New Approach to Nonlinear Dynamics of Fullerenes and Fullerites

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Abstract

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 does 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, 5, 6, 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 $\Gamma_0$ 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 $\Gamma_j$ ($j \neq 0$), 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, 5, 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 $x_i(t)$ (i =
The $1, 2, \ldots, N$ determine the displacement of the $i$-th atom from its equilibrium position at time $t$. The $3 \times N$-dimensional vector $\mathbf{X}(t) = \{x_1(t), x_2(t), \ldots, x_N(t)\}$, describing the full set of atomic displacements, can be decomposed into the basis vectors (symmetry-adapted coordinates) of all irreps $\Gamma_j$ of the group $G$ contained in the mechanical representation \[ \mathbf{X}(t) = \sum_{ji} \mu_{ji}(t) \phi_{i}^{(j)} = \sum \Delta_j. \] Here $\phi_{i}^{(j)}$ is the $i$-th basis vector of the $n_j$-dimensional irrep $\Gamma_j$. 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 $\Delta_j$ from the individual irreps $\Gamma_j$ 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 preserved in time; its elements cannot disappear during time evolution except in 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 operators $\hat{g} \in \hat{G}$ acting on the $3N$-dimensional vectors $\mathbf{X}(t)$, which correspond to elements $g \in G$ acting on three-dimensional vectors $\mathbf{x}_i(t)$, we can write the above condition of preservation of $G_D$ as a condition of invariance of the vector $\mathbf{X}(t)$ under the action of the elements of the group $G_D$:

$$\hat{g} \mathbf{X}(t) = \mathbf{X}(t), \; g \in G_D.$$ \hspace{1cm} (2)

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

$$(\Gamma_j \downarrow G_D) \mathbf{c}_j = \mathbf{c}_j.$$ \hspace{1cm} (3)

\footnote{Considering vibrational regimes only, we can treat $\Gamma$ as a $3N - 6$ vibrational representation of the group $G$.}
Here $\Gamma_j \downarrow G_D$ is the restriction of the irrep $\Gamma_j$ of the group $G$ to the subgroup $G_D$, i.e. the set of matrices of $\Gamma_j$ which correspond to the elements $g \in G_D$ only. The $n_j$-dimensional vector $c_j$ in Eq. (3) is the invariant vector in the carrier space of the irrep $\Gamma_j$ corresponding to the given subgroup $G_D \subset G$. Note that each invariant vector of a given irrep $\Gamma_j$ 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 $c_j \neq 0$, then the irrep $\Gamma_j$ does contribute to the dynamical regime $X(t)$ with the symmetry group $G_D$. Moreover, the invariant vector $c_j$ determines the explicit form of the mode of the irrep $\Gamma_j$ belonging to the bush of modes associated with the given nonlinear dynamical regime.

We will illustrate the general statements of bush theory with the $C_{60}$ fullerene with buckyball structure and with 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 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 $G = I_h$)\[3]\:

\begin{equation}
B7 : \text{[symmetry } C_{5v} \text{]: } A_g(a) - I_h, \quad H_g(a, 0.577a, 0, 0.516a, -0.258a) - D_{5d}
\end{equation}

\begin{equation}
F_{1u}(0, 0, a) - C_{5v}, \quad F_{2u}(a, 0.258a, 0.197a) - C_{5v}.
\end{equation}

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

\footnote{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.}
for each of the four irreps). The structure Eq. (4) of the bush B7 shows that there exist only four contributions \( \Delta_j \) to the appropriate dynamical regime \( X(t) \). We denote them as \( \Delta[A_g], \Delta[H_g], \Delta[F_{1u}], \Delta[F_{2u}] \). The invariant vectors listed in Eq. (4) permit us immediately to write the explicit form of the dynamical regime \( X(t) \) corresponding to the bush B7 by replacing the arbitrary constants with the four functions of time \( \mu(t), \nu(t), \gamma(t) \) and \( \xi(t) \):

\[
X(t) = \Delta[A_g] + \Delta[H_g] + \Delta[F_{1u}] + \Delta[F_{2u}] = \\
\mu(t) \varphi[A_g] + \nu(t)\{\varphi_1[H_g] + 0.577 \varphi_2[H_g] + 0.516 \varphi_4[H_g] - 0.258 \varphi_5[H_g]\} + \\
\gamma(t) \varphi_3[F_{1u}] + \xi(t)\{\varphi_1[F_{2u}] + 0.258 \varphi_2[F_{2u}] + 0.197 \varphi_3[F_{2u}]\}. \tag{5}
\]

Eq. (5) is a consequence of the relation of the group \( G \) and its subgroup \( G_D \) only, and now we must take into account the concrete structure of our physical system to find the explicit form of the basis vectors \( \varphi_i^{(j)} \) 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 the \( C_{60} \) 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 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 \( \Gamma_j \) enters into the vibrational representation. Each contribution \( \Delta_j \) “splits” into \( m_j \) copies \( \Delta_{jk} \), where \( k = 1, 2, \ldots, m_j \) and, therefore,

\[
X(t) = \sum_j \Delta_j = \sum_j (\sum_{k=1}^{m_j} \Delta_{jk}). \tag{6}
\]

For the case of bush B7 we have \( \Delta[A_g] = \Delta_1[A_g] + \Delta_2[A_g], \ \Delta[F_{1u}] = \Delta_1[F_{1u}] + \Delta_2[F_{1u}] + \Delta_3[F_{1u}] + \Delta_4[F_{1u}], \ etc. \)

\( ^3 \)Hereafter we write the symbol \( j \) of the irrep \( \Gamma_j \) generating the contribution \( \Delta_j \) in square brackets next to symbol \( \Delta \).
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 $\mu(t), \nu(t), \gamma(t)$ and $\xi(t)$:

$$\mu(t) = [\mu_1(t), \mu_2(t)],$$

$$\nu(t) = [\nu_1(t), \ldots, \nu_5(t)],$$

$$\gamma(t) = [\gamma_1(t), \ldots, \gamma_4(t)],$$

$$\xi(t) = [\xi_1(t), \ldots, \xi_5(t)].$$

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 $[C_1]$ (5, 87).

Supposing that nonlinearity of the considered system is weak, we can estimate the relative values of the contributions from different irreps to a given bush. For example,

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4 According to results obtained in the paper this hypothesis valid for $C_{60}$ fullerene vibrations.
for above discussed infrared active bush B7 we have

\[ \Delta[F_{1u}](\text{root}) = O(\varepsilon); \quad \Delta[F_{1u}](\text{secondary}) = O(\varepsilon^3); \]
\[ \Delta[F_{2u}] = O(\varepsilon^3); \quad \Delta[A_g] = O(\varepsilon^2); \quad \Delta[H_g] = O(\varepsilon^2). \]

Here \( \varepsilon \) 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 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 the \( C_{60} \) 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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