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Theory of intrinsic localized modes in diatomic chains: beyond the rotating wave approximation

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Abstract

Intrinsic localized modes in the gap of a diatomic chain with free ends are discussed in detail by going beyond the rotating wave approximation. We include in the time dependence of the displacements terms up to $\cos(2\omega t)$. We consider a finite chain of particles interacting with nearest-neighbour interactions. We study amplitudes of the intrinsic localized modes smaller than 0.25 Å. In this range of amplitudes the full potential can be well represented by an expansion in powers of the displacements up to fourth-order terms. The use of a force constant model allows us to simplify the problem. As a test case we consider a chain of LiI atoms. We found intrinsic localized modes in the gap. The amplitudes of the first harmonic term ($\cos(\omega t)$) are of even or odd parity, whereas we prove that the amplitudes of the static part and those of the second harmonic can have only even symmetry. The main result of the paper is that the amplitudes associated with the second harmonic are two or three orders of magnitude less than those of the first harmonic. Furthermore, the frequency of the localized modes are modified by less than 1% by the inclusion of the second harmonic.

1. Introduction

The existence of highly localized modes in anharmonic crystals is by now well established [1,5]. These modes have been termed intrinsic localized modes (ILMs), reflecting the fact that no external defects are needed for their creation. The first studies [1, 3] showed the existence of ILMs above the top of the harmonic phonon branch for monoatomic one-dimensional lattices with harmonic and quartic anharmonic interactions. In a diatomic chain with realistic potentials, however, Kiselev *et al* [4] showed that ILMs arise in the gap between the acoustic and the optical branches. The above treatments are based on the rotating wave approximation (RWA) in which the atomic displacements contain a static part and a vibrational

part proportional to $\cos(\omega t)$, where ω is the frequency of the stationary localized mode. Molecular dynamics (MD) simulations [6] verify that those modes do not depend on the dimensionality and are also present in diatomic 3D crystals. In these MD simulations a Fourier extension of the RWA was made by introducing a part of the vibrational displacement proportional to $\cos(2\omega t)$. However, the contributions to the displacements pattern associated with the second harmonic were not analysed. Recently ILMs have been observed [7] in crystalline arrays of charged linear chains of PtCl with resonant Raman scattering. ILM have been observed also in different systems, such as waveguide arrays [8], spin waves in an antiferromagnet [9] and small Josephson junction ladders [10]. In this work we consider a diatomic chain with two alternating masses to represent a one-dimensional LiI crystal. The study of one-dimensional systems provides a simple interpretative scheme to understand the more complex results of the 3D MD simulations. We present a detailed study of the equations of motion going beyond the RWA, including the second harmonic to prove numerically the common understanding that the RWA is an approximation which is of practical use if higher harmonics contributions are small. Even if there are general theorems stating the existence of the ILMs [11–13] for on-site potentials and for potential energy functions strictly convex, i.e. with even anharmonic terms only, we need numerical calculations, because of the form of our potential which also contains odd anharmonic terms and because, even more importantly, the general theorems do not provide a numerical evaluation of the displacements pattern [14]. In a previous paper [15] we have shown that the full potential containing a Born–Mayer repulsive term and an attractive Coulombic part gives ILMs which are qualitatively the same as those derived from a force constant model which includes harmonic as well as cubic and quartic anharmonic interactions derived by a Taylor expansion of the full potential. The results of the two approaches essentially coincide for amplitudes of the ILMs on the order of 0.25 Å or less. Since these amplitudes are in the range accessible to experiments, we simplify the analysis by using the force constant method. We examine ILM modes in a diatomic chain with free ends and like atoms at the ends. We obtain ILM modes of odd or even parity. As a specific case we investigate LiI which has a large gap because of the large difference in mass of the Li and I atoms. In section 2 we first introduce the two-body potential. Then we discuss the equations of motion beyond the RWA. In section 3 we discuss the results for the ILM modes. We draw the conclusions in section 4.

2. Theoretical development

We consider a diatomic chain of particles interacting via nearest-neighbour forces. The equations of motion of the particles are

$$m_n \ddot{u}_n = V'_{n+1}(u_{n+1} - u_n) - V'_n(u_n - u_{n-1}) \tag{1}$$

where u_n is the displacement of the nth particle and $V_n(u_{n+1} - u_n)$ is the interaction potential of neighbouring atoms. We use a potential formed by a repulsive Born–Mayer part and an attractive Coulomb part, which is appropriate for alkali halide crystals. The parameters are fitted to bulk properties of LiI [16]. In the following we will focus on displacements with maximum amplitude of 0.05–0.25 Å. As we have shown in a previous paper [15] this restriction allows us to expand the potential in a power series of the displacements up to fourth order. The equations of motion then become

$$\begin{aligned} m_n \ddot{u}_n = {} & K_2(u_{n+1} + u_{n-1} - 2u_n) + K_3[(u_{n+1} - u_n)^2 - (u_{n-1} - u_n)^2] \\ & + K_4[(u_{n+1} - u_n)^3 + (u_{n-1} - u_n)^3] \end{aligned} \tag{2}$$

where K_2, K_3, K_4 are the harmonic, cubic and quartic force constants derived from the total potential V. We remind that in the RWA equation (2) represents a chain of atoms which

are anharmonic oscillators with respect to the space coordinates, while they are harmonic oscillators of frequency ω with respect to the time coordinate. To go beyond the RWA we include the next term, i.e. the second harmonic 2ω. The displacement for the nth particle for stationary modes is then of the form

$$u_n = A(\phi_n + \xi_n \cos(\omega t) + \chi_n \cos(2\omega t)) \tag{3}$$

where A is the maximum amplitude of the mode. The relative vibrational amplitudes ξ_n and χ_n and the static displacement ϕ_n are independent of time. Substituting equation (3) into (2) we get

$$\begin{aligned} m_n\omega^2\xi_n + m_n 4\omega^2\chi_n = {} & K_2\big\{(\phi_n - \phi_{n-1}) + (\phi_n - \phi_{n+1}) + [(\xi_n - \xi_{n-1}) \\ & + (\xi_n - \xi_{n+1})]\cos(\omega t) + [(\chi_n - \chi_{n-1}) + (\chi_n - \chi_{n+1})]\cos(2\omega t)\big\} \\ & + AK_3\big[(\phi_{n+1} - \phi_n) + (\xi_{n+1} - \xi_n)\cos(\omega t) + (\chi_{n+1} - \chi_n)\cos(2\omega t)\big]^2 \\ & - AK_3\big[(\phi_{n-1} - \phi_n) + (\xi_{n-1} - \xi_n)\cos(\omega t) + (\chi_{n-1} - \chi_n)\cos(2\omega t)\big]^2 \\ & + A^2K_4\big[(\phi_{n+1} - \phi_n) + (\xi_{n+1} - \xi_n)\cos(\omega t) + (\chi_{n+1} - \chi_n)\cos(2\omega t)\big]^3 \\ & + A^2K_4\big[(\phi_{n-1} - \phi_n) + (\xi_{n-1} - \xi_n)\cos(\omega t) + (\chi_{n-1} - \chi_n)\cos(2\omega t)\big]^3. \end{aligned} \tag{4}$$

To be consistent with the displacement expansion up to the second harmonic of equation (3) we consider in equation (4) only all the contributions pertinent to our ansatz: i.e. we replace the terms in $\cos^3(n\omega t)$ by $3/4\cos(n\omega t)$ for $n = 1$ and 2, the terms in $\cos^2(\omega t)\cos(2\omega t)$ by $(1 + 2\cos(2\omega t))/4$ etc. In this way we get the constant term as well as the term linear in $\cos(\omega t)$ and $\cos(2\omega t)$. Equating in equation (4) the coefficients of the $\cos(\omega t)$ terms we get

$$\begin{aligned} & K_2\big[(\xi_n - \xi_{n-1}) + (\xi_n - \xi_{n+1})\big] + AK_3\big[2(\phi_n - \phi_{n-1})(\xi_n - \xi_{n-1}) + (\chi_n - \chi_{n-1})(\xi_n - \xi_{n-1}) \\ & \quad - 2(\phi_n - \phi_{n+1})(\xi_n - \xi_{n+1}) - (\chi_n - \chi_{n+1})(\xi_n - \xi_{n+1})\big] \\ & \quad + \tfrac{3}{4}A^2K_4\big[(\xi_n - \xi_{n-1})^3 + (\xi_n - \xi_{n+1})^3 + 4(\phi_n - \phi_{n-1})^2(\xi_n - \xi_{n-1}) \\ & \quad + 4(\chi_n - \chi_{n-1})(\phi_n - \phi_{n-1})(\xi_n - \xi_{n-1}) + 2(\chi_n - \chi_{n-1})^2(\xi_n - \xi_{n-1}) \\ & \quad + 4(\phi_n - \phi_{n+1})^2(\xi_n - \xi_{n+1}) + 4(\chi_n - \chi_{n+1})(\phi_n - \phi_{n+1})(\xi_n - \xi_{n+1}) \\ & \quad + 2(\chi_n - \chi_{n+1})^2(\xi_n - \xi_{n+1})\big] = m_n\omega^2\xi_n. \end{aligned} \tag{5}$$

Equating the coefficients of the $\cos(2\omega t)$ terms we obtain

$$\begin{aligned} & K_2\big[(\chi_n - \chi_{n-1}) + (\chi_n - \chi_{n+1})\big] + \frac{AK_3}{2}\big[4(\phi_n - \phi_{n-1})(\chi_n - \chi_{n-1}) + (\xi_n - \xi_{n-1})^2\big] \\ & \quad - \frac{AK_3}{2}\big[4(\phi_n - \phi_{n+1})(\chi_n - \chi_{n+1}) + (\xi_n - \xi_{n+1})^2\big] + \frac{3}{4}A^2K_4\big[(\chi_n - \chi_{n-1})^3 \\ & \quad + (\chi_n - \chi_{n+1})^3 + 4(\phi_n - \phi_{n-1})^2(\chi_n - \chi_{n-1}) + 2(\phi_n - \phi_{n-1})(\xi_n - \xi_{n-1})^2 \\ & \quad + 2(\chi_n - \chi_{n-1})(\xi_n - \xi_{n-1})^2 + 4(\phi_n - \phi_{n+1})^2(\chi_n - \chi_{n+1}) \\ & \quad + 2(\phi_n - \phi_{n+1})(\xi_n - \xi_{n+1})^2 + 2(\chi_n - \chi_{n+1})(\xi_n - \xi_{n+1})^2\big] = m_n(2\omega)^2\chi_n \end{aligned} \tag{6}$$

and of the constant term

$$\begin{aligned} & K_2\big[(\phi_n - \phi_{n-1}) + (\phi_n - \phi_{n+1})\big] + \frac{AK_3}{2}\big[2(\phi_n - \phi_{n-1})^2 + (\chi_n - \chi_{n-1})^2 + (\xi_n - \xi_{n-1})^2\big] \\ & \quad - \frac{AK_3}{2}\big[2(\phi_n - \phi_{n+1})^2 + (\chi_n - \chi_{n+1})^2 + (\xi_n - \xi_{n+1})^2\big] \\ & \quad + A^2K_4\big[(\phi_n - \phi_{n-1})^3 + (\phi_n - \phi_{n+1})^3\big] \\ & \quad + \tfrac{3}{4}A^2K_4\big[2(\phi_n - \phi_{n-1})(\chi_n - \chi_{n-1})^2 + 2(\phi_n - \phi_{n-1})(\xi_n - \xi_{n-1})^2 \\ & \quad + 2(\phi_n - \phi_{n+1})(\chi_n - \chi_{n+1})^2 + 2(\phi_n - \phi_{n+1})(\xi_n - \xi_{n+1})^2 \\ & \quad + (\chi_n - \chi_{n-1})(\xi_n - \xi_{n-1})^2 + (\chi_n - \chi_{n+1})(\xi_n - \xi_{n+1})^2\big] = 0. \end{aligned} \tag{7}$$

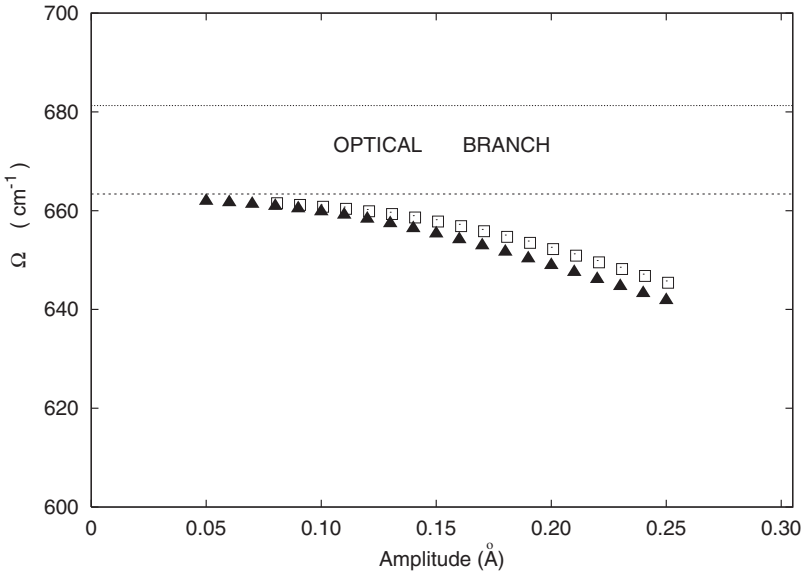

Figure 1. Frequency of bulk gap localized modes versus amplitude A for even modes ▲ and odd modes □.

Equations (5)–(7) are very useful to study the symmetries of the various amplitudes. By considering these equations for the central atom $n = 0$ one sees that the ξ_{-1} and ξ_1 displacements can have an even or odd symmetry, while the static displacements ϕ_{-1} and ϕ_1 and the displacements χ_{-1} and χ_1 can have only even parity. The static displacements give rise to an expansion of the crystal. To solve the system of coupled equations of motion (5)–(7) we use a technique based on a standard routine of the Newton scaled gradient method. We start with three atoms and an initial guess of the displacements. One atom is then added to each end of the chain. The iterative procedure is continued up to 200 atoms. The addition of a couple of atoms acts as a perturbation on the chain. If in the iterative procedure this perturbation does not alter the mode, we consider the mode to be a stable solution.

3. Localized modes in the gap

We start by considering the chain formed by $-100 < n < 100$ atoms, with a light atom at the origin $n = 0$. The initial guess for the displacements is $\xi_0 = 1, \xi_{-1} = \xi_1$ (odd modes) and $\phi_0 = \phi_{-1} = \phi_1 = 0$. In our analysis of the RWA we showed that this initial guess gives odd ILM modes coming from the bottom of the optical branch. The initial conditions for the χ_n are $\chi_0 = 0$, $\chi_{-1} = -\chi_1$. If one chooses $\chi_{-1} = \chi_1$ stable modes are not obtained, even for small values of the amplitude A in agreement with out previous discussion of equation (6). In figure 1 we present the results for the frequencies of the gap modes obtained by solving equations (5)–(7). We consider maximum displacements up to 0.25 Å. As previously mentioned, we have proved in a recent paper [15] that the full potential containing a Born–Mayer repulsive term and an attractive Coulombic part gives ILMs which are qualitatively the same as those derived from a force constant model which includes harmonic as well as cubic and quartic anharmonic interactions derived by a Taylor expansion of the full potential in the range of amplitudes up to 0.25 Å. The pattern of the static and first harmonic displacements are shown in figure 2. The second harmonic displacements are presented in figure 3. These

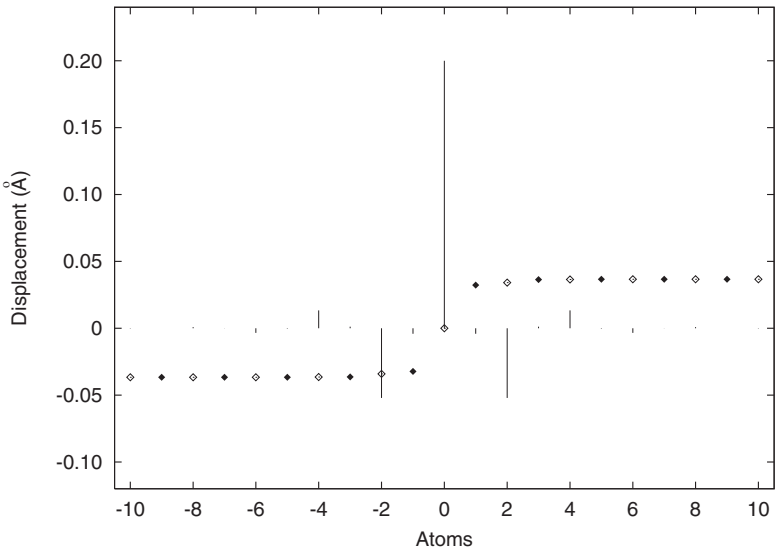

Figure 2. First harmonic displacements $A\xi_n$ of the odd localized mode for amplitude $A = 0.20$. Only the central part of the chain is shown. The static displacements $A\phi_n$ are shown as $\diamondsuit$. Open diamonds indicate the light atoms, full diamonds indicate the heavy atoms.

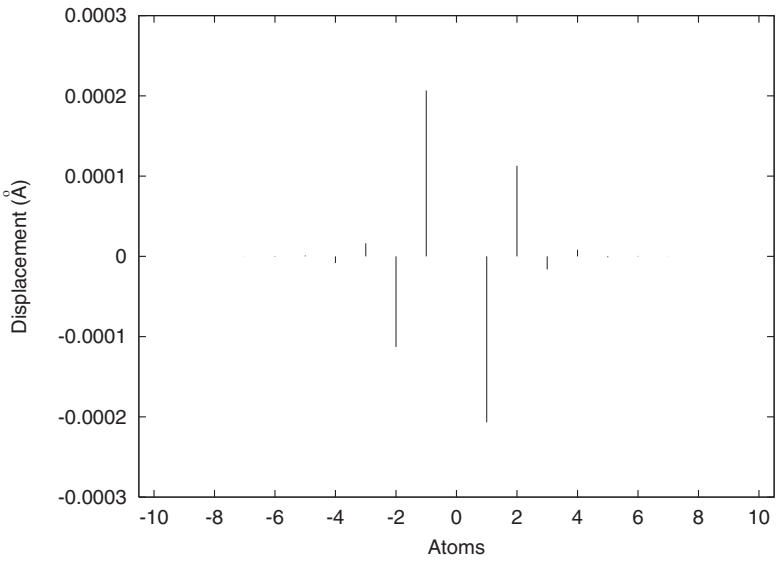

Figure 3. Second harmonic displacements $A\chi_n$ of the odd localized mode for amplitude $A = 0.20$. Only the central part of the chain is shown.

contributions have even parity like the static displacements and their maximum amplitude is two order of magnitude less than those associated with the first harmonic. This indicates that the RWA is adequate to describe ILM modes. In figure 4 we present for the odd case the behaviour of the second harmonic displacement of site $n = -1$, i.e. χ_{-1}, as a function of the maximum amplitude A of the mode. One sees that in the range of amplitudes considered here the $|\chi_{-1}|$ is always much less than the first harmonic amplitude. We now consider the chain

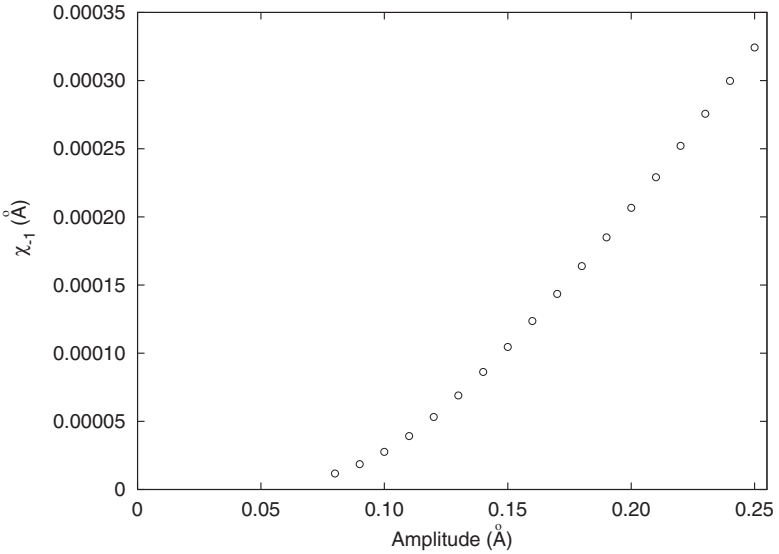

Figure 4. Second harmonic displacement $A\chi_{-1}$ of the odd localized mode versus the maximum amplitude A of the mode.

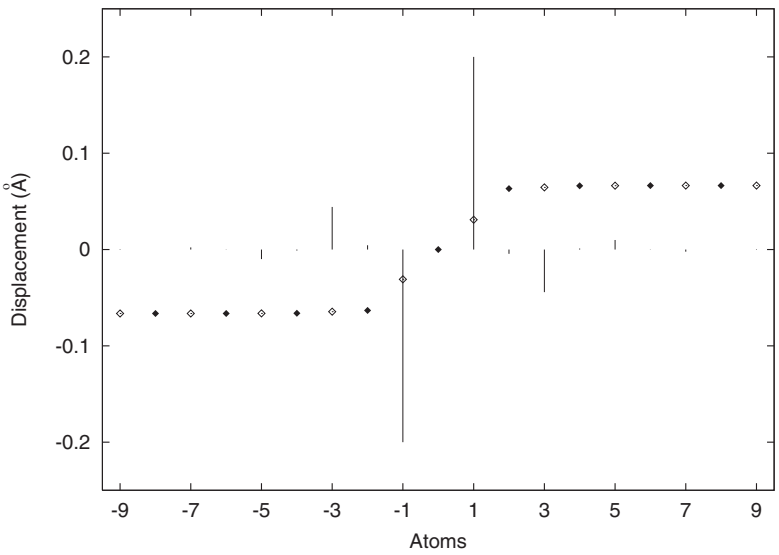

Figure 5. First harmonic displacements $A\xi_n$ of the even localized mode for amplitude $A = 0.20$. Only the central part of the chain is shown. The static displacements $A\phi_n$ are shown as $\diamondsuit$. Open diamonds indicate the light atoms, full diamonds indicate the heavy atoms.

with a heavy atom at the centre $n = 0$. In this case we obtain solutions with even symmetry for the ξ_n displacements and odd symmetry for the ϕ_n and χ_n displacements. The frequencies of these modes differ by less than 1% compared to those with the light central atom and therefore are not presented. The displacement patterns for the ξ_n even displacements and for the static ϕ_n odd displacements are shown in figure 5. The static displacements produce an expansion of the chain. The displacement patterns of the χ_n contributions are presented in figure 6. We note

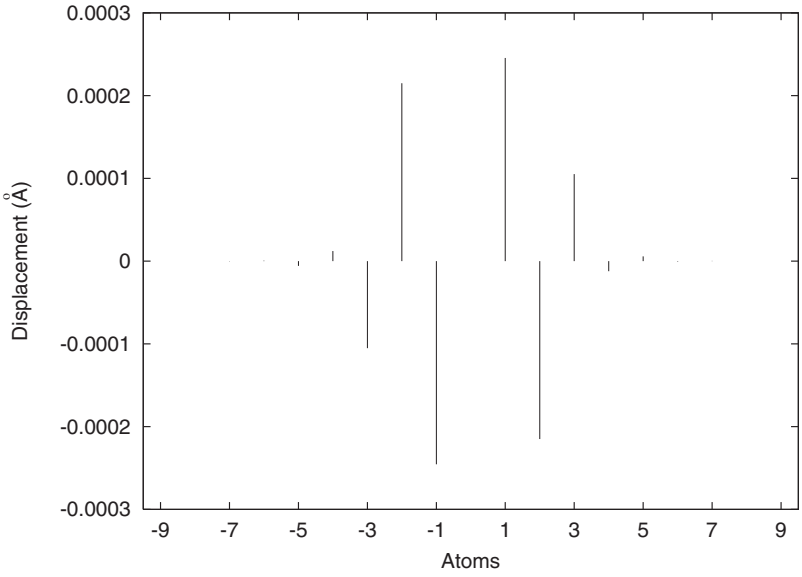

Figure 6. Second harmonic displacements $A\chi_n$ of the even localized mode for amplitude $A = 0.20$. Only the central part of the chain is shown.

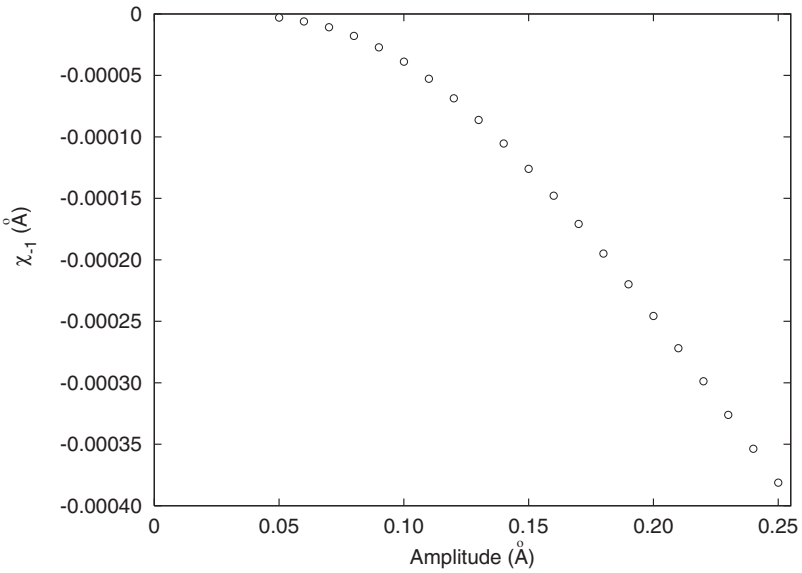

Figure 7. Second harmonic displacement $A\chi_{-1}$ of the even localized mode versus the maximum amplitude A of the mode.

that even in this case of a heavy atom at the centre the displacements associated with the second harmonic are two orders of magnitude less than those of the ξ_n contributions. The behaviour of the second harmonic displacement χ_{-1} as a function of the maximum mode amplitude A is given in figure 7.

4. Conclusions

We have studied anharmonic localized modes present in a finite diatomic chain by going beyond the RWA. We have included in the calculations second harmonic terms. The calculations are performed for amplitudes no larger than 0.25 Å which is in the range of amplitudes that can be detected experimentally without damaging the crystal. For these amplitudes it is possible to make a power series expansion of the potential retaining force constants up to fourth order. The displacements related to the first harmonic have either even or odd symmetry according to whether the central atom of the chain is a light or a heavy atom.

We have shown that the displacements associated with the second harmonic terms have even symmetry. The maximum amplitude of these displacements is two orders of magnitude less than those of the first harmonic contributions. These results are consistent with the intensities of the first and second harmonic present in the power spectrum evaluated with MD simulations [4]. In conclusion we have shown that the inclusion of the second harmonic terms in the equations of motion does not alter significantly the results obtained with the rotating wave in the range of amplitudes we have considered.

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