

Perturbation approach to the impurity problem in lattice dynamics

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1982 J. Phys. C: Solid State Phys. 15 2115

(<http://iopscience.iop.org/0022-3719/15/10/012>)

[The Table of Contents](#) and [more related content](#) is available

Download details:

IP Address: 80.230.39.157

The article was downloaded on 26/07/2009 at 18:46

Please note that [terms and conditions apply](#).

Perturbation approach to the impurity problem in lattice dynamics

Itzhak Dana and Joshua Zak

Department of Physics, Technion—Israel Institute of Technology, Haifa, Israel

Received 14 April 1981, in final form 4 November 1981

Abstract. Using the localisation ideas in the kq representation for perfect lattices, an equation is postulated defining perturbed localised modes for the impurity problem in lattice dynamics. The equation is solved by perturbation theory in the unit-cell scheme, up to second order. Multibranch and one-branch effective equations of motion are derived. The formalism is illustrated through the example of a molecular diatomic chain with a strongly localised impurity and in the tight-binding limit. A first-order correction is found for the displacement function of the optical localised mode.

1. Introduction

In a series of papers (Zak 1977a, 1977b, 1979) perturbative procedures were developed and applied to problems of electron dynamics in solids. These procedures were based on equations defining localised states for perturbations caused by impurities, magnetic fields and electric fields. The equations were postulated using basic facts about the localisation problem in the kq representation. The localised states were used to derive one-band effective Hamiltonians containing interband effects.

In the present article similar procedures are developed for the impurity problem in lattice dynamics. Classical equations of motion and the harmonic approximation are assumed. Unlike the methods based on the Green function formalism (see for example, Maradudin *et al* 1971) our approach makes use of direct perturbative procedures, with an explicit expression for the perturbation caused by impurities. The term impurity will be used here to indicate any alteration of the force constants which preserves the number of degrees of freedom per unit-cell. Interstitial or vacancy cases (Montroll and Potts 1955) are therefore not considered here.

The formal similarity between the equations describing phonons and those describing electrons is well known (Elliott *et al* 1974). There are, however, some differences between the two problems, arising from their different physical nature. First, the number of electronic energy bands for certain periodic potentials may be infinite, while the number of vibrational branches is always bounded by the number of degrees of freedom per unit cell. Second, unlike the Hamiltonian of an electron in a crystalline potential, the force-constants matrix is not an arbitrary Hermitian operator but has to satisfy relations of two kinds (Maradudin *et al* 1971): (*a*) those imposed by invariance against rigid-body translations and rotations of the crystal and (*b*) those imposed by the special structure and symmetry of a particular crystal. As a consequence, assumptions about

general features of perturbations in the force constants usually differ from the ones made for impurity potentials in electron dynamics.

A brief summary of the kq representation in lattice dynamics (Zak and Birman 1974) is given in § 2. In § 3 an equation defining perturbed localised modes of lattice vibrations is postulated. The equation is solved by perturbation theory in the unit-cell scheme up to second order. In § 4 multibranch effective equations of motion are derived. In principle, these can be diagonalised in the branch index to obtain one-branch effective equations up to any order in the perturbation expansion. Explicit results are given up to first order. The formalism is illustrated in § 5, where a model calculation is made for a two-branch problem. The model considered is that of a molecular diatomic chain with a strongly localised impurity. The problem is solved in the tight-binding limit and a first-order correction is found for the displacement function of the optical localised mode. The result, being due to the interbranch interaction, is a correction to a Koster-Slater one-branch approximation (Koster and Slater 1954).

2. kq representation in lattice dynamics: summary

Let the deviation of an atom from equilibrium be $d(\mathbf{R}_n + \mathbf{q}_f)$, where \mathbf{R}_n is the position vector of a unit cell and \mathbf{q}_f is the location of the atom relative to the unit cell. The description of the deviations d as a function of the discrete radius vector $\mathbf{r} = \mathbf{R}_n + \mathbf{q}_f$ leads to the lattice dynamics in the coordinate representation. In this representation the equations of motion are

$$\sum_{n'f'\beta} \varphi_{\alpha\beta}(\mathbf{R}_n + \mathbf{q}_f, \mathbf{R}_{n'} + \mathbf{q}_{f'}) b_{\beta}(\mathbf{R}_{n'} + \mathbf{q}_{f'}) = \omega^2 b_{\alpha}(\mathbf{R}_n + \mathbf{q}_f) \quad (1)$$

where d has been renormalised to b (the displacement function) in order to eliminate the masses, and the renormalised force-constants matrix φ is symmetric in the triple index (α, n, f) .

The transformation from the r representation to the kq_f representation is given by

$$C_{\alpha}(\mathbf{k}, \mathbf{q}_f) = V_b^{-1/2} \sum_n \exp(-i\mathbf{k} \cdot \mathbf{R}_n) b_{\alpha}(\mathbf{R}_n + \mathbf{q}_f) \quad (2)$$

$$\varphi_{\alpha\beta}(k\mathbf{q}_f, k'\mathbf{q}_{f'}) = V_b^{-1} \sum_{nn'} \exp(-i\mathbf{k} \cdot \mathbf{R}_n) \varphi_{\alpha\beta}(\mathbf{R}_n + \mathbf{q}_f, \mathbf{R}_{n'} + \mathbf{q}_{f'}) \exp(i\mathbf{k}' \cdot \mathbf{R}_{n'}) \quad (3)$$

for the displacement function and the force-constants matrix, respectively. V_b is the volume of a unit cell in the reciprocal lattice.

For an ideal crystal, $\varphi_{\alpha\beta} = \varphi_{\alpha\beta}^{(0)}$, the latter depends only on the difference $\mathbf{R}_n - \mathbf{R}_{n'}$. The displacement function is a Bloch wave with a branch index m and a wavevector \mathbf{k}_B . From (2) and (3) we obtain then

$$\begin{aligned} C_{\alpha m \mathbf{k}_B}(\mathbf{k}, \mathbf{q}_f) &= V_b^{1/2} \Delta(\mathbf{k} - \mathbf{k}_B) b_{\alpha m \mathbf{k}_B}(\mathbf{q}_f) \\ \varphi_{\alpha\beta}^{(0)}(k\mathbf{q}_f, k'\mathbf{q}_{f'}) &= V_b \Delta(\mathbf{k} - \mathbf{k}') D_{\alpha\beta}^{(0)}(\mathbf{k}, \mathbf{q}_f \mathbf{q}_{f'}) \end{aligned} \quad (4)$$

where the dynamical matrix $D_{\alpha\beta}^{(0)}$ is given by

$$D_{\alpha\beta}^{(0)}(\mathbf{k}, \mathbf{q}_f \mathbf{q}_{f'}) = \sum_n \exp(-i\mathbf{k} \cdot \mathbf{R}_n) \varphi_{\alpha\beta}^{(0)}(\mathbf{R}_n + \mathbf{q}_f, \mathbf{q}_{f'})$$

and we have

$$\sum_{f'\beta} D_{\alpha\beta}^{(0)}(\mathbf{k}_B, \mathbf{q}_f \mathbf{q}_{f'}) C_{\beta m \mathbf{k}_B}(\mathbf{k}, \mathbf{q}_{f'}) = \omega_m^2(\mathbf{k}_B) C_{\alpha m \mathbf{k}_B}(\mathbf{k}, \mathbf{q}_f). \quad (5)$$

In an ideal crystal one can define Wannier functions for lattice vibrations (Kohn 1973). These are given, in the kq_f representation, by

$$a_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) = \int_{V_b} d\mathbf{k}_B \exp(-i\mathbf{k}_B \cdot \mathbf{R}_n) C_{\alpha m \mathbf{k}_B}(\mathbf{k}, \mathbf{q}_f) \\ = \exp(-i\mathbf{k} \cdot \mathbf{R}_n) b_{\alpha m \mathbf{k}}(\mathbf{q}_f) \tag{6}$$

and are localised around \mathbf{R}_n . The simple relation (6) between the Wannier function in the kq_f representation and a Bloch wave, leads to the following equation:

$$\sum_{f'\beta} D_{\alpha\beta}^{(0)}(\mathbf{k}, \mathbf{q}_f \mathbf{q}_{f'}) a_{\beta mn}(\mathbf{k}, \mathbf{q}_{f'}) = \omega_m^2(\mathbf{k}) a_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) \tag{7}$$

which, unlike (5), is an eigenvalue problem only in the the unit-cell scheme (the quasi-coordinate \mathbf{k} is held constant).

3. Perturbed localised modes of lattice vibrations

The equations of motion (1) read, in the kq_f coordinates, as follows:

$$\sum_{f'\beta} \int_{V_b} d\mathbf{k}' \varphi_{\alpha\beta}(\mathbf{k} \mathbf{q}_f, \mathbf{k}' \mathbf{q}_{f'}) C_{\beta}(\mathbf{k}', \mathbf{q}_{f'}) = \omega^2 C_{\alpha}(\mathbf{k}, \mathbf{q}_f).$$

Defining the perturbation caused by impurities by

$$V_{\alpha\beta} = \varphi_{\alpha\beta} - \varphi_{\alpha\beta}^{(0)}$$

and using (4), we obtain

$$\sum_{f'\beta} [D_{\alpha\beta}^{(0)}(\mathbf{k}, \mathbf{q}_f \mathbf{q}_{f'}) C_{\beta}(\mathbf{k}, \mathbf{q}_{f'}) + \int d\mathbf{k}' V_{\alpha\beta}(\mathbf{k} \mathbf{q}_f, \mathbf{k}' \mathbf{q}_{f'}) C_{\beta}(\mathbf{k}', \mathbf{q}_{f'})] = \omega^2 C_{\alpha}(\mathbf{k}, \mathbf{q}_f). \tag{8}$$

We now write an equation, closely related to the original problem (8), but defining localised modes in the presence of the perturbation.

Let us compare (5) with (7). In (7), the dependence of ω_m^2 on the quasicordinate \mathbf{k} is related to the localised character of the Wannier functions. Such a dependence is absent in (5) and the eigenfunctions, reflecting the symmetry of the problem, are extended in nature. A similar relation should exist between the eigenvalue problem (8) and an equation defining perturbed localised modes. The latter is postulated as follows:

$$\sum_{f'\beta} [D_{\alpha\beta}^{(0)}(\mathbf{k}, \mathbf{q}_f \mathbf{q}_{f'}) A_{\beta mn}(\mathbf{k}, \mathbf{q}_{f'}) + \int d\mathbf{k}' V_{\alpha\beta}(\mathbf{k} \mathbf{q}_f, \mathbf{k}' \mathbf{q}_{f'}) A_{\beta mn}(\mathbf{k}' \mathbf{q}_{f'})] \\ = \Omega_m(\mathbf{k}, \mathbf{R}_n) A_{\alpha mn}(\mathbf{k}, \mathbf{q}_f). \tag{9}$$

The quantity Ω_m in (9), besides being \mathbf{k} -dependent, depends on the site of localisation of the perturbed localised modes $A_{\alpha mn}$. This is due to the loss of translational symmetry by the introduction of impurities, which also leads, in the \mathbf{r} representation, to a separate dependence of $A_{\alpha mn}$ on \mathbf{r} and \mathbf{R}_n . A branch index m has been introduced, since (9) is now solved by perturbation theory in the unit-cell scheme, starting from the unperturbed problem (7).

Let us expand $A_{\alpha mn}$ in the complete set of the Wannier functions (6):

$$A_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) = \sum_{\mathbf{l}} B_{ml}(\mathbf{k}, \mathbf{R}_n) a_{\alpha n}(\mathbf{k}, \mathbf{q}_f) \tag{10}$$

where the summation is over the branch index l . Using (10) and (7), (9) can be written in the Wannier functions representation (unit-cell scheme):

$$\begin{aligned} \omega_s^2(\mathbf{k}) B_{ms}(\mathbf{k}, \mathbf{R}_n) + \sum_l \int d\mathbf{k}' V_{sl}(\mathbf{R}_n, \mathbf{k}\mathbf{k}') B_{ml}(\mathbf{k}', \mathbf{R}_n) \\ = \Omega_m(\mathbf{k}, \mathbf{R}_n) B_{ms}(\mathbf{k}, \mathbf{R}_n) \end{aligned} \tag{11}$$

where

$$V_{sl}(\mathbf{R}_n, \mathbf{k}\mathbf{k}') = V_b \sum_{\substack{f, \alpha \\ f', \beta}} a_{\alpha sn}^*(\mathbf{k}, \mathbf{q}_f) V_{\alpha\beta}(\mathbf{k}\mathbf{q}_f, \mathbf{k}'\mathbf{q}_{f'}) a_{\beta ln}(\mathbf{k}', \mathbf{q}_{f'}). \tag{12}$$

Assuming the existence of a small parameter of perturbation theory, B_{ms} and Ω_m are expanded in powers of it:

$$B_{ms}(\mathbf{k}, \mathbf{R}_n) = B_{ms}^{(0)}(\mathbf{k}, \mathbf{R}_n) + B_{ms}^{(1)}(\mathbf{k}, \mathbf{R}_n) + B_{ms}^{(2)}(\mathbf{k}, \mathbf{R}_n) + \dots \tag{13}$$

$$\Omega_m(\mathbf{k}, \mathbf{R}_n) = \omega_m^2(\mathbf{k}) + \Omega_m^{(1)}(\mathbf{k}, \mathbf{R}_n) + \Omega_m^{(2)}(\mathbf{k}, \mathbf{R}_n) + \dots \tag{14}$$

When (13) and (14) are substituted in (11), we obtain, up to second order of perturbation theory (Landau and Lifshitz 1977),

$$B_{ms}^{(0)}(\mathbf{k}, \mathbf{R}_n) = \delta_{ms}$$

$$B_{ms}^{(1)}(\mathbf{k}, \mathbf{R}_n) = \frac{V_{sm}(\mathbf{k}, \mathbf{R}_n)}{\omega_m^2(\mathbf{k}) - \omega_s^2(\mathbf{k})} \quad s \neq m \quad B_{mm}^{(1)}(\mathbf{k}, \mathbf{R}_n) = 0$$

$$\Omega_m^{(1)}(\mathbf{k}, \mathbf{R}_n) = V_{mm}(\mathbf{k}, \mathbf{R}_n)$$

$$\begin{aligned} B_{ms}^{(2)}(\mathbf{k}, \mathbf{R}_n) = \frac{1}{\omega_m^2(\mathbf{k}) - \omega_s^2(\mathbf{k})} \sum_l \int d\mathbf{k}' V_{sl}(\mathbf{R}_n, \mathbf{k}\mathbf{k}') B_{ml}^{(1)}(\mathbf{k}', \mathbf{R}_n) \\ - \frac{V_{mm}(\mathbf{k}, \mathbf{R}_n) V_{sm}(\mathbf{k}, \mathbf{R}_n)}{[\omega_m^2(\mathbf{k}) - \omega_s^2(\mathbf{k})]^2} \quad s \neq m \end{aligned} \tag{15}$$

$$B_{mm}^{(2)}(\mathbf{k}, \mathbf{R}_n) = -\frac{1}{2} \sum_l |B_{ml}^{(1)}(\mathbf{k}, \mathbf{R}_n)|^2 \tag{16}$$

$$\Omega_m^{(2)}(\mathbf{k}, \mathbf{R}_n) = \sum_l \int d\mathbf{k}' V_{ml}(\mathbf{R}_n, \mathbf{k}\mathbf{k}') B_{ml}^{(1)}(\mathbf{k}', \mathbf{R}_n) \tag{17}$$

where

$$V_{sm}(\mathbf{k}, \mathbf{R}_n) = \int d\mathbf{k}' V_{sm}(\mathbf{R}_n, \mathbf{k}\mathbf{k}'). \tag{18}$$

When obtaining the results above, we assumed that no branch degeneracy exists at the \mathbf{k} considered. When two branches intersect at some \mathbf{k}_0 (the acoustic branches, for example, are dynamically degenerate at $\mathbf{k} = 0$), degenerate perturbation theory should be used in the neighbourhood of \mathbf{k}_0 .

Since the number of branches is finite, the sums in (15)–(17) and in higher order expressions always converge. Using the positive-definite nature of the unperturbed problem (7), one can also write upper bounds for the perturbation theory expressions (Dana 1978).

4. Multibranch and one-branch effective equations

The similarity between equations (8) and (9) will now be used to derive effective equations which contain the small parameter of perturbation theory in a natural way. The decoupling of these equations in the branch-index leads then to one-branch effective equations, which are correct up to any desired order in the small parameter.

We start by expanding the displacement function $C_\alpha(\mathbf{k}, \mathbf{q}_f)$ in the set of the perturbed localised modes $A_{\alpha mn}$:

$$C_\alpha(\mathbf{k}, \mathbf{q}_f) = \sum_{lp} F_l^{(P)}(\mathbf{R}_p) A_{\alpha p}(\mathbf{k}, \mathbf{q}_f). \tag{19}$$

Substituting (19) into (8) and using (9) we obtain

$$\sum_{lp} [\Omega_l(\mathbf{k}, \mathbf{R}_p) - \omega^2] F_l^{(P)}(\mathbf{R}_p) A_{\alpha p}(\mathbf{k}, \mathbf{q}_f) = 0. \tag{20}$$

The perturbation $V_{\alpha\beta}$ is generally not Hermitian in the unit-cell scheme. As a consequence, the perturbed localised modes do not form an orthogonal set. In fact, from (10) and (13) we have, up to second order of the perturbation expansion,

$$\begin{aligned} s_{mn,lp}(\mathbf{k}) &= V_b \sum_{f\alpha} A_{\alpha mn}^*(\mathbf{k}, \mathbf{q}_f) A_{\alpha p}(\mathbf{k}, \mathbf{q}_f) \\ &= \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_p)] [\delta_{ml} + s_{mn,lp}^{(1)}(\mathbf{k}) + s_{mn,lp}^{(2)}(\mathbf{k})] \end{aligned}$$

where

$$\begin{aligned} s_{mn,lp}^{(1)}(\mathbf{k}) &= B_{ml}^{(1)*}(\mathbf{k}, \mathbf{R}_n) + B_{lm}^{(1)}(\mathbf{k}, \mathbf{R}_p) \\ s_{mn,lp}^{(2)}(\mathbf{k}) &= B_{ml}^{(2)*}(\mathbf{k}, \mathbf{R}_n) + B_{lm}^{(2)}(\mathbf{k}, \mathbf{R}_p) + \sum_s B_{ms}^{(1)*}(\mathbf{k}, \mathbf{R}_n) B_{ls}^{(1)}(\mathbf{k}, \mathbf{R}_p) \end{aligned}$$

are non-vanishing overlap elements of the first and the second order respectively. On multiplying (20) from the left by $A_{\alpha mn}^*(\mathbf{k}, \mathbf{q}_f)$, summing over f and α and integrating over \mathbf{k} , we obtain

$$\begin{aligned} \sum_{lp} [w_m(\mathbf{R}_n - \mathbf{R}_p) \delta_{ml} + D_{mn,lp}^{(1)} + \dots] F_l^{(P)}(\mathbf{R}_p) &= \omega^2 F_m^{(P)}(\mathbf{R}_n) \\ &+ \omega^2 \sum_{lp} (S_{mn,lp}^{(1)} + \dots) F_l^{(P)}(\mathbf{R}_p) \end{aligned} \tag{21}$$

where

$$w_m(\mathbf{R}_n - \mathbf{R}_p) = V_b^{-1} \int d\mathbf{k} \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_p)] \omega_m^2(\mathbf{k}) \tag{22}$$

$$D_{mn,lp}^{(1)} = V_b^{-1} \int d\mathbf{k} \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_p)] [\delta_{ml} \Omega_m^{(1)}(\mathbf{k}, \mathbf{R}_p) + s_{mn,lp}^{(1)}(\mathbf{k}) \omega_l^2(\mathbf{k})] \tag{23}$$

$$S_{mn,lp}^{(1)} = V_b^{-1} \int d\mathbf{k} \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_p)] s_{mn,lp}^{(1)}(\mathbf{k}).$$

The set of multibranch effective equations (21) can be put into the form of an eigenvalue problem by an orthogonalisation procedure (Zak 1977c). The orthonormal perturbed localised modes which diagonalise the right-hand side of (21) in the branch index, are given by

$$\psi_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) = A_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) - \frac{1}{2} \sum_{m'n'} S_{m'n',mn}^{(1)} a_{\alpha n'n'}(\mathbf{k}, \mathbf{q}_f) \tag{24}$$

where (24) and all the equations hereafter in this section are written, for the sake of

simplicity, only up to first order of perturbation theory. The $\psi_{\alpha mn}$ s lead to the following multibranch effective equations:

$$\sum_{lp} [w_m(\mathbf{R}_n - \mathbf{R}_p) \delta_{ml} + K_{mn,lp}^{(1)}] F_l^{(0)}(\mathbf{R}_p) = \omega^2 F_m^{(0)}(\mathbf{R}_n), \quad (25)$$

where

$$K_{mn,lp}^{(1)} = D_{mn,lp}^{(1)} - \frac{1}{2} \sum_{p'} [w_m(\mathbf{R}_n - \mathbf{R}_{p'}) S_{mp',lp}^{(1)} + S_{mn,lp'}^{(1)} w_l(\mathbf{R}_p - \mathbf{R}_{p'})]$$

and the coefficients $F_m^{(0)}(\mathbf{R}_n)$ are defined by the expansion

$$C_\alpha(\mathbf{k}, \mathbf{q}_f) = \sum_{lp} F_l^{(0)}(\mathbf{R}_p) \psi_{\alpha lp}(\mathbf{k}, \mathbf{q}_f).$$

The last step is to decouple the equations (25) in the branch index. This is effected by a diagonalisation procedure (Zak 1977c). The final result for the effective one-branch equations is

$$\sum_p [w_m(\mathbf{R}_n - \mathbf{R}_p) + D_{mn,mp}^{(1)}] F_m(\mathbf{R}_p) = \omega_m^2 F_m(\mathbf{R}_n) \quad (26)$$

where, from (23),

$$D_{mn,mp}^{(1)} = V_b^{-1} \int d\mathbf{k} \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_p)] \Omega_m^{(1)}(\mathbf{k}, \mathbf{R}_p) \quad (27)$$

and $F_m(\mathbf{R}_n)$ is the displacement function in the representation of the orthonormal perturbed localised modes

$$\varphi_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) = A_{\alpha mn}(\mathbf{k}, \mathbf{q}_f) + \sum_{m'n'} (iT_{m'n',mn}^{(1)} - \frac{1}{2} S_{m'n',mn}^{(1)}) a_{\alpha m'n'}(\mathbf{k}, \mathbf{q}_f) \quad (28)$$

where $T_{mn,mp}^{(1)} = 0$ and, for $m \neq l$,

$$T_{mn,lp}^{(1)} = \frac{i}{V_b^2} \sum_{n'p'} \iint d\mathbf{k} d\mathbf{k}' \exp[i\mathbf{k} \cdot (\mathbf{R}_{p'} - \mathbf{R}_p) - i\mathbf{k}' \cdot (\mathbf{R}_{n'} - \mathbf{R}_n)] \\ \times \frac{K_{mn',lp'}^{(1)}}{\omega_m^2(\mathbf{k}') - \omega_l^2(\mathbf{k})}.$$

Effective one-branch equations which are exact up to higher orders of perturbation theory can be similarly obtained by diagonalisation procedures (Zak 1977c). These equations are more complicated than (26), because of their dependence on expressions which contain the interbranch interaction.

An explicit expression for the perturbation has been used from the beginning. In some cases one may prefer to work with a ω^2 -dependent perturbation which would lead, after a solution of the effective equations is obtained, to algebraic equations for the vibrational frequencies (Maradudin *et al* 1971).

5. A model calculation

We consider a linear chain of molecules of the same mass $2M$, connected by identical nearest-neighbour force constants β . Each molecule consists of two atoms, each of mass M , connected by a force constant α , $\alpha \gg \beta$ (Case A in the paper of Kohn). This chain has a centre of inversion and the type of impurity introduced preserves this symmetry. We

simply change the force constant α , in the unit cell $n = 0$, to α' . This corresponds to a strongly localised perturbation. The impurity is felt only when the atoms in the unit cell $n = 0$ move in antiphase. In this case, and when $\alpha' > \alpha$, the impurity is identical in effect to an inert interstitial, symmetrically situated between the two atoms, and connected with them by force constants $2(\alpha' - \alpha)$. The model has an exact solution (Dana 1978), which can be compared with that obtained here by means, and as an illustration, of our formalism.

Let the lattice constant be a and define

$$\varphi_1 = \frac{\alpha}{M} \quad \varphi_2 = \frac{\beta}{M} \quad \varphi = \varphi_1 + \varphi_2 \quad \rho = \frac{4\varphi_1\varphi_2}{(\varphi_1 + \varphi_2)^2} \quad \Delta\varphi = \frac{\alpha' - \alpha}{M}.$$

For the unperturbed chain, the two branches are given by

$$\omega_m^2(k_B) = \varphi\{1 + (-1)^m[1 - \rho \sin^2(k_B a/2)]^{1/2}\} \\ m = 1, 2 \quad -\pi/a < k_B \leq \pi/a. \tag{29}$$

We substitute (29) into the equations of motion and solve for the displacement functions. Using (6) and the localisation criteria of Kohn for this chain, we obtain the Wannier functions

$$a_{mn}(k, q_1) = \left(\frac{a}{4\pi}\right)^{1/2} e^{if(k)/2} e^{-ikna}, \tag{30}$$

$$a_{mn}(k, q_2) = \left(\frac{a}{4\pi}\right)^{1/2} (-1)^m e^{-if(k)/2} e^{-ikna} \tag{31}$$

where the proper phase factor in (30) and (31) is given by

$$e^{if(k)} = \left(\frac{\varphi_1}{\varphi} + \frac{\varphi_2}{\varphi} e^{-ika}\right) \left[1 - \rho \sin^2\left(\frac{ka}{2}\right)\right]^{-1/2}.$$

The perturbation can be written in the r representation as

$$V(na + q_f, n'a + q_{f'}) = \Delta\varphi\delta_{n,0}\delta_{n',0}(2\delta_{f,f'} - 1),$$

and in the kq_f representation as (see (3))

$$V(kq_f, k'q_{f'}) = \frac{a}{2\pi} \Delta\varphi(2\delta_{f,f'} - 1). \tag{32}$$

When $\alpha \gg \beta$, as in our case, $\rho \ll 1$, and the two branches are very narrow. In this case one can decide to work only up to first order in ρ . From now on all the equalities will be exact only within this approximation.

Using (30), (31) and (32) in (12), and integrating over k' as in (18), we obtain

$$V_{11}(k, n) = \Omega_1^{(1)}(k, n) = \frac{1}{8}i\Delta\varphi(\delta_{n,-1} - \delta_{n,1}) \sin(ka) e^{ikna} \tag{33}$$

$$V_{22}(k, n) = \Omega_2^{(1)}(k, n) = 2\Delta\varphi\delta_{n,0} e^{ikna} \tag{34}$$

$$B_{12}^{(1)}(k, n) = -\frac{1}{8}\lambda\rho(\delta_{n,-1} - \delta_{n,1}) e^{ikna} \tag{35}$$

$$B_{21}^{(1)}(k, n) = \frac{1}{8}i\lambda\rho\delta_{n,0} \sin(ka) e^{ikna}. \tag{36}$$

The parameter

$$\lambda = \Delta\varphi/\varphi$$

in (35) and (36) is related to the interbranch interaction via the perturbation. We shall assume that $\lambda \ll 1$ and work up to first order of the perturbation expansion. It turns out, as a matter of fact, that all the second order expressions of perturbation theory are also of the second order in ρ . This is a consequence of the proper choice of the phase factor in (30) and (31).

Substituting (35), (36), (30) and (31) into (10), and using the inverse transformation of (2), we can write the perturbed localised modes in the r representation

$$A_{mn}(pa + q_f) = a_m(pa + q_f - na) + \frac{1}{32}2^{1/2} \lambda \rho [\delta_{m,1}(\delta_{n,-1} - \delta_{n,1}) \times \delta_{p,0}(\delta_{f,2} - \delta_{f,1}) + \delta_{m,2}\delta_{n,0}(\delta_{p,-1} - \delta_{p,1})]. \tag{37}$$

From (37) we see that up to first order in λ and ρ , the perturbation affects only the acoustic modes which are localised at both sides of the impurity, and the optical mode which is localised at the impurity itself. This is consistent with physical expectations.

We can now explicitly write the effective one-branch equations (26) for our model. Using (29) in (22), and (33), (34) in (27), we obtain

$$w_1(p - n) = -\frac{1}{8}\varphi\rho[\delta_{p-n,-1} - 2\delta_{p-n,0} + \delta_{p-n,1}] = 2\varphi - w_2(p - n) \tag{38}$$

$$D_{1n,1p}^{(1)} = 0 \tag{38}$$

$$D_{2n,2p}^{(1)} = 2\Delta\varphi\delta_{n,0}\delta_{p,0}. \tag{39}$$

From (38) we see that within our approximation no localised mode of vibration can emerge from the acoustic branch, and all the solutions of (26) with $m = 1$ correspond to extended modes with ω_1^2 lying in the acoustic branch. This result was expected from the nature of the perturbation, and remains valid also when terms of the second order in λ and ρ are kept. The optical one-branch equation ($m = 2$) is of the Koster–Slater type. By substituting (39) into (26), one obtains the localised solution

$$F_2(n) = \exp[i(1 + \text{sgn}(\Delta\varphi))\frac{1}{2}\pi n - z|n|] \tag{40}$$

where

$$\sinh(z) = 8|\lambda|/\rho.$$

The corresponding frequency is given by

$$\omega_2^2 = 2\varphi(1 - \frac{1}{8}\rho) + 2 \text{sgn}(\Delta\varphi) [(\frac{1}{8}\varphi\rho)^2 + (\Delta\varphi)^2]^{1/2}. \tag{41}$$

The coefficients (40) serve to expand the displacement function in the set of the orthonormal perturbed localised modes (28). These, however, are equal to the A_{mn} s, since a short calculation reveals that $S^{(1)}$ and $T^{(1)}$ in (28) are of the second order in ρ and can therefore be neglected within our approximation. From (40) and (37) we then obtain the displacement function of the optical localised mode

$$b_2(pa + q_f) = \sum_{n=-\infty}^{\infty} F_2(n) a_2(pa + q_f - na) + \frac{1}{32}2^{1/2} \lambda \rho (\delta_{p,-1} - \delta_{p,1}). \tag{42}$$

The second term on the right-hand side of (42) is entirely due to the interbranch interaction via the perturbation, and it can be interpreted as a correction term to the Koster–Slater one-branch approximation.

On the other hand, the vibrational frequency, as given by (41), does not contain

interbranch effects. The latter emerge when one includes into (26) higher order expressions of perturbation theory.

Let us compare our results with the exact solution. This can be obtained as follows. For the ideal crystal the displacement function has the form

$$b(na + q_f) = u(q_f) e^{ikna}.$$

When the impurity is introduced k acquires, for the localised modes, an imaginary part, and we can assume that the displacement function, at both sides of the impurity, is

$$\begin{aligned} b(na + q_f) &= u^+(q_f) b^n & n > 0 \\ b(na + q_f) &= u^-(q_f) b^{-n} & n < 0 \end{aligned} \tag{43}$$

where $|b| < 1$. Because of the inversion symmetry around the impurity, we must have

$$u^+(q_1) = \pm u^-(q_2) \quad u^-(q_1) = \pm u^+(q_2) \tag{44}$$

where $q_2 > q_1$. On comparing the equations of motion for $n = 0$ with those for $n = \pm 1$, we obtain

$$b(q_1) = u^-(q_1) = \pm u^+(q_2) = \pm b(q_2). \tag{45}$$

The plus sign in (45), because of the nature of the perturbation, cannot give rise to a localised mode. We then choose the minus sign in (44) and (45), which indeed corresponds to an optical-like localised mode. On substituting (43)–(45) into the equations of motion, we obtain, after some algebra,

$$b = \frac{\varphi_1 w - \tilde{\varphi}}{\varphi_2 \tilde{\varphi}} \tag{46}$$

$$\frac{u^-(q_1)}{u^-(q_2)} = \frac{u^+(q_2)}{u^+(q_1)} = -\frac{\varphi_1}{\tilde{\varphi}} \tag{47}$$

$$\tilde{\varphi} w^3 - (\tilde{\varphi}^2 + \varphi_1^2) w^2 + \tilde{\varphi}(\varphi_1^2 - \varphi_2^2) w = 0 \tag{48}$$

where

$$w = \omega_2^2 - \varphi \quad \tilde{\varphi} = \varphi_1 + 2\Delta\varphi.$$

The expressions (46), (47) define the displacement function of the localised mode, while (48) is an equation for its frequency of vibration. In our case $\alpha > \beta$ ($\varphi_1 > \varphi_2$), so that the solution $w = 0$ of (48) leads to $|b| > 1$ and it is not physical. The other solutions of (48) are given by

$$w = \frac{\tilde{\varphi}^2 + \varphi_1^2}{2\tilde{\varphi}} \pm \left[\varphi_2^2 + \left(\frac{\tilde{\varphi}^2 - \varphi_1^2}{2\tilde{\varphi}} \right)^2 \right]^{1/2}. \tag{49}$$

The sign in (49) must be chosen so that $|b| < 1$. Using (46), (48) and (49), we can verify that when $\Delta\varphi$ is sufficiently small, $|\Delta\varphi| \ll \varphi_2$, the sign in (49) is the same as the sign of $\Delta\varphi$. We then have, in this case,

$$\omega_2^2 = \varphi + \frac{\tilde{\varphi}^2 + \varphi_1^2}{2\tilde{\varphi}} + \text{sgn}(\Delta\varphi) \left[\varphi_2^2 + \left(\frac{\tilde{\varphi}^2 - \varphi_1^2}{2\tilde{\varphi}} \right)^2 \right]^{1/2}. \tag{50}$$

The condition $|\Delta\varphi| \ll \varphi_2$ is equivalent to $|\lambda| \ll \rho$ (see definition of λ and ρ). It means that the strength of the perturbation is smaller than the width of the unperturbed branch. It can be shown (Dana 1978) that in this case (41) is consistent with working only up to first order in ρ . On retaining now in (50) only first-order terms in λ and ρ , one can easily check that (50) reduces indeed to (41).

6. Summary and final remarks

The paper introduces the concept of perturbed localised modes for the impurity problem in lattice dynamics. It is parallel to the concept of generalised Wannier functions in the dynamics of electrons in solids (Kohn and Onnifroy 1973, Gay and Smith 1974, Zak 1977a, 1977b, 1977c, 1979). The equation defining these modes is postulated using the localisation ideas in the kq representation for lattice dynamics (Zak and Birman 1974). The equation is solved by perturbation theory in the unit-cell scheme and effective one-branch equations of motion are derived. These equations contain the 'interbranch interaction' in the small parameter of perturbation theory and give corrections to a Koster-Slater (1954) one-branch approximation. The solution of the equations corresponds to the extended and the localised modes of vibration, arising from unperturbed branches when impurities are introduced.

Alternatively, one may apply the ideas of Kohn and Onnifroy (1973), or their generalisation to three dimensions (Gay and Smith 1974), to lattice dynamics in order to define perturbed localised modes. The latter can be calculated by means of variational procedures similar to those used in electron dynamics (Kohn and Onnifroy 1973, Gay and Smith 1975).

Because of their localised character, one expects the perturbed localised modes not to differ drastically from the localised basis of the perfect crystal (Kohn 1973). At the same time these modes reflect the influence of impurities on the vibrations of atoms at different crystal sites. This is well demonstrated by our model calculation which gives an explicit expression for the perturbed localised modes. For these reasons, the concept itself of perturbed localised modes may turn out to be quite useful in the framework of the impurity problem in lattice dynamics.

With regard to the solution of the equations of motion for the perturbed crystal, one may compare the method proposed in this paper with the usual one based on the Green function formalism (Maradudin *et al* 1971). Consider the case of a slowly varying perturbation in the force constants caused by an extended impurity. In the Green function formalism the frequencies corresponding to the localised modes of vibration are found by solving an eigenvalue problem whose dimension is equal to the number of degrees of freedom in the crystal directly affected by the presence of the impurity. In the case of an extended impurity this generally involves an excessively difficult calculation. On the other hand, the assumption of a slowly varying perturbation, in the framework of the formalism presented in this paper, may itself facilitate in some cases the derivation of one-branch effective equations of motion. This is similar to the situation one has in the impurity problem in electron dynamics (Zak 1977a, 1977c). The one-branch effective equations of motion are in general much easier to solve than the original equations, since they only involve the space of one branch. For well-localised impurities, however, the methods based on the Green function formalism may be preferable in practice for many cases.

References

- Dana I 1978 *Thesis* Technion (unpublished)
- Elliott R J, Krumhansl J A and Leath P L 1974 *Rev. Mod. Phys.* **46** 465–9
- Gay J C and Smith J R 1974 *Phys. Rev. B* **9** 4151–64
- 1975 *Phys. Rev. B* **11** 4906–15
- Kohn W 1973 *Phys. Rev. B* **7** 2285–7
- Kohn W and Onnfroy J R 1973 *Phys. Rev. B* **8** 2485–95
- Koster G F and Slater J C 1954 *Phys. Rev.* **95** 1167–76
- Landau L D and Lifshitz E M 1977 *Quantum Mechanics* (Oxford: Pergamon)
- Maradudin A A, Montroll E W, Weiss G H and Ipatova I P 1971 *Solid State Physics* supp. 3, ed H Ehrenreich, F Seitz and D Turnbull (New York and London: Academic Press)
- Montroll E W and Potts R B 1955 *Phys. Rev.* **100** 525–43
- Zak J 1977a *Phys. Rev. B* **15** 771–8
- 1977b *Phys. Rev. B* **16** 4154–63
- 1977c *Phys. Rev. B* **16** 1334–43
- 1979 *Phys. Rev. B* **19** 1946–53
- Zak J and Birman J L 1974 *Phys. Rev. B* **10** 1315–8