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Ab initio refining of quasibreathers in graphane

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A method for refining the profile of quasibreathers in the space of all initial atoms displacements is developed in the framework of the density functional theory. The method is exemplified by the procedure of constructing the discrete breathers in graphane.

Keywords: discrete breathers, *ab initio* calculations, density functional theory, quasibreathers.

Introduction

According to the conventional definition [1,2], discrete breathers (DBs) represent localized in space and periodic in time oscillations in homogeneous nonlinear Hamiltonian lattices. The existence of such objects is not obvious. Indeed, the localization (exponential in the most cases) of a discrete breather means that the oscillation amplitudes of peripheral («tail») atoms are essentially smaller than those of the central breather atoms. On the other hand, in nonlinear systems, it is typical for the frequency to depend on the amplitude. Thus, it seems that atoms in the tail should oscillate with frequencies that differ from those of breather core atoms and, therefore, DB couldn't be strictly periodic in time dynamical object.

Despite that, there are a series of model systems in which the existence of exact discrete breathers was rigorously proved. In this regard, let us refer to the proof provided in [3] for systems of weakly coupled nonlinear oscillators, *i.e.* for the lattice models with on-site potentials, and also to the proof of exact discrete breathers existence in the Fermi-Pasta-Ulam models [4], in which the local interactions between atoms and lattice nodes are absent. Due to the rather abstract nature of these proofs, it is hard to understand the physical underground of the possibility for exact discrete breathers to exist. In our work [5], an attempt was made to give a clear interpretation of such possibility. Its essence can be described as follows.

Let's consider the chain of weakly coupled oscillators, and let's displace from the equilibrium state only one of them (we will refer to it as the «central» oscillator). In the absence of interactions with neighbors, it will oscillate with the natural frequency ω_0. Under the weak interactions between the oscillators, the excitation spreads to its neighbors and their oscillations can be described by a sum of terms which possess different frequencies. Among these terms, there are both describing forced vibrations with frequency ω_0 (due to the interactions with the central oscillator), and those associated with natural frequencies ω_j of the peripheral oscillators ($\omega_j \neq \omega_0$ because of the difference in oscillators' amplitudes). For DB to be a periodical dynamical object with frequency ω_0, it is needed the fine tuning of the initial conditions (the profile of DB) for solving the Cauchy problem of nonlinear differential equations that govern the lattice dynamics. Such tuning is necessary for elimination of the terms with frequencies that are not equal to ω_0.

Small deviations in the initial breather profile lead to the situation where vibrational contributions of the peripheral oscillators (particles of the chain) with frequencies $\omega_j \neq \omega_0$ are not suppressed completely. As a result, some quasi-periodical vibrational regime arises and this regime was called quasi-breather (QB) in the work [6].

It is essential for the quasibreather that different lattice particles vibrate with different but close frequencies, and the frequency of its' central particle «drifts» in time around a certain average value. That makes an exact DB to be a very unusual dynamical object. The difficulty of its construction is connected with the necessity of very fine tuning of the initial displacements of all lattice particles at the moment $t=0$ (their velocities are supposed to be equal to zero). For this tuning one can use continuation from the anti-continuous limit [7], pair synchronization method [5] or different descent methods for minimization of some objective functions in many-dimensional space of all initial conditions [8]. Let us note that QBs turn out to be more adequate dynamical objects compared to exact breathers, since neither physical experiment allows one to proceed from the exact initial profile of the DB.

Below we consider the problem of the exact breathers construction in crystal lattices by means of computer simulations. Studies of this type are of great importance, as far as the exact analytical solutions of nonlinear differential equations are known only in very rare cases.

Almost all works on computer simulations of discrete breathers in 1D, 2D, 3D lattices rely on the models of mass points (MP-models) with interactions governed by some phenomenological potentials. However, such models are not rather adequate for discrete breathers description since they do not take into account the effects of the electron shell polarization of atoms in crystal. Moreover, the effects of that kind require the quantum mechanical methods to be well described.

In this connection, in the paper [9], we have investigated the discrete breathers in graphane by means of *ab initio* simulations, based on the density functional theory (DFT) [10, 11]. It was proved in the frame of this theory that the Schrodinger wave function, which is determined in many-dimensional coordinate space of all electrons, can be expressed via a certain functional of the electron density function $\rho(r)$ that is determined in the three-dimensional coordinate space. Since the exact expressions of exchange-correlation functionals used in DFT are not known, many different their approximate forms were suggested (see [12]).

For *ab initio* calculations of discrete breathers in graphane we used ABINIT package [13,14] that implements the main methods of the density functional theory. In fact, our calculations have been made under certain approximations. The Born-Oppenheimer approximation was used to separate the fast movement of electrons and slow movements of atom nuclei. The behavior of electron subsystem was described by quantum-mechanical Kohn-Sham equations, while atom cores were considered as classical particles (the forces acting on them are calculated with the aid of the current state of the electron subsystem that reacts instantly on the change of nuclei configuration). The exchange-correlation functionals were taken in the standard local density approximation (LDA) form. To speed up the computational runs, we used the pseudo-potentials describing the atom nuclei with their core electrons. To solve the Kohn-Sham equations the basis of plane waves are used, with the maximum energy of these waves determined by a certain value of the parameter CutOff.

Taking into account all above-mentioned approximations, it can be actually stated that using ABINIT package we have studied a certain mathematical model which is named hereafter the ABINIT-model. This model seems to be much more adequate compared to any MP-model, because it takes into account the complex quantum-mechanical effects of electron shells polarization in the process of the breather oscillations. Let us note that in the papers [15,16], devoted to studying breathers in some perovskites, the attempt was made to consider the electron shell polarization of some atoms within a very simple MP-model. Indeed, the authors of [15,16] described the electron shell as only one additional degree of freedom.

In this regard, let us note that the *ab initio* calculations based on the density functional theory usually give very good values of structural parameters of molecules, crystals and nano-objects of different type (often with the error that does not exceed 1%) [12].

Now let's consider the main difference between the graphane gap-breathers properties that were obtained in [17], based on the MP-model with Brenner potential, and those obtained in [9] within the ABINIT-model. A striking difference was found in the function ω(A), representing dependence of the frequency ω of DB on its amplitude A. Indeed, ω(A) found in [17] is a complex non-monotonic function which demonstrates existence of three different regions in amplitude A with two changes of the nonlinearity type (from soft to hard and backward). In contrast to this behavior, the function ω(A) found in [9] monotonically decreases with increasing of the amplitude A. Moreover, it can be well approximated by a segment of the straight line situated inside the gap of the phonon spectrum. This result shows the significant errors produced by the mass-point model of graphane for large amplitudes. Such errors emerge because the MP-models can't describe the complex polarization mechanism of the electron shells. On the other hand, this mechanism plays an essential role in the large amplitude dynamics of the breather (remember that in ABINIT-models the behavior of electron subsystem is taken into account by means of the quantum mechanics). Let us also note that the parameters of the phenomenological potentials for MP-models are usually obtained to provide the correct equilibrium configuration and phonon spectrum of the considered physical system. In fact, this means that the above-mentioned parameters are estimated in the small-amplitude approximation, while in the case of discrete breather the atom amplitudes are rather large (about 10% of the crystal interatomic distance or even more). This could be another reason of the difference between results reported in [17] and [9].

2. Quasi breathers in graphane

Graphane can be considered as a system that consists of the carbon plane of graphene (XY plane) with hydrogen atoms attached to that plane (along the perpendicular to it Z-direction) at the opposite sides of the plane in a staggered manner. In fact, in the equilibrium state of graphane, carbon atoms are slightly displaced from XY plane, again in a staggered manner (see Fig.1).

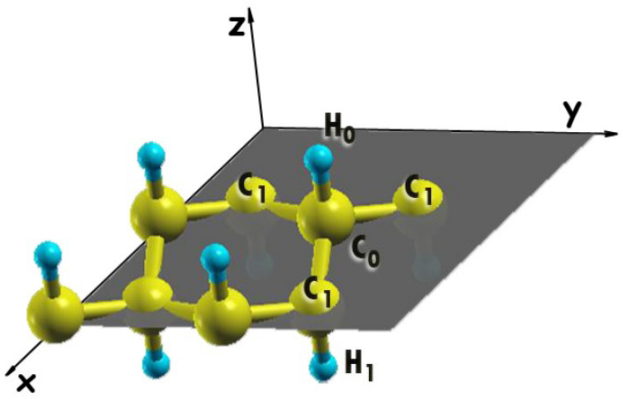

Fig. 1. (Color online) The structure of graphane. Carbon and Hydrogen atoms are depicted in yellow and blue color respectively. C_0 and H_0 atoms represent the breather core.

In both works [17] and [9], discrete breathers were excited by displacing one of Hydrogen atoms (H_0) in Z direction, while all initial velocities, as well as displacements of all other graphane atoms, were equal to zero. In the process of free oscillations, the initial excitation partially spreads to the neighbor atoms. First of all, these are the carbon atom C_0, situated under the H_0 atom, and its three symmetrically placed nearest neighbors named by C_1 (the hydrogen atoms H_1 attached to them lay under the XY plane). As a result, the highly localized in space quasi-periodic vibrational regime is excited in the graphane system. Obviously, this dynamical object is not an exact DB, but it represents a certain QB.

In Fig.2, one can see the typical time evolution of the central atoms H_0 and C_0 of such quasi-breather. It is clearly seen that oscillations of these atoms are not strictly periodic because their amplitudes are spread in some region around a certain average value. As a numerical characteristic of the «quasibreather rate», *i.e.* the rate of deviation of the obtained dynamical object from the exact DB, one can choose various functions $\Delta[P(0)]$ of the breather shape $P(0)$ at t=0 which we call «breather profile». This profile represents the full set of the initial displacements of all graphane atoms which are taken into account in the *ab initio* calculations (remember that initial velocities of all atoms are assumed to be equal to zero).

Any exact breather represents a strictly periodic dynamical object and, therefore, each atom also must vibrate periodically. If we look at Fig.2, we find that oscillations of the hydrogen atom H_0 are not periodic because its maxima differ in value. Therefore, we have to choose such initial profile $P(0)$ that leads to fully periodic oscillations of H_0 atom. This necessary condition turns out to be also sufficient for DB to be exact dynamical object. Indeed, a deviation from periodicity of any atom leads to the deviation from periodicity of the whole DB because of interactions between all graphane atoms. Thus, we can choose the following quasibreather rate function:

$$\Delta\left[P(0)\right]=\sqrt{\sum_{i=1}^{M}\frac{\left(Zh_0(0)-Zh_0(i\cdot T)\right)^2}{M(M-1)}}, \qquad (1)$$

where $Zh_0(t)$ is the displacement of H_0 atom in z direction at the instant t, while M is the number of the breather periods to take into account. Obviously, the ideal minimal value of the function Δ[P(0)] is equal to zero, and this value can be reached only for the strictly periodic function $Zh_0(t)$. Therefore, for the exact DB construction, one may use (1) as an objective function for any descent method in the many-dimensional space of all initial atomic displacements. For the QB we obtained in [9] with the amplitude A=0.469Å (which is defined as $Zh_0(0)$), we find the following value of the rate function (1) for M=3 can be found:

$\Delta[P(0)]=0.0147$.

Note that the amplitude A=0.469Å corresponds to DB situated near the center of the phonon gap.

In this regard, one can ask: «Could the quasibreather rate be refined by choosing more accurate initial conditions for breather construction (compared to the simple displacement of only one H_0 atom)?» The more fundamental question is: «Could we construct the exact DB in the framework of ABINIT-model?» The present paper is devoted to the discussion on these problems.

3. The descent method for quasibreathers refining

To refine the profile of the QB depicted in Fig.2, we apply a certain descent procedure based on the simplex method in the Nelder-Mead form [18] (do not confuse with the simplex-method in the linear programming!). Unlike the steepest descent or conjugate gradients methods, this method does not require calculations of any gradients. It is very important for our purpose because *ab initio* calculations based on density functional theory demands a lot of computing time that makes difficult to find gradients of the objective function.

The objective function *explicitly* depends only on the time-evolution of the Hydrogen atom H_0. However, it depends *implicitly* on the initial displacements of *all* graphane atoms. Therefore, we have to refine the quasibreather profile by tuning the initial values of all atom displacements, *i.e.* to perform the descent procedure in many-dimensional coordinate space. Nevertheless, to speed up the calculations, one can choose only those parameters which produce the main contribution to the objective function. Really, we have used two free parameters for our descending: the displacement of C_0 atom in Z-direction, and the distance between C_0 and C_1 atoms in XY-plane. These parameters are believed to be the most important ones for the QB dynamics (let us note, that displacement of C_1 atoms in Z-direction are defined from the condition of immovability of the mass-center). As a result of application of the minimization procedure to the quasibreather with amplitude A=0.469Å, we have obtained the following rate-function value (1):

$\Delta[P(0)]=0.0013$.

One can see that the rate function for DB in Fig.3 is 10 times less than that for the original QB depicted in Fig.2. Thus, we have found the quasibreather that visually seems to be almost ideal (compare Fig.2 and Fig.3).

The further improvement of the QB depicted in Fig.3

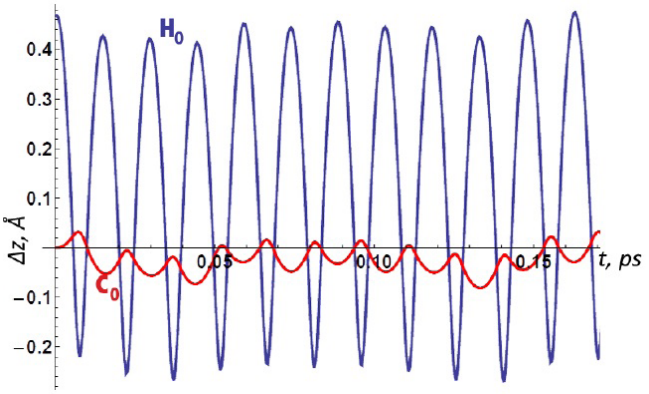

Fig. 2. (Color online) The time evolution of the C_0 (red) and H_0 (blue) atoms of the breather found in [8].

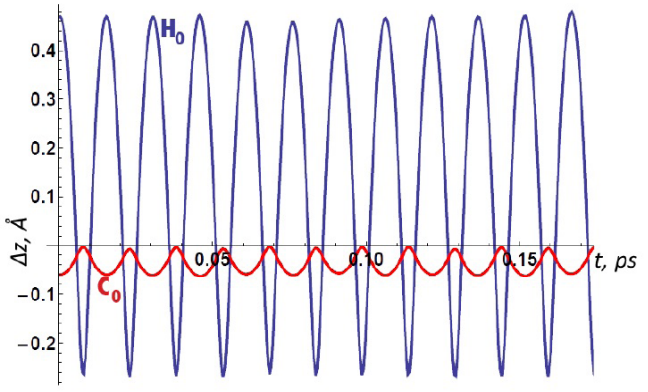

Fig. 3. (Color online) The time evolution of the C_0 (red) and H_0 (blue) atoms of the quasibreather refined by the minimization of the rate function $\Delta[P(0)]$ (1).

requires great computing time and we did not fulfill such refining in the present work. Our purpose was to show how one can refine the profile of QBs obtained by *ab initio* calculations using as an example quasibreathers from [9].

4. Conclusion

To the best of our knowledge, all papers treated discrete breathers in crystals consider atoms as mass-points whose interactions are described by some phenomenological potentials. Only in our recent paper [9], these dynamical objects were studied in the framework of the ABINIT-model based on the density functional theory using as example QBs in graphane. Such *ab initio* approach permits one to take into account polarization of electron shells of the crystal atoms induced by breather vibrations.

In the present paper, we outline a method for refining quasibreathers in this model. The more detailed investigation on this subject will be published elsewhere.

To exemplify the above method we have refined the shape of one of quasibreathers in graphane that was obtained earlier in [9].

As a future work, it is tempting to apply the procedure of refinement of initial conditions, developed in this work, to the discrete breathers in other systems [20] including 2D Morse crystal [21—23], crystals with NaCl structure [24] and graphene [25,26].

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