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The generalised pseudoatom potential in solids: relation to screening and lattice dynamics

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Abstract. The change in potential when an ion is displaced is shown to have pseudoatom qualities i.e. the total potential can be divided exactly into atomic-like potentials which move rigidly with the ions to first order in the displacement. An additional non-rigid potential arises under the ionic distortion. Relations between the pseudoatom potential and the pseudoatom charge density of Ball, which is mathematically similar, are pointed out. Some previous approximations to the dielectric screening are shown to be inconsistent; it is suggested that, for transition metal systems, a consistent treatment of the pseudoatom potential may be necessary to achieve further progress. This pseudoatom behaviour of the potential will have consequences for lattice dynamics and the electron–phonon interaction.

1. Introduction

In the adiabatic approximation, electrons in a molecule or solid respond instantaneously to the motion of the ions. When a single ion is displaced from its equilibrium position, a change in the electronic charge density results. In the early (weak) pseudopotential theory, the concept of a 'pseudoatom' was developed (Ziman 1964). An ion, together with a rigidly attached charge distortion and accompanying potential, could be treated as a single entity. This pseudoatom could be used to construct two-body potentials, and hence to calculate dynamic properties such as phonon spectra and liquid-metal structure factors. This simplification unfortunately survives only to lowest order in the pseudopotential: higher-order terms introduce N-body interactions, where $N \geqslant 3$, and the pseudoatom concept loses its usefulness.

Ball (1975) made the important observation that a pseudoatom concept for the charge density of any solid can be retained, to first order in the ionic displacements. His main result, that the total electronic charge density can be decomposed uniquely into 'pseudoatom'-like contributions which move rigidly with the nuclei, is a conceptual breakthrough which facilitates understanding of the processes that are involved and suggests the construction of reasonable approximation schemes, even if it does not simplify exact calculations. This new pseudoatom also contains a non-rigid charge density distortion and, we emphasise, is valid only to first order in the nuclear displacements.

We develop a similar 'decomposition theorem' for the total one-electron potential. We find that, to first order in nuclear displacements, the potential decomposes straightforwardly into components which move rigidly with the nuclei. This 'rigid-atom-like'

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potential is supplemented by a non-rigid potential, mathematically similar to the corresponding charge distortion. This separation of the potential is qualitatively different for simple metals, transition metals and compounds, covalent semiconductors, and insulators. Our primary interest here is in transition metal systems, where poorly understood peculiarities in electronic screening are known to produce phonon anomalies. These anomalies have been strongly correlated with high-temperature superconductivity and reflect actual or incipient lattice instabilities. The potentials we describe ultimately become the basis of many electronically-driven phase transitions. In particular, we are interested in structural instabilities and the superconducting transition.

The plan of the paper is as follows: after presenting the theorem in § 2, we discuss in § 3 the relationship between the pseudoatom potential and the pseudoatom charge density. A reformulation of the screening problem in crystals in terms of the pseudoatom potential is presented in § 4, where two widely used approximations are reviewed. Section 5 contains a short discussion of the role of the pseudoatom potential in lattice dynamics.

2. The decomposition theorem

The many-body problem of N interacting electrons in a region of external potential v_{ext} is usually reduced to a one-electron problem involving an effective potential v. In this 'mean-field approximation' the potential $v(r, R)$ is a parametric function of the nuclear coordinates $\{\boldsymbol{R}_j\} \equiv R$. The change, $\boldsymbol{\delta}_j v \equiv \partial v(r; R)/\partial \boldsymbol{R}_j$, of the potential per unit displacement of nucleus j is a vector field which can be decomposed into its irrotational and purely rotational parts:

$$\boldsymbol{\delta}_j v(\boldsymbol{r}, R^0) = -\nabla u_j(\boldsymbol{r} - \boldsymbol{R}_j^0) + \nabla \times \boldsymbol{\omega}_j(\boldsymbol{r} - \boldsymbol{R}_j^0), \tag{1}$$

where the equilibrium position of atom j is denoted R_j^0. In this equation, u_j may be interpreted as a potential which moves rigidly with the nucleus and is defined only to within a constant. The potential $\boldsymbol{\omega}_j$ is undetermined to within the gradient of an arbitrary scalar function and describes non-rigid potential distortions around $\boldsymbol{R}_j^0$.

It is reasonable to consider u_j and $\boldsymbol{\omega}_j$ to be defined (uniquely) through the Helmholtz construction

$$u_j(\boldsymbol{r} - \boldsymbol{R}_j^0) = -(1/4\pi) \int [\nabla . \boldsymbol{\delta}_j v(\boldsymbol{r}', R^0)/|\boldsymbol{r} - \boldsymbol{r}'|]\, \mathrm{d}^3 r' \tag{2a}$$

$$\boldsymbol{\omega}_j(\boldsymbol{r} - \boldsymbol{R}_j^0) = -(1/4\pi) \int [\nabla \times \boldsymbol{\delta}_j v(\boldsymbol{r}', R^0)/|\boldsymbol{r} - \boldsymbol{r}'|]\, \mathrm{d}^3 r' \tag{2b}$$

although only ∇u_j and $\nabla \times \boldsymbol{\omega}_j$ are physical quantities. Of course $\boldsymbol{\delta}_j v$, which we refer to as the pseudoatom potential, is determined from the electron dynamics; equations (2a) and (2b) are simply more explicit forms of equation (1) which eliminate the arbitrariness in u_j and $\boldsymbol{\omega}_j$. With these definitions it follows that u_j and $\boldsymbol{\omega}_j$ vanish at large distances. Some mathematical details relating to equations (2a) and (2b) and to the manipulations which follow, are given in the Appendix.

Translational invariance implies that, for a rigid displacement of the system by an amount $\boldsymbol{\epsilon}$,

$$v(\boldsymbol{r} + \boldsymbol{\epsilon}, R^0 + \epsilon) = v(\boldsymbol{r}, R^0). \tag{3}$$

Expanding in powers of $|\boldsymbol{\epsilon}|$, we have

$$v(r+\boldsymbol{\epsilon}, R^0+\epsilon) = v(r, R^0) + \boldsymbol{\epsilon}.\left[\nabla v(r, R^0) + \sum_l \delta_l v(r, R^0)\right] + \theta(\epsilon^2) \tag{4}$$

and upon using equation (1) and (3), the first-order term gives

$$\nabla\left[v(\boldsymbol{r}, R^0) - \sum_j u_j(\boldsymbol{r}-\boldsymbol{R}_j^0)\right] + \nabla\times\left[\sum_j \omega_j(\boldsymbol{r}-\boldsymbol{R}_j^0)\right] = 0. \tag{5}$$

Since the first term is irrotational and the second is purely rotational, they are each identically zero. Thus we have

$$v(r, R^0) = \sum_j u_j(\boldsymbol{r}-\boldsymbol{R}_j^0) \tag{6}$$

up to a constant, which can be made zero by a trivial shift of the scale of v, and

$$\sum_j \omega_j(\boldsymbol{r}-\boldsymbol{R}_j^0) = \nabla f(r). \tag{7}$$

Accepting equation (2b) as the definition of ω_j requires in addition that the scalar function f be harmonic:

$$\nabla^2 f = 0. \tag{8}$$

Gathering these results together, we find that the total potential v can be written, to first order in $\boldsymbol{\delta R}_j = \boldsymbol{R}_j - \boldsymbol{R}_j^0$,

$$v(r, R) = \sum_j \{u_j(r-\boldsymbol{R}_j) + \delta\boldsymbol{R}_j.[\nabla\times\omega_j(r-\boldsymbol{R}_j^0)]\} \tag{9}$$

In making the change $\boldsymbol{R}_j^0 \rightarrow \boldsymbol{R}_j$ in the argument of u_j, we have changed only second- and higher-order corrections, which do not concern us here.

Equation (9) holds for a collection of nuclei at arbitrary positions $\boldsymbol{R}_j^0$. Although R^0 will ordinarily be an equilibrium configuration in applications, no such requirement has been used in the derivation. There are two important consequences: firstly, the total potential decomposes into rigid-atom potentials u_j given by equation (2a), and secondly, an atomic displacement gives rise to two potentials with distinctive characters. Previous attempts to divide the potential into atomic-like contributions have been plagued by the arbitrariness believed to be inherent in any such procedure. The unique procedure given above constitutes the proper decomposition for calculating electronic transition rates, phonon spectra and any other quantities involving only first-order lattice displacements. The distinctive characters of u_j and ω_j will be studied in subsequent sections.

One important function of the relation (6) may be to provide a constraint on models of u_j. For many crystalline systems it is now quite possible to solve for the self-consistent potentials $v(\boldsymbol{r}, R^0)$. Calculating u_j or $\delta_j v$ is a much more difficult problem, involving the computation of the full dielectric matrix or the self-consistent treatment of a large cluster with a single atom displaced from the reference configuration. Hence the introduction of models of, or approximations to, u_j becomes a reasonable approach. From equation (6) it follows that, for a crystal, u_j can be expanded in lattice harmonics consistent with the point group of atom j. (Similarly ω_j, or $\nabla\times\omega_j$, can be expanded in the corresponding symmetrised vector harmonics.) Equivalent ions in a crystal will produce identical pseudoatom potentials. On the other hand, identical nuclei at inequivalent sites or in the amorphous state will be associated with different pseudoatom potentials. The new and important restriction, is, of course, that $\sum_j u_j(\boldsymbol{r} - \boldsymbol{R}_j^0)$ must actually be a good approximation to $v(\boldsymbol{r}, R^0)$, and that $\sum_j \boldsymbol{\nabla} \times \boldsymbol{\omega}_j(\boldsymbol{r} - \boldsymbol{R}_l^0)$ must vanish. We show in § 3 that u_j and $\boldsymbol{\omega}_j$ are not independent, since they arise from the same physical screening mechanisms. In addition, we discuss some of the approximations for the pseudoatom potential which have been used previously.

3. Relationship of the potential to the charge density

We discuss the connection between the change $\boldsymbol{\delta}_j n = \partial n(\boldsymbol{r}, R)/\partial \boldsymbol{R}_j$ in the charge density $n(r, R)$ where atom j is displaced and the corresponding pseudoatom potential $\boldsymbol{\delta}_j v$. Ball's original result is that the electron charge density can be expressed as

$$n(\boldsymbol{r}, R) = \sum_j \{\rho_j(\boldsymbol{r} - \boldsymbol{R}_j) + \boldsymbol{\delta R}_j . [\boldsymbol{\nabla} \times \boldsymbol{B}(\boldsymbol{r} - \boldsymbol{R}_j^0)]\}, \tag{10}$$

valid to first order in the nuclear displacement. We do *not* include the nuclear (or ionic) charge in ρ_j. Following the density functional formalism, we begin with the relation (Hohenberg and Kohn 1964, Kohn and Sham 1965)

$$v(\boldsymbol{r}) = v_{\text{ext}}(\boldsymbol{r}) + \int v_{\text{c}}(\boldsymbol{r} - \boldsymbol{r}')n(\boldsymbol{r}')\, \mathrm{d}^3 r' + \mu_{\text{xc}}(\boldsymbol{r}). \tag{11}$$

The dependence on nuclear coordinates will not be denoted explicitly unless necessary. The exchange–correlation potential μ_{xc} is the functional derivative, $\delta E_{\text{xc}}[n]/\delta n(\boldsymbol{r})$, of E_{xc}, the exchange–correlation contribution to the total energy, and v_{c} denotes the Coulomb interaction. We can write

$$\boldsymbol{\delta}_j v(\boldsymbol{r}) = \boldsymbol{\delta}_j v_{\text{ext}}(\boldsymbol{r}) + \int [v_{\text{c}}(\boldsymbol{r} - \boldsymbol{r}') + v_{\text{xc}}(\boldsymbol{r}, \boldsymbol{r}')]\boldsymbol{\delta}_j n(\boldsymbol{r}')\, \mathrm{d}^3 r' \tag{12}$$

where we have defined an exchange-correlation *interaction* v_{xc} (Pickett 1975) by

$$v_{\text{xc}}(\boldsymbol{r}, \boldsymbol{r}') \equiv \delta\mu_{\text{xc}}(\boldsymbol{r})/\delta n(\boldsymbol{r}') = \delta^2 E_{\text{xc}}/\delta n(\boldsymbol{r})\delta n(\boldsymbol{r}'). \tag{13}$$

The contribution from the external potential is rigid:

$$\boldsymbol{\delta}_j v_{\text{ext}}(\boldsymbol{r}) = \boldsymbol{\nabla} v_{\text{ext}}^j(\boldsymbol{r} - \boldsymbol{R}_j^0). \tag{14}$$

Rigorously, v_{ext}^j should be the nuclear potential $-Ze/|\boldsymbol{r} - \boldsymbol{R}_j|$, but in practice, the difficulties in screening the bare nucleus require that the core electrons be removed from the problem and replaced by an effective pseudopotential.

Defining the screening part of the rigid potential

$$\tilde{u}_j \equiv u_j - v_{\text{ext}}^j, \tag{15}$$

substitution of equation (12) into equations (2a) and (2b) gives, after some manipulation, a Coulomb contribution

$$\begin{Bmatrix} \tilde{u}_j(\boldsymbol{r}) \\ \boldsymbol{\omega}_j(\boldsymbol{r}) \end{Bmatrix} = \int \mathrm{d}^3 r'\, v_{\text{c}}(\boldsymbol{r} - \boldsymbol{r}') \begin{Bmatrix} \rho_j(\boldsymbol{r}') \\ \boldsymbol{B}_j(\boldsymbol{r}') \end{Bmatrix}, \tag{16a}$$

and an exchange-correlation contribution

$$\begin{Bmatrix} \tilde{u}_j(\boldsymbol{r}) \\ \boldsymbol{\omega}_j(\boldsymbol{r}) \end{Bmatrix} = -\frac{1}{4\pi} \int \frac{\mathrm{d}^3 r'}{|\boldsymbol{r} - \boldsymbol{r}'|} \int \mathrm{d}^3 r'' \boldsymbol{\nabla}_{r'} v_{\text{xc}}(\boldsymbol{r}', \boldsymbol{r}'') \begin{Bmatrix} \cdot \\ \times \end{Bmatrix} [-\boldsymbol{\nabla}\rho_j(\boldsymbol{r}'') + \boldsymbol{\nabla} \times \boldsymbol{B}_j(\boldsymbol{r}'')]. \tag{17}$$

The Coulomb interaction preserves the 'rotationality' of the fields, so that the rigid charge produces a rigid potential and the rotational charge produces a rotational potential. The exchange–correlation interaction evidently produces complicated cross terms arising from its non-diagonality $[v_{xc}(\boldsymbol{r},\boldsymbol{r}'') \neq v_{xc}(\boldsymbol{r}-\boldsymbol{r}')]$.

4. Screening of crystalline solids

The decomposition of the potential that was achieved in §2 can be applied to study the screening of perturbations arising from lattice displacements and finally to give a better understanding of the restrictions imposed by the various approximations which have been used previously. We begin with a relation which defines the dielectric function ϵ:

$$\begin{aligned}\delta_j v(\boldsymbol{r}) &= \int \mathrm{d}^3 r' \epsilon^{-1}(\boldsymbol{r},\boldsymbol{r}')\delta_j v_{\mathrm{ext}}(\boldsymbol{r}') \\ &= -\int \mathrm{d}^3 r' \epsilon^{-1}(\boldsymbol{r},\boldsymbol{r}')\nabla v^j_{\mathrm{ext}}(\boldsymbol{r}-\boldsymbol{R}^0_j).\end{aligned} \tag{18}$$

We also introduce the polarisability χ which describes the density response to an external perturbation, defined by

$$\delta_j n(\boldsymbol{r}) = \int \mathrm{d}^3 r' \chi(\boldsymbol{r},\boldsymbol{r}')\delta_j v_{\mathrm{ext}}(\boldsymbol{r}') \tag{19}$$

and using equation (12), we find that ϵ^{-1} is given by

$$\epsilon^{-1}(\boldsymbol{r},\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') + \int V(\boldsymbol{r},\boldsymbol{r}'')\chi(\boldsymbol{r}'',\boldsymbol{r}')\,\mathrm{d}^3 r'' \tag{20}$$

where

$$V(\boldsymbol{r},\boldsymbol{r}') = v_c(\boldsymbol{r}-\boldsymbol{r}') + v_{xc}(\boldsymbol{r},\boldsymbol{r}') \tag{21}$$

is the total electron–electron interaction. This relation in fact defines the electron dielectric function (Ballentine 1967, Kleinman 1967, 1968, Kugler 1975, Pickett 1975). The test-charge dielectric function is defined similarly but with v_{xc} replaced by zero, since a test charge feels no exchange–correlation interaction; exchange–correlation corrections are of course still present in χ. We show that the electron dielectric function enters naturally into lattice dynamical expressions. All of the above results hold for an arbitrary configuration of atoms. Now we restrict ourselves to crystalline solids.

Defining the Fourier transforms appropriate for a crystal

$$v^j_{\mathrm{ext}}(\boldsymbol{r}) = \sum_{\boldsymbol{Q},\boldsymbol{G}} v^j_{\mathrm{ext}}(\boldsymbol{Q}+\boldsymbol{G}) \exp[\mathrm{i}(\boldsymbol{Q}+\boldsymbol{G}).\boldsymbol{r}] \tag{22a}$$

$$\epsilon^{-1}(\boldsymbol{r},\boldsymbol{r}') = \sum_{\boldsymbol{QGG}'} \exp[\mathrm{i}(\boldsymbol{Q}+\boldsymbol{G}).\boldsymbol{r}]\epsilon(\boldsymbol{Q}+\boldsymbol{G},\boldsymbol{Q}+\boldsymbol{G}')\exp[-\mathrm{i}(\boldsymbol{Q}+\boldsymbol{G}').\boldsymbol{r}'] \tag{22b}$$

where $\boldsymbol{Q}$ is restricted to the first Brillouin zone and $\boldsymbol{G}$, $\boldsymbol{G}'$ are reciprocal lattice vectors, we insert equation (18) into equations (2a) and (2b) to find

$$\begin{aligned}\begin{Bmatrix} u_j(\boldsymbol{r}-\boldsymbol{R}^0_j) \\ \omega_j(\boldsymbol{r}-\boldsymbol{R}^0_j)\end{Bmatrix} &= \frac{1}{4\pi}\sum_{\boldsymbol{QGG}'} v_c(\boldsymbol{Q}+\boldsymbol{G})\epsilon^{-1}(\boldsymbol{Q}+\boldsymbol{G},\boldsymbol{Q}+\boldsymbol{G}')v^j_{\mathrm{ext}}(\boldsymbol{Q}+\boldsymbol{G}') \\ &\quad\times \begin{Bmatrix} (\boldsymbol{Q}+\boldsymbol{G}).(\boldsymbol{Q}+\boldsymbol{G}') \\ (\boldsymbol{Q}+\boldsymbol{G})\times(\boldsymbol{Q}+\boldsymbol{G}')\end{Bmatrix} \exp(\mathrm{i}(\boldsymbol{Q}+\boldsymbol{G})\boldsymbol{r}) \exp(\mathrm{i}\boldsymbol{Q}.\boldsymbol{R}^0_j).\end{aligned} \tag{23}$$

Since the cross product vanishes if $\boldsymbol{G} = \boldsymbol{G}'$, ω_j is seen to arise solely from the off-diagonal ($\boldsymbol{G} \neq \boldsymbol{G}'$) screening. There are contributions to u_j from both diagonal and off-diagonal screening.

In simple s–p metals a common practice is to use the (diagonal) electron-gas dielectric function to screen the bare electron–ion pseudopotential. In this approximation $\epsilon(\boldsymbol{r}, \boldsymbol{r}') = \epsilon(\boldsymbol{r} - \boldsymbol{r}')$ and ω_j is zero. This procedure is consistent to first order in the pseudopotential and gives the traditional pseudoatom again. To higher order in the pseudopotential, which may have to be considered in this approach (Bertoni *et al* 1974), the diagonal elements of ϵ are altered. In addition, the off-diagonal elements become non-zero, giving rise to a potential deformation ω_j, and perturbation theory in the pseudopotential rapidly becomes complicated.

Where the pseudopotential $v_{\mathrm{ext}}^{\mathrm{ps}}$ is weak, it has a linear relationship with the total potential v and ϵ^{-1}:

$$v(\boldsymbol{r}) = \int \mathrm{d}^3 r' \epsilon^{-1}(\boldsymbol{r} - \boldsymbol{r}') v_{\mathrm{ext}}^{\mathrm{ps}}(\boldsymbol{r}'). \tag{24}$$

Since the dielectric function ϵ is a linear response function, this equation does not hold for strong potentials. Instead we have the relation (18), as for small displacements, $\delta_j v_{\mathrm{ext}}$ is small. There does however exist a generalisation of equation (24) to arbitrary potentials. If equation (23) is written in real-space form

$$\begin{Bmatrix} u_j(\boldsymbol{r} - \boldsymbol{R}_j^0) \\ \omega_j(\boldsymbol{r} - \boldsymbol{R}_j^0) \end{Bmatrix} = -\frac{1}{4\pi} \iint \frac{\mathrm{d}^3 r' \mathrm{d}^3 r''}{|\boldsymbol{r} - \boldsymbol{r}'|} \boldsymbol{\nabla}_{r'} \begin{Bmatrix} \cdot \\ \times \end{Bmatrix} \epsilon^{-1}(\boldsymbol{r}', \boldsymbol{r}'') \boldsymbol{\nabla} v_{\mathrm{ext}}^{j}(\boldsymbol{r}'' - \boldsymbol{R}_j^0) \tag{23$'$}$$

integrating by parts on $\boldsymbol{r}''$ and summing over j gives

$$v(\boldsymbol{r}) = +\frac{1}{4\pi} \int \frac{\mathrm{d}^3 r' \mathrm{d}^3 r''}{|\boldsymbol{r} - \boldsymbol{r}'|} v_{\mathrm{ext}}(\boldsymbol{r}'') [\boldsymbol{\nabla}_{r'} . \boldsymbol{\nabla}_{r''} \epsilon^{-1}(\boldsymbol{r}', \boldsymbol{r}'')]. \tag{24$'$}$$

Thus we have, from (6) and (18) a linear relation between v, v_{ext} and (v_{c} multiplied by derivatives of) ϵ^{-1}. When $\epsilon^{-1}(\boldsymbol{r}, \boldsymbol{r}') = \epsilon^{-1}(\boldsymbol{r} - \boldsymbol{r}')$, we can use $\boldsymbol{\nabla}_{r'} . \boldsymbol{\nabla}_{r''} L^{-1}(\boldsymbol{r}', \boldsymbol{r}'') = -\boldsymbol{\nabla}_{r'}^2 \epsilon^{-1}(\boldsymbol{r}' - \boldsymbol{r}'')$ to integrate over $\boldsymbol{r}'$ by parts to give equations (24). As stated above, ϵ^{-1} is only diagonal for weak potentials, showing that equation (24′) is consistent with, and indeed is, a generalisation of, equation (24). Equation (24) is, however, valid for arbitrary configurations R, as the screening of the pseudopotential is the same for the band structure ($R = R^0$) and for lattice dynamics ($R = R^0 + \delta R$) (Heine *et al* 1966). Equations (18) and (24′) show how these screening processes differ for strong lattice potentials.

For semiconductors and insulators it has long been recognised that the $\boldsymbol{G} \neq \boldsymbol{G}'$ matrix elements must be included consistently. Due to the lack of metallic screening, a diagonal approximation for ϵ will not give acoustic modes with the correct long-wavelength behaviour. The acoustic sum rule (Pick *et al* 1970) gives a necessary condition for the dielectric matrix to have the proper acoustic-mode behaviour. The principle effect of the off-diagonal screening is to set up long-range dipolar potentials (in insulators) or to describe 'bond-bending forces' or 'bond-charge displacements' (in semiconductors) (Sinha 1973). Only recently have proper calculations of the full dielectric matrix for covalently bonded semiconductors become practical (Louie *et al* 1975, Baldereschi and Maschke 1978, Wendel and Martin 1978); study of the longitudinal (u_j) and rotational (ω_j) parts of the pseudoatom potential should provide physical insight into the screening processes.

In transition metals and compounds, the $G \neq G'$ terms in ϵ are known to be important. The complexity of the screening mechanisms in these systems is evident from the great variety of structures in their phonon spectra (for a review see Sinha 1978). Johnson (1974) has given a sum rule which allows an estimation, from the charge density, of the number of reciprocal lattice vectors which contribute to off-diagonal screening. Crude estimates suggest this number to be $\sim 10^3$. One approach for attempting to circumvent these mathematical difficulties is to study (screened) potentials of simplified form. In the remainder of this section we study two such model potentials in the light of the previous developments.

4.1. Rigid-ion and deformable ion models

The difficulty in calculating the full dielectric matrix has led to derivation of model potentials which attempt to account for the full matrix in some approximate way. Typically this reduces to the (inconsistent) modelling of u_j and discarding of ω_j. The rigid muffin-tin (RMT) approximation (Gaspari and Gyorffy 1972, Evans *et al* 1973), in which it is assumed that

$$u_j(r - R_j) = \begin{cases} v_j^{\mathrm{MT}}(|r - R_j|), & |r - R_j| < R^{\mathrm{MT}}, \\ \text{constant}, & \text{otherwise}, \end{cases} \tag{25}$$

probably accounts rather well in transition metals for the diagonal plus off-diagonal screening contributions to u_j inside the muffin-tin radius R^{MT}. Otherwise, it is difficult to understand the rather impressive successes (Butler 1977, Papaconstantopoulos *et al* 1977) of the model. A screened Coulomb tail (Sinha and Harmon 1976), proposed to account for the non-neutrality of the muffin-tin region, may contain the main corrections to u_j outside the muffin-tin for transition metals. It has apparently never been argued, let alone proven, that contributions to the scattering of electrons from ω_j are negligible. It would appear likely that these corrections are not negligible, and that developments in the theory await a consistent modelling of the potential deformation ω_j. Without going into detail, we suggest that these corrections are even more important in transition metal compounds than in the transition elements themselves.

The RMTA discussed above is just one form of the more general rigid-ion (RI) (or rigid-atom) potential, a model which has also been used extensively in tight-binding calculations. In general, a rigid-ion potential has the form of a sum of atomic-like potentials

$$v^{\mathrm{RI}}(r) = \sum_j v_j^{\mathrm{RI}}(r - R_j), \tag{26}$$

leading to the change in potential

$$\delta_v v^{\mathrm{RI}}(r) = -\nabla v_j^{\mathrm{RI}}(r - R_j^0) \tag{27}$$

which completely ignores the possibility of a rotational contribution like ω_j. An alternative form which relaxes this restriction is the deformable-ion (DI) model, defined by

$$v^{\mathrm{DI}}(r, R) = v(r - \xi(r, R), R^0) \tag{28}$$

where $\xi(r)$ is the local dilation of the lattice, defined by

$$\xi(r, R) \equiv \sum_j \sum_Q \delta R_j \exp[\mathrm{i}Q.(r - R_j^0)]. \tag{29}$$

The DI model assumes that the potential deforms smoothly with the lattice. This model is usually only applied to single long-wavelength phonons and its limitations are well known. For the general case, Sham and Ziman (1963) have noted that the definition, equation (29), is not unique and probably not even 'best', although the model seems never to have been carefully tested.

Nevertheless, it can be instructive to consider the predictions of the DI model. For a single displaced nucleus δR_0, taken to be at the origin, we have

$$\xi(\boldsymbol{r}) = \delta R_0 \sum_Q \exp(\mathrm{i}\boldsymbol{Q}.\boldsymbol{r}) = \delta R_0 d(\boldsymbol{r}). \tag{30}$$

The deformation function d depends on the lattice type but has the general properties

$$d(\boldsymbol{R}_j^0) = \delta_{j,0}, \tag{31a}$$

$$d(\boldsymbol{r}) \overset{|\boldsymbol{r}|\to\infty}{\propto} [\sin(Q_\mathrm{D}r) - (Q_\mathrm{D}r)\cos(Q_\mathrm{D}r)]r^{-3} \tag{31b}$$

where the second relation follows from approximating the Brillouin zone by a Debye sphere of radius Q_D. This 'kinematical deformation' of the potential vanishes at all nuclear sites except the origin and decreases in an oscillatory r^{-2} fashion.

From equations (29) and (30) we find

$$\delta_j v^\mathrm{DI}(\boldsymbol{r}) = -\nabla v(\boldsymbol{r}).[\delta_j\xi(\boldsymbol{r})] = -d(\boldsymbol{r})\nabla v(\boldsymbol{r}) \tag{32}$$

for $\boldsymbol{R}_j^0 = 0$. Thus in the DI model the potential deformation is just the gradient modulated by the kinematical deformation d. To see that $\delta_j v^\mathrm{DI}$ contains both rigid and rotational components, it is only necessary to substitute equation (32) into equations (2a), (2b) to obtain

$$\begin{Bmatrix} u_j^\mathrm{DI}(\boldsymbol{r}) \\ \omega_j^\mathrm{DI}(\boldsymbol{r}) \end{Bmatrix} = -\frac{1}{4\pi}\int \frac{\mathrm{d}^3r'}{|\boldsymbol{r}-\boldsymbol{r}'|} \begin{Bmatrix} \nabla.[d(\boldsymbol{r}')\nabla v(\boldsymbol{r}')] \\ \nabla d(\boldsymbol{r}') \times \nabla v(\boldsymbol{r}') \end{Bmatrix}. \tag{33}$$

In this form, it becomes obvious that the rotational contribution ω_j must come from the radial part of ∇d coupling to a non-radial part of ∇v, or vice versa. The non-radial part of ∇d, which is missing from equation (31b) due to the spherical approximation used there, is present in every crystal and is largest for very anisotropic unit cells and low-symmetry sites.

As a final application, we consider a model where a muffin-tin potential (at equilibrium) is considered to deform according to the DI model; this could be called the deformable muffin-tin (DMT) model. The rotational potential becomes (setting the origin at R_j^0)

$$\omega_j^\mathrm{DI}(\boldsymbol{r}) = \sum_{j'} \boldsymbol{X}_{j'}(\boldsymbol{r}) \times \boldsymbol{R}_{j'}^0, \tag{34}$$

with

$$\boldsymbol{X}_{j'}(\boldsymbol{r}) = \frac{1}{4\pi}\int \frac{\mathrm{d}^3r'}{|\boldsymbol{r}-\boldsymbol{r}'|} \frac{d'(\boldsymbol{r}')v_{j'}^{\prime\mathrm{MT}}(\boldsymbol{r}'-\boldsymbol{R}_j^0)}{|\boldsymbol{r}'-\boldsymbol{R}_{j'}^0|^2}(\boldsymbol{r}'-\boldsymbol{R}_{j'}^0) \tag{35}$$

where d', v'^MT denote the radial derivatives. There is no contribution from the muffin-tin at the origin, since the deformation d is (assumed) spherical. The distortion field $\boldsymbol{X}_{j'}$ arises because the spherical potentials centred at $\boldsymbol{R}_{j'} \neq 0$ are distorted by the spherical (about the origin) deformation function d. From the expression for u^DI (equation 33), we see that the rigid-potential change is given by

$$\nabla u_j^\mathrm{DI}(\boldsymbol{r}) = d(\boldsymbol{r})\nabla\left[\sum_{j'} v_{j'}^\mathrm{MT}(\boldsymbol{r}-\boldsymbol{R}_{j'}^0)\right] = d(\boldsymbol{r})\sum_{j'} v_{j'}^{\prime\mathrm{MT}}(\boldsymbol{r}-\boldsymbol{R}_j^0)(\boldsymbol{r}-\boldsymbol{R}_{j'}^0)/|\boldsymbol{r}-\boldsymbol{R}_{j'}^0| \tag{36}$$

This expression is different from the corresponding rigid-ion term in two ways: (i) the rigid shift $v_0'^{\mathrm{MT}}(r)$ arising from the muffin-tin at the origin is modulated by the deformation function d and (ii) additional contributions arise from other muffin-tins. This kinematical deformation, $d \sim r^{-2}$ for large r, probably overestimates the true potential deformation at large distances in metals, since the screening is not taken into account properly.

The use of the DI model has been confined primarily to long-wavelength deformations. In view of the relative successes of the RMT approximation in transition metals, it would be most interesting to know the changes that the DMT model would make. The main difficulty in studying the DMT model is in the evaluation of matrix elements, so simple for RMTs, but complicated for DMTs (see equations (34) and (35)). A formalism developed by Whitfield (1961), in which the Bloch functions are deformed according to equation (29), could simplify the treatment of the potential in a DI approximation.

5. Lattice dynamics and the pseudoatom potential

In view of the formidable problem of screening in transition metal systems, it has recently become necessary to formulate and calculate lattice dynamics in terms of the unknown screened (pseudoatom) potential rather than the known bare (ionic) potential. The pseudoatom potential is then approximated in an appropriate fashion. The relations have so often been presented in a form of limited applicability (generally the RI approximation) that is is worthwhile to present the general relationships.

Within the adiabatic approximation, a rigorous expression for the change in energy of the electronic system $\delta_j E = \partial E(R)/\partial \boldsymbol{R}_j$ when the ion at $\boldsymbol{R}_j$ is moved, is (Sham 1969)

$$\delta_j E = \int [\delta_j v^{\mathrm{ext}}(r)] n(r)\, \mathrm{d}^3 r. \tag{37}$$

The harmonic force constants require the second derivative, of which only the $\boldsymbol{R}_i \neq \boldsymbol{R}_j$ term need be kept. Using equation (19), we can write

$$\begin{aligned} \delta_i \delta_j E &= \int \delta_j v_{\mathrm{ext}}(r) \delta_i n(r)\, \mathrm{d}^3 r, \qquad i \neq j \\ &= \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \delta_j v_{\mathrm{ext}}(r) \chi(r, r') \delta_i v_{\mathrm{ext}}(r'). \end{aligned} \tag{38}$$

Together with the ion–ion Coulomb force constants

$$\delta_i \delta_j U(r) = \tfrac{1}{2} \left[\delta_i \delta_j \sum_{i' \neq j'} \frac{Z_{i'} Z_{j'} e^2}{|\boldsymbol{R}_{i'} - \boldsymbol{R}_{j'}|} \right]_{\mathrm{R}=\mathrm{R}^0}, \tag{39}$$

where Z_j denotes the ionic (or nuclear) charge associated with v^j_{ext}, the dynamics of the lattice in the harmonic approximation are completely determined.

Introducing the susceptibility χ_0 which describes the response of the density to the total potential change

$$\delta_j n(r) = \int \mathrm{d}^3 r' \chi_0(r, r') \delta_j v(r'), \tag{40}$$

which can be written in an abbreviated real-space matrix notation

$$\delta_j n = \chi_0 \delta_j v, \tag{40'}$$

we have from equations (18)–(21) that

$$\chi = \chi_0 \epsilon^{-1} \tag{41}$$

and

$$\epsilon = 1 - V\chi_0. \tag{42}$$

The force constants can be written (for $i \neq j$)

$$\Phi_{ij} = \delta_i\delta_j U + \delta_i\delta_j E = (\delta_i\delta_j U - \delta_i v\chi_0 V\chi_0\delta_j v) + \delta_i v\chi_0\delta_j v. \tag{43}$$

This regrouping was advocated by Pickett and Gyorffy (1976) to study phonon spectra, and especially anomalies, in transition metal systems. The 'neutral-object' force constants (in brackets) are short range, as was demonstrated explicitly by Allen (1978), and are not reponsible for the phonon anomalies. The 'band-structure force constant', Φ^{BS}, as the last term in equation (42) has been referred to, has been shown to give rise to long-range force constants. Using the result of § 2 for the pseudoatom potential $\delta_j v$, the force constant Φ^{BS} is the sum of four terms

$$\Phi^{BS} = \nabla u_i\chi_0\nabla u_j + \nabla u_i\chi_0(\nabla \times \omega_j) + (\nabla \times \omega_i)\chi_0\nabla u_j + (\nabla \times \omega_i)\chi_0(\nabla \times \omega_j). \tag{44}$$

The last three contributions are not present if an RI model for the potential is used. However, when off-diagonal screening is crucial, as is the case in transition metals systems, ω_j is necessarily present and the contributions from $\nabla \times \omega_j$ to Φ^{BS} may not be negligible. The recent calculation of Varma and Weber (1977), which is based on equation (43) but ignores $\nabla \times \omega_j$, seems to account fully for the phonon anomalies in the Nb-Mo alloy system.

The more traditional approach to the description of phonon anomalies has utilised expression (38) (rather than equation (43)), which when added to the ion–ion force constant (39), can be rewritten as (again, for $i \neq j$)

$$\Phi_{ij} = \delta_i\delta_j U + \delta_i v^{\text{ext}}(\chi_0\epsilon^{-1})\delta_j v^{\text{ext}}. \tag{45}$$

Both Sinha and Harmon (1975) and Hanke *et al* (1976) have suggested models in which 'resonant screening', or resonant denominators in expressions for ϵ^{-1}, can give rise to the observed anomalies. Although the two models differ in spirit and in some predictions, each assumes a local pseudopotential for v_{ext} and includes large local-field corrections. The predictions of the models were studied only in relation to the effect on the dynamical matrix. From the present point of view, a study of the screened potential $\epsilon^{-1}\delta v^{\text{ext}}$ e.g. the magnitude and character of ω and of the corrections to u, would be a more fundamental approach. Such a study will be left to a later publication.

Another approach (Gupta and Freeman 1976, Gupta *et al* 1977 and Myron *et al* 1977) uses the fact that the underlying band structure entering through χ_0 [in either equation (45) or in Φ^{BS} in equation (43)], can account for the anomalies whenever the intraband contributions are dominant. For the well studied case of Nb (Cooke *et al* 1974, Pickett 1975), however, it appears that the matrix elements of the potential are necessary (Pickett and Allen 1977) even for a qualitative understanding of the anomalies. The question of the effect of $\nabla \times \omega_j$ on Φ^{BS} may be an important one in the understanding of anomalous phonons.

6. Summary

Our main result is the decomposition of the one-electron potential into atom-like contributions which (1) move rigidly with the ions to first order in the displacement, and (2) at equilibrium, sum exactly to the total potential. The formalism provides an explicit prescription for this rigid-ion-like potential. When the ions are displaced, an additional potential deformation is produced which is explicitly non-rigid. Although this latter deformation can be thought of as involving no 'net potential', its effects are crucial in semiconductors and insulators. It is suggested that its effects in transition metal systems may be important in crystalline screening effects and phonon spectra.

We have not given any explicit discussion of the application of our results to the electron–phonon interaction. This is so fundamental to the theory of metals that it deserves special attention. Transport properties, deformation potentials and ultrasonic attenuation are examples of properties crucially dependent on the electron–phonon matrix element. The electron-displaced ion cross section, i.e. matrix elements of $\delta_j v$, is, however, the fundamental quantity entering into the electron–phonon interaction; this partially justifies our study of the somewhat *ad hoc* rigid-ion and deformable-ion models for $\delta_j v$. This same cross section is involved in phonon spectra and anomalies, and strong electron–phonon interactions and is intimately related to electronically-driven phase transitions.

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Appendix

The Helmholtz decomposition of a continuous vector field $\boldsymbol{F}$ into longitudinal (l) and transverse (t) fields

$$\boldsymbol{F} = \boldsymbol{F}_l + \boldsymbol{F}_t \tag{A1}$$

such that

$$\nabla \times \boldsymbol{F}_l = 0 \qquad \nabla . \boldsymbol{F}_t = 0, \tag{A2}$$

can be accomplished by using

$$\begin{Bmatrix} \boldsymbol{F}_l \\ \boldsymbol{F}_t \end{Bmatrix} = -\frac{1}{4\pi} \begin{Bmatrix} \nabla \\ \nabla \times \end{Bmatrix} \int \frac{\mathrm{d}^3 r'}{|r - r'|} \begin{Bmatrix} \nabla . \boldsymbol{F} \\ \nabla \times \boldsymbol{F} \end{Bmatrix}. \tag{A3}$$

It is straightforward to substitute (A1) into (A3), integrate by parts, use

$$\nabla^2 \frac{1}{|r - r'|} = -4\pi\delta(r - r'), \tag{A4}$$

and find (A3) to be consistent. (A2) is satisfied by construction.

The use of the Helmholtz construction in the text requires that the integrals over the crystal volume Ω

$$\int_{\Omega} \frac{\mathrm{d}^3 r'}{|r - r'|} \left\{ \begin{array}{l} \nabla \cdot \\ \nabla \times \end{array} \right\} \delta_l v(r') \tag{A5}$$

exist. In metals, the itinerant electrons screen the perturbation and result in an exponential decay of u and ω. The worst case occurs for semiconductors and insulators, where the energy gap prevents metallic screening. For other than elemental crystals, ionicity may be present, with the result that $u(r) \sim r^{-1}$ for large r. It is easily verified that, even for this case, the integrals converge and that partial integration, which is used freely, introduces no surface terms.

The decomposition theorem and following formulae are expressed in terms of the total potential, which in principle contains a discontinuity at the nucleus. It is a straightforward matter to separate out the nuclear term, apply the Helmholtz construction to the (continuous) electronic screening contribution to δv, and then to restore the nuclear term to obtain the displayed equations.

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