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LETTERS
TO THE EDITOR

Quantum-Chemical Calculations of the Variance of Phonons in Crystals: Convergence of Results Depending on Cyclic Cluster Growth

R. A. Evarestov and M. V. Losev

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: re1973@re1973.spb.edu

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At present ab initio quantum-chemical calculations of phonon spectra of crystals are carried out using cyclic cluster models with imposition of cyclic boundary conditions on a crystal fragment in the form of an extended unit cell [1]. In such model vibrational frequencies are calculated precisely (within the limits of the accepted calculation scheme) for those points of the initial Brillouin zone which have a wave vector comparable with the selected unit cell [2].

Let matrix (l) determine the transformation of translation vectors when passing from a primitive cell to an extended cell.

$$A_j = \sum_i \mathrm{l}_{ji}\, a_i,\ i, j = 1, 2, 3. \qquad (1)$$

Here a_i and A_j are translation vectors of the primitive and extended cells, respectively.

The extended lattice cell contains L = det (l) primitive cells. Points K^s, s = 1, 2, … L in the Brillouin zone of the primitive cell comparable with the translations are determined by relation (2):

$$K^s = \sum_i n_{si} b_i. \qquad (2)$$

Here b_i are translation vectors of the reciprocal lattice for the selected extended unit cell and n_{si} are integers.

In particular, phonon frequencies for the centre of the Brillouin zone (point Γ) are obtained upon imposing cyclic boundary conditions on a primitive cell and remain constant as the cell is extended. The calculation of the dispersion of phonons demands the interpolation of the vibrational frequencies calculated for points K^s by means of the Fourier transformation of the force-field matrix found for the cyclic cluster. As the cyclic cluster increases the dissimilarity of its force-field matrix from that for an infinite crystal decreases, so that the calculated phonon spectra of the cyclic cluster and the crystal become close. Unfortunately, as far as we know, practically in all publications on the calculations of phonon spectra of crystals the size of a cyclic cluster is selected on the basis of available computing resources, and the calculated phonon spectra are compared to the experimental data for a bulk crystal. In this case, as a rule, the convergence of the results obtained for a certain system depending on the cyclic cluster growth is not considered.

Here we briefly report the results of our calculation in a harmonic approximation of such convergence for the LiF crystal with a face-centered cubic lattice and two atoms in a primitive cell. We used the cubic cyclic clusters containing 8, 27, 64 (two-, three-, and four-fold expanding translation vectors of the face-centered lattice), 16 (transition to a body centered cubic lattice), and 32 (transition to a simple cubic lattice with the subsequent doubling translation vectors) primitive cells. The displacement forces for the cyclic cluster atoms were calculated in the LCAO basis by the program Crystal06 [3]. For lithium and fluorine atoms we used the full-electron TZV basis [4], excluding diffusive gaussian atomic *s* functions with orbital exponents 0.0770 and 0.0289 in the case of the lithium atom and optimizing remaining most diffusive orbital exponents (one for *s* functions of the Li atom and four for the F atom, two at a time for *s*-and *p*-functions). When optimizing the basis and the lattice constant a_0

we used hybrid Hamiltonian B3LYP [5] (a_0 of 4.07 Å was obtained, whereas the experimental value is 4.03 Å).

The Crystal06 program version in use considers only point symmetry of the extended lattice cell [6], so that its practical application for large cells is difficult. Therefore we used the program fropho [7] for the calculation of phonon spectra. It allows us to consider completely the space symmetry of a cyclic cluster (both the point symmetry operations and "interior" primitive translations) when building up a force-field matrix using forces on atoms calculated before. The complete consideration of the symmetry allows us to restrict ourselves to two independent displacements (one for each of atoms in a primitive cell) for all considered cells.

Let us consider the calculated phonon frequencies for the point with the coordinates 1/4 1/4 1/4 on the direction Λ (Γ–L) in the Brillouin zone for a primitive cell. The corresponding wave vector is comparable with translation vectors only for the greatest cyclic cluster of 64 primitive cells obtained by the fourfold extension of each of translation vectors of the primitive cell. The values of the phonon frequencies (in THz, degeneration is specified in parentheses) are given below.

Cluster		8	16	27	32	64
Frequencies	(2)	3.78	3.42	4.45	4.11	4.23
	(1)	8.59	7.95	7.32	7.91	7.86
	(2)	9.23	9.33	9.25	10.54	9.05
	(1)	14.44	15.66	17.29	16.18	19.80

It is seen that the convergence of the results becomes rather poor as the size of a cyclic cluster increases, and even for the cyclic cluster of 32 primitive cells (with the translation vector length $2a_0$ ~8 Å) the difference of the calculated and exact values of phonon frequencies remains fairly large (for example, for the greatest frequency it is 18%). The results obtained agree with the general criteria offered in the literature for the selection of a cyclic cluster: when calculating phonons in crystals the translation vector of a cyclic cluster should be no less than 8–10 Å [8]. At the same time, for particular systems the calculation of phonon spectra should be accompanied by studying the convergence of results for increasing cyclic cluster size. Only such approach is hopeful for obtaining rather reliable thermodynamic characteristics of a crystal (entropy, Gibbs free energy, and heat capacity) calculated by summing over phonon spectra.

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