each contribution $\mathbf{\Delta}_j$ "splits" into m_j copies $\mathbf{\Delta}_{jk}$, where $k = 1, 2, \dots, m_j$ and, therefore,

$$\mathbf{X}(t) = \sum_j \mathbf{\Delta}_j = \sum_j \left(\sum_{k=1}^{m_j} \mathbf{\Delta}_{jk} \right). \quad (6)$$

For the case of the bush B7 we have $\mathbf{\Delta}[A_g] = \mathbf{\Delta}_1[A_g] + \mathbf{\Delta}_2[A_g]$, $\mathbf{\Delta}[F_{1u}] = \mathbf{\Delta}_1[F_{1u}] + \mathbf{\Delta}_2[F_{1u}] + \mathbf{\Delta}_3[F_{1u}] + \mathbf{\Delta}_4[F_{1u}]$, etc.

The bush B7 in the C_{60} fullerene structure forms a 19-dimensional dynamical object: its evolution is described by the dynamical variables listed below as components of the four vectorial variables $\boldsymbol{\mu}(t)$, $\boldsymbol{\nu}(t)$, $\gamma(t)$ and $\boldsymbol{\xi}(t)$: $\boldsymbol{\mu}(t) = [\mu_1(t), \mu_2(t)]$, $\boldsymbol{\nu}(t) = [\nu_1(t), \dots, \nu_8(t)]$, $\gamma(t) = [\gamma_1(t), \dots, \gamma_4(t)]$, $\boldsymbol{\xi}(t) = [\xi_1(t), \dots, \xi_5(t)]$.

Thus, although only four of the ten irreps contribute to the bush B7, its dimension is equal to 19 because several copies of each of these four irreps are contained in the full vibrational representation of C_{60} fullerene. We cannot predict the concrete evolution of the amplitudes of the bush modes without specific information of the nonlinear interactions in the considered physical systems, but we can assert that there does exist an exact nonlinear regime which involves only the modes belonging to a given bush.

3. Optical bushes for C_{60} fullerene

As was already noted, there are 22 bushes of vibrational modes for C_{60} fullerene structure. Five of them are infrared active and six are Raman active. We call these bushes by the term "optical". The root modes of the optical bushes belong to the infrared active irrep F_{1u} or to the Raman active irreps A_g and H_g. We want to emphasize that some modes associated with the irreps which are not active in optics can be contained in a given optical bush.

All optical bushes with their symmetry groups (in square brackets), numbers of irreps contributing to them, and their dimensions (in parentheses) are listed below.

Infrared active bushes:

B7 $[C_{5v}]$ (4, 19); B11 $[C_{3v}]$ (6, 31); B15 $[C_{2v}]$ (7, 46);
B19 $[C_s]$ (9, 89); B22 $[C_1]$ (10, 174).

Raman active bushes:

B1 $[I_h]$ (1, 2); B4 $[D_{5d}]$ (2, 10); B5 $[D_{3d}]$ (3, 16);
B10 $[D_{2h}]$ (3, 24); B16 $[C_{2h}]$ (5, 45); B20 $[C_i]$ (5, 87).

Supposing that nonlinearity of the considered system is weak[4] we can estimate the relative values of the contributions from different irreps to a given bush. For example, for above discussed infrared active bush B7 we have

$$\mathbf{\Delta}[F_{1u}](root) = O(\varepsilon), \quad \mathbf{\Delta}[F_{1u}](secondary) = O(\varepsilon^3),$$

$$\mathbf{\Delta}[F_{2u}] = O(\varepsilon^3), \quad \mathbf{\Delta}[A_g] = O(\varepsilon^2), \quad \mathbf{\Delta}[H_g] = O(\varepsilon^2).$$

Here ε is an appropriate small parameter characterizing the value of the root mode.

Thus, in the case of weak nonlinearity, the contributions of different irreps can be of essentially different value. This property seems to be important for the interpretation of the vibrational spectra of bushes of modes.

[4] According to results obtained in the paper [3] this hypothesis is valid for C_{60} fullerene vibrations.

4. Conclusion

In the present paper, we consider a new type of possible nonlinear excitations — bushes of normal modes — in vibrational spectra of fullerenes and fullerites, using as an example the C_{60} buckyball structure. We believe that special experiments for revealing the bushes of vibrational modes in their pure form will be important for further elucidation of the role of these fundamental dynamical objects in various phenomena in fullerenes and fullerites. It seems that such experiments may be similar to those by Martin and others reported in [3]. However, unlike these experiments, we must use the monochromatic incident light with frequency close to that of the root mode and with polarization along the symmetry axis of the chosen bush.

The first-principle calculations are desirable for obtaining the coefficients of the anharmonic terms in C_{60} fullerene for a more detailed description of the bush dynamics.

The concept of bushes of normal modes and the appropriate mathematical methods for their analysis are valid for both molecular and crystal structures. Such a possibility can simplify the assignment of the different optical lines in fullerites brought about by both intra- and inter-vibrations of the C_{60} molecular clusters.

It will be very interesting to study interactions between bushes of vibrational modes and electron subsystems in fullerenes and fullerites.

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