

# Ab initio calculations of the lattice dynamics of crystals

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**Abstract.** A review is given of the use of the density functional theory in calculations of the lattice dynamics of crystals. This approach is based on calculation, in the first order in nuclear displacements, of changes in the potential and charge density. This is done using the linear response theory and the linear muffin-tin (MT) orbitals. This makes it possible to treat in a unified manner both simple systems with almost-free electrons and transition metals. The suitability of the method is demonstrated by calculations of the phonon dispersion curves of Nb and Mo. The calculated results are found to be in good agreement with the experimental data.

## 1. Introduction

Calculations of the lattice dynamics of crystals are among the most important tasks in solid-state physics. The main interest lies in the transition metals, and in their alloys and compounds. The interest in these materials is due to an enormous variety of the structure of their phonon curves and also due to the phenomena of lattice instability and of superconductivity; in the latter case, phonons play the central role and the effect is observed at relatively high temperatures (8–23 K). The bulk of the available information on the phonon spectra of these materials has been obtained experimentally from inelastic neutron diffraction. In some cases such information has been deduced from measurements of the elastic constants, specific heat, and tunneling characteristics of superconductors.

Initially, in spite of the considerable progress in the microscopic theory of the phonon spectra of metals with almost-free electrons, which has been stimulated by the development and application of the pseudopotential method (see, for example, Ref. [1]), the progress in the understanding of the phonon spectra of transition metals has been relatively slow and difficult. This has primarily been due to the difficulty encountered in the application of the pseudopotential concept when discussing the effects of the electron screening in systems with a strong  $d$  nature of the conduction band. Consequently, in the past it has been usually necessary to bring in phenomenological force constants in order to reproduce the dispersion curves (without any real understanding of the nature of the observed anomalies) or the transition metals have been regarded as materials with almost-free electrons and attempts have been made to account for the phonon dispersion by model pseudopotentials and also by models of screening by free electrons. Naturally, such methods are not theoretically justified.

More recently, there have been many attempts to develop a complete microscopic theory of the phonon spectra of the transition metals both formally and by complex computer calculations. In the final analysis this has resulted in a better understanding of the nature of the dispersion curve anomalies. However, up to now (apart from the very latest contributions [2–5]) there have been no published completely ab initio calculations of the phonon spectra which would agree with the experimental results along all the symmetric directions.

In this review we shall consider the main reasons for this theoretical situation and give a state-of-the-art account of the microscopic theory of lattice dynamics with special attention to the transition metals.

## 2. Many-body theory of lattice dynamics

The microscopic approach to the calculation of the electron contribution to the lattice dynamics is based on the very old idea of Born and Oppenheimer [6] of adiabatic

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Received 15 September 1994; revision received 21 November 1994  
*Uspekhi Fizicheskikh Nauk* **165** (7) 773–797 (1995)  
Translated by A Tybulewicz

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separation of the slow motion of nuclei from the fast motion of electrons in calculation of the energies of molecules. A similar approach was later generalised to crystals. The essence of this approximation can be stated as follows. In view of the considerable difference between the velocities of electrons and nuclei, characterised by  $(m/M)^{1/2}$ , where  $m$  and  $M$  are the masses of an electron and a nucleus, it is permissible to consider two uncoupled [apart from small nonadiabatic corrections of the order of  $(m/M)^{1/2}$ ] systems of electrons and nuclei. The system of electrons is described by the Schrodinger equation for electrons which are in the field of arbitrarily distributed nuclei and are characterised by the Hamiltonian

$$H_e = T_e + V_{ee} + V_{ne}, \quad (2.1)$$

where  $T_e$  is the kinetic energy of electrons,  $V_{ee}$  is the Coulomb interaction between electrons, and  $V_{ne}$  is the nuclear–electron interaction. The nuclear system which determines, in particular (in the harmonic approximation), the spectrum of phonon excitations, has the Hamiltonian

$$H_n = T_n + V_{nn} + E\{\mathbf{R}\}. \quad (2.2)$$

Here,  $T_n$  is the kinetic energy of nuclei,  $V_{nn}$  is the Coulomb interaction of nuclei, and  $E\{\mathbf{R}\}$  is the electron energy described by the Hamiltonian (2.1). This quantity can be represented as the average, for any given set of  $\{\mathbf{R}\}$ , value of the Hamiltonian  $H_e$ :

$$E\{\mathbf{R}\} = \langle 0_R | H_e | 0_R \rangle, \quad (2.3)$$

where  $|0_R\rangle$  is the ground state of the electron system for a given distribution of nuclei  $\{\mathbf{R}\}$ .

The above approach makes it possible to derive quite simply, at least from the formal point of view, an expression for the electron contribution to the force acting on a nucleus when it is displaced slightly from an equilibrium position in an ideal crystal, as well as the electron contribution to the dynamic matrix of vibrations. In particular, the electron contribution to the force can be represented by

$$\mathbf{F}_R = -\frac{dE}{d\mathbf{R}} = -\frac{d}{d\mathbf{R}} \langle 0 | H_e | 0 \rangle, \quad (2.4)$$

where the averaging is carried out over the ground state of the crystal. It follows from the Hellman–Feynman theorem, that expression (2.4) can be rewritten in the form

$$\mathbf{F}_R = -\left\langle 0 \left| \frac{\partial V_{ne}}{\partial \mathbf{R}} \right| 0 \right\rangle = -\int \rho(\mathbf{r}) \frac{\partial V_{ne}(\mathbf{r})}{\partial \mathbf{R}} d\mathbf{r}. \quad (2.5)$$

Therefore, the force acting on a nucleus when it is displaced in a crystal is of purely electrostatic origin and, at first sight, it should be easy to find it if we know the electron density distributions  $\rho(\mathbf{r})$ . In fact, calculation of the function  $\rho(\mathbf{r})$  for a crystal is a far from simple task and we shall return later to the problem of actual calculation of this quantity.

The electron contribution to the dynamic matrix of vibrations can also be obtained quite readily and it can be expressed in terms of the second derivative of the total energy:

$$A_{\mu\mu'}(\mathbf{R} - \mathbf{R}') = \frac{d}{dR_\mu} \frac{d}{dR'_{\mu'}} \langle 0 | H_e | 0 \rangle, \quad (2.6)$$

where  $\mu = \{x, y, z\}$ . Applying again the Hellman–Feynman theorem we can rewrite the matrix  $A_{\mu\mu'}(\mathbf{R} - \mathbf{R}')$  in the form

$$A_{\mu\mu'}(\mathbf{R} - \mathbf{R}') = \int \frac{d\rho(\mathbf{r})}{dR_\mu} \frac{\partial V_{ne}(\mathbf{r})}{\partial R'_{\mu'}} d\mathbf{r} + \int \rho(\mathbf{r}) \frac{\partial^2 V_{ne}(\mathbf{r})}{\partial R_\mu \partial R'_{\mu'}} d\mathbf{r}. \quad (2.7)$$

It follows from formula (2.7) that in order to calculate the dynamic matrix it is not sufficient, in contrast to calculation of the force, to know just the electron density distribution in an ideal crystal: we also need to know the change in the electron density due to a change in the potential of the nuclei due to their displacement. This change in the electron density should be found, in the linear approximation, from the change in the potential and within the framework of the linear response theory it can be written as follows:

$$\frac{d\rho(\mathbf{r})}{dR_\mu} = \int \frac{\partial V_{ne}(\mathbf{r}')}{\partial R_\mu} \chi(\mathbf{r}', \mathbf{r}) d\mathbf{r}'. \quad (2.8)$$

Here,  $\chi(\mathbf{r}, \mathbf{r}')$  is simply the susceptibility of a system of interacting electrons which are in the periodic field of nuclei.

This many-body ab initio approach is most readily applied to the description of the dynamics of a lattice of a simple metal. The relationships obtained are general and they apply to a system of ‘bare nuclei plus all the electrons in a crystal, including localised electrons in the inner shells’. In general, the ion core electrons may be excluded from calculations by introducing the electron–ion pseudopotential in place of the simple Coulomb electron–nuclear interaction. For simple metals this electron–ion pseudopotential proves to be a fairly small quantity, so that we can use perturbation theory not only because of smallness of the shift of an ion from an equilibrium position (only this approach has been used in the above discussion), but also because of the smallness of the pseudopotential. Since the expressions for the dynamic matrix (2.7) and (2.8) are quadratic in terms of the pseudopotential, the susceptibility of the electron system can be described by the expression for a homogeneous electron gas. In this case the Fourier representation of the dynamic matrix can be written in the form

$$\begin{aligned} A_{\mu\mu'}(\mathbf{q}) &= A_{\mu\mu'}^i(\mathbf{q}) + \sum_G (q + G)_\mu V_{ic}(\mathbf{q} + \mathbf{G}) \chi(\mathbf{q} + \mathbf{G}) \\ &\quad \times V_{ic}(\mathbf{q} + \mathbf{G}) (q + G)_{\mu'} \\ &\quad - \sum_G G_\mu V_{ic}(\mathbf{G}) \chi(\mathbf{G}) V_{ic}(\mathbf{G}) G_{\mu'}. \end{aligned} \quad (2.9)$$

Here,  $A_{\mu\mu'}^i(\mathbf{q})$  is the contribution of ions to the dynamic matrix; the wave vector  $\mathbf{q}$  lies in the first Brillouin zone;  $\mathbf{G}$  is the reciprocal lattice vector;  $\chi(\mathbf{q} + \mathbf{G})$  is the susceptibility of an interacting homogeneous electron gas. The third term in expression (2.9) follows from the second term in expression (2.7) and it is due to the translational invariance. Formula (2.9) applies to crystals with one atom per unit cell, but it is easily generalised to the case of crystals with a basis. The electron susceptibility can be expressed simply in terms of the static dielectric function of a homogeneous electron gas  $\epsilon(\mathbf{q}, 0)$ :

$$\chi(\mathbf{q}) = \frac{1}{V(\mathbf{q})} \left[ \frac{1}{\epsilon(\mathbf{q}, 0)} - 1 \right], \quad (2.10)$$

where  $V(\mathbf{q})$  is the Fourier component of the Coulomb interaction

$$V(\mathbf{q}) = \frac{4\pi e^2}{q^2}. \quad (2.11)$$

Calculations of the phonon spectra of a whole range of simple metals, carried out with the aid of various approximate expressions for the static dielectric function, are in very reasonable agreement with the experimental data (see, for example, Ref. [1]).

When the pseudopotential is no longer small or if all the electrons in a crystal are considered in a calculation of the electron contribution to the dynamic matrix of vibrations  $A_{\mu\mu'}(\mathbf{q})$ , it is necessary to know the susceptibility of the electron subsystem which takes account of the band structure of the electron spectrum. In this case the Fourier representation of the susceptibility is no longer a function of the momentum  $\mathbf{q}$  alone, but is a matrix in the space of the reciprocal lattice vectors  $\mathbf{G}$  and  $\mathbf{G}'$ . The exact expression for  $A_{\mu\mu'}(\mathbf{q})$  can be written, in accordance with formulas (2.7) and (2.8), in the form

$$\begin{aligned} A_{\mu\mu'}(\mathbf{q}) = & \sum_{\mathbf{G}, \mathbf{G}'} (q + \mathbf{G})_{\mu} V_{\text{nc}}(\mathbf{q} + \mathbf{G}) \chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}') \\ & \times V_{\text{nc}}(\mathbf{q} + \mathbf{G}') (q + \mathbf{G}')_{\mu'} \\ & - \sum_{\mathbf{G}, \mathbf{G}'} G_{\mu} V_{\text{nc}}(\mathbf{G}) \chi(\mathbf{G}, \mathbf{G}') V_{\text{nc}}(\mathbf{G}') G'_{\mu'}, \end{aligned} \quad (2.12)$$

where  $\chi(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$  is the electron susceptibility matrix. This expression has been derived by many authors over two decades ago (see, for example, Refs [1, 7]), but there have been no consistent ab initio calculations based on this approach for crystals other than those of simple metals.

As is known (see, for example, Ref. [8]), even calculations of the dielectric response functions of a homogeneous electron gas at densities corresponding to real metals represent a very difficult and only partly solved problem. The difficulties in calculations of the same functions for an electron subsystem of a crystal, carried out within the framework of the standard many-body theory, are incomparably greater. However, it should be pointed out that a general and absolutely rigorous expression (2.12) for the electron contribution to the dynamic matrix has proved very useful in solid-state theory. This expression has been used to demonstrate a number of rigorous and exact relationships describing lattice dynamics, and to develop a multitude of approximate and semiphenomenological approaches to the calculations of phonon spectra (see, for example, Refs [7, 9]).

### 3. Density functional method and lattice dynamics

The many-body approach to the theory of crystal lattice dynamics presented in the preceding section leads to simple and physically clear expressions for the electron contribution to the forces acting on the nuclei and for the same contribution to the dynamic matrix. However, as pointed out already, this approach is not very suitable for real ab initio calculations. It is clear from expressions (2.5) and (2.7) for the force and the dynamic matrix that both these quantities are determined solely by the distribution of the

electron charge in an ideal crystal and by changes in this quantity which are induced by displacements of nuclei or of ion cores. The most general and rigorous approach to calculations of these quantities is at present the density functional method, proposed by Kohn, Hohenberg, and Sham [10, 11] (see also Ref. [12]). An undoubted advantage of this method is a practical technique for specific calculations carried out within the framework of this method.

Briefly, the method can be described by a theorem proved in Ref. [10]: the energy of the ground state of a system of interacting electrons which are in an external field  $V_{\text{ext}}(\mathbf{r})$  is a single-valued functional of the electron density distribution  $\rho(\mathbf{r})$ . This functional is extremal when  $\rho(\mathbf{r})$  is varied and it reaches its minimum for a true distribution of the electron density, i.e.

$$\frac{\delta E\{\rho(\mathbf{r})\}}{\delta \rho(\mathbf{r})} = 0. \quad (3.1)$$

The energy functional  $E\{\rho(\mathbf{r})\}$  can be written in the form

$$\begin{aligned} E\{\rho(\mathbf{r})\} = & T\{\rho(\mathbf{r})\} + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ & + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \tilde{E}_{\text{xc}}\{\rho(\mathbf{r})\}. \end{aligned} \quad (3.2)$$

Here,  $T\{\rho(\mathbf{r})\}$  is the kinetic energy functional and the second term is the energy of the interaction with an external field which in the case of crystals becomes

$$V_{\text{ext}}(\mathbf{r}) = - \sum_{\mathbf{R}, \mathbf{t}} \frac{Z_{\mathbf{R}} e^2}{|\mathbf{r} - \mathbf{R} - \mathbf{t}|}, \quad (3.3)$$

where  $\mathbf{R}$  are the positions of the basis sites in a unit cell and  $\mathbf{t}$  are primitive translations. The third term in expression (3.2) is the contribution of the electrostatic Coulomb interaction between electrons (Hartree energy) and the last (fourth) term is the exchange–correlation functional, describing the contribution of the electron–electron exchange–correlation interaction to the potential energy of the electron system. Unfortunately, the exact form of the expressions for the functionals of the kinetic and exchange–correlation energies, needed in specific calculations, are not yet known. Nevertheless, a whole range of approximate expressions has been proposed and they can be used to carry out calculations whose results are in very good agreement with the experimental data. The problem of the explicit representation of the energy functional will be discussed many times later in this review: at this stage we shall discuss the derivation of the expressions for the force and for the dynamic matrix on the basis of the density functional method.

As usual, the force acting on a nuclei at a site  $\mathbf{R}$  by the electrons when the nucleus is displaced will be described by

$$\mathbf{F}_{\mathbf{R}} = - \frac{dE\{\rho(\mathbf{r})\}}{d\mathbf{R}}, \quad (3.4)$$

and the total derivative will be represented in the form

$$\frac{dE\{\rho(\mathbf{r})\}}{d\mathbf{R}} = \frac{\partial E\{\rho(\mathbf{r})\}}{\partial \mathbf{R}} + \frac{\delta E\{\rho(\mathbf{r})\}}{\delta \rho(\mathbf{r})} \frac{d\rho(\mathbf{r})}{d\mathbf{R}}. \quad (3.5)$$

In view of the extremality of the total energy functional (3.1), the second term in Eqn (3.5) vanishes. Since in the expression for the total energy (3.1) only the second

term, describing the interaction with the external field, depends explicitly on  $\mathbf{R}$ , it follows that

$$\mathbf{F}_R = - \int \rho(\mathbf{r}) \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}} d\mathbf{r}. \quad (3.6)$$

Similarly, the electron contribution to the dynamic matrix, given by

$$A_{\mu\mu'}(\mathbf{R} - \mathbf{R}') = - \frac{dF_{R_\mu}}{dR'_{\mu'}}, \quad (3.7)$$

can be rewritten in the form

$$A_{\mu\mu'}(\mathbf{R} - \mathbf{R}') = \int \frac{d\rho(\mathbf{r})}{dR'_{\mu'}} \frac{\partial V_{\text{ext}}(\mathbf{r})}{\partial R_\mu} d\mathbf{r} + \int \rho(\mathbf{r}) \frac{\partial^2 V_{\text{ext}}(\mathbf{r})}{\partial R_\mu \partial R'_{\mu'}} d\mathbf{r}. \quad (3.8)$$

Therefore, the formal expressions for the electron contributions to the force and the dynamic matrix, obtained within the framework of the many-body approach [expressions (2.5) and (2.7)], are completely identical with the expressions (3.6) and (3.8) obtained by the density functional method. This is not surprising, because in both methods we start from a consideration of the electron energy in a given field of nuclei and then deal with the change in this energy under the action of the displacements of the nuclei. The difference between these approaches lies in the methods used to calculate the energy, the electron density distribution and the changes in these quantities.

Before we discuss the current and most consistent methods of calculation within the framework of the density functional, we shall consider briefly some of the simplest but very effective approaches to the theory of lattice dynamics based on simple approximations for the functional (3.2). Let us consider a weakly nonuniform electron system. In this case the density functional (3.2) can be described by what is known as the local approximation:

$$E\{\rho(\mathbf{r})\} = \int \rho(\mathbf{r}) t[\rho(\mathbf{r})] d\mathbf{r} + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}[\rho(\mathbf{r})] d\mathbf{r}. \quad (3.9)$$

Here,  $t[\rho(\mathbf{r})]$  is the kinetic energy of electrons per particle in a homogeneous electron gas in which the density is everywhere  $\rho$ , and  $\varepsilon_{\text{xc}}(\rho)$  is the corresponding exchange–correlation energy. The values of  $t(\rho)$  and  $\varepsilon_{\text{xc}}(\rho)$  are quite well known for a wide range of densities of a homogeneous electron gas; in particular, they have been calculated by the Monte Carlo method [13]. If only the exchange energy is included,  $t(\rho)$  and  $\varepsilon_{\text{xc}}(\rho)$  can be described by the following exact analytic expressions

$$\begin{aligned} t(\rho) &= c_0 \rho^{2/3}, \\ \varepsilon_{\text{xc}}(\rho) &= c_1 \rho^{1/3}, \end{aligned} \quad (3.10)$$

where  $c_0$  and  $c_1$  are constants independent of the electron density. Substitution of these expressions in the functional (3.9) leads to the Thomas–Fermi theory which has been well known since the thirties. If  $\varepsilon_{\text{xc}}(\rho)$  in expression (3.10) is supplemented by the correlation energy, the resultant expression represents the Thomas–Fermi–Dirac functional. We shall not discuss in detail this theory and its applications in solid-state physics (see, for example, the first chapter in Ref. [12]), but we shall consider briefly only one of these applications used frequently and effectively to

calculate the properties of ionic and molecular crystals. These crystals can be regarded as consisting of saturated ‘elementary’ units: ions, atoms, or molecules with filled electron shells. After separation of the Madelung Coulomb energy of ionic compounds, the remaining part is found to be determined by the short-range forces and is related primarily to the pair overlaps between the nearest neighbours. This makes it possible to regard quite accurately the total electron density of a crystal as a superposition of the densities of the individual elementary units and the latter can be found in turn from any program for atomic calculations. The energy of the pair interactions is described by the expression

$$\begin{aligned} \Delta E(\mathbf{R}) &= E\{\rho_{\text{at}}(\mathbf{r}) + \rho_{\text{at}}(\mathbf{r} + \mathbf{R})\} \\ &\quad - E\{\rho_{\text{at}}(\mathbf{r})\} - E\{\rho_{\text{at}}(\mathbf{r} + \mathbf{R})\}, \end{aligned} \quad (3.11)$$

where  $E\{\rho(\mathbf{r})\}$  is the local Thomas–Fermi–Dirac approximation. The short-range pair interaction of ions is determined by the difference between the expression (3.11) and that describing the interaction of point ions, and it can be found numerically. The total energy of a crystal can thus be written as follows:

$$E = E_M + \sum_{R,R'} U_{RR'}, \quad (3.12)$$

where  $E_M$  is the Madelung Coulomb energy for point ions and  $U_{RR'}$  is the short-range pair interion potential discussed above.

First calculations of this type were carried out back in the thirties by Jensen, Lentz and Gombas [14]. The current series of calculations was started in the seventies by Gaydenko and Nikulin [15] who found the parameters of the interatomic interactions within the framework of the Thomas–Fermi functional. The work has since been developed on the basis of what is known as the Gordon–Kim electron gas model [16]. This model has been used in calculations of the binding energy, equilibrium interatomic distances, elastic constants, pressures of polymorphic transformations, etc., for a large number of ionic and molecular crystals. A good agreement with the experimental data has been achieved. The phonon spectra of these crystals have not been calculated. This has been done later [17] in connection with various types of lattice instabilities in ionic crystals: melting, transition to a superionic state, and structural instability.

The method under discussion has a number of shortcomings and the most important of these is the rigid ion approximation. This means that any possible deformations of ions, including those related to their dipole polarisability, are ignored in this approach. These shortcomings of the Gordon–Kim model have recently been eliminated. First, a suggestion has been made to include the influence, on the ions, of the crystal Madelung Coulomb potential, which is due to the presence of the surrounding ions. This requires calculation of the distribution of the electron density for a single ion not in its free state, but in a charged Watson sphere. The charge on this sphere is assumed to be equal to the charge of an ion but opposite in sign, and the radius of the sphere is calculated by equating the potential inside the sphere to the Madelung potential on the ion. This procedure leads first of all to some compression of negative ions in a crystal and expansion of positive ions, which

describes much better (compared with the superposition of the densities of free ions) the experimentally found densities in ionic crystals. A change in the interionic distances alters also the Madelung potential and, consequently, the radius of the Watson sphere and as a consequence also the effective radius of an ion. Ions thus seem to ‘breathe’ in a crystal so that the model has been called the potential-induced breathing (PIB) [18]. The total energy of a crystal considered in this approximation is

$$E = E_M + \sum_R S(U_R) + \sum_{R,R'} V(U_R, U_{R'}) \quad (3.13)$$

where  $S_R$  is the energy of a single ion which depends on the Madelung potential  $U_R$  and  $V_{RR'}(U_R, U_{R'})$  is the short-range pair interaction, which also depends on the Madelung potentials  $U_R$  and  $U_{R'}$  of the ions at  $\mathbf{R}$  and  $\mathbf{R}'$ . Calculations of the static and dynamic properties of a whole range of ionic crystals carried out within the framework of this approximation has made it possible to improve considerably the agreement with the available experimental data, compared with that attainable on the basis of the original Gordon–Kim model.

In fact, the PIB approximation is a method for including the monopole polarisability of ions. An equally important role in ionic crystals is played also by the dipole polarisability, describing in the appropriate approximation the contribution to the total polarisability energy of the electron subsystem. A generalisation of the Gordon–Kim model proposed recently [19] takes into account quite simply also the dipole polarisation of ions in lattice dynamics calculations. This is done by calculating first the behaviour of a single ion in an external electric field  $\mathbf{E}$ . It is well known that an atom or an ion subjected to an external field acquires a dipole moment

$$\mathbf{P} = \alpha \mathbf{E} \quad (3.14)$$

where  $\alpha$  is the dipole polarisability of the atom or ion involved. The dipole moment  $\mathbf{P}$  can be described quite simply in terms of the change in the electron density  $\delta\rho(\mathbf{r})$  due to the action of the field:

$$\mathbf{P} = \int \mathbf{r} \delta\rho(\mathbf{r}) d\mathbf{r} \quad (3.15)$$

The function  $\delta\rho(\mathbf{r})$  can be calculated by any program designed to give the parameters of free atoms. Details of such calculations can be found in Mahan’s paper [20]. The next step, in full agreement with the Gordon–Kim approach, is a calculation of the pair interaction of two ions with given dipole moments  $\mathbf{P}_R$  and  $\mathbf{P}_{R'}$ . This is done with the aid of formula (3.11) for the pair energy with the Thomas–Fermi–Dirac functional. At large distances this interaction reduces to the standard interaction between point dipoles. However, at short distances, when ions overlap, this interaction differs considerably from that of point dipoles, which can be deduced from formula (3.11) by numerical methods. Calculations are also carried out relating to the interaction between an ion with a given dipole moment  $\mathbf{P}_R$  and the electric field of a spherically symmetric ion. At large distances this interaction is again identical with that deduced for point objects. However, at short distances it can be found by numerical methods applying formula (3.11). The final expression for the energy of a crystal regarded as the function of the density

and of the dipole moment in this approximation can be written in the form

$$\begin{aligned} E = E_M + \sum_R S(U_R) + \sum_{R,R'} V(U_R, U_{R'}) + \sum_R \frac{P_R^2}{2\alpha_R} \\ + \sum_{R,R'} \mathbf{P}_R \Phi_{RR'} \mathbf{P}_{R'} + \sum_{R,R'} \mathbf{P}_R \gamma_{RR'} \mathbf{P}_{R'} \\ + \sum_{R,R'} \mathbf{P}_R M_{RR'} - \sum_R \mathbf{P}_R E_R \end{aligned} \quad (3.16)$$

The first three terms in the above expression represent the PIB model. The other five terms, which depend on the dipole moments  $\mathbf{P}_R$ , determine the polarisation contribution to the crystal energy. The fourth term describes the energy needed for the creation of a dipole moment  $\mathbf{P}_R$  of an ion with a polarisability  $\alpha_R$ . The fifth term is the energy of the interaction between point dipoles described by the matrix  $\Phi_{RR'}$ , defined as

$$\Phi_{RR'} = R^{-3}(1 - \hat{R}\hat{R}') \quad (3.17)$$

where  $\hat{R} = \mathbf{R}/R$ . The sixth term represents the short-range interaction of extended dipoles. The matrix  $\gamma_{RR'}$  is determined by the difference between the real interaction of the point dipoles described by expression (3.11) and the interaction of dipole moments. The last two terms describe the energy of the interaction of dipoles with the electric field of point ions (eighth term) and also the short-range interaction between an extended dipole and a spherically symmetric ion (seventh term). The matrix  $M_{RR'}$ , usually called the deformability matrix by analogy with the terminology of a phenomenological theory of a deformable ion put forward by Hardy [21], vanishes for an ideal cubic lattice. It differs from zero for a deformed crystal and it is then proportional to the amplitude  $U_R$  of the displacement of an ion from its equilibrium position. Calculations of the electron polarisability and of the phonon frequencies, carried out for a large number of binary ion crystals with cubic symmetry on the basis of expression (3.18) for the total energy [19], are in surprisingly good agreement with the experimental data.

As pointed out above, the method for calculation of lattice dynamics just described and based on the use of the simplest density functionals of the Thomas–Fermi–Dirac type can be used to tackle a fairly limited class of systems. These are mainly the systems composed of ‘saturated’ elements and on top of that these elements should not change greatly on transition from the free to the crystalline state. However, in calculations of such extremely important (from the theoretical and practical points of view) materials as metals and covalent semiconductors it is necessary to employ more modern and (unfortunately) more time-consuming methods. The main error in the calculation of the parameters of crystals by the Thomas–Fermi–Dirac functional method comes from the local approximation for the kinetic energy. This difficulty is avoided by Kohn and Sham [11] by adding to and then subtracting from the functional (3.12), the kinetic energy  $T_0$  of an interacting electron gas which experiences an inhomogeneous external field that depends on the electron density:

$$\begin{aligned} E\{\rho(\mathbf{r})\} = T_0\{\rho(\mathbf{r})\} + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}\{\rho(\mathbf{r})\} \end{aligned} \quad (3.18)$$

Here,  $E_{xc}\{\rho(\mathbf{r})\}$  is the total exchange–correlation energy, which includes the contributions of both the potential and kinetic energies:

$$E_{xc}\{\rho(\mathbf{r})\} = \tilde{E}_{xc}\{\rho(\mathbf{r})\} + T\{\rho(\mathbf{r})\} - T_0\{\rho(\mathbf{r})\}. \quad (3.19)$$

The electron density  $\rho(\mathbf{r})$  is then

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} f_{\mathbf{k}\lambda} \psi_{\mathbf{k}\lambda}^*(\mathbf{r}) \psi_{\mathbf{k}\lambda}(\mathbf{r}), \quad (3.20)$$

where  $f_{\mathbf{k}\lambda}$  are the occupation numbers of single-particle states (here  $\mathbf{k}$  is the wave vector which lies in the irreducible part of the Brillouin zone and  $\lambda$  numbers the energy bands), which are equal to unity for states with energies  $\varepsilon_{\mathbf{k}\lambda}$  lower than or equal to the chemical potential (Fermi energy)  $\varepsilon_F$ , and which vanish for all other states with energies higher than  $\varepsilon_F$ . Minimalisation of expression (3.1) gives the following equation for the wave function  $\psi_{\mathbf{k}\lambda}(\mathbf{r}) = |\mathbf{k}\lambda\rangle$ :

$$\left[ -\nabla^2 + V_{\text{ext}}(\mathbf{r}) + e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}) - \varepsilon_{\mathbf{k}\lambda} \right] |\mathbf{k}\lambda\rangle = 0. \quad (3.21)$$

Here,  $V_{xc}(\mathbf{r})$  is the exchange–correlation potential:

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}\{\rho(\mathbf{r})\}}{\delta \rho(\mathbf{r})}. \quad (3.22)$$

Rewriting Eqn (3.21) in the form

$$\left[ -\nabla^2 + V_{\text{eff}}(\mathbf{r}) - \varepsilon_{\mathbf{k}\lambda} \right] |\mathbf{k}\lambda\rangle = 0, \quad (3.23)$$

we obtain the usual single-particle Schrodinger equation with the self-consistent effective potential

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_C(\mathbf{r}) + V_{xc}(\mathbf{r}). \quad (3.24)$$

The total energy of the system of interacting electrons can be expressed as follows in terms of the solutions of Eqn (3.23):

$$E\{\rho(\mathbf{r})\} = \sum_{\mathbf{k}, \lambda} f_{\mathbf{k}\lambda} \varepsilon_{\mathbf{k}\lambda} - \int \rho(\mathbf{r}) V_{\text{eff}}(\mathbf{r}) d\mathbf{r} + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}\{\rho(\mathbf{r})\}. \quad (3.25)$$

The first and second terms in this equation represent the kinetic energy of noninteracting electrons. We shall not discuss in detail the Kohn–Sham method or the fundamental, for this method, problem of deriving the exchange–correlation potential  $V_{xc}(\mathbf{r})$ . The most widely used approximation for this quantity is at present the local approximation, i.e. exactly the same approximation as in the Thomas–Fermi–Dirac method. A detailed discussion of the feasibility of using the local approximation and the methods of going beyond this approximation can be found in a monograph on the subject [12] and in a recent review of Jones and Gunnarsson [22].

The Kohn–Sham method combined with the expression (3.25) for the total energy and with a suitably selected expression for the exchange–correlation functional  $E_{xc}\{\rho(\mathbf{r})\}$  makes it possible, in principle, to carry out a self-consistent calculation of the properties of the ground state of a crystal, including its energy and electron density. A detailed discussion of such self-consistent methods will be given in the following section of this review. Even at the stage of calculation of the total energies it is possible to find the phonon frequencies of some of the vibrational modes of

a crystal by the ‘frozen phonon’ method [23]. This method involves direct calculation of the total energy of a crystal with an ideal lattice and also in the presence of a distortion corresponding to one of the normal vibrational modes. The phonon frequency can then be found quite simply from the difference between these two energies:

$$M \omega_q^2 = \frac{\Delta E(U_q)}{|U_q|^2},$$

where  $U_q$  is the amplitude of a normal mode and  $M$  is the reduced mass. The frozen phonon method is, in principle, suitable for the calculation of the phonon modes with a wave vector  $\mathbf{q}$  commensurate with any reciprocal lattice vector, because only then the distorted lattice remains periodic and the single-particle Kohn–Sham equations can be solved. A new unit cell of the distorted structure should not be too large so as to avoid major technical problems in solving the equations. Some examples of such calculations will be given in later sections of this review.

In calculation of the phonon spectra at an arbitrary point of the Brillouin zone it is necessary to apply, as mentioned earlier in the discussion of the many-body approach, the linear response method. The calculations are quite simple, at least in the formal sense.

Let us assume that displacements of atoms from an equilibrium configuration described by the positions  $\{\mathbf{R} + \mathbf{t}\}$  are

$$\delta \mathbf{t}_R = \delta \mathbf{A} \exp(i\mathbf{q} \cdot \mathbf{t}) + \delta \mathbf{A}^* \exp(-i\mathbf{q} \cdot \mathbf{t}),$$

where  $\delta \mathbf{A}$  is a complex polarisation vector and  $\mathbf{q}$  is the phonon wave vector within the first Brillouin zone. The presence of such a displacement field in a crystal alters the external Coulomb potential of the nuclei, which acts on electrons:

$$\tilde{V}_{\text{ext}}(\mathbf{r}) = \sum_{R, \mathbf{t}} \frac{-Z_R e^2}{|\mathbf{r} - \mathbf{R} - \mathbf{t} - \delta \mathbf{t}_R|}, \quad (3.26)$$

where  $Z_R$  are the nuclear charges. We shall expand the external field in terms of the displacements and retain only the terms of the first order of smallness. Then, the change in the external potential can be represented by a superposition of two fields:

$$\delta V_{\text{ext}}(\mathbf{r}) = \sum_R \delta \mathbf{A}_R \sum_{\mathbf{t}} \exp(i\mathbf{q} \cdot \mathbf{t}) \nabla \frac{Z_R e^2}{|\mathbf{r} - \mathbf{R} - \mathbf{t}|} + \sum_R \delta \mathbf{A}_R^* \sum_{\mathbf{t}} \exp(-i\mathbf{q} \cdot \mathbf{t}) \nabla \frac{Z_R e^2}{|\mathbf{r} - \mathbf{R} - \mathbf{t}|}, \quad (3.27)$$

which have the wave vectors  $+\mathbf{q}$  and  $-\mathbf{q}$ , i.e.

$$\delta V_{\text{ext}}(\mathbf{r}) = \sum_R \delta \mathbf{A}_R \delta_R^+ V_{\text{ext}}(\mathbf{r}) + \sum_R \delta \mathbf{A}_R^* \delta_R^- V_{\text{ext}}(\mathbf{r}). \quad (3.28)$$

We must point out straight away a very important property of an external perturbation. If the radius vector  $\mathbf{r}$  acquires an increment equal to the primitive translation vector, then both components of expression (3.27) transform as the Bloch-type waves:

$$\delta^\pm V_{\text{ext}}(\mathbf{r} + \mathbf{t}) = \exp(i\mathbf{q} \cdot \mathbf{t}) \delta^\pm V_{\text{ext}}(\mathbf{r}).$$

(For simplicity, the index  $R$  of the variation  $\delta$  will be omitted.) This means that if a perturbation in one unit cell is known, it can be found quite simply for the whole crystal, which will be shown to be a very important

circumstance. It should also be mentioned that both components have the Hermitian property, i.e.

$$[\delta^\pm V_{\text{ext}}(\mathbf{r})]^* = \delta^\mp V_{\text{ext}}(\mathbf{r}).$$

Thus the presence of a phonon with a wave vector  $\mathbf{q}$  is associated with the given external perturbation of the type described by formula (3.28) and our next problem is to find what happens to the charge density distribution. According to the Kohn–Sham theory, the distribution of the density  $\rho$  is a sum of the occupied states of absolute squares of one-electron wave functions described by expression (3.20). In the linear response theory [24] the change in the distribution of the electron density  $\delta\rho$  can, in the first order, be written in exactly the same form as  $\delta V_{\text{ext}}$ , i.e.

$$\delta\rho = \sum_R \delta A_R \delta^+ \rho + \sum_R \delta A_R^* \delta^- \rho,$$

and can be expressed in terms of  $\psi_{k\lambda}$  and also in terms of the first-order corrections  $\delta^+ \psi_{k\lambda}$  and  $\delta^- \psi_{k\lambda}$ :

$$\delta^\pm \rho = \sum_{k,\lambda} f_{k\lambda} (\delta^\pm \psi_{k\lambda}^* \psi_{k\lambda} + \psi_{k\lambda}^* \delta^\pm \psi_{k\lambda}), \quad (3.29)$$

where  $\delta^\pm \psi_{k\lambda}^* = (\delta^\mp \psi_{k\lambda})^*$ . The first-order correction  $|\delta^\pm k\lambda\rangle = \delta^\pm \psi_{k\lambda}$  is a Bloch function with the wave vector  $\mathbf{k} \pm \mathbf{q}$ , which can be seen quite easily on the basis of an expression derived by applying standard perturbation theory:

$$|\delta^\pm k\lambda\rangle = \sum_{\lambda'} |k \pm q\lambda'\rangle \frac{\langle k \pm q\lambda' | \delta^\pm V_{\text{eff}} | k\lambda \rangle}{\epsilon_{k\lambda} - \epsilon_{k \pm q\lambda'}}. \quad (3.30)$$

Since the electron density, induced by the displacements of nuclei, screens the external perturbation described by expression (3.27), it follows that the matrix element of this expression should include a screened perturbation  $\delta^\pm V_{\text{eff}}$  expressed in terms of  $\delta^\pm \rho$  is as follows:

$$\begin{aligned} \delta^\pm V_{\text{eff}} &= \delta^\pm V_{\text{ext}} + \delta^\pm V_C + \delta^\pm V_{\text{xc}} \\ &= \sum_{\mathbf{t}} \exp(\pm i\mathbf{q} \cdot \mathbf{t}) \nabla \frac{Z_R e^2}{|\mathbf{r} - \mathbf{R} - \mathbf{t}|} \\ &\quad + \int \frac{\delta^\pm \rho \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} + \frac{dV_{\text{xc}}}{d\rho} \delta^\pm \rho, \end{aligned} \quad (3.31)$$

where the exchange and correlation effects are considered in the local density approximation. We shall now substitute the expression for the first-order corrections (3.30) into formula (3.29). The change in the density is then expressed in terms of what is known as the static polarisability function of noninteracting electrons

$$\begin{aligned} \pi_{\pm q}(\mathbf{r}, \mathbf{r}') &= \sum_{k,\lambda,\lambda'} \frac{f_{k\lambda} - f_{k \pm q\lambda'}}{\epsilon_{k\lambda} - \epsilon_{k \pm q\lambda'}} \\ &\quad \times \psi_{k \pm q\lambda'}(\mathbf{r}) \psi_{k\lambda}^*(\mathbf{r}) \psi_{k \pm q\lambda'}^*(\mathbf{r}') \psi_{k\lambda}(\mathbf{r}') \end{aligned} \quad (3.32)$$

as an integral of this function and of the screened perturbation:

$$\delta^\pm \rho(\mathbf{r}) = \int \pi_{\pm q}(\mathbf{r}, \mathbf{r}') \delta^\pm V_{\text{eff}}(\mathbf{r}') \, d\mathbf{r}', \quad (3.33)$$

or in symbolic operator notation:  $\delta\rho = \hat{\pi} \delta V_{\text{eff}}$ . Calculation of a screened perturbation in a self-consistent manner, i.e. by calculation of the response of electrons to an external

field  $\delta^\pm V_{\text{ext}}$  in accordance with formulas (3.29) and (3.30), followed by screening the response in accordance with expression (3.31) and repetition of the whole cycle can be avoided if the reciprocal of the static dielectric function of a crystal is calculated. We shall rewrite expression (3.31) in the symbolic form:  $\delta V_{\text{eff}} = \delta V_{\text{ext}} + (\hat{v}_C + \hat{v}_{\text{xc}}) \delta\rho$ , where

$$v_C = \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad v_{\text{xc}} = \frac{dV_{\text{xc}}}{d\rho} \delta(\mathbf{r} - \mathbf{r}')$$

are integral operators. Then,  $\delta V_{\text{eff}} = \hat{\epsilon}^{-1} \delta V_{\text{ext}}$  and  $\delta\rho = \hat{\chi} \delta V_{\text{ext}}$ , where  $\epsilon^{-1}$  is the reciprocal dielectric function defined as  $\epsilon^{-1} = (1 - v_C \pi - v_{\text{xc}} \pi)^{-1}$  and  $\chi$  is the generalised susceptibility function which can be expressed in terms of  $\epsilon^{-1}$  as follows:  $\chi = \hat{\epsilon}^{-1} \pi$ . This approach requires inversion of the dielectric function matrix  $\epsilon = 1 - v_C \pi - v_{\text{xc}} \pi$  in some representations (for example, the representation of plane waves or of the angular momentum). The only limitation that may have to be imposed concerns the dimensions of this matrix. Historically, the success of the pseudopotential theory in the case of simple metals has led to the use of the plane wave representation. For example, in the limit of free electrons all the linear response functions depend only on the difference  $\mathbf{r} - \mathbf{r}'$ , so that application of the Fourier transformation yields directly the formulas for simple metals discussed in the preceding section. However, even in the case of covalent semiconductors with a fairly small pseudopotential, the dimensions of the matrices which have to be calculated in the plane wave representation are so large that only a few attempts have been made to complete these calculations. The problem becomes even more complex in the case of the transition metals.

It is thus clear that calculation of the static susceptibility function of a crystal or directly of the induced electron density is the key to the problem of lattice dynamics. In spite of full mathematical rigour of the derivation of Eqn (3.8), this equation is quite unsuitable for any practical calculations of the dynamic matrix of a transition metal. The main reason for this is the need for a large basis set in the representation of one-electron wave functions of the valence electrons in the calculation of the polarisability (3.32). This has held up this part of solid-state physics for over 20 years. It is well known that in the valence range the energy band structure can be reproduced with a small basis of test functions. For example, in the method of linear muffin-tin (MT) orbitals discussed in the next section the one-electron spectrum can be calculated with a precision of the order of  $10^{-3}$  Ry employing just 9 orbitals per atom. On the other hand, the expression for the polarisability (3.32) contains a sum over all the filled and empty states, which requires knowledge of highly excited Bloch functions and, as a minimum, it is necessary to calculate them in advance. The latter can be found formally only by diagonalisation of very large Hamiltonian matrices, which limits the practical value of the method. Physically, such slow convergence of the polarisability in the case of a transition metal is related to a very simple circumstance: both the one-electron wave functions  $|k\lambda\rangle$  and the first-order corrections  $|\delta^\pm k\lambda\rangle$  to these functions oscillate in the region of an ion core. In the case of substances with almost-free electrons these oscillations can be excluded by replacing the real crystal potential with a weak pseudopotential. Unfortunately, as the energy bands become narrower, expansion of pseudowave functions in terms of plane waves converges increasingly slowly and the

pseudopotential concept loses its advantages. A calculation of the dynamic matrix in accordance with formula (3.8) using expression (3.32) for the polarisability proves to be very sensitive to the errors in the wave functions because of incompleteness of the basis. We shall now illustrate this by a simple example of the acoustic sum rule. We shall assume that all the nuclei of the lattice atoms are displaced by an infinitesimally small distance  $\mathbf{d}$ . We can then expect all the electrons to follow the motions of their nuclei and this results simply in a rigid shift of the charge density:  $\delta\rho = \mathbf{d} \times \nabla\rho$ . Let us now see what happens to the wave functions perturbed by a potential of the  $\mathbf{d} \times \nabla V$  type. We then have

$$\begin{aligned} |\delta k\lambda\rangle &= \mathbf{d} \sum_{\lambda'} |k\lambda'\rangle \frac{\langle k\lambda' | \nabla V | k\lambda \rangle}{\varepsilon_{k\lambda} - \varepsilon_{k\lambda'}} \\ &= \mathbf{d} \sum_{\lambda'} |k\lambda'\rangle \langle k\lambda' | \nabla | k\lambda \rangle = \mathbf{d} \times \nabla | k\lambda \rangle. \end{aligned} \quad (3.34)$$

We can see that the last equality can be derived only if use is made of the mathematical property of completeness of the wave functions, which is acquired over the whole energy scale. In the opposite case a large error is made in determination of the long-wave limit of the dynamic matrix and, consequently, the error has an influence for any value of  $\mathbf{q}$ .

In spite of the unsatisfactory quantitative description of the phonon spectra by the response function method, based on standard perturbation theory, the structure of the anomalies of the dispersion curves of transition metals has been explained qualitatively by numerous phenomenological models. The simplest of these models ignores the matrix element of the electron–electron interaction. The quantities most readily amenable to standard band calculations are the one-electron energies  $\varepsilon_{k\lambda}$  and, therefore, it is very interesting to follow the behaviour of the pure band factor  $(f_{k\lambda} - f_{k+q\lambda'}) / (\varepsilon_{k\lambda} - \varepsilon_{k+q\lambda'})$  in expression (3.32), considered as a function of the wave vector  $\mathbf{q}$ , and to check what effect it has on the structure of the phonon spectrum. As demonstrated by Keeton and Loucks [25], and also by Liu et al. [26], if the Fermi surface has pronounced singularities of the ‘nesting’ type (i.e. singularities resulting from the addition of one part of the surface to another by translation through a certain wave vector  $\mathbf{q}_0$ ), one can expect a peak in the absolute values of the polarisability and susceptibility functions. However, there are serious difficulties associated with ignoring the  $\mathbf{q}$  dependence of the matrix elements of the electron–phonon interaction and those related to the fact that the peaks of this type are small in magnitude against a fairly smooth background, particularly when all the interband transitions are included. These circumstances should be taken into account in any attempts to analyse of the anomalies of the phonon spectra of the transition metals. A review of other model theories can be found in Ref. [7].

#### 4. Linear MT orbital method for band structure calculations

It follows from the foregoing discussion, that in the theory of calculations of the force and lattice dynamics the central place is occupied by self-consistent calculations of the electron density distribution for an arbitrary configuration of atoms in a unit cell of a crystal. It is therefore of interest

to consider the state-of-the-art of the problem of self-consistent solution of single-particle equations by the density functional method and the application of the method of frozen phonons to phonon frequency calculations. In spite of the obvious shortcomings of the frozen phonon method, associated with its limited applicability to just the high-symmetry wave vectors, it is nevertheless highly universal and can be applied both to systems with wide bands (simple metals and semiconductors) and to transition metals. This advantage of the method is primarily due to the development and application of what are known as the all-electron methods in the band theory of solids.

In calculation of the total energy of a crystal as a function of the displacements of nuclei an important aspect is the correct inclusion of the effects of the nonsphericity of the distribution of the electron density and potential at interstices of the unit cell of a crystal, since the vibrations of atoms directed towards one another distort considerably the electron density in the interstitial region. The standard technique for the solution of the Schrodinger equation with an arbitrary potential involves the use of the variational principle. A functional is derived and its minimisation by variation of the one-electron wave functions leads to the Schrodinger equation. The one-electron wave function is represented by an expansion in terms of a certain basis  $|\chi_\alpha^k\rangle$ :

$$|k\lambda\rangle = \sum_{\alpha} |\chi_\alpha^k\rangle A_\alpha^{k\lambda}, \quad (4.1)$$

where  $A_\alpha^{k\lambda}$  are the coefficients of the expansion which, for a fixed basis  $|\chi_\alpha^k\rangle$ , provide the variational freedom of the functional and are found by solving the matrix eigenvalue problem:

$$\sum_{\alpha} \langle \chi_\beta^k | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | \chi_\alpha^k \rangle A_\alpha^{k\lambda} = 0. \quad (4.2)$$

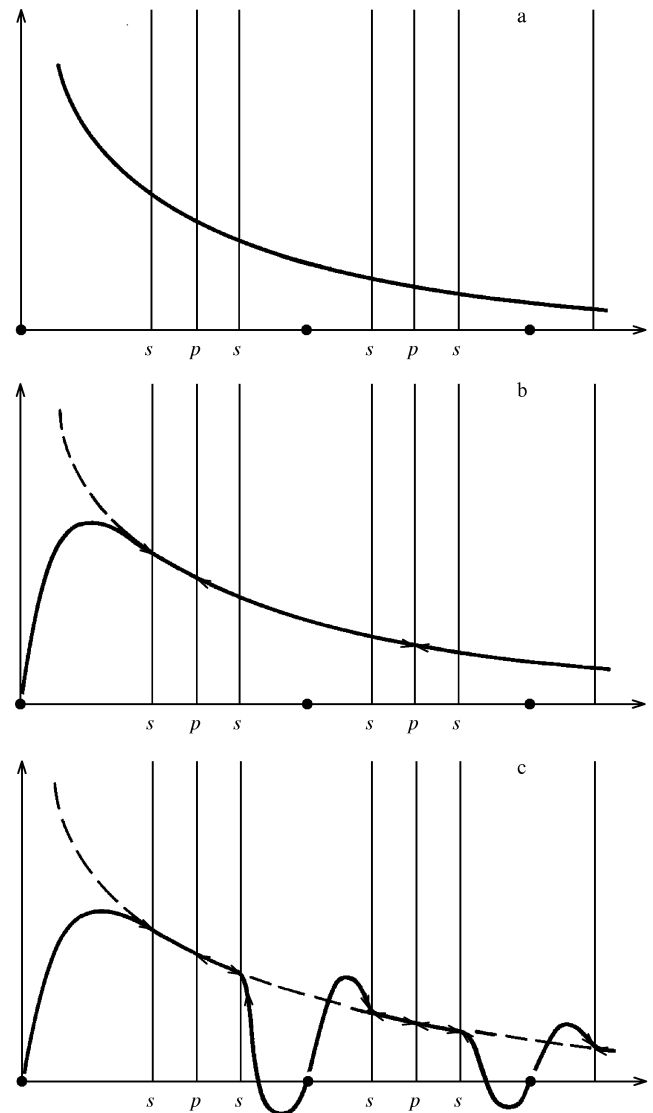
The main problem is related to the construction of suitable test functions which represent a Bloch state of a valence electron. In the pseudopotential method the basis functions are plane waves and this factor simplifies particularly the finding of the algorithm for the calculation of the band structure. However, as mentioned above, as the width of the valence band decreases, the expansion of pseudowave functions in terms of plane waves converges more and more slowly, and the pseudopotential loses its advantages. In all-electron methods the space in a crystal is divided into nonoverlapping spheres centred on each atom, known as muffin-tin (MT) spheres, and the remaining interstitial region. Within the MT spheres the basis functions are linear combinations of numerical solutions of the radial Schrodinger equation containing the spherical part of the potential. These numerical solutions are multiplied by spherical harmonics. Such a representation ensures rapid convergence of the basis both for delocalised and localised states. In the interstitial region, where the potential is fairly smooth, the basis functions are selected from the solution of the Helmholtz equation:  $(-\nabla^2 - \kappa^2)f(\mathbf{r}) = 0$  (here,  $\kappa^2$  is the average kinetic energy of an electron in the interstitial region). In the well-known linear augmented plane wave (LAPW) method [27, 28], the solutions are plane waves which are matched smoothly to the solutions of the radial Schrodinger equation at the boundaries of the MT spheres. In spite of the fact that this complete basis set may, in



principle, reproduce the correct behaviour of the Bloch states in the interstitial region, the slow convergence of the plane waves in the case of structures which are not close-packed or loose or in the case of supercells leads to serious restrictions on the convergence of this method.

On the other hand, the representation of localised orbitals and, in particular, the representation of linear MT orbitals (LMTO) [29] is well known for its rapid divergence of the basis. In the interstitial region the linear MT orbitals represent linear combinations of the Bessel and Hankel functions at some fixed energy  $\varepsilon = \kappa^2$ . In particular, in the standard LMTO method [27], in which the atomic sphere approximation (ASA) and the condition  $\kappa^2 = 0$  are used, all that is needed is 9 orbitals per atom in order to reproduce the energy bands with an error not exceeding  $10^{-3}$  Ry. Several approaches have been developed recently for taking account of the nonsphericity of the potential (these are known as the non-MT corrections) within the framework of this method. Weyrich [30] proposed the use of the Fourier transformation for the LMTO in the interstitial region. Such formulation does not increase the size of the Hamiltonian matrices or the overlap. However, a calculation of the contribution of the interstitial region to the Hamiltonian and of the distribution of the charge density makes this generalisation of the method very time-consuming. Blochl [31] made an attempt to use the tight-binding approximation in the case of the MT orbitals and to find directly the density at certain points in space. Unfortunately, this approach has been tested only on a small number of materials [31] and further application of the method remains in doubt. It has recently been proposed [32] that the total electron density in all space can be represented by the values and first derivatives of the MT orbitals at the boundaries of the MT spheres, where the product of two MT orbitals is made to fit a linear combination of two Hankel functions. The density distribution can thus be found approximately by interpolation.

A new approach to the solution of this problem is proposed in Ref. [33] where use is made of the representation of the spherical harmonics near the MT spheres and at the interstices. The space in a crystal is divided into polyhedral Wigner–Seitz cells and the MT orbitals are represented by one-centre expansions in terms of the spherical harmonics inside the spheres surrounding the polyhedra. Such one-centre expansions describe correctly the density only in the regions within the atomic cells. Consequently, the problems of solution of the Poisson equation and calculation of the matrix elements of the potential of the region between the spheres are reduced to finding an effective method for integration of the functions in the region between a sphere and the boundary of a polyhedron. This can be done either by applying the technique of expansion in terms of the spherical harmonics of the  $\theta$  function [29] or, as shown in Ref. [33], by reducing the volume to the surface integrals with the aid of the Gauss theorem. The advantage of the proposed method is a unified representation of all the quantities in terms of the spherical harmonics for both regions of space in a crystal, which leads to a calculation method the rate of which is only several times less than the rate of the standard LMTO–ASA method. This approach also retains the simplicity and physical clarity of the LMTO–ASA method and can be readily incorporated in the existing computer programs.



**Figure 1.** Plotting of an MT orbital: (a) initial shell function; (b) replacement of the diverging part of a linear combination of the numerical radial functions and of the regular Bessel functions in an MT sphere at the origin of the coordinate system, and also replacement in all other polyhedra (excluding that at the origin of coordinates) of tails with one-centre expansions in terms of the Bessel functions (as illustrated by the arrows); (c) replacement of the Bessel functions in all the MT spheres with the numerical radial functions. The vertical lines identify the boundaries of the MT spheres and of the polyhedra.

We shall now discuss in greater detail the task of construction of the linear MT orbitals. The space in a crystal is divided in a certain way into polyhedra Wigner–Seitz cells surrounding each atom. Inscribed MT spheres as well as the spheres surrounding the polyhedron are introduced for these atomic cells. Both types of spheres are centred at the lattice sites. We shall consider what is known as the shell function, which in the LMTO method is the singular Hankel function  $K_L(\mathbf{r}_R - \mathbf{t})$  centred at a site  $\mathbf{R} + \mathbf{t}$ , as shown in Fig. 1a, and having the energy  $\varepsilon = \kappa^2$ . (Here and later it is assumed that all the radial functions with the vectors in braces are multiplied by spherical harmonics, where  $L$  denotes a combined index for  $lm$ ; the subscript  $R$  over  $\mathbf{r}$  denotes the difference  $\mathbf{r} - \mathbf{R}$ , where  $\{\mathbf{R}\}$  are the positions of atoms in a unit cell, and  $\{\mathbf{t}\}$  are

primitive translations.) Inside the sphere centred at  $\mathbf{R} + \mathbf{t}$  the diverging part of the shell function is replaced by a linear combination of numerical radial functions subject to the condition of smooth matching at the boundary of the sphere. The radial functions are here the solutions  $\phi_{RL}(\mathbf{r}_R - \mathbf{t}, \varepsilon_{vRI})$  of the Schrodinger equation which contains the spherical part of the potential and which applies at certain energies  $\varepsilon_{vRI}$  in the region of interest to us, as well as the energy derivatives of these functions  $\phi'_{RL}(\mathbf{r}_R - \mathbf{t}, \varepsilon_{vRI})$ . Inside every other atomic cell centred at  $\mathbf{R}' + \mathbf{t}'$  the shell function tail is replaced by its own one-centre expansion in terms of the Bessel functions:

$$K_L(\mathbf{r}_R - \mathbf{t}) = \sum_{L'} J_{L'}(\mathbf{r}_{R'} - \mathbf{t}') S_{R'L'RL}(\mathbf{t}' - \mathbf{t}), \quad (4.3)$$

where  $J_L(\mathbf{r}_R - \mathbf{t})$  is a Bessel function and  $S_{R'L'RL}(\mathbf{t})$  are structural constants in the coordinate space. (This is illustrated in Fig. 1b.) Since the Hankel and Bessel functions are described by the expressions

$$K_l(r) = -\frac{i(\kappa w)^{l+1}}{(2l-1)!!} h_l(\kappa r), \quad (4.4)$$

$$J_l(r) = \frac{1}{2} \frac{(2l-1)!!}{(\kappa w)^l} j_l(\kappa r), \quad (4.5)$$

where  $h_l = j_l - n_l$  are the usual spherical Hankel functions, and  $j_l, n_l$  are the spherical Bessel and Neumann functions, the expression for the structure constants is

$$S_{R'L'RL}(\mathbf{t}) = \sum_{L''} \frac{8\pi(2l''-1)!!}{(2l'-1)!!(2l-1)!!} C_{LL''}^{L''} (\kappa w)^{l+l''-l''} \times K_l(|\mathbf{t} - \mathbf{R}' + \mathbf{R}|) (-i)^{l''} Y_{L''}^*(\mathbf{t} - \mathbf{R}' + \mathbf{R}), \quad (4.6)$$

where  $w$  is the average radius of a Wigner-Seitz cell and  $C_{LL''}^{L''}$  are the Gaunt coefficients. Finally, the linear MT orbitals are found by replacing the Bessel functions in all the MT spheres with linear combinations of  $\phi_{RL}$  and  $\phi'_{RL}$  (Fig. 1c), which are selected so that the LMTO is everywhere continuous and differentiable.

The last step is the summation over a lattice of MT orbitals, centred at various sites, with a phase shift  $\exp(i\mathbf{k} \cdot \mathbf{t})$  so that the basis functions satisfy the Bloch theorem. This can be done quite simply: it involves just summation of the structure constants given by expression (4.6) since the orbitals constructed in this way are already represented everywhere by one-centre expansions. The basis functions are then

$$\begin{aligned} \chi_{RL}^k(\mathbf{r}_{R'}) &= \Phi_{RL}^k(\mathbf{r}_R) \delta_{RR'} + \sum_{L'} \Phi'_{R'L'}(\mathbf{r}_{R'}) S_{R'L'RL}^k, \quad r_{R'} < s_R, \\ \chi_{RL}^k(\mathbf{r}_{R'}) &= K_{RL}(\mathbf{r}_R) \delta_{RR'} + \sum_{L'} J_{R'L'}(\mathbf{r}_{R'}) S_{R'L'RL}^k, \quad r_{R'} \in \Omega_{R'}^{\text{int}}, \end{aligned} \quad (4.7)$$

where  $s_R$  is the radius of an MT sphere,  $\Omega_{R'}^{\text{int}}$  is the interstitial region of a given atom, and  $S_{R'L'RL}^k$  is the Fourier representation of the structure constants given by expression (4.6):

$$S_{R'L'RL}^k = \sum_{\mathbf{t}} \exp(i\mathbf{k} \cdot \mathbf{t}) S_{R'L'RL}(\mathbf{t}). \quad (4.8)$$

The radial functions  $\Phi_{RL}^k(\mathbf{r}_R)$  and  $\Phi'_{RL}(\mathbf{r}_R)$  are now such linear combinations of the solutions  $\phi_{RL}$  and  $\phi'_{RL}$  which are

matched smoothly to the Hankel and Bessel functions at the boundary of a sphere.

We shall now make some comments about the expansions described by expressions (4.7). Inside nonoverlapping MT spheres these expansions converge rapidly and are readily calculated. On the other hand, in the interstitial region  $\Omega_R^{\text{int}}$  of a given atom such expansions converge slowly and are generally converging only for radii  $r_R$  smaller than the distance between the nearest sites. This means, in particular, that the space should be separated into polyhedra which are similar in shape to the compact Wigner-Seitz cells of close-packed structures in which the distances between  $r_R \in \Omega^{\text{int}}$  and the nearest neighbours amount approximately to  $\frac{1}{2}$ . In the case of loose structures the technique of empty spheres should be used [34], first in order to remove the regions of divergences of the one-centre expansions and, second, in order to reduce the number of terms in the sums over  $L$  in expressions (4.7). The frozen phonon calculations have shown that the summation up to  $l_{\text{max}} = 8$  ensures a convergence of the phonon frequencies to a value of the order of several percent. In particular, in the case of Al and Si with two empty spheres, such precision can be achieved for  $l_{\text{max}} = 6$ , whereas for Nb with the valence states that are strongly of  $d$  nature we must have  $l_{\text{max}}$  of at least 8.

Let us now consider the selection of fixed energy tails  $\varepsilon = \kappa^2$ . In his original paper, Andersen [27] developed the LMTO method making use of the  $\kappa^2 = 0$  approximation when, in particular, all the formulas become simple. This approximation is justified because in the case of close-packed structures the average kinetic energy of the valence electrons is approximately zero within one energy 'window' of the order of 1 Ry. The systems of interest to us are distorted lattices where the interstitial region should be treated more rigorously. Many approaches are known for the improvement of the basis set of the LMTO method [35, 36]. It is worth mentioning one of them [36], which has become popular [37] and in which the size of the basis is increased by use of one more value of  $\kappa^2$ . While the first energy  $\kappa^2$  is usually placed close to the average potential in the interstitial region (known as the MT zero), the second (and possibly the third) are taken to be large and negative (from  $-1$  to  $-2$  Ry). The advantage of this method is an improvement in the variational freedom of the basis by inclusion of orbitals of the type used in the method of linear combination of atomic orbitals (LCAO). On the other hand, a shortcoming of this method is the tripling of the size of the basis, which increases the computer time 27-fold.

It is proposed in Ref. [33] that one or possibly two energies  $\kappa^2$  in the filled part of the band be used. This may be justified directly by the energy-dependent multiple scattering theory. It can be applied to materials with the valence bands  $\lesssim 0.8$  Ry wide, where it is expected that contributions of the  $\partial K / \partial \kappa$  and  $\partial^2 K / \partial \kappa^2$  type to the expansion are small. In the case of materials with wide valence bands or when the MT spheres are very small, one should use a basis set consisting of two or more values of  $\kappa$ . The corresponding tail energies may be located near the bottom and top of the valence band and separated from them by  $\geq 1.0$  Ry. (Smaller separations may lead to almost-linear MT orbitals and a singular overlap matrix.)

In any case we have to select positive rather than negative values of  $\kappa$  and this may give rise to some

complications in calculations. The problem is this: the use of positive tail energies makes the structure constants singular when  $\kappa^2$  is equal to the energy of a free electron. The singularity occurs also at  $\mathbf{k} = \mathbf{0}$  in the standard LMTO method, but it is bypassed by displacement from the point  $\Gamma$  by a certain small vector. Here we can consider formally  $\kappa^2$  as a complex quantity and the addition of a small imaginary region (usually amounting to several hundredths of a rydberg) avoids this technical difficulty.

We shall now consider expressions for the Hamiltonian matrices and for the overlap. In the case of the basis LMTO set defined by expressions (4.7) the wave functions of the valence electrons  $|k\lambda\rangle$  are represented in the form of linear combinations  $|\chi_{RL}^k\rangle$  with the coefficients  $A_{RL}^{k\lambda}$  found from the variational principle. In the case of the one-electron Hamiltonian in the density functional theory, these coefficients are found from the following generalised eigenvalue problem:

$$\begin{aligned} & \sum_{L,R} [ \langle \chi_{R'L'}^k | -\nabla^2 + V^{\text{MT}}(\mathbf{r}) + V^{\text{NMT}}(\mathbf{r}) | \chi_{RL}^k \rangle \\ & - \varepsilon_{k\lambda} \langle \chi_{R'L'}^k | \chi_{RL}^k \rangle ] A_{RL}^{k\lambda} \\ & = \sum_{L,R} (H_{R'L'RL}^k - \varepsilon_{k\lambda} O_{R'L'RL}^k) A_{RL}^{k\lambda} = 0, \end{aligned} \quad (4.9)$$

where  $V^{\text{MT}}(\mathbf{r})$  denotes the spherical and  $V^{\text{NMT}}(\mathbf{r})$  the nonspherical part of the potential. We can easily see that the contributions of various regions of space are separable. The Hamiltonian and the overlap matrices are

$$H_{R'L'RL}^k = H_{R'L'RL}^{k,\text{MT}} + H_{R'L'RL}^{k,\text{NMT}} + \kappa^2 O_{R'L'RL}^{k,\text{int}} + V_{R'L'RL}^{k,\text{int}}, \quad (4.10)$$

$$O_{R'L'RL}^k = O_{R'L'RL}^{k,\text{MT}} + O_{R'L'RL}^{k,\text{int}}. \quad (4.11)$$

The first and second terms in expression (4.10) and the first term in expression (4.11) represent integrals over MT spheres, whereas the other terms in expression (4.11) represent integrals over the interstitial region. Here,  $H_{R'L'RL}^{k,\text{MT}}$  is a matrix element of the operator  $-\nabla^2 + V^{\text{MT}}(\mathbf{r})$  and  $H_{R'L'RL}^{k,\text{NMT}}$  is a matrix element of the nonspherical part of the potential. The third term in expression (4.10) is a matrix element of the kinetic energy in the interstitial region. Since the basis functions are the solutions of the Helmholtz equation, they can be described in a trivial manner in terms of the interstitial overlap integral [second term in expression (4.11)]. The last term in expression (4.10) is a matrix element of the interstitial potential.

All these contributions are represented by one-centre, two-centre, and three-centre integrals, and are simple generalisations of the formulas employed in the standard LMTO method. The radial matrix elements are calculated employing the properties of the radial Schrodinger equation and of its energy derivative.

The interstitial element of the overlap matrix is an integral of the two-centre type, which is expressed in terms of the product of two Hankel functions centred at the sites  $\mathbf{R}$  and  $\mathbf{R}'$ . Since they are eigenfunctions of the operator  $-\nabla^2$ , they can be expanded in terms of the Bessel functions and represented in the form of one-centre expansions of expressions (4.7), which formally are infinite series. On the other hand, such one-centre expansions can be used in estimating an integral by means of a technique proposed in

Ref. [33], but this complicates finding the overlap matrix. The best method is to use many-centre expansions and to calculate the interstitial overlap matrix with the help of the Green identity [38].

The all-potential method described above has the same advantages as the familiar Green function (or the Korringa–Kohn–Rostocker) method. The non-MT corrections from both regions of space have the same form and can be considered together. They can be separated into  $\mathbf{k}$ -dependent structure constants and a potential-dependent part. The latter part can be calculated only once ahead of a cycle carried out over points in the  $\mathbf{k}$  space. Consequently, the bulk of the computer time is used in calculation of the convolutions of the radial matrix elements with the  $S$  matrix. The one-centre expansions of expressions (4.7) converge inside the MT spheres with  $l_{\text{max}} \leq 4$  and in the interstitial region with  $L_{\text{max}} \leq 8$ . This means that the sums in the two-centre and three-centre integrals should include also higher angular momenta. The computer time is then approximately equal to the time needed to solve the eigenvalue problem and, therefore, in the case of the basis sets with one value of  $\kappa$  the total time needed for the calculation of the matrices  $H$  and  $O$  and their subsequent diagonalisation is only 2–2.5 times greater than the time needed in the standard calculations by the LMTO-ASA method.

The potential  $V_{\text{eff}}(\mathbf{r}) = V^{\text{MT}}(\mathbf{r}) + V^{\text{NMT}}(\mathbf{r})$  is understood to be expanded in terms of spherical harmonics both inside the MT sphere and in the interstitial region. Its exchange–correlation part is usually found by direct calculation at a given set of points in space, which is followed by expansion in terms of the spherical harmonics. The Coulomb contribution is calculated by solving the Poisson equation inside a sphere surrounding an atomic cell. The contribution of the external space is then included by multipole charges in each cell.

## 5. Calculations of the forces and total energy by the linear MT orbital method

As pointed out above, the density functional theory makes it possible to calculate directly the change in the total energy of a crystal caused by displacements of the atomic nuclei. This can be done by the LMTO band method just discussed, which takes account of the nonsphericity of the density and potential. However, although the total energy can usually be calculated to within a few percent, this method is unsatisfactory in predicting the frequencies of atomic vibrations because of the need to carry out several self-consistent calculations in order to determine the dependence of the total energy on the displacements of atoms. Another shortcoming of the frozen phonon method is subtraction of energies of the order of  $10^4$  Ry, which yields a phonon energy  $\sim 10^{-3}$  Ry. The best approach is an analytic differentiation of the expression for the total energy with respect to displacements, followed by calculation of the atomic forces, which should be much more accurate. In the development of the method for calculation of the dynamic matrix at an arbitrary point in the Brillouin zone, which is given below, we shall find this a very important circumstance, because analytic calculation of the first derivative of the force with respect to displacements is a simpler task than calculation of the second derivative of the total energy.

According to the Hellman–Feynman theorem, the force experienced by an atom is electrostatic and it acts on the nucleus of an atom. Consequently, this force can be determined precisely if the distribution of the total charge density in a crystal is known. Unfortunately, this distribution is derived from one-electron wave functions, which are only approximate solutions of the Schrodinger equation obtained by the variational principle. Consequently, the forces calculated on the basis of the Hellman–Feynman formula may be highly inaccurate. On the other hand, the atomic forces deduced by numerical differentiation of the total energy with respect to displacements give good results, so that the Hellman–Feynman force should be supplemented by a correction associated with the use of an incomplete basis set in the representation of wave functions. This is known as the Pulay correction [39], which vanishes in the theory of multiple scattering [40] and also in calculations carried out by the pseudopotential method for materials containing the *s* and *p* electrons. There have been several investigations of this problem within the framework of the all-electron LMTO and LAPW methods [31, 41]. Unfortunately, the validity of the proposed formulas is very doubtful in view of the absence of concrete calculations. On the other hand, the conclusion reached in Ref. [33] is supported by a series of specific calculations of the phonon frequencies. The results of these calculations have been compared with those made by the total energy method and the agreement is sufficiently good for the practical use of the proposed formula. (A similar derivation of the formula for the calculation of the forces within the framework of the LAPW method has recently been proposed independently in Ref. [42].)

Two approaches to the calculation of the forces acting on atoms in a crystal have been proposed. These approaches are based on the fundamental property of the total energy functional  $E\{\rho, V_{\text{ext}}\}$ , which depends on the overall distribution of the electron density  $\rho$  and on the external Coulomb potential  $V_{\text{ext}}$  of the nuclei: for a given value of  $V_{\text{ext}}$  this functional is extremal when  $\rho$  is varied and it reaches its minimum for a true distribution of the electron density. This gives rise to an important property: when the external potential is altered, the total derivative of  $E$  with respect to the displacement of an atom is equal to its partial derivative, i.e.  $dE/d\mathbf{R} = \partial E/\partial\mathbf{R}$ , whereas

$$\frac{\delta E}{\delta\rho} \frac{d\rho}{d\mathbf{R}} = 0$$

follows from the steady-state condition. This is the Hellman–Feynman theorem and it represents the first of the known approaches to the calculation of the forces based on its use. As demonstrated in the preceding sections of this review, according to this theorem the forces expressed solely in terms of the change of the external field are described by the integral

$$\frac{dE}{d\mathbf{R}} = \int \rho \frac{\partial V_{\text{ext}}}{\partial\mathbf{R}} d\mathbf{r}, \quad (5.1)$$

and—at first sight—may be found in a trivial manner if the electron density distribution is known. However, this is true only for calculations carried out within the framework of the pseudopotential method, in which the basis is formed by plane waves independent of the positions of atoms. However, the majority of the calculations, carried

out with the aid of other basis functions within the framework of the LMTO and LAPW methods, demonstrate that this formula may give results which differ by two or three orders of magnitude from reality. The second approach is based on Andersen’s theorem of forces (see, for example, Ref. [43]), which deals with the total energy not as a function of the density but of the potential. According to this theorem, the force acting on a nucleus and all the electrons which are inside an arbitrary surface  $\Sigma$  surrounding a given nucleus is

$$\frac{dE}{d\mathbf{R}} = \frac{\delta}{\delta\mathbf{R}} \left( \sum_{k,\lambda} f_{k\lambda} \varepsilon_{k\lambda} \right) + \mathbf{F}_{\text{ES}} + \mathbf{F}_{\text{xc}}, \quad (5.2)$$

where the first term represents the change in the one-electron energies associated with the virtual displacements of the frozen potential,  $\mathbf{F}_{\text{ES}}$  is the electrostatic force between the electron and nuclear charges outside and inside the surface, and  $\mathbf{F}_{\text{xc}}$  is the exchange–correlation contribution. If the motion of electrons is self-consistent, the force acting on them vanishes and, consequently, the quantity calculated from formula (5.2) represents the required force acting on a nucleus. This formulation is more general than the preceding one, since it makes it possible to deal with the contribution of electrons to an arbitrary total energy, which may differ from zero if the one-electron wave functions are found approximately. One of the problems encountered here is a prescription for selection of the surface  $\Sigma$ .

In fact, in practical calculations the energy is *not* a functional of the charge density or of the potential. In minimisation of the functional the electron density is represented by

$$\sum_{k,\lambda} f_{k\lambda} |\psi_{k\lambda}|^2,$$

where the wave functions are expanded in terms of a certain basis set

$$|k\lambda\rangle = \sum_{\alpha} |\chi_{\alpha}^k\rangle A_{\alpha}^{k\lambda}.$$

Consequently, for a fixed basis, the variational freedom of the functional applies only to the coefficients  $A_{\alpha}^{k\lambda}$  and the total energy remains constant when only these coefficients are varied. This variational principle leads to the matrix eigenvalue problem of the kind described by expression (4.2), which is obtained not only as a variational solution of the one-electron Schrodinger equation, but also as a result of global minimisation of the total-energy functional. This quite obvious (but missing from the published literature) statement is very important for the understanding of the derivation of any formula for the forces. It follows from this statement that the total derivative  $dE/d\mathbf{R}$  is equal to the partial derivative  $\partial E/\partial\mathbf{R}$ , whereas

$$\frac{dE}{d\{A_{\alpha}^{k\lambda}\}} \frac{d\{A_{\alpha}^{k\lambda}\}}{d\mathbf{R}} = 0.$$

Let us now consider a very simple and *practical* method for finding the forces based on the theorem under discussion. Let us assume that a self-consistent calculation of the atomic configuration  $\{\mathbf{R}\}$  is carried out and that it yields the coefficients  $A_{\alpha}^{k\lambda}\{\mathbf{R}\}$  and  $E\{\mathbf{R}\}$ . We shall also assume that the calculation is carried out for the  $\{\mathbf{R} + \delta\mathbf{R}\}$  configuration and that the solution to the eigenvalue

problem is not sought, but variational coefficients are substitute from the preceding stage of the calculation, i.e. the coefficients  $A_\alpha^{k\lambda}\{\mathbf{R}\}$  are substituted again. Since our basis is made to fit the potential, it is in fact essential to ensure partial self-consistency, but at each stage it is possible to use the old coefficients  $A_\alpha^{k\lambda}\{\mathbf{R}\}$ . In this way we obtain the total energy of a distorted configuration  $\tilde{E}\{\mathbf{R} + \delta\mathbf{R}\}$ . (The tilde symbol means that the energy found is not the exact total energy for the investigated configuration). It follows from the theorem just formulated that the force field can be found for the configuration  $\{\mathbf{R}\}$  if the function  $\tilde{E}\{\mathbf{R} + \delta\mathbf{R}\}$ , rather than the exact dependence  $E\{\mathbf{R} + \delta\mathbf{R}\}$ , is differentiated. This requires ensuring full self-consistency only once and no significant modification of the computer programs, so that the approach should be very effective. However, at this stage we shall try to derive directly the formula for the calculation of the forces, which should be even more effective, and it will be needed in the development of the linear response theory discussed in the next section.

We shall carry out a direct differentiation of the total energy of a crystal, described by formula (3.25), with respect to the position of an atom at a site  $\mathbf{R}$ . If the electron density is self-consistent, we find that

$$\frac{dE}{d\mathbf{R}} = \int \rho \frac{\partial V_{\text{ext}}}{\partial \mathbf{R}} d\mathbf{r} + \sum_{k,\lambda} f_{k\lambda} \left\langle \frac{d\psi_{k\lambda}}{d\mathbf{R}} \middle| -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | k\lambda \right\rangle,$$

where the first term represents the Hellman–Feynman result and the second is the Pulay correction, associated with incompleteness of the basis set. We shall represent the one-electron wave function by an expansion in terms of linear MT orbitals. The Pulay correction can be found if we calculate the following matrix element:

$$\langle \delta\chi_{RL}^k | -\nabla^2 + V - \varepsilon_{k\lambda} | k\lambda \rangle, \quad (5.3)$$

which obviously does not vanish if  $|k\lambda\rangle$  are found by the variational method. [The contribution made by the change in the variational coefficients  $A$  disappears because  $|k\lambda\rangle$  satisfy the matrix eigenvalue problem of the type described by expression (4.2).] The change

$$|\delta\chi_{RL}^k\rangle = \left| \frac{d\chi_{RL}^k}{d\mathbf{R}} \right\rangle$$

in the MT orbital is the difference between the MT orbitals  $|\chi_{R+\delta RL}^k\rangle$  and  $|\chi_{RL}^k\rangle$ , defined for the final and initial atomic configurations, respectively. We shall consider their approximation involving replacement of the exact orbital  $|\chi_{R+\delta RL}^k\rangle$  with an orbital  $|\tilde{\chi}_{R+\delta RL}^k\rangle$  derived from the solutions  $\phi_{RL}$  and  $\dot{\phi}_{RL}$  for an unperturbed crystal. This leads to the ‘rigid’ part of the change  $|\delta\chi_{RL}^k\rangle$  which contains  $-\delta\mathbf{R}'\nabla\chi_{RL}^k(\mathbf{r}_{R'})$  in each atomic cell  $R'$  plus a contribution associated with the change in the structure constants. This rigid part of the response can be used quite simply to estimate the matrix element (5.3). The ignored contribution is the ‘soft’ part  $|\delta^s\chi_{RL}^k\rangle$  associated with changes  $\delta^s\phi$ ,  $\delta^s\phi$ . Therefore, our next task will be to prove that the soft contribution to the force can be ignored. Since our test functions for the interstitial region are independent of the parameters of the potential, the soft contribution differs from zero only inside the MT spheres. Consequently, the

error in the determination of the force will be proportional to the following matrix element:

$$\langle \delta^s\chi_{RL}^k | -\nabla^2 + V - \varepsilon_{k\lambda} | k\lambda \rangle_{\Omega_{\text{MT}}}, \quad (5.4)$$

where the integration volume is extended to the region occupied by the MT spheres and where the induced orbital  $|\delta^s\chi_{RL}^k\rangle$  vanishes and has a zero radial derivative at the boundary of a sphere. The equation for the change in the radial functions can be written as follows:

$$(-\nabla^2 + V^{\text{MT}} - \varepsilon_v)\delta^s\phi + \delta^sV^{\text{MT}}\phi = 0, \quad (5.5)$$

where  $\delta^sV^{\text{MT}}$  is the soft change in the spherical part of the potential. [The equation for the energy derivatives is obtained by direct differentiation of Eqn (5.5).] Since the potential depends on the density, we can write

$$\delta^sV^{\text{MT}} = (\delta^sV_{\text{ext}})^{\text{MT}} + \frac{dV^{\text{MT}}}{d\rho} \frac{d\rho}{d\phi} \delta^s\phi,$$

where the contribution representing the change in the coefficients  $\delta A_\alpha^{k\lambda}$ , i.e.

$$\frac{d\rho}{d\{A_\alpha^{k\lambda}\}} \delta A_\alpha^{k\lambda},$$

vanishes on the basis of the variational principle formulated at the beginning of this section. This is important in our analysis, because—in principle—we can deal with the self-consistent equation (5.5) at the radial level and we can thus find the exact force. However, it is obvious that the bulk of the change in the spherical part of the potential is related to a certain constant shift  $V^{\text{MT}}$  on the energy scale inside each MT sphere:  $\delta^sV^{\text{MT}}(r) = \text{const}$ . Then, according to Eqn (5.5), the change in the radial functions is  $\delta^s\phi = -\text{const} \times \phi$  and its energy derivative is  $\delta^s\phi = -\text{const} \times \dot{\phi}$ , and the first part of the error in the determination of the force is estimated by means of the integral

$$\int_{s_{\text{MT}}} V^{\text{NMT}} \dot{\rho} d\mathbf{r},$$

which is negligibly small, since the electron density is practically independent of the linearisation centres  $\varepsilon_v$ . The second part of the error, which originates from the matrix element of the operator  $-\nabla^2 + V^{\text{MT}}$  in expression (5.4) is related directly to the linearised nature of the MT orbitals and can also be quite small if the parameters  $\varepsilon_v$  are selected at the centres of gravity of the filled part of the energy band. This discussion justifies theoretically our approximation.

If only the rigid displacement of the MT orbitals centred on the atoms is included, whereas the change in the shape of these MT orbitals is ignored, the theorem of forces can be formulated even more clearly. We shall do this by dividing, as in the preceding section, the space in a crystal into Wigner–Seitz cells. Then the total force can be written in the form [33]

$$\mathbf{F}_R = \sum_{k,\lambda} f_{k\lambda} \frac{\delta\varepsilon_{k\lambda}}{\delta\mathbf{R}} + \mathbf{F}_R^{\text{M}} + \int_{\Omega_R} \nabla[\rho(\mathbf{r})V_C(\mathbf{r})] d\mathbf{r} + \int_{\Omega_R} \nabla[\rho(\mathbf{r})\varepsilon_{\text{xc}}(\mathbf{r})] d\mathbf{r} - V_0 \int_{\Omega_R} \nabla\rho(\mathbf{r}) d\mathbf{r}, \quad (5.6)$$

where the last three contributions are also obviously integrals over the surfaces of a polyhedron. This result is simply the familiar Andersen theorem on forces [43] and

it gives the force in terms of the change in the sum of one-electron energies under the influence of virtual displacements of the frozen potentials plus the electrostatic Madelung contribution  $F_R^M$  and the surface terms. (Here,  $V_0$  is the point on the energy scale which is regarded as the origin and is called the MT zero.) This is not surprising, because in accordance with this theorem, in the force calculations it is necessary to assume that the self-consistent crystal potential remains constant when atoms are displaced. Since the basis set is made to match this potential, the result is simply a rigid shift of the basis functions centred on the atoms and this shift reproduces the shift of all the frozen potentials.

We shall now consider briefly the practical side of the calculations. Since all the surface integrals and  $F_R^M$  can be found quite simply, the main difficulty is a calculation of the change in the eigenvalues  $\delta\epsilon_{k\lambda}/\delta\mathbf{R}$  for each point  $\mathbf{k}$  and each band  $\lambda$ . It has been estimated that in this case the computer time has to be increased by about 50% compared with the time needed to solve the eigenvalue problem and, consequently, such calculation of the forces should be very effective.

We shall now give the results of calculations carried out by the total energy method and with the aid of the force formula. We shall do this for a number of phonon modes in Si, Nb, and Al. The results will be compared with the corresponding calculations carried out by the LAPW method, by the pseudopotential method, and by another version of the LMTO method; they will also be compared with the experimental data. Some comments should be made about the calculations. First, a basis set with one  $\kappa$  is selected for all the materials, so that the Hamiltonian and overlap matrices are low-dimensional. Second, since the method relies on one-centre expansions in terms of the spherical harmonics for the wave functions, charge density, and potential in the interstitial region, it follows that summation over  $L$  should include higher angular momenta. Use has been made of  $l_{\max} = 6-8$  (as specified below) in the expansion of the tails of the  $s$ ,  $p$ , and  $d$  orbitals. (The overlap integral converges much faster as a result of many-centre expansions for the MT orbitals in the interstitial region.) Although convergence of the total energy to within  $10^{-3}$  Ry per atom can be achieved for  $l_{\max} = 10-12$ , the convergence of the difference between the energies of distorted and undistorted lattices or of the atomic forces calculated for a given geometry is achieved for  $l_{\max} = 6-8$ , which is quite satisfactory for our purposes. The wave functions are expanded up to  $l_{\max} = 4$  in all the calculations, but the charge density and the potential are expanded up to  $l_{\max} = 8$ . This is related to the consideration of the half-core states. Since the MT spheres should remain unchanged for all the distorted configurations of a given lattice and since they should not overlap, they become quite small. Consequently, the amplitude of the high (from  $-10$  Ry and higher) core states has a finite value at the boundary of a sphere. Such states are regarded as of the band type and are calculated for separate energy ‘windows’ on the assumption that there is no hybridisation with the valence band. On the other hand, deep core levels are found from atomic calculations as the solutions of the Dirac equation, used with the spherical part of the potential, and are recalculated for each self-consistency iteration state.

We shall consider the results of calculations for an optical  $\Gamma$  phonon in Si. This phonon mode is calculated for

a shift of two silicon atoms along the  $[111]$  direction. The geometry of the positions of the atoms is  $\pm(1/8+x)a(1, 1, 1)$ , where  $a = 10.26$  a.u. is the experimental lattice parameter. The calculations include also two empty spheres, which follow behind the silicon atoms; this is a standard practice in the LMTO method. The positions of these spheres are also altered in order to conserve the total number of symmetry operations under distortion conditions. The basis set, representing the wave functions, can be expanded in terms of spherical harmonics up to  $l_{\max} = 6$ . The fixed tail energy is selected to be 0.1 Ry. The core states  $2s$  and  $2p$  are regarded as the valence states and the tail energies are  $-9.4$  and  $-6.4$  Ry, respectively. The radii of all the MT spheres are assumed to be 2.10 a.u. The exchange–correlation potential is taken from Ref. [44] and the method of tetrahedra [45] is used for integration over the Brillouin zone.

The results of this calculation are presented in Table 1. It lists the frequency of the investigated phonon mode, and also the third-order force constants calculated with the aid of formulas for the total energy and force. The results are compared also in Table 1 with the calculations reported by Yu, Singh, and Krakauer [42] carried out by the LAPW method, with the pseudopotential calculations of Yin and Cohen [46], with the results of another calculation by the LMTO method reported by Methfessel, Rodriguez, and Andersen [37]; they are also compared with the experimental data. Once again, we can see that the agreement between the calculations based on the total energy and on the atomic forces is excellent. The error is 0.5% and it is comparable with the error in the LAPW and pseudopotential methods. All the results are in good agreement with the experiments; the precision of the calculations is close to the precision of another LMTO calculation, and also to the results of Yu, Singh, and Krakauer [42] and of Yin and Cohen [46].

**Table 1.** Frequency of the optical  $\Gamma$  phonon in Si and the third-order force constant  $k_{xyz}$  of Si (results of calculations by various methods and experimental data).

Method	$\omega/\text{THz}$	$k_{xyz}/(\text{Ry}/a_B^3)$
Our results:	15.43	0.4304
total energy	15.51	0.4338
atomic forces		
LAPW [42]:	15.37	0.4026
total energy	15.40	0.4030
atomic forces		
Pseudopotential [46]:	15.16	0.357
total energy	15.14	0.355
atomic forces		
LMTO [37]:	15.47	0.4212
total energy		
Experiment	15.53 [47]	0.3820 [48]

The total energies and forces were calculated for an  $H$  phonon in Nb. The longitudinal and transverse modes of the bcc lattice at the point  $H = (0, 0, 1)(2\pi/a)$  are degenerate ( $a = 6.22$  a.u. is the experimental lattice parameter). The details of the calculations are as follows. A basis  $s$ ,  $p$ ,  $d$  with one  $\kappa$ , which has a one-centre expansion, is cut off at  $l_{\max} = 8$ . The fixed energy of an MT orbital tail is selected to be 0.5 Ry at approximately the centre of gravity of the filled part of the energy band and subject to a small

correction of 0.03 Ry. The levels  $4s$  and  $4p$  are also regarded as the valence levels with the edges of the tails amounting to  $-3$  and  $-5$  Ry, respectively. The radius of the MT sphere in Nb is taken to be 2.568 a.u. and integration over the Brillouin zone by the method of tetrahedra is carried out for 60  $\mathbf{k}$  points. Table 2 gives the calculated total energies of four distorted configurations, measured relative to the equilibrium configuration. The displacements  $\delta$  are converted to a value per atom and expressed in units of the lattice parameter. The forces are calculated by polynomial sixth-order interpolation with an even series (because of symmetry). Such interpolation can give the values of the force for each displacement  $\delta$ . Table 2 includes, for the sake of comparison, also the results of calculations based on formula (5.6). We can see that the difference between them is less than 1.8%, which is close to the error of 0.8% found earlier for Si. If these results are used, a calculation of the total energy can be used to estimate the frequency of an  $H$  phonon: the value obtained is 6.56 THz. A calculation based on the expression for the forces gives 6.60 THz, which is only 0.7% greater than the earlier value and by 1.7% greater than the experimental frequency which is 6.47 THz [49]. We can therefore draw the conclusion that the agreement with the experiments is good.

**Table 2.** Total energy, measured from the equilibrium configuration, and atomic forces as functions of the displacements  $\delta$  (in units of the lattice parameter) for the  $H$  phonon in Nb.

$\delta$	0.005	0.010	0.015	0.020
$\Delta E_{\text{tot}}/10^{-3}$ Ry	0.1668	0.6781	1.5696	2.8403
$F_{\text{num}}/(\text{Ry}/a_{\text{B}})$	0.01073	0.02241	0.03494	0.04623
$F_{\text{calc}}/(\text{Ry}/a_{\text{B}})$	0.01070	0.02233	0.03453	0.04706

The last example in this section is a calculation of an  $X$  phonon in the fcc lattice of Al. The valence electrons with  $\kappa^2 = 0.3$  Ry can be represented by the MT orbitals  $3s$ ,  $3p$ , and  $3d$  ( $\text{Im}\kappa^2 = 0.03$  Ry, exactly as in the preceding calculations). The MT orbitals  $3s$  and  $2p$  are used to describe the low-lying levels with  $\kappa^2 = -6.5$  Ry and  $\kappa^2 = -4$  Ry, respectively. The basis has a one-centre expansion to  $l_{\text{max}} = 6$ . The lattice parameter is 7.64 a.u. and the radius of an MT sphere in Al is selected to be 2.623 a.u. Since for an fcc lattice the longitudinal and transverse modes are not degenerate at the point  $X = (0, 0, 1)(2\pi/a)$ , two separate calculations are needed. In integration over the Brillouin zone the longitudinal mode is calculated at 75  $\mathbf{k}$  points and 75  $\mathbf{k}$  points for a low-symmetry transverse mode. The calculated results are compared in Table 3 with the measured frequencies [49]. The agreement between the calculations based on formulas for the total energy and those based on the forces is good, but the difference is greater than that found for Si and Nb, and it amounts to 7%. All the theoretical values are close to the experimental data to within 4.5%.

**Table 3.** Frequencies of the  $X$  phonon (in terahertz) in Al calculated from the total energy and atomic forces, and found experimentally.

Mode	Total energy	Atomic forces	Experiment [49]
Longitudinal	9.38	10.05	9.69
Transverse	5.62	6.07	5.79

## 6. Variational theory of the linear response

We shall now consider the development of the linear response theory, based on the use of MT-basis sets, the advantages of which have been demonstrated in detail in the preceding two sections. The problem of convergence of the polarisability described by expression (3.32), associated with the summation over highly excited states and, consequently, violation of the acoustic sum rule seems to be artificial. Let us consider a calculation of the parameters of any phonon within the framework of the total energy method described in the preceding section. For simplicity, we shall assume that  $\mathbf{q}$  vanishes. Then, the displacement of all the atoms in the basis in a unit cell by a certain distance  $\mathbf{d}$  does not alter anything in the calculation process, i.e. it simply shifts the origin in the coordinate space. The self-consistent density is obviously invariant under such a displacement of the basis and it depends only on the relative distances between the atoms. The acoustic sum rule is then satisfied identically and if we wish to find the change in the density in the coordinate system of the undistorted lattice, the result is  $\mathbf{d} \times \nabla \rho$ . Hence, we may conclude that the main problem appears in the attempt to expand the displaced density and the wave functions relative to the origin of the coordinates of the original lattice. Since the wave functions oscillate in the region of the ion core, their rigid displacement leads to first-order corrections in the original coordinate system and these corrections are of the  $\mathbf{d} \times \nabla |k\lambda\rangle$  type; this, in turn, is also subject to strong short-wavelength oscillations and these can be found by the use of a mathematically complete system of functions. Consequently, any theory of atomic vibrations should automatically describe such rigid shifts.

A very elegant method, which makes it possible to eliminate the sum over the filled states in expression (3.32) for the polarisability, was proposed by Sternheimer [50] in connection with calculations of the atomic polarisability. It is based on the solution of the differential equation which is satisfied by the first-order corrections. Let us consider the one-electron Schrodinger equation in which the effective potential in the density functional theory is supplemented by a weak perturbation. Expansion of one-electron wave functions as a series in terms of the small parameter of this perturbation and retention of only the first-order terms gives

$$(-\nabla^2 + V - \varepsilon_{k\lambda})|\delta k\lambda\rangle + (\delta V_{\text{eff}} - \delta \varepsilon_{k\lambda})|k\lambda\rangle = 0.$$

Since in the theory of lattice dynamics a perturbation is in the form of a superposition of waves of the type described by an expression such as (3.28), this applies also to the first-order corrections, as shown in the preceding section. In the case of nonzero wave vectors  $\mathbf{q}$ , we may conclude that the first-order corrections to the one-electron energies always vanish, since

$$\delta \varepsilon_{k\lambda} = \langle k\lambda | \delta V_{\text{eff}} | k\lambda \rangle = 0$$

because the integrand behaves as the function

$$\exp(-i\mathbf{k} \cdot \mathbf{r}) \exp(\pm i\mathbf{q} \cdot \mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) = \exp(\pm i\mathbf{k} \cdot \mathbf{r}),$$

multiplied by a function which is periodic over the lattice. The integral of the above expression over the whole space is identically equal to zero. Consequently, we can write down

$$(-\nabla^2 + V - \varepsilon_{k\lambda})|\delta^\pm k\lambda\rangle + \delta^\pm V_{\text{eff}}|k\lambda\rangle = 0. \quad (6.1)$$

The result is therefore an inhomogeneous second-order differential equation for the corrections to the wave functions. Since the wave functions are of the Bloch type, the above equation can be solved only for one unit cell. The sole condition is, as in the original Schrodinger equation, that the boundary conditions imposed by the Bloch theorem should be obeyed.

Let us consider the advantages of this method. First, it does not require introduction of supercells, as is done in the frozen phonon method, so that we can use the former method for *any* value of  $\mathbf{q}$ . Second, the proposed method does not require knowledge of any excited states, since Eqn (6.1) relates the first-order corrections—which, according to expression (3.29), have to be found only for the filled states—to the filled states themselves. This avoids the difficulty encountered in applying perturbation theory to the response functions and related to the summation over highly excited energy levels. As a consequence, the acoustic sum rule is satisfied identically since the wave function gradient obeys Eqn (6.1) with a potential of the  $\nabla V$  type, i.e.

$$(-\nabla^2 + V - \varepsilon_{k\lambda})\nabla|\mathbf{k}\lambda\rangle + \nabla V|\mathbf{k}\lambda\rangle = 0.$$

This approach to the problem of lattice dynamics is proposed in Ref. [51] and, independently, in Ref. [52], where the Sternheimer method is generalised within the framework of the pseudopotential formalism and its use is demonstrated by a calculation of the phonon spectrum of Si. The use of plane waves as the basis [53] is very elegant and makes it possible to ignore the corrections associated with the change in the basis functions as a result of displacements. It is this that makes it possible to calculate the atomic forces by the frozen phonon method and the dynamic matrix in the linear response theory by means of formulas based on the Hellman–Feynman theorem. Unfortunately, as mentioned several times earlier, the very slow convergence of the expansion of the pseudopotential wave functions in terms of plane waves for narrow-band systems makes this method unsuitable for the calculation of the properties of phonons in a transition metal.

Construction of a rapidly converging basis set for representation of first-order corrections occupies the central place in the method proposed in Ref. [4]. The MT orbital representation is used there and this makes it possible to calculate the phonon spectra of *any* crystals, including transition metals. The method is quite fast and accurate: the time needed to calculate the dynamic matrix for an arbitrary vector  $\mathbf{q}$  is comparable with the time required for a self-consistent calculation of the band structure of an unperturbed crystal; the error in the calculated phonon frequencies is usually a few percent.

Two problems are encountered when the MT-basis functions are used in the linear response theory. The first problem is due to the fact that the unperturbed energy bands  $\varepsilon_{k\lambda}$  and the wave functions  $|\mathbf{k}\lambda\rangle$  are obtained in this basis with the help of the Rayleigh–Ritz variational principle. These wave functions are not the *exact* solutions of the one-electron Schrodinger equation. It is therefore necessary to adopt the variational formulation of the linear response theory. The second problem, discussed several times above, is related to the fact that the MT-basis functions are matched to an unperturbed one-electron potential and, therefore, they cannot be used directly as

the basis for expansion of the first-order corrections. They should be reconstructed in order to take account of the perturbation characteristics. In particular, the augmented partial waves inside the MT spheres should track the motion of their atoms, so as to allow for the rigid shift of the wave function in the region of the atomic core.

The variational formulation of the linear response method is needed in connection with the solution of the linearised Schrodinger equation (6.1) with the help of an expansion of the first-order corrections (to the one-electron wave functions) in terms of the basis of the MT orbitals. The energy functional should be found the minimisation of which with respect to  $|\delta^\pm \mathbf{k}\lambda\rangle$  leads to Eqn (6.1). If the initial Schrodinger equation is obtained subject to the condition which should be satisfied by the wave functions that minimise the total energy functional, the functional of interest to us can be derived by expanding the total energy in terms of a change in the external potential (in terms of the displacements of the nuclei) up to the terms of the second order of smallness. The most general form of such an expansion is

$$\begin{aligned} \delta^{(2)}E = & \sum f_{k\lambda} \langle \delta^+ \delta^- \mathbf{k}\lambda + \delta^+ \delta^- \mathbf{k}\lambda | -\nabla^2 + V - \varepsilon_{k\lambda} | \mathbf{k}\lambda \rangle \\ & + 2 \sum f_{k\lambda} \langle \delta^+ \mathbf{k}\lambda | -\nabla^2 + V - E_{k\lambda} | \delta^+ \mathbf{k}\lambda \rangle \\ & + \int \delta^+ \rho \delta^- V_{\text{eff}} \, d\mathbf{r} + \int \delta^+ \rho \delta^- V_{\text{ext}} \, d\mathbf{r} \\ & + \int \rho \delta^+ \delta^- V_{\text{ext}} \, d\mathbf{r} + \text{c.c.}, \end{aligned} \quad (6.2)$$

where  $|\delta^\pm \delta^\mp \mathbf{k}\lambda\rangle$  represents second-order corrections to the wave functions. We have retained deliberately the first term in the above expression, because the unperturbed wave functions are only approximate solutions of the Schrodinger equation, as is true of the LMTO method which is used to find them by solving the matrix eigenvalue problem of the type described by expression (4.9). Variation of this expression with respect to  $|\delta^\pm \mathbf{k}\lambda\rangle$  and use of the induced density given by formula (3.29) leads to the condition which should be satisfied by the first-order corrections that minimise  $\delta^2 E$ , i.e. it leads to the differential Sternheimer equation in which the change in the one-electron potential  $\delta^\pm V_{\text{eff}}$  should be found in a self-consistent manner in accordance with expression (3.31). The expression given above—representing the second-order change in the total energy in the density functional theory (specifically, the electron part of this energy)—describes simply the electron contribution to the dynamic matrix. (The contribution of the nuclei is given by the appropriate Ewald sum and finding it is a trivial matter.) The property of extremality follows directly from the Hohenberg–Kohn principle and it can be used to calculate the dynamic matrix quite accurately: since the first-order corrections and the charge densities themselves are variationally correct, the error is only of the second order of smallness in terms of the error in  $|\delta^\pm \mathbf{k}\lambda\rangle$ . The second and third terms are missing from expression (6.2) at its minimum and, therefore, the result can be interpreted as that obtained from the Hellman–Feynman theorem (last two contributions) plus a correction for incompleteness of the basis set [first term in expression (6.2)]. This correction is due to the approximate nature of the unperturbed states  $|\mathbf{k}\lambda\rangle$  and it is completely



analogous to the Pulay force, as used in the calculations of the atomic forces described in Section 3.

There is one more important property which follows from extremality of the dynamic matrix and is associated with calculation of the third derivative of the total energy. This may apply to the anharmonic coefficients, the Gruneisen coefficients, and other nonlinear coefficients. Let us consider the derivative of  $\delta^{(2)}E$  with respect to some parameter  $x$  (for example, the lattice parameter in calculation of the Gruneisen coefficient or the displacement of a nucleus in calculation of the anharmonic coefficient of any one vibrational mode). We then have

$$\frac{d\delta^{(2)}E}{dx} = \frac{\partial\delta^{(2)}E}{\partial x} + \frac{d\delta^{(2)}E}{d\{|\delta^{\pm}\mathbf{k}\lambda\rangle\}} \frac{d\{|\delta^{\pm}\mathbf{k}\lambda\rangle\}}{dx},$$

and the last contribution should vanish if the variational derivative  $d\delta^{(2)}E/d\{|\delta^{\pm}\mathbf{k}\lambda\rangle\}$  is found at the minimum of the functional  $\delta^{(2)}E$ . This property makes it possible to express all the nonlinear coefficients in terms of the known first-order corrections and variation of the latter due to a change in  $x$  can be ignored. We must comment here on the second-order changes in the wave functions that occur in the dynamic matrix. These functions make only a limited contribution to the first term of expression (6.2) and they are easily calculated for a given set of the basis functions [see formula (6.4) given later]. In view of this limitation, which is defined below, it is easy to calculate also the derivatives of these functions with respect to the selected parameter  $x$ , so that these functions do not affect the statement made above.

Let us now consider the problem of constructing the Hilbert space for representing the first-order corrections. Let us return to the MT-basis set  $\{|\chi_{\alpha}^k\rangle\}$  of dimension  $N$  (where  $\alpha$  is a combined index denoting  $RL$ ), which represents the unperturbed functions  $|\mathbf{k}\lambda\rangle$ . The space is separated into MT spheres, centred on the atoms, and the interstitial region. Inside the spheres the MT orbitals are linear combinations of the numerically calculated radial functions multiplied by spherical harmonics. In the interstitial region they are the Hankel functions. The one-electron wave function can be represented by a linear combination

$$|\mathbf{k}\lambda\rangle = \sum_{\alpha}^N |\chi_{\alpha}^k\rangle A_{\alpha}^{k\lambda},$$

where  $A_{\alpha}^{k\lambda}$  are the coefficients in the expansion found by solving the eigenvalue matrix problem:

$$\sum_{\alpha}^N \langle \chi_{\beta}^k | -\nabla^2 + V - \varepsilon_{k\lambda} | \chi_{\alpha}^k \rangle A_{\alpha}^{k\lambda} = 0.$$

(We recall that this result is not only obtained by solving the one-electron Schrodinger equation with the aid of the variational method, but can be regarded as the result of global minimisation of the total energy functional in terms of the coefficients  $A_{\alpha}^{k\lambda}$  for a fixed basis  $\{|\chi_{\alpha}^k\rangle\}$ .)

In the linear response method the first-order variation  $|\delta^{\pm}\mathbf{k}\lambda\rangle$  should include the change  $|\delta^{\pm}\chi_{\alpha}^k\rangle$  in the basis of the MT orbitals and the change  $\delta^{\pm}A_{\alpha}^{k\lambda}$  in the expansion coefficients:

$$|\delta^{\pm}\mathbf{k}\lambda\rangle = \sum_{\alpha}^N [|\delta^{\pm}\chi_{\alpha}^k\rangle A_{\alpha}^{k\lambda} + |\chi_{\alpha}^{k\pm q}\rangle \delta^{\pm}A_{\alpha}^{k\lambda}]. \quad (6.3)$$

Since this function is a Bloch wave with the wave vector  $\mathbf{k} \pm \mathbf{q}$ , the functions  $|\chi_{\alpha}^{k\pm q}\rangle$ ,  $|\delta^{\pm}\chi_{\alpha}^k\rangle$  are also Bloch waves.

The first of them is the initial MT orbital with the wave vector  $\mathbf{k} + \mathbf{q}$  and the second is a linearised MT orbital constructed as follows: inside the MT spheres the basis  $|\delta^{\pm}\chi_{\alpha}^k\rangle$  represents a change in the numerical radial functions plus a contribution associated with the change in the structure constants. The change in the radial functions is described by an incomplete set of differential equations, derived by linearisation of the radial Schrodinger equation in terms of the perturbation  $\delta^{\pm}V_{\text{eff}}$  [2]. This change contains two contributions. The first is trivial and it is associated with a rigid shift of the potential inside an MT sphere and the second is related to the change in the profile of the potential. In the interstitial region the basis  $|\delta^{\pm}\chi_{\alpha}^k\rangle$  can be represented as the sum

$$\sum_{\mathbf{t}} \exp[i(\mathbf{k} \pm \mathbf{q}) \cdot \mathbf{t}] \nabla K_{\alpha}(\mathbf{r}_R - \mathbf{t})$$

of the gradients of the Hankel functions centred at the lattice sites. The expansion of  $|\delta^{\pm}\mathbf{k}\lambda\rangle$ , written in the form of expression (6.3), converges rapidly because the basis  $|\delta^{\pm}\chi_{\alpha}^k\rangle$  matches a perturbation in exactly the same way as the initial basis  $|\chi_{\alpha}^k\rangle$  matches the unperturbed crystal potential. Expression (6.3) can also be interpreted as an expansion of  $|\delta^{\pm}\mathbf{k}\lambda\rangle$  in terms of the basis  $|\chi_{\alpha}^{k\pm q}\rangle$  in a local coordinate system shifted together with its nucleus; in this case the convergence in respect of the number of orbitals per atom should be approximately the same as for the unperturbed states.

We should also consider the second-order corrections. They appear in the formulation of the method described here because the states  $|\mathbf{k}\lambda\rangle$  are not exact and represent only the variational solutions [see the first term in expression (6.2)]. The second-order change in the wave functions is

$$|\delta^{\pm}\delta^{\mp}\mathbf{k}\lambda\rangle = \sum_{\alpha}^N (|\chi_{\alpha}^k\rangle \delta^{\pm}\delta^{\mp}A_{\alpha}^{k\lambda} + |\delta^{\mp}\chi_{\alpha}^{k\pm q}\rangle \delta^{\pm}A_{\alpha}^{k\lambda} + |\delta^{\pm}\chi_{\alpha}^{k\mp q}\rangle \delta^{\mp}A_{\alpha}^{k\lambda} + |\delta^{\pm}\delta^{\mp}\chi_{\alpha}^k\rangle A_{\alpha}^{k\lambda}), \quad (6.4)$$

where  $\delta^{\pm}\delta^{\mp}A_{\alpha}^{k\lambda}$  and  $|\delta^{\pm}\delta^{\mp}\chi_{\alpha}^k\rangle$  are the second-order changes in the expansion coefficients and in the basis functions, respectively. Substitution of the above expression into the first term of formula (6.2) demonstrates that the contribution representing the second-order changes in the coefficients can be ignored, because they occur in expression (6.4) only as the coefficients of the unperturbed basis functions, i.e.

$$\sum_{\alpha}^N \delta^{\pm}\delta^{\mp}A_{\alpha}^{k\lambda} \langle \chi_{\beta}^k | -\nabla^2 + V - \varepsilon_{k\lambda} | \mathbf{k}\lambda \rangle = 0.$$

On the other hand, the last three contributions to expression (6.4) are important in calculation of  $\delta^{(2)}E$ .

There are a number of fundamental consequences of the fact that the second-order changes in the coefficient  $A_{\alpha}^{k\lambda}$  can be ignored. We can see that in the second-order change in the wave function described by expression (6.4) only the last three terms are really needed. In selection of the Hilbert space  $\{|\chi\rangle; |\delta\chi\rangle\}$  of the basis functions the variational freedom of the functional (6.2) arises only from the coefficients  $\delta^{\pm}A_{\alpha}^{k\lambda}$ . This is fully analogous to the variational freedom of the total energy functional represented solely by the coefficients  $A_{\alpha}^{k\lambda}$ , as shown in the preceding

section. There, this aspect has a consequence in the calculation of the forces acting on atoms: if the variations in the total energy are considered in terms of the displacements, the steady-state condition means that there is no need to include the contribution corresponding to the change in the variational coefficients. In the present case the consequence is the same: in calculation of the nonlinear parameters, discussed in the preceding section, the steady-state nature of  $\delta^{(2)}E$  implies that there is no need to include the contribution corresponding to the changes in the coefficients  $\delta^\pm A_\alpha^{k\lambda}$ . The coefficients  $\delta^\pm A_\alpha^{k\lambda}$  themselves are found by a minimisation procedure. Variation of  $\delta^{(2)}E$  with respect to  $\delta^\pm A_\alpha^{k\lambda}$  gives the following matrix system of linear equations:

$$\begin{aligned} & \sum_{\alpha}^N \langle \chi_\beta^{k\pm q} | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | \chi_\alpha^{k\pm q} \rangle \delta^\pm A_\alpha^{k\lambda} \\ & + \sum_{\alpha}^N [ \langle \chi_\beta^{k\pm q} | \delta^\pm V_{\text{eff}} | \chi_\alpha^k \rangle \langle \delta^\pm \chi_\beta^{k\mp q} | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | \chi_\alpha^k \rangle \\ & + \langle \chi_\beta^{k\pm q} | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | \chi_\alpha^k \rangle ] A_\alpha^{k\lambda} = 0. \end{aligned} \quad (6.5)$$

This system of linear equations represents, as expected, a variant of the initial matrix eigenvalue problem described by expression (4.9). It gives the minimum of the functional  $\delta^{(2)}E$  in the space of the coefficients  $\delta^\pm A_\alpha^{k\lambda}$  and any second-order changes in the basis, such as  $|\delta^\pm \delta^\mp \chi_\alpha^k\rangle$ , do not influence the position of the minimum. On the other hand, the functions  $|\delta^\pm \delta^\mp \chi_\alpha^k\rangle$  determine the value of  $\delta^{(2)}E$  at its minimum and should be included in calculation of the dynamic matrix.

The linear system of equations (6.5) is readily solved for  $\delta^\pm A_\alpha^{k\lambda}$ . This requires inversion of the matrix

$$\langle \chi_\beta^{k\pm q} | -\nabla^2 + V - \varepsilon_{k\lambda} | \chi_\alpha^{k\pm q} \rangle,$$

whose eigenvalues are known to be  $\varepsilon_{k\lambda} - \varepsilon_{k\pm q\lambda'}$  and whose eigenvectors are  $A_\alpha^{k\pm q\lambda'}$ , where  $\lambda' = 1, \dots, N$ . The result for  $\delta^\pm A_\alpha^{k\lambda}$  is then substituted into formula (6.3), which yields the final expression for  $|\delta^\pm k\lambda\rangle$  in the following form:

$$\begin{aligned} |\delta^\pm k\lambda\rangle &= \sum_{\alpha}^N |\delta^\pm \chi_\alpha^k\rangle A_\alpha^{k\lambda} \\ &+ \sum_{\lambda'}^N |k\pm q\lambda'\rangle \frac{\langle k\pm q | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | \sum_{\alpha}^N \delta^\pm \chi_\alpha^k A_\alpha^{k\lambda} \rangle}{\varepsilon_{k\lambda} - \varepsilon_{k\pm q\lambda'}} \\ &+ \sum_{\lambda'}^N |k\pm q\lambda'\rangle \frac{\langle \sum_{\alpha}^N \delta^\pm \chi_\alpha^{k\mp q} A_\alpha^{k\pm q\lambda'} | -\nabla^2 + V_{\text{eff}} - \varepsilon_{k\lambda} | k\lambda \rangle}{\varepsilon_{k\lambda} - \varepsilon_{k\pm q\lambda'}} \\ &+ \sum_{\lambda'}^N |k\pm q\lambda'\rangle \frac{\langle k\pm q | \delta^\pm V_{\text{eff}} | k\lambda \rangle}{\varepsilon_{k\lambda} - \varepsilon_{k\pm q\lambda'}}. \end{aligned} \quad (6.6)$$

This formula has a simple physical meaning. The first three terms, containing  $\{|\delta\chi\rangle\}$ , appear because of the use of the *variational* solutions. They can be regarded as corrections, associated with incompleteness of the basis set, to the last contribution (with  $\delta^\pm V_{\text{eff}}$ ), which has the form of expression (3.30) deduced by standard perturbation theory. If all the unperturbed states are found rigorously and represent a *mathematically* complete system of functions, then the first and second terms cancel out and

the third term disappears: we again obtain expression (3.30). However, the use of the functions  $|\delta\chi\rangle$  in the basis reduces considerably the number of states  $|k\pm q\lambda'\rangle$  needed to reach convergence in expression (6.6). Following this conclusion, the summation in the last three contributions is carried out only over the lowest  $N$  energy states, where  $N$  is the size of the basis for the unperturbed system. Moreover, the acoustic sum rule is obeyed. If  $\mathbf{q} = \mathbf{0}$  and  $\delta^\pm V_{\text{eff}} = \mathbf{d} \times \nabla V_{\text{eff}}$  and  $|\delta\chi_\alpha^k\rangle = \mathbf{d} \times \nabla |\chi_\alpha^k\rangle$  are substituted, the last three contributions in expressions (6.6) are combined together in an integral of the gradient of the periodic function, which vanishes, and which is calculated over the surface of a unit cell. This comment is related to excited states. It follows from the logic of the above conclusion that the change in the charge density associated with a phonon, which is a property of the ground state of unperturbed and perturbed crystals, should be calculated beginning from knowledge of just the occupied states, whereas all the empty states can (in principle) be arbitrary. The LMTO method has a major advantage in tackling this problem: it is fast and exact within a certain energy ‘window’. The states  $|k\pm q\lambda'\rangle$  are the eigenstates of the matrix of the Hamiltonian  $\langle \chi_\beta^{k\pm q} | -\nabla^2 + V_{\text{eff}} | \chi_\alpha^{k\pm q} \rangle$  which is constructed specifically to reproduce well only the filled bands. (The energy window of interest to us contains the centres  $\varepsilon_v$  of linearisation.) Consequently, the excited states in expression (6.6) should not be interpreted as the real states: in this formulation the linear response theory requires knowledge only of the filled energy bands.

It is interesting to consider the interpretation of the excited states in the exact Green function (or the Korringa–Kohn–Rostocker) methods and in the augmented plane wave method. Since the energy bands  $\varepsilon_{k\lambda}$  and the eigenvectors  $A_\alpha^{k\lambda}$  in the Korringa–Kohn–Rostocker (and the augmented plane wave) methods can be obtained from the matrices of the Hamiltonian  $\langle \chi_\beta^k(\varepsilon_v) | -\nabla^2 + V_{\text{eff}} | \chi_\alpha^k(\varepsilon_v) \rangle$  of the LMTO (LAPW) methods for all values of  $\varepsilon_v = \varepsilon_{k\lambda}$ , the states  $|k\pm q\lambda'\rangle$  in expression (6.6) should be regarded as the eigenstates of the matrix

$$\langle \chi_\beta^{k\pm q}(\varepsilon_{k\lambda}) | -\nabla^2 + V_{\text{eff}} | \chi_\alpha^{k\pm q}(\varepsilon_{k\lambda}) \rangle,$$

and only the bands  $\varepsilon_{k\pm q\lambda'}$  with energies close to  $\varepsilon_{k\lambda}$  will then be described correctly. In this case knowledge of such an *auxiliary* spectrum for *each* filled band  $\varepsilon_{k\lambda}$  is needed in order to find  $|\delta^\pm k\lambda\rangle$ .

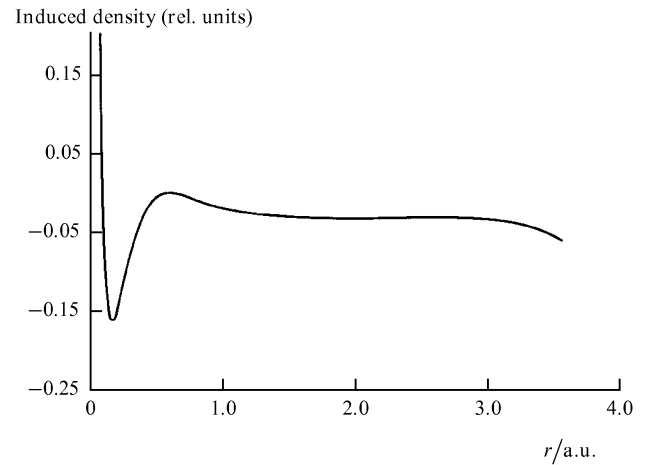
We shall now demonstrate application of the linear response method to the phonon spectra of Nb and Mo. We shall make a number of comments about these calculations. The first comment relates to selection of the size of the basis set used in expansion of the one-electron wave functions and of the first-order corrections to these functions. In many cases it is sufficient to use the MT orbitals  $s$ ,  $p$ , and  $d$  selected with one tail energy  $\kappa^2$  approximately at the centre of the filled part of the band. However, this is insufficient in the case of some phonon wave vectors (this applies in particular to a longitudinal mode along the [001] direction in Mo). The variational freedom of the dynamic matrix functional is improved by the use of the basis functions representing linear combinations of the orbitals  $s$ ,  $p$ , and  $d$  with two energies  $\kappa^2$ . The first energy is selected, as usual, approximately at the ‘centre of gravity’ and it is close to 0.5 Ry, whereas the second one is 1 Ry higher, i.e. it represents 1.5 Ry. Both energies have small imaginary

parts (0.03 Ry) by bypassing the singularities of the structure constants at positive energies.

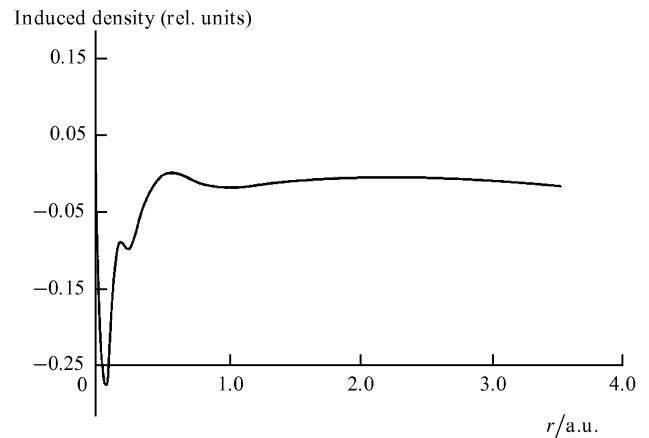
The second comment is related to the one-centre expansion of the response functions in the interstitial region. As in the standard LMTO method, when expansions in terms of spherical harmonics are used, the higher angular momenta must be included. In the majority of calculations of the expansions of the tails of the MT orbitals it has been assumed that  $l_{\max} = 8$ , which implies a procedure of internal summation in three-centre integrals representing changes in the Hamiltonian and overlap matrices. The wave functions and the first-order corrections are expanded up to  $l_{\max} = 4$ , but the changes in the charge density and in the potential are expanded to  $l_{\max} = 8$ . It is also found that in some cases (this applies particularly to a transverse Nb mode along the [111] direction at low values of  $q$ ), the dynamic matrix converges only for  $l_{\max} = 10-12$ .

The third comment is related to selection of the number of the  $k$  points in the irreducible part of the Brillouin zone, which are needed in integration by the method of tetrahedra [45]. For all the wave vectors  $q$  the number of points is selected to ensure that the dynamic matrix converges to within 0.1%–0.3%. In the majority of cases, convergence of this order is reached for about 100 points, although in final calculations this number was selected to be 256. In rare cases this number had to be increased to 508. The last comment is related to the number of iterations needed for self-consistency of the induced density. The number of iterations for finding a self-consistent change in the density depends strongly on how close is a given phonon wave vector  $q$  to the centre of the Brillouin zone. For those wave vectors which lie near the zone boundary, this number is approximately 50. However, in the long-wavelength limit the number of iterations had to be increased greatly because of the Coulomb divergence of the  $\delta Q/q^2$  type, where  $\delta Q$  are charge oscillations inside a cell. In principle, such a divergence can be summed by introducing an effective permittivity  $\varepsilon(q)$ , which for metals increases proportionately to  $q^2$  if  $q$  is small. This is fully analogous to the summation of all the loop diagrams in the random phase approximation. However, this procedure has not yet been implemented and self-consistency in the long-wavelength limit is achieved, as in the case of large values of  $q$ , by the method of admixing the density from the preceding iteration step. In the limit  $q \rightarrow 0$ , the admixing parameter is selected to be very small (of the order of 0.01), so that the number of iterations needed for self-consistency is of the order of 150–250.

Since from the computational point of view the linear response method is fairly difficult, it is necessary to test all the computer algorithms and programs. Such testing should involve first a calculation of the charge density induced by the atomic displacements in a unit cell. In a comparison of the induced densities the reference standard can be a calculation carried out by the frozen phonon technique, based on the all-potential LMTO method described in Sections 2 and 3. By way of example, let us consider a longitudinal phonon mode at the point  $(0, 0, \frac{1}{2})$  in the Brillouin zone of Nb. A suitable selection of a supercell with four atoms enables us to construct self-consistent distributions of the charge density as a function of the displacements of nuclei from equilibrium positions. The density change associated with this phonon was found by

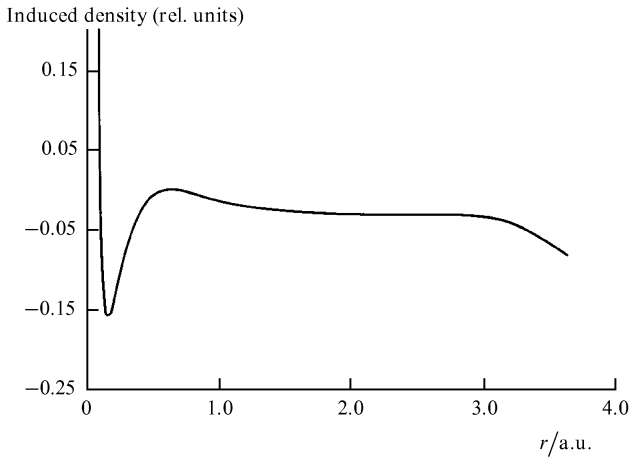


**Figure 2.** Self-consistent change in the charge density for an arbitrary phonon mode with  $q = (0, 0, \frac{1}{2})$  in Nb, deduced within the framework of the all-potential LMTO method. The dependence of the radial component for  $l = 0$  and  $m = 0$  is shown.

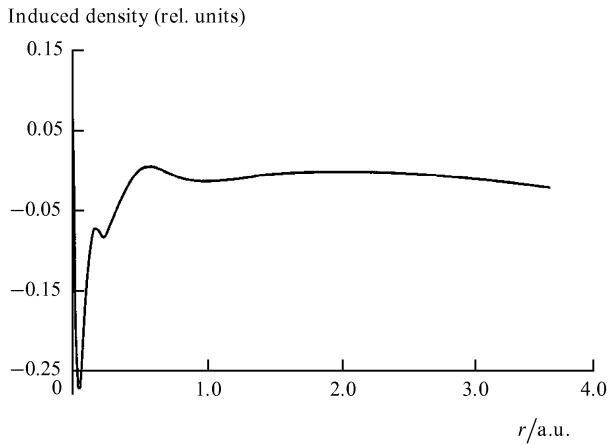


**Figure 3.** Self-consistent change in the charge density for an arbitrary phonon mode with  $q = (0, 0, \frac{1}{2})$  in Nb, obtained within the framework of the all-potential LMTO method. The dependence of the radial component for  $l = 2$  and  $m = 0$  is shown.

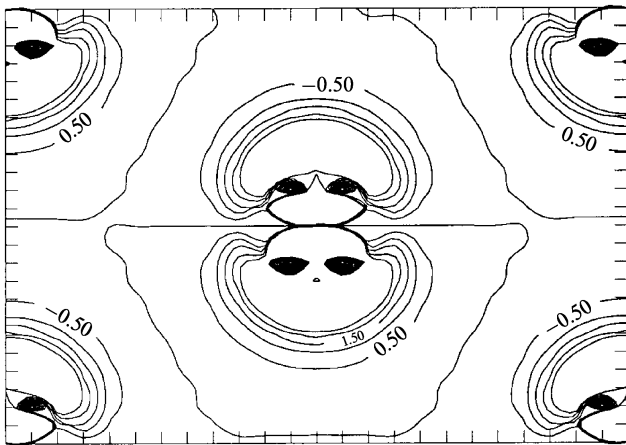
numerical differentiation of this displacement function at each point of the unit cell. This was the method used to find the induced density (Figs 2 and 3). In view of the use of an expansion in spherical harmonics, these figures show only two examples of the dependences of the radial components of the change in the density on the distance from a nucleus:  $l = 0, m = 0$  in Fig. 2 and  $l = 2, m = 0$  in Fig. 6. The linear response methods was applied to the investigated phonon mode: this did not require any supercells or numerical differentiation procedures. The calculated dependences of the induced density are shown in Figs 4 and 5. Comparison of the figures in pairs (Figs 2 and 4, and Figs 3 and 5) demonstrates that the corresponding curves are practically identical, illustrating strikingly the advantages of the linear response method: the method is accurate and fast. Moreover, it is evident that a change in the density is an oscillatory function in the core region of an atom. Let us consider in detail the nature of these oscillations and the related topics. The initial electron density oscillates in the core region and this is a consequence of the shell structure of the atoms. It is natural to expect that a rigid shift of this



**Figure 4.** Self-consistent change in the charge density for an arbitrary phonon mode with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in Nb, obtained by the linear response method. The dependence of the radial component for  $l = 0$  and  $m = 0$  is shown.

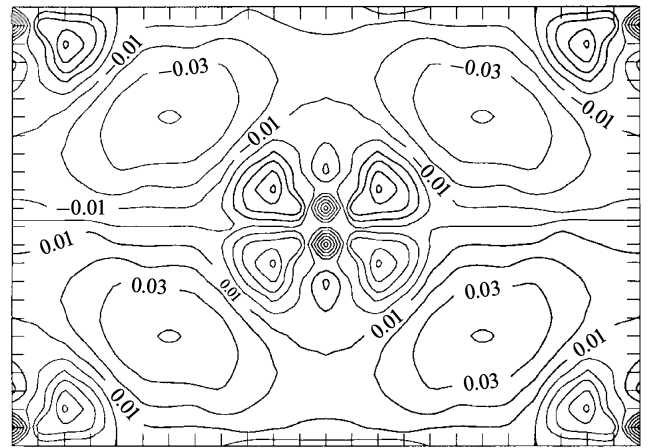


**Figure 5.** Self-consistent change in the charge density for a longitudinal optical mode with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in Nb, deduced within the linear framework method. The dependence of the radical component for  $l = 2$  and  $m = 0$  is shown.

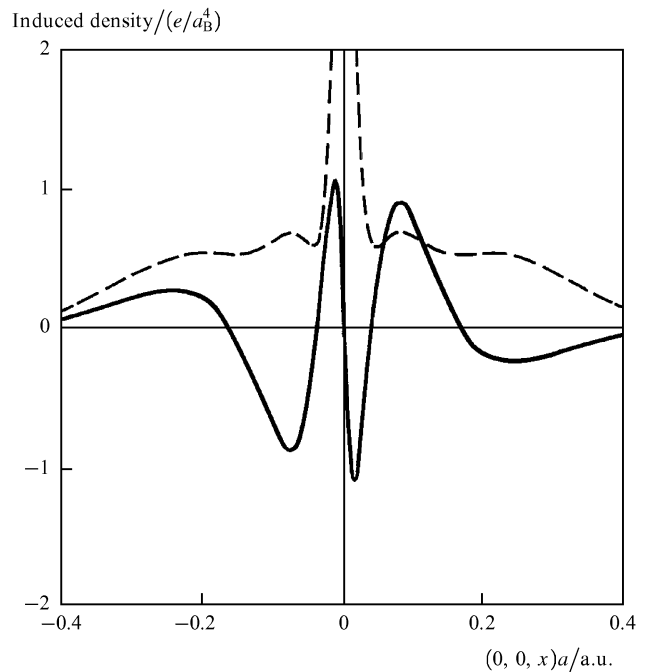


**Figure 6.** Calculated distribution of the charge density gradient for Nb in a (110) plane.

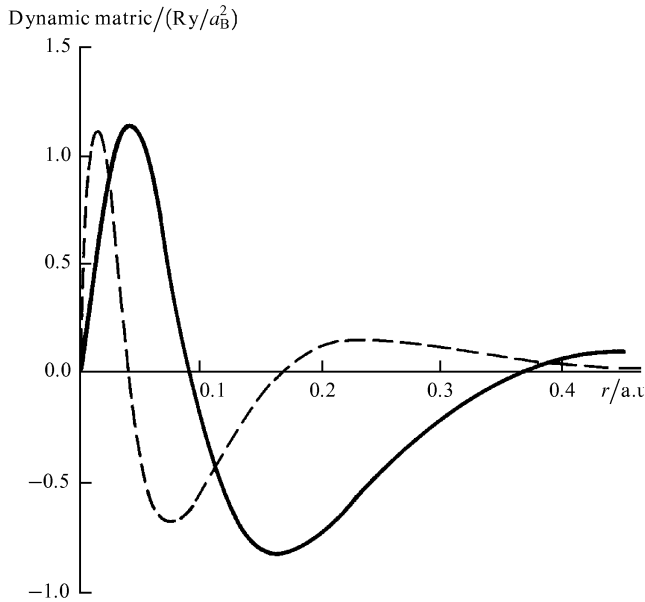
density in the core also gives rise to oscillations of the change in the density, because  $\delta\rho = \nabla \times \rho$  applies in this region. This is evident from Fig. 6, which gives the distribution of the density gradient in a (110) plane. However, oscillations of this kind are subtracted from the induced densities shown in Figs 2–5, i.e. only the soft contribution to the linear response is shown. Fig. 7 demonstrates the pattern of the behaviour of the soft contribution to a change in the density for a phonon with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in a (110) plane, which also reveals oscillations of the dipole nature, but of much smaller amplitude. A direct comparison of these oscillations with those of the valence density is made in Fig. 8, which demonstrates that the spatial positions of the peaks of



**Figure 7.** Calculated soft contribution to the density, induced by the formation of a longitudinal phonon mode with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in Nb. The (110) plane is shown.



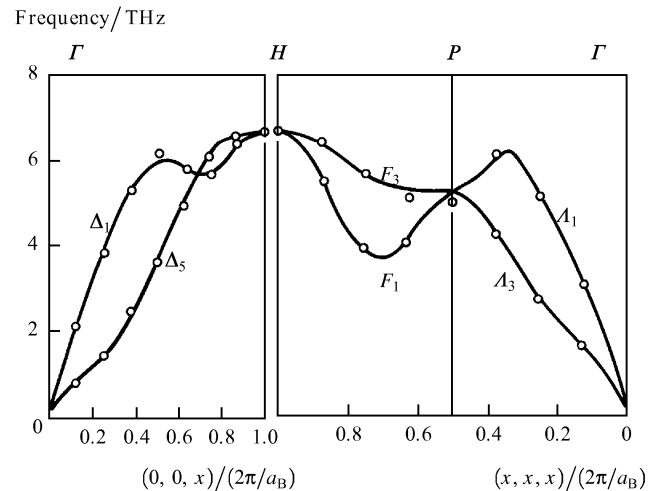
**Figure 8.** Comparison of the oscillations of the valence density and of the density induced by a longitudinal phonon mode with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in Nb.



**Figure 9.** Contribution to the dynamic matrix made by the dipole oscillations in the region of an atomic core, induced by a longitudinal phonon mode with  $\mathbf{q} = (0, 0, \frac{1}{2})$  in Nb.

both functions coincide and, consequently the oscillations of the soft contribution to the linear response are also due to the shell structure of the atomic cores. At first sight, it seems that the force acting on a nucleus is established inside the core region and is then screened by the distribution of the valence charge. However, we shall now show that this is incorrect. Fig. 9 shows that the contribution to the dynamic matrix, (within the framework of the Hellman–Feynman theorem) can be represented in the form of a force which is a function of the distance to a nucleus (continuous curve). The dashed curve in this figure is the induced density distribution. We can see (and this follows also from Fig. 6) that within the core the nucleus is inside nesting dipoles and the contributions of these dipoles fully compensate one another. The first peak in the dependence of the force established at a distance of about 0.05 a.u. corresponds to the innermost induced dipole. The amplitude of this peak is an order of magnitude higher than the real value of the dynamic matrix. The force is then screened by the second inner dipole and it can be seen to vanish near  $r = 0.1$  a.u. On emergence from the core region the contribution to the dynamic matrix decreases continuously and at about 0.4 a.u. it almost reaches the expected value. We can see that there is a sum rule according to which the combined contribution to the force made by the core region is negligible. This result helps us to understand the great sensitivity of the expression for the dynamic matrix derived within the framework of the Hellman–Feynman theorem for a transition metal. Since this force is purely electrostatic, acts on a nucleus, and is related to a change in the density around a nucleus, the contribution made by the oscillations inside the core (which is not eliminated by introduction of a pseudopotential) should be enormous and it should be calculated very accurately. Any slight error in the determination of  $\delta\rho$  results in a major error in the dynamic matrix.

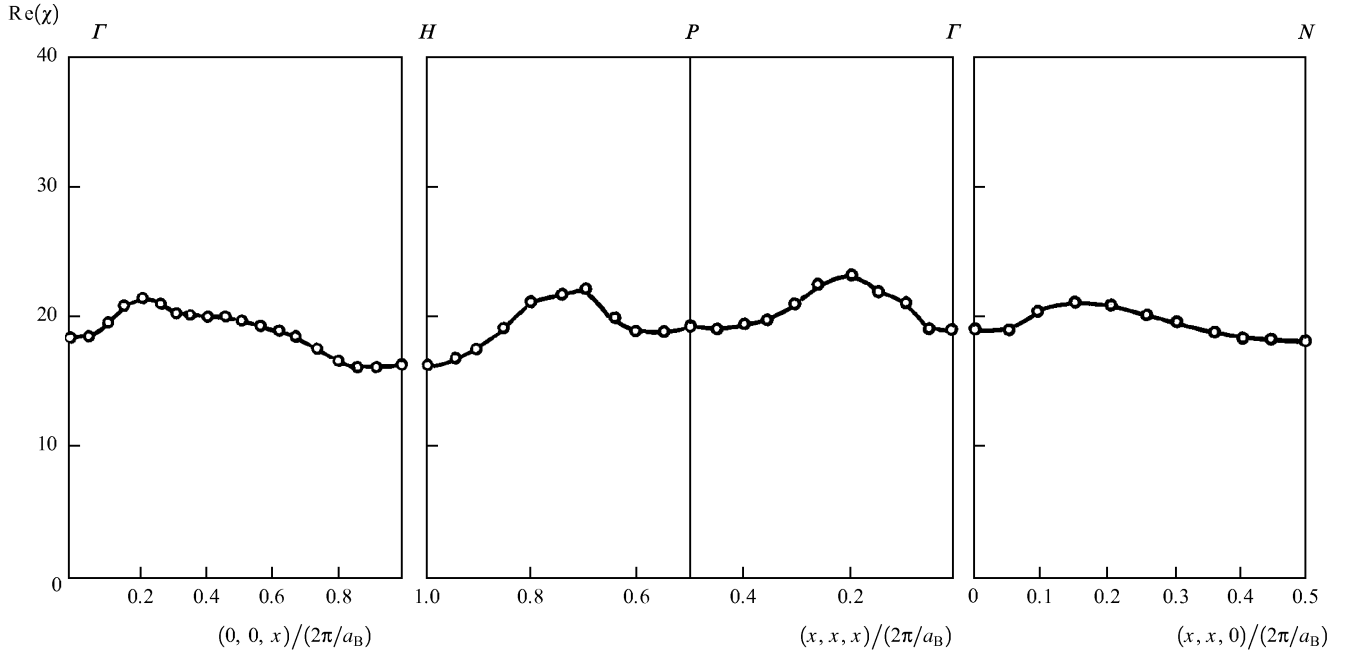
We shall now discuss the results of calculations of the phonon spectra. We shall begin with Nb. The dispersion



**Figure 10.** Phonon dispersion curves for Nb: the continuous curves are the experimental data obtained by inelastic neutron diffraction; the points are the values calculated by the linear response method.

curves of this metal have been calculated along the  $\Gamma$ – $H$ ,  $\Gamma$ – $P$ , and  $P$ – $H$  directions in the Brillouin zone, which correspond to the  $[00x]$  and  $[xxx]$  directions in the reciprocal space. The lattice parameter is selected to be 6.15 a.u., as predicted theoretically by calculations based on the total energy method. (The experimental lattice parameter is 6.22 a.u.) The radius of an MT sphere is selected to be 2.72 a.u. An exchange–correlation potential from Ref. [44] is used. The valence states are represented by the basis set  $s, p, d$ , with  $\kappa_1^2 = 0.55$  Ry and  $\kappa_2^2 = 1.5$  Ry. In addition to the real valence states, the half-core states  $4s$  and  $4p$  also remain of the valence kind (in some energy windows) when calculated by the linear response method. The corresponding energies are  $\kappa_{4s}^2 = -3$  Ry and  $\kappa_{4p}^2 = -1.5$  Ry. Fig. 10 gives, for the sake of comparison, the calculated dispersion dependences (points) and the experimental results of Ref. [49] (continuous curves). We can see that along all the directions the agreement between the theory and experiment is very good and the error does not exceed 3.4%. In particular, the theory reproduces satisfactorily the anomalous behaviour of the dispersion curve of a longitudinal mode in the range of the wave vectors  $\mathbf{q}$  near the point  $(0, 0, 0.7)$  and near the point  $(0.7, 0.7, 0.7)$ , and also of a transverse mode along the  $\Gamma$ – $H$  direction if  $\mathbf{q}$  is low. All the curves behave correctly at long wavelengths and this means that the acoustic sum rule is obeyed. This correct behaviour of the curves in the long-wavelength limit also makes it possible to draw the conclusion that the calculated velocities of propagation of longitudinal and transverse acoustic waves along various directions are close to their experimental values. Moreover, this means that the theory describes well also the elastic constants of this material.

We shall analyse the nature of the anomalies of the longitudinal modes near the points  $(0.7, 0.7, 0.7)$  and  $(0, 0, 0.7)$ . We shall do this by considering the behaviour of the band structure factor in the crystal polarisability described by expression (3.32). The dispersion of this function along the high-symmetry directions is shown in Fig. 11. (Only the contribution of the intraband transitions is shown: at  $\mathbf{q}$  approaching zero, this contribution becomes the density of states in matter.) The dependence in question has a small



**Figure 11.** Calculated band contribution to the real part of the polarisability. Only the intraband transitions are considered.

singularity near the point  $(0.7, 0.7, 0.7)$  related to nesting of the Fermi surface for this wave vector and usually employed to account for the anomalous behaviour of this longitudinal mode. We can also see that the function under consideration has a number of singularities near which there are no significant anomalies; also this function has *no singularities* at the point where the anomaly of the longitudinal mode  $\Delta_1$  is observed. This anomaly was elucidated by calculating the distribution patterns of the induced densities for the wave vectors  $\mathbf{q} = (0, 0, x)$ , which are plotted in Fig. 12 for a (110) plane at  $x = 0.9, 0.8, 0.7$ , and  $0.6$  (from top to bottom). It is evident from these results that at  $x = 0.9$  and  $0.8$  a nucleus is inside a quadrupole charge induced in the interstitial region and this charge disappears on passing through the region of the anomaly ( $x = 0.7$  and  $0.6$ ). Consequently, the force acting on the nucleus changes there abruptly. This behaviour of the density should be attributed to the nonsmooth behaviour of a matrix element of the electron–phonon interaction, which has a singularity near the point in question. We can summarise the results by concluding that the anomalies of the vibrational modes of transition metals are most likely related to a very fine interplay which establishes the distribution of the induced electron charge, as reflected in the electrostatic contribution to the dynamic matrix. It cannot be explained by the simple nesting theory.

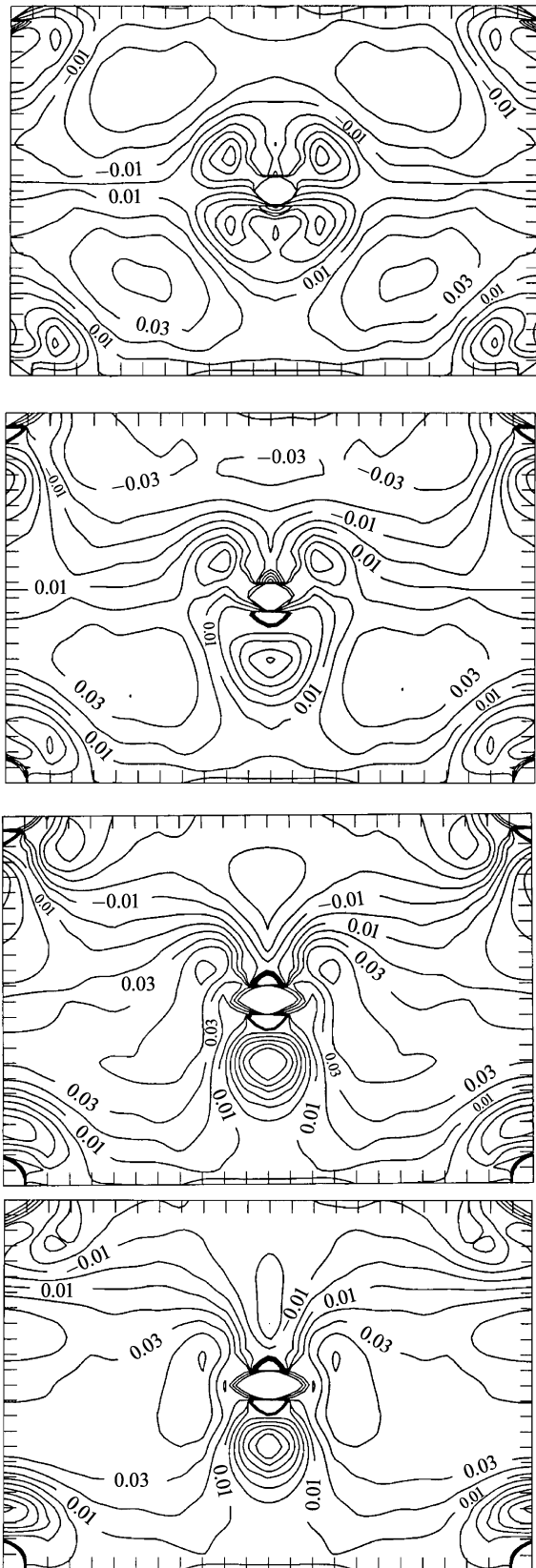
In particular, a dip of the phonon dispersion curve near the momentum  $\mathbf{q} = (0.7, 0.7, 0.7)$  is observed for practically all the bcc metals, both simple and transition. This dip is most likely related to the behaviour of a structure factor of the type

$$\sum_{\mathbf{R}} \exp(i\mathbf{q} \cdot \mathbf{R}) \nabla_{\mu} \nabla_{\mu'} \frac{1}{R},$$

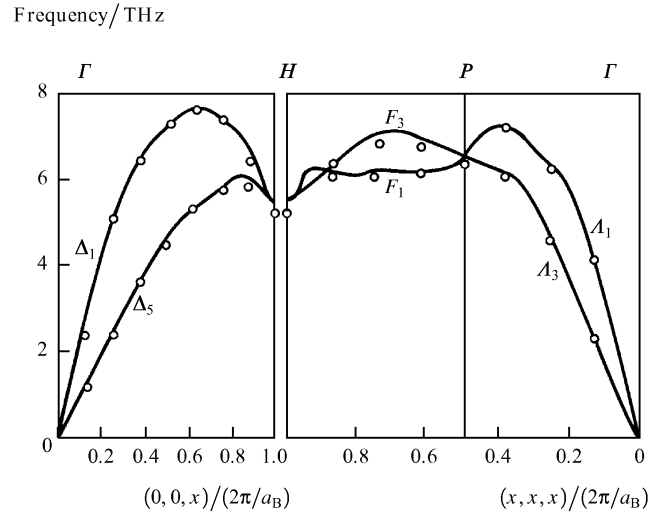
which appears in calculations of the band structure and phonon spectra. For bcc metals the dependence of this factor has a strong dip near the momentum  $\mathbf{q} = (0.7, 0.7, 0.7)$ .

We shall conclude with a discussion of the results of calculations of the phonon spectrum of Mo. As in the case of Nb, the dispersion curves of this metal were calculated along the  $\Gamma$ – $H$ ,  $\Gamma$ – $P$ , and  $P$ – $H$  directions in the Brillouin zone. The lattice parameter was selected to be  $5.89$  a.u., as predicted theoretically by calculations based on the total energy method. (The experimental lattice parameter is  $5.95$  a.u.) The radius of an MT sphere was taken to be  $2.55$  a.u. The exchange–correlation potential was taken from Ref. [44]. The valence states were represented by a basis set  $s$ ,  $p$ , and  $d$  with  $\kappa_1^2 = 0.51$  Ry and  $\kappa_2^2 = 1.5$  Ry. In addition to the real valence states, the half-core states  $4s$  and  $4p$  were also assumed to be of the valence type (in separate energy windows) in the linear response calculations. The corresponding energies were taken to be  $\kappa_{4s}^2 = -3.3$  Ry and  $\kappa_{4p}^2 = -1.6$  Ry. A comparison of the calculated dispersion curves (points) with the experimental results [49] (continuous curves) is made in Fig. 13. As in the case of Nb, the agreement between the theory and experiment [49] is very good along all the directions and the error does not exceed  $4.1\%$ . In particular, the theory reproduces well the familiar anomalous behaviour of the dispersion curves of the longitudinal and transverse modes in the range of the wave vectors  $\mathbf{q}$  near the point  $(0, 0, 1)$ . All the curves behave in the expected manner at long wavelengths, which means that the calculated velocities of the longitudinal and transverse waves travelling along various directions and also the elastic constants of this metal are close to their experimental values.

**Acknowledgements.** We are grateful to the Russian Fund for Fundamental Research and to the International Science Foundation (Soros Foundation) for financial support. One of us (S Yu S) is grateful to O K Andersen for valuable discussions and hospitality during his visit to the Max Planck Institute at Stuttgart, when a large part of the reported work was carried out.



**Figure 12.** Charts of the densities induced by vibrations of atoms near a longitudinal mode  $(0, 0, x)$  anomaly at  $x = 0.7$ . The changes in the densities for  $x = 0.9, 0.8, 0.7,$  and  $0.6$  (from top to bottom) are shown.



**Figure 13.** Phonon dispersion curves for Mo: the continuous curves are the experimental data obtained by inelastic neutron diffraction; the points are the values calculated by the linear response method.

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