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Microscopic calculation of phonon spectrum of KCl and KBr

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A microscopic calculation is performed of the phonon spectrum of the alkali halide crystals KCl and KBr in the approximation where the dielectric matrix is assumed to be of separable form. The calculations involve two adjustable microscopic parameters. Reasonable agreement with experiment is obtained. A detailed discussion is also given of the microscopic treatment of effective charges and overlap interactions in ionic crystals. It is shown how qualitative conclusions regarding the nature of the overlap forces may be drawn from a simple consideration of the nature of the valence- and conduction-band orbitals.

I. INTRODUCTION

The lattice dynamics of alkali halides has been a subject of very considerable interest for the past few decades. For a recent review we refer the reader to the paper by Cochran.[1] The phonon dispersion curves obtained from neutron scattering data are usually analyzed in terms of the shell model.[2,3] Hardy and Karo have also performed extensive calculations for the alkali halides using the deformation dipole model,[4,5] while several calculations are also available using the formalism developed by Tolpygo and co-workers.[6,7] More recently, deformable shell generalizations of the shell model have been used with considerable success to fit the dispersion curves, requiring fewer parameters than the shell model to give equivalent agreement with experiment. These include the breathing shell model[8,9] and its recent generalizations to include deformations of more general symmetry,[10] the model of Verma and Singh,[11,12] which takes into account charge-transfer effects,[1] and the model of Basu and Sengupta.[13] In general, the number of adjustable parameters in these models is typically six or greater. A calculation based on a more microscopic theory might be expected to reduce the number of parameters further. Recently, there have been several attempts to formulate such a microscopic theory for the alkali halides.[14-17]

In this paper, we extend and develop the approach given previously by one of the authors[17] and show that even after making rather gross simplifications, the theory is capable of yielding reasonable agreement with experiment in the case of two alkali halides investigated, namely, KCl and KBr, using only two adjustable microscopic parameters. We also discuss how the nature of the "overlap" forces between ions and the "overlap" contribution to the effective charge can be understood qualitatively in terms of the microscopic theory.

II. THEORY

We first briefly review the formalism developed in Ref. 17 (henceforth referred to as I), and then derive some further consequences of this approach. The method is based on two main simplifications. The first is the assumption that the microscopic dielectric function matrix[18] may be written approximately in the form

$$\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}') \simeq \delta_{\vec{G}\vec{G}'} + v(\vec{q}+\vec{G}) \sum_{\substack{\alpha\beta \\ \kappa\kappa'}} (\vec{q}+\vec{G})_\alpha \times f^{\kappa}(\vec{q}+\vec{G}) a^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) f^{*\kappa'}(\vec{q}+\vec{G}')\,(\vec{q}+\vec{G}')_\beta \times \exp[-i(\vec{G}\cdot\vec{r}_\kappa - G'\circ\vec{r}_{\kappa'})] \ , \qquad (2.1)$$

where $v(\vec{Q})$ is the Fourier transform of the effective electron-electron interaction; $\vec{G}$, $\vec{G}'$ are vectors of the reciprocal lattice; κ, κ' refer to basis ions in the unit cell with basis vectors $\vec{r}_\kappa$, $\vec{r}_{\kappa'}$; $f^{\kappa}(\vec{Q})$ is a form factor associated with the κth ion; and $a^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is a generalized $\vec{q}$-dependent polarizability matrix. A more general form of Eq. (2.1) may be written and has in fact been used to calculate the phonon spectra of semiconducting crystals[19] but for systems with reasonably well-localized electrons, such as the alkali halides, Eq. (2.1) is expected to be sufficient. The inverse of the dielectric function given by Eq. (2.1) may then shown to be

$$\epsilon^{-1}(\vec{q}+\vec{G},\ \vec{q}+\vec{G}') = \delta_{\vec{G}\vec{G}'} - v(\vec{q}+\vec{G}) \sum_{\substack{\alpha\beta \\ \kappa\kappa'}} (\vec{q}+\vec{G})_\alpha \times f^{\kappa}(\vec{q}+\vec{G}) S^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) f^{*\kappa'}(\vec{q}+\vec{G}')\,(\vec{q}+\vec{G}')_\beta \times \exp[-i(\vec{G}\cdot\vec{r}_\kappa - \vec{G}'\cdot\vec{r}_{\kappa'})] \ , \qquad (2.2)$$

where the matrix $S^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is given by

$$\underline{S} = (\underline{V} + \underline{a}^{-1})^{-1} \ , \qquad (2.3)$$

where

$$V^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = \sum_{\vec{G}} (\vec{q}+\vec{G})_\alpha (\vec{q}+\vec{G})_\beta f^{*\kappa}(\vec{q}+\vec{G}) \times f^{\kappa'}(\vec{q}+\vec{G}) v(\vec{q}+\vec{G}) e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \tag{2.4}$$

[the vector $\vec{r}_{\kappa\kappa'}$ is used to denote $(\vec{r}_\kappa - \vec{r}_{\kappa'})$]. The physical basis of the above model has been discussed in I and elsewhere.[19,20] It corresponds to assuming that the polarization of the electrons in response to an externally applied field may be described in terms of dipole distributions centered on the ionic sites $\vec{r}_\kappa$ with form factors given by the $f^\kappa(\vec{Q})$. [This may be seen by writing the electron density response matrix $\chi(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$ in terms of $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$.][19]

Let us write the valence-electron wave functions ψ_k in the form

$$\psi_k(\vec{r}) = N^{-1/2} \exp[i\vec{k}\cdot(\vec{r}_l + \vec{r}_\kappa)]\varphi^\kappa_k(\vec{r} - \vec{r}_l - \vec{r}_\kappa) \quad , \tag{2.5}$$

where N is the total number of unit cells in the crystal, k specifies both the Bloch wave vector $\vec{k}$ and the band index, $\vec{r}_l$ is the position of the origin of the lth unit cell, $\vec{r}_\kappa$ is the basis vector for the κth ion, and the function $\varphi^\kappa_k(\vec{r}-\vec{r}_l-\vec{r}_\kappa)$ is defined in the (l,κ) subcell only. In the tight-binding limit, $\varphi^\kappa_k(\vec{r}-\vec{r}_l-\vec{r}_\kappa)$ is the atomic orbital (of type specified by the index κ) associated with the ion at (l,κ), but in the general case $\varphi^\kappa_k(\vec{r}-\vec{r}_l-\vec{r}_\kappa)$ in a given subcell (l,κ) will have contributions from the orbital on the ion in the subcell (l,κ) as well as orbitals from neighboring subcells. In I, it was shown that an explicit expression for $a^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ consistent with Eq. (2.1) is

$$a^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = \frac{\hbar^2}{m^2} \sum_{k,k'}{}' \frac{n(k)-n(k')}{E_k - E_{k'}} r^{kk'}_\alpha(\kappa) \times r^{k'k}_\beta(\kappa') \Delta_{\vec{k}'-\vec{k},\vec{q}}\, e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \quad , \tag{2.6}$$

where m is the electron mass, E_k, $E_{k'}$ are the one-electron energy levels of states k, k', respectively, the symbol $\Delta_{\vec{k}'-\vec{k},\vec{q}}$ means $\vec{k}' = \vec{k} + \vec{q}$ *modulo* a reciprocal-lattice vector $\vec{G}$ (which also defines $\vec{G}$), the prime over the summation in Eq. (2.6) implies that the case $k = k'$ is to be excluded, and $r^{kk'}_\alpha(\kappa)$ is the dipole matrix element in subcell κ, defined by

$$r^{kk'}_\alpha(\kappa) = \frac{1}{E_k - E_{k'}} \int_{(0,\kappa)} d\vec{r}\, \varphi^{*\kappa}_k(\vec{r} - \vec{r}_\kappa) \times p_\alpha \varphi^\kappa_{k'}(\vec{r} - \vec{r}_\kappa) \quad , \tag{2.7}$$

where $\vec{p}$ is the electron momentum operator, and the integration is to be performed over the subcell κ in the origin unit cell.

The cross-polarizability terms in Eq. (2.6) for the case $\kappa \neq \kappa'$ are seen to result from overlap in the sense that they vanish unless the states k, k' each have nonzero amplitudes in *both* subcells κ, κ'. Physically, they correspond to the fact that a local field applied at one site κ may also induce dipole moments on other sites κ', corresponding to virtual electronic transitions from states on one ion to excited states on neighboring ions. In the tight-binding limit, as $\vec{q} \to 0$, Eq. (2.6) reduces to the standard expression for the ionic polarizability (apart from a constant factor). As $\vec{q} \to 0$, the expression for the electrical polarizability per unit volume is[17]

$$\alpha_{\alpha\beta} = \frac{e^2}{\Omega} \sum_{\kappa\kappa'} a^{\kappa\kappa'}_{\alpha\beta}(0) \quad (\Omega = \text{volume of unit cell}). \tag{2.8}$$

An explicit expression for the electronic contribution to the dielectric constant (for frequencies ≫ the lattice frequencies) for cubic crystals may be obtained from Eq. (2.2). It is given by[19,20]

$$\epsilon_\infty = 1 + \frac{4\pi e^2}{\Omega} \sum_{\kappa,\kappa'} \bar{S}_{\kappa\kappa'} \quad , \tag{2.9}$$

where

$$\bar{S}_{\kappa\kappa'} = (\bar{V} + a^{-1})^{-1}_{\kappa\kappa'} \tag{2.10}$$

and

$$\bar{V}_{\kappa\kappa'} = \frac{1}{3} \sum_{\vec{G}}{}' G^2 f^{*\kappa}(\vec{G}) f^{\kappa'}(\vec{G})\, v(\vec{G}) \times e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}} \quad , \tag{2.11}$$

where the prime over the summation excludes the singular contribution from $\vec{G} = 0$. Note that because of cubic symmetry, and because we are considering the limit $\vec{q} \to 0$ the matrices $\underline{a}$, $\underline{\bar{V}}$, $\underline{\bar{S}}$ are expressed in (κ,κ') space alone, the (α,β) components having been factored out via the trivial factor $\delta_{\alpha\beta}$. Thus $\bar{V}_{\kappa\kappa'}\delta_{\alpha\beta}$ is the limit as $\vec{q} \to 0$ of the matrix $V^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ in Eq. (2.4) with the singular contribution from $\vec{G} = 0$ removed.

The exchange and correlation corrections to $v(\vec{Q})$ are not known at all accurately for any system other than a free-electron gas. For highly localized systems, we may include all the interactions between electrons on the same ion as a many-electron correction to the expression for the polarizabilities $a^{\kappa\kappa'}_{\alpha\beta}$ given in Eq. (2.6) (since these are going to be taken as parameters in any case) and consider interactions between more distant electrons as being pure Coulomb-like, i.e., unmodified by exchange and correlation effects (which are generally short range in character). Thus we may crudely represent the effective electron-electron interaction as given by

$$v(\vec{r}) = e^2/r, \quad r \geq r_{xc}$$
$$= 0, \quad r \leq r_{xc} \tag{2.12}$$

where r_{xc} is an adjustable parameter which is typically approximately an ionic radius. From Eq. (2.12), we obtain

$$v(\vec{Q}) = (4\pi e^2/\Omega Q^2)\cos(Q r_{xc}) \quad . \tag{2.13}$$

We should point out, however, that this approximation is not likely to be very accurate in regions of overlapping electron density from neighboring ions and hence for systems where such overlapping regions are a significant fraction of the total volume.

In the case that the real-space distributions corresponding to the form factors $f^{\kappa}(\vec{Q})$ do not overlap on neighboring sites, it has been shown elsewhere[19,20] that Eq. (2.9) is equivalent to the Lorentz-Lorenz formula

$$\epsilon_\infty = (1+\tfrac{8}{3}\pi\alpha)/(1-\tfrac{4}{3}\pi\alpha) \;, \tag{2.14}$$

which one obtains in the point-dipole models. However, in the general case, Eq. (2.14) is modified by the so-called local-field corrections to the point-dipole fields, and as we shall see this effect is probably significant, even in the alkali halides.

The explicit expression for $\epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$ [Eq. (2.2)] enables us to obtain an analytic expression for the dynamical matrix. In order to do this, however, a second important simplification is necessary. This is based on an identity obeyed by the electron-phonon matrix element, and the method has been developed in Ref. 21 and in I. The initial step is to choose an arbitrary (in practice, spherical) volume $V_0(\kappa)$ around each ion of type κ. It may then be shown that the total electron-nucleus interaction may be replaced by the sum of two terms: (i) a weak residual potential $W_\kappa(\vec{r})$, which is approximately constant inside $V_0(\kappa)$ and outside $V_0(\kappa)$ is equal to the interaction between the electron and the total "pseudoion" inside $V_0(\kappa)$ and (ii) a nonlocal pseudopotential whose matrix element $M_{k'k}$ between states $\psi_{k'}$ and ψ_k may be written as a surface integral over the surface of $V_0(\kappa)$. We may also, in principle, absorb the nonlocal (exchange) part of $W_\kappa(\vec{r})$ inside this matrix element although we shall neglect this complication here. The net result of this transformation is that the nuclei (or the ion cores) may now be replaced by the "pseudoions" consisting of all the charge inside the volumes $V_0(\kappa)$. These may be regarded as moving rigidly with the nuclei, and the remainder of the electron density deformation can be calculated by perturbation theory in terms of the transformed electron-phonon matrix element. We may write[22]

$$W_\kappa(\vec{Q}) = -Z_\kappa \frac{4\pi e^2}{\Omega Q^2}\, \frac{\sin Q r_s(\kappa)}{Q r_s(\kappa)} \tag{2.15}$$

where $Z_\kappa e$ is the total charge inside $V_0(\kappa)$, and $r_s(\kappa)$ is the radius of the (spherical) volume $V_0(l,\kappa)$, and

$$\begin{aligned} M_{k'k} = i\,\Omega^{-1/2} \sum_{\kappa,\alpha} \bigl[& Q_{\vec{q}j}\, e_\alpha(\kappa\,|\,\vec{q}j)\Delta_{\vec{k}'-\vec{k},\vec{q}} \\ & + Q^*_{\vec{q}j} e^*_\alpha(\kappa\,|\,\vec{q}j)\Delta_{\vec{k}',-\vec{k},-\vec{q}}\bigr] I_\alpha^{k'k}(\kappa) \;, \end{aligned} \tag{2.16}$$

where

$$\begin{aligned} I_\alpha^{k'k}(\kappa) = \frac{1}{N}\Biggl[\frac{\hbar^2}{2m}\int_{S\,0(\kappa)} dS \Biggl(& \frac{\partial}{\partial n}\varphi^{*\kappa}_{k'}(\vec{r}-\vec{r}_\kappa) \\ & \times \frac{\partial}{\partial x_\alpha}\varphi^{\kappa}_{k}(\vec{r}-\vec{r}_\kappa) - \varphi^{*\kappa}_{k'}(\vec{r}-\vec{r}_\kappa)\frac{\partial^2}{\partial n\,\partial x_\alpha}\varphi^{\kappa}_{k}(\vec{r}-\vec{r}_\kappa)\Biggr)\Biggr] \;, \end{aligned} \tag{2.17}$$

where the integral is over the surface of the volume $V_0(\kappa)$ in the origin unit cells. $Q_{\vec{q}j}$, $e_\alpha(\kappa/\vec{q}j)$ are, respectively, the normal coordinate and polarization vector for the phonon mode $(\vec{q}j)$. We have assumed in Eq. (2.15) that the potential seen by an electron outside $V_0(\kappa)$ due to the pseudoion inside $V_0(\kappa)$ is pure Coulomb-like, i.e., exchange and correlation effects are neglected. This is likely to be a good approximation in the limit where the $V_0(\kappa)$ can be chosen so that they actually separate wave functions of electrons inside and outside $V_0(\kappa)$, i.e., in the nonoverlapping limit. Although this condition is never actually satisfied in practice, the exchange and correlation corrections to $W_\kappa(\vec{r})$ are likely to be small for many of the ionic crystals. Note that the exchange and correlation corrections for electrons *inside* the $V_0(\kappa)$ (in practice, the largest part of the exchange and correlation effects) is transformed away with the rest of the strong potential in the region by means of the formalism.

Using the above results, it may be demonstrated following the results in I, that the dynamical matrix may be written

$$\begin{aligned} D^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = {} & \bar{D}^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) \\ & - \delta_{\kappa\kappa'} \lim_{\vec{q}\to 0}\Bigl(\sum_{\kappa''} \bar{D}^{\kappa\kappa''}_{\alpha\beta}(\vec{q})\Bigr) \;, \end{aligned} \tag{2.18}$$

where

$$\begin{aligned} \bar{D}^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = {} & Z_\kappa Z_{\kappa'} C^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) + R'^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) \\ & + (\underline{J}\,\underline{a}^{-1}\underline{J}^\dagger)^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) - (\underline{W}'\,\underline{S}\,\underline{W}'^\dagger)^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) \,, \end{aligned} \tag{2.19}$$

where $C^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ is the usual Coulomb-coupling coefficient between charges $|e|$ on sublattices κ, κ',

$$\begin{aligned} R'^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = {} & -\frac{1}{\Omega}\sum_{k,k'}{}' \frac{n(k)-n(k')}{E_k - E_{k'}}\,[I_\alpha^{k'k}(\kappa)]^*\,[I_\beta^{k'k}(\kappa')] \\ & \times e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}}\,\bigl[\tfrac{1}{2}(\Delta_{\vec{k}'-\vec{k},\vec{q}} + \Delta_{\vec{k}'-\vec{k},-\vec{q}})\bigr] \end{aligned} \tag{2.20}$$

(where $\vec{G}$ is the reciprocal-lattice vector which equates $(\vec{k}'-\vec{k})$ and $\pm\vec{q}$ in the appropriate terms in the last set of square brackets),

$$\begin{aligned} J^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = {} & -\frac{\hbar}{m}\frac{1}{\Omega}\sum_{k,k'}{}' \frac{n(k)-n(k')}{E_k - E_{k'}} \\ & \times [I_\alpha^{k'k}(\kappa)]^*\,[r_\beta^{k'k}(\kappa')] \times e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}}\,\Delta_{\vec{k}'-\vec{k},\vec{q}} \end{aligned} \tag{2.21}$$

[where $r_\beta^{k'k}(\kappa')$ has been defined in Eq. (2.7)],

$$W'^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = W^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) + (\underline{J}\,\underline{a}^{-1})^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) \;, \tag{2.22}$$

where

$$W^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=\sum_{\vec{G}}(\vec{q}+\vec{G})_\alpha(\vec{q}+\vec{G})_\beta\, W_\kappa(\vec{q}+\vec{G})$$
$$\times f^{\kappa'}(\vec{q}+\vec{G})e^{i\vec{G}\cdot\vec{r}_{\kappa\kappa'}}\quad . \tag{2.23}$$

The matrix $\underline{a}$ has already been defined in Eq. (2.6). The last term on the right-hand side in Eq. (2.18) arises from translational invariance. A necessary condition for this term to be well defined is that the singular contributions to $\bar{D}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ cancel as $\vec{q}\to 0$. This is ensured by the effective-charge sum rule,[23–25] which was not discussed in I. We shall return to this condition later. For the present, we anticipate this result and write the value of this term as $D^{(0)\kappa\kappa'}_{\alpha\beta}$. Equation (2.19) is equivalent to the pair of equations

$$\omega^2\underline{M}\,\underline{U}=(\underline{Z}\,\underline{C}\,\underline{Z}+\underline{R}'+\underline{J}\,\underline{a}^{-1}\underline{J}^\dagger+\underline{D}^{(0)})\underline{U}+\underline{W}'\underline{w}\quad , \tag{2.24a}$$

$$0=\underline{W}'^\dagger\,\underline{u}+(\underline{V}+\underline{a}^{-1})\underline{w}\quad . \tag{2.24b}$$

Here $\underline{M}$ is the diagonal matrix $M_\kappa\delta_{\alpha\beta}\delta_{\kappa\kappa'}$, $\underline{Z}$ is the diagonal matrix $Z_\kappa\delta_{\alpha\beta}\delta_{\kappa\kappa'}$, and $\underline{u}$ is a $3r$-element column matrix (r is equal to the number of ions in the unit cell) denoting the nuclear displacement amplitude vectors. $\underline{w}$ is also a $3r$-element column matrix, which represents the amplitudes of the periodic array of dipole distributions arising from the charge deformation on the ionic sites. Note that these do not represent *total* electronic dipole moments on the ions as part of the latter has already been represented in terms of a displacement dipole moment corresponding to the rigid motion of the valence charge inside the pseudoion $V_0(l\kappa)$ along with the ion core. Thus, Eqs. (2.24) are not really identical to the shell model equations as was implied in I. The correct relationship between the two sets of equations is derived later in this section.

The meaning of the coupling-coefficient matrices in Eqs. (2.24) may be made more explicit by rewriting Eqs. (2.24) as the set of equations

$$\omega^2\underline{M}\,\underline{u}=(\underline{Z}\,\underline{C}\,\underline{Z}+\underline{R}'+\underline{D}^{(0)})\underline{u}+\underline{W}\,\underline{w}+\underline{J}\,\underline{E}, \tag{2.25a}$$

$$0=\underline{W}^\dagger\,\underline{u}+\underline{V}\,\underline{w}+\underline{E}\quad , \tag{2.25b}$$

$$0=\underline{J}^\dagger\,\underline{u}+\underline{w}-\underline{a}\,\underline{E}\quad , \tag{2.25c}$$

where it is clear that the $3r$-component column matrix $\underline{E}$ is proportional to the amplitude of the effective *local field* at the ion sites. Equation (2.25b) may be regarded as serving as a definition of $\underline{E}$. Equation (2.25c) then expresses the deformation dipole moment as depending linearly on the local field as also on the displacements $\underline{u}$ via the short-range coupling coefficient $\underline{J}$, which may thus be thought of as the "mechanical" or "overlap" polarizability. In fact, in the limit of nonoverlapping atomic orbitals, it is obvious from Eq. (2.17) that $V_0(\kappa)$ can be chosen large enough so that $I^{kk'}_\alpha(\kappa)$ vanishes and hence by Eqs. (2.20) and (2.21), so do the matrices $\underline{J}$ and $\underline{R}'$. Equation (2.25a) expresses the equation of motion of the pseudoions, the first term on the right-hand side representing the force due to the Coulomb field of the other pseudoions, as well as the "overlap" interaction $\underline{R}'$; the second term the force due to the electrostatic field due to the deformation dipoles $\underline{w}$, and the last term representing the "overlap" force due to distortion of the charge density inside the pseudoion via the local field. It is worth noting that although the latter is a long-range force, when $\underline{E}$ is eliminated from the equations of motion (2.25) to yield Eqs. (2.24), the effective overlap forces that are left are all short-range. It should be also noted that there are two types of "short-range" forces in Eqs. (2.24), namely, those arising from the $\vec{q}$-dependent parts of the matrices $\underline{R}'$, $\underline{J}$, and $\underline{a}^{-1}$, which may properly be termed "mechanical-overlap" forces, and those arising from the deviations of the $\underline{W}$ and $\underline{V}$ matrices from the point-dipole Coulomb coupling matrices due to overlap of the *dipole distributions* corresponding to the form factors $f^\kappa(\vec{Q})$, i.e., from local-field corrections to the point-dipole fields. In the shell model or other phenomenological dipole models these two types of short-range forces are not explicitly differentiated.

The dynamic effective charge can be derived as follows. We consider the limit $\vec{q}\to 0$. The bulk polarization $\vec{P}$ is given by

$$P_\alpha=\frac{|e|}{\Omega}\sum_\kappa\left[(\underline{Z}\,\underline{u})_\alpha(\kappa)-w_\alpha(\kappa)\right]\quad . \tag{2.26}$$

The corresponding macroscopic field, neglecting retardation effects, may be written[26]

$$E^{\text{mac}}_\alpha=-4\pi q_\alpha(\vec{q}\cdot\vec{P})/q^2\quad . \tag{2.27}$$

We also note that as $\vec{q}\to 0$,

$$C^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=\frac{4\pi e^2}{\Omega}\,\frac{q_\alpha q_\beta}{q^2}+\bar{C}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})\quad , \tag{2.28}$$

$$W^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=-Z_\kappa\frac{4\pi e}{\Omega}\,\frac{q_\alpha q_\beta}{q^2}+\bar{W}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})\quad , \tag{2.29}$$

$$V^{\kappa\kappa'}_{\alpha\beta}(\vec{q})=\frac{4\pi e^2}{\Omega}\,\frac{q_\alpha q_\beta}{q^2}+\bar{V}^{\kappa\kappa'}_{\alpha\beta}(\vec{q})\quad , \tag{2.30}$$

where $\underline{\bar{C}}$, $\underline{\bar{W}}$, $\underline{\bar{V}}$ are as regular as $\vec{q}\to 0$. All the other matrices in Eqs. (2.24) are regular as $\vec{q}\to 0$.

As is well known,[26,27] singular terms in Eqs. (2.24) can be associated with the macroscopic field, and we obtain, as $\vec{q}\to 0$,

$$\omega^2\underline{M}\,\underline{u}=(\underline{Z}\,\underline{C}\,\underline{Z}+\underline{R}'+\underline{J}\,\underline{a}^{-1}\underline{J}^\dagger+\underline{D}^{(0)})\underline{u}$$
$$+(\underline{W}+\underline{J}\,\underline{a}^{-1})\underline{w}-|e|\underline{Z}\,\underline{E}^{\text{mac}}\quad , \tag{2.31a}$$

$$0=(\underline{\bar{W}}^{\dagger}+\underline{a}^{-1}\underline{J}^{\dagger})\underline{u}+(\underline{\bar{V}}+\underline{a}^{-1})\underline{w}+|e|\,\underline{E}^{\mathrm{mac}}\quad, \tag{2.31b}$$

where $\underline{E}^{\mathrm{mac}}$ is the $3r$-element column matrix formed from the $E_{\alpha}^{\mathrm{mac}}$ at each ion site. On eliminating $\underline{w}$, we obtain, from Eqs. (2.31) and (2.26),

$$\omega^2\underline{M}\,\underline{u}=(\underline{Z}\,\underline{\bar{C}}\,\underline{Z}+\underline{R}'+\underline{J}\,\underline{a}^{-1}\underline{J}^{\dagger}+\underline{D}^{(0)}-\underline{\bar{W}}'\,\underline{\bar{S}}\,\underline{\bar{W}}'^{\dagger})\underline{u}$$

$$-|e|\underline{Z}^{\mathrm{eff}}+\underline{E}^{\mathrm{mac}} \tag{2.32a}$$

and

$$P_{\alpha}=\frac{|e|}{\Omega}\sum_{\kappa}\left[(\underline{Z}^{\mathrm{eff}}\underline{u})_{\alpha}(\kappa)+|e|(\underline{\bar{S}}\,\underline{E}^{\mathrm{mac}})_{\alpha}(\kappa)\right]\quad, \tag{2.32b}$$

where

$$\underline{\bar{S}}=(\underline{\bar{V}}+\underline{a}^{-1})^{-1}\quad, \tag{2.33}$$

$$\underline{\bar{W}}'=\underline{\bar{W}}+\underline{J}\,\underline{a}^{-1}\quad, \tag{2.34}$$

$$\underline{Z}^{\mathrm{eff}}=\underline{Z}+\underline{\bar{S}}\,\underline{\bar{W}}'^{\dagger}\quad. \tag{2.35}$$

We restrict ourselves once again to cubic crystals, so that the matrices $\underline{Z}$, $\underline{\bar{S}}$, $\underline{\bar{W}}'$ are diagonal in (α,β) space and, as before, we may drop the Cartesian indices. From Eqs. (2.32) it is clear that the effective charge on the κth ion is

$$Z^{\mathrm{eff}}(\kappa)=Z_{\kappa}+\sum_{\kappa'}(\underline{\bar{W}}'\underline{\bar{S}})_{\kappa\kappa'}\quad. \tag{2.36}$$

The acoustic sum rule may then be written[20]

$$\sum_{\kappa}Z^{\mathrm{eff}}(\kappa)=\sum_{\kappa}Z_{\kappa}+\sum_{\kappa\kappa'}(\underline{\bar{W}}'\underline{\bar{S}})_{\kappa\kappa'}=0\quad. \tag{2.37}$$

It may be shown that in the limit as $\vec{q}\rightarrow 0$, the singular part of $D_{\alpha\beta}^{\kappa\kappa'}(\vec{q})$ given by Eq. (2.19) is equal to $(4\pi e^2/\Omega\epsilon_{\infty})Z^{\mathrm{eff}}(\kappa)Z^{\mathrm{eff}}(\kappa')q_{\alpha}q_{\beta}/q^2$. Hence, the sum rule [Eq. (2.37)] ensures that $\sum_{\kappa''}D_{\alpha\beta}^{\kappa\kappa''}(\vec{q})$ has a well-defined limit as $\vec{q}\rightarrow 0$. It may also be shown via Eqs. (2.26), (2.27), and (2.31b) that the macroscopic field vanishes for acoustic modes on account of the acoustic sum rule, a result which is derivable from more general considerations.[23–25]

Using Eqs. (2.33) and (2.34) the expression for $Z^{\mathrm{eff}}(\kappa)$ may also be written in the alternative form

$$Z^{\mathrm{eff}}(\kappa)=Z_{\kappa}+\sum_{\kappa'}J_{\kappa\kappa'}+\sum_{\kappa'}\left[(\underline{\bar{W}}-\underline{\bar{J}}\,\underline{\bar{V}})\underline{\bar{S}}\right]_{\kappa\kappa'}\quad. \tag{2.38}$$

Let us consider the limit where the dipole distributions corresponding to the $f^{\kappa}(\vec{Q})$ are spherically symmetric and so well localized on the ions that they do not overlap. By elementary electrostatics it is obvious that in this case there are no local-field corrections to the point-dipole Coulomb fields in the $\underline{W}$ and $\underline{V}$ coefficients, i.e., in this case

$$\underline{\bar{W}}=-\underline{Z}\,\underline{\bar{C}},\quad \underline{\bar{V}}=\underline{\bar{C}}\quad. \tag{2.39}$$

We also have the well-known result[1]

$$\bar{C}_{\kappa\kappa'}=-4\pi e^2/3\Omega \tag{2.40}$$

Then Eq. (2.38) may be written

$$Z^{\mathrm{eff}}(\kappa)=\Big(Z_{\kappa}+\sum_{\kappa'}J_{\kappa\kappa'}\Big)\quad\Big(1+\frac{4\pi e^2}{3\Omega}\sum_{\lambda\lambda'}\bar{S}_{\lambda\lambda'}\Big)$$

$$=\frac{\epsilon_{\infty}+2}{3}\Big(Z_{\kappa}+\sum_{\kappa'}J_{\kappa\kappa'}\Big)\quad. \tag{2.41}$$

The last step follows using the result (2.9). Equation (2.41) shows that in this limit the Szigeti charge $Z^s(\kappa)$ is given by

$$Z^s(\kappa)=Z_{\kappa}+\sum_{\kappa\kappa'}J_{\kappa\kappa'}\quad. \tag{2.42}$$

It might appear that the quantity on the right-hand side of Eq. (2.42) is arbitrary in the sense that Z_{κ} is the total charge on the pseudoion inside the volume $V_0(\kappa)$ and hence depends on the choice of $V_0(\kappa)$. However, it should be remembered that the surface integral $I_{\alpha}^{k'k}(\kappa)$ and hence the $J_{\kappa\kappa'}$ also depend on the choice of $V_0(\kappa)$ and will tend to compensate the dependence of Z_{κ} on $V_0(\kappa)$, so that (within the approximations of the model) the charge $Z^s(\kappa)$ is still a unique quantity. Note that in the above Lorentz-field limit, the effective charge sum rule, together with Eq. (2.40), requires that

$$\sum_{\kappa}Z_{\kappa}+\sum_{\kappa\kappa'}J_{\kappa\kappa'}=0\quad. \tag{2.43}$$

In the case that the $V_0(\kappa)$ is taken to be the total volume of the subcell "belonging" to the κth ion, Z_{κ} becomes the total ionic charge on the κth ion. Due to over-all charge neutrality the sum rule then requires that

$$\sum_{\kappa\kappa'}J_{\kappa\kappa'}=0\quad. \tag{2.44}$$

Inspection of Eq. (2.21) reveals that the quantity on the left-hand side contains (inside the sum over states k, k') the factor $[\sum_{\kappa}I_{\alpha}^{k'k}(\kappa)]^*$. From the definition of $I_{\alpha}^{k'k}(\kappa)$ in Eq. (2.17), it may be seen that $\sum_{\kappa}I_{\alpha}^{k'k}(\kappa)$ involves an integral over the surface of the whole unit cell of a *periodic* function (we are working in the limit $\vec{q}\rightarrow 0$, so that $k'=k$). Thus the integral must vanish, and hence Eq. (2.44) is identically satisfied.

Thus we see that in the Lorentz-field limit (i.e., nonoverlapping dipole distributions), the effective charge sum rule is identically satisfied without imposing any further restriction on the dielectric matrix. In the general case, however, Eq. (2.42) is no longer valid, the Szigeti charge loses its significance, and we must go back to the formula (2.38), or Eq. (2.36). In this case, the sum rule imposes a relation between the pseudopotential $W_{\kappa}(\vec{Q})$, the overlap coupling coefficients, and the parameters of the dielectric matrix. In the limit where overlap is neglected, it imposes a restriction on the parameters of the dielectric matrix, a fact we shall use in the calculation described in

Sec. III.

In addition to the effective charge sum rules, there is a set of similar sum rules arising from the fact that for a uniform displacement of the crystal, the total electron density perturbation must correspond to a similar uniform translation of the electron density.[25,19] In the limit $\vec{q} \to 0$, the only nonzero Fourier components of the electron-density perturbation are for $\vec{Q}=$ a vector of the reciprocal lattice. According to the formalism developed in I, we may write

$$\Delta\rho(\vec{G}) = \Delta\rho_d(\vec{G}) + \Delta\rho^{(0)}(\vec{G}) \quad , \tag{2.45}$$

where $\Delta\rho_d$, $\Delta\rho^{(0)}$ are, respectively, the deformation and "rigid-pseudoion" contribution to the electron density perturbation. If $\vec{u}$ is the (arbitrary) uniform displacement given to the lattice, we have

$$\Delta\rho^{(0)}(\vec{G}) = i\sum_{\kappa} [Z_\kappa - Z_n(\kappa)] \sum_{\alpha} u_\alpha G_\alpha f_v^\kappa(\vec{G}), \tag{2.46}$$

where $f_v^\kappa(\vec{Q})$ is the form factor associated with the unperturbed electron density inside $V_0(\kappa)$, $Z_n(\kappa)$ is the nuclear charge on the κth ion, and[17]

$$\Delta\rho_d(\vec{G}) = -i\sum_{\kappa\alpha} w_\alpha(\kappa) G_\alpha f^\kappa(\vec{G}) \quad . \tag{2.47}$$

On the other hand, the sum rules require that

$$\Delta\rho(\vec{G}) = i\sum_{\kappa} [Z_t(\kappa) - Z_n(\kappa)] \sum_{\alpha} u_\alpha G_\alpha f_t^\kappa(\vec{G}) \quad , \tag{2.48}$$

where $Z_t(\kappa)$ is the *total* ionic charge on the κth ion, and $f_t^\kappa(\vec{Q})$ is the form factor for the total ionic charge. In the limit where $V_0(\kappa)$ is chosen as the *total* subcell volume $f_v^\kappa(\vec{G}) = f_t^\kappa(\vec{G})$, and it was shown in I that $\Delta\rho_d(\vec{G}) = 0$. Thus, the above sum rules are identically satisfied.

In the general case, by Eq. (2.31b), since $\underline{E}^{\text{mac}}$ vanishes in the limit $\vec{q} \to 0$ by the effective charge sum rule, we have

$$w_\alpha(\kappa) = -\sum_{\kappa'} (\underline{\overline{S}}\,\underline{\overline{W}}'^{\dagger})_{\kappa\kappa'}\, u_\alpha \quad . \tag{2.49}$$

Let us define

$$Y_\kappa = \sum_{\kappa} (\underline{\overline{S}}\,\underline{\overline{W}}'^{\dagger})_{\kappa\kappa'} = \sum_{\kappa'} (\underline{\overline{W}}\,\underline{\overline{S}})_{\kappa'\kappa} \quad . \tag{2.50}$$

Then, combining Eqs. (2.45)–(2.48), we obtain

$$\sum_{\kappa} \{[Z_\kappa - Z_n(\kappa)] f_v^\kappa(\vec{G}) - [(Z_t(\kappa) - Z_n(\kappa)] \times f_t^\kappa(\vec{G}) + Y_\kappa f^\kappa(\vec{G})\} = 0 \quad . \tag{2.51}$$

The sum of the first two terms in the sum on the left-hand side of Eq. (2.51) is $[Z_\kappa - Z_t(\kappa)] f_0^\kappa(\vec{G})$, where $f_0^\kappa(\vec{Q})$ is the form factor for the electron distribution in the subcell κ *outside* $V_0(\kappa)$. Thus, a solution (although not necessarily a unique one) to Eq. (2.51) is

$$Y_\kappa = Z_t(\kappa) - Z_\kappa \tag{2.52}$$

and

$$f^\kappa(\vec{Q}) = f_0^\kappa(\vec{Q}) \quad . \tag{2.53}$$

If the electron-density distribution in the subcells are known fairly accurately, Eq. (2.52) may be imposed as additional restrictions on $(\underline{\overline{W}}'\underline{\overline{S}})_{\kappa'\kappa}$ which are more stringent than the effective-charge sum rule [Eq. (2.37)]. It is also obvious that if Eq. (2.52) are satisfied then the effective-charge sum rule is also identically satisfied. The second set of relations, Eq. (2.53), may be used to define the functions $f^\kappa(\vec{Q})$ involved in the original factorization hypothesis for $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$, in the absence of any other information about the dielectric matrix. If the volume $V_0(\kappa)$ is chosen to include only the core electrons and contains only a negligible fraction of the valence electron density on the ion κ, Eq. (2.53) imply that the form factors should be chosen to be the valence electron shell form factors for the κth ion. We should bear in mind, however, that the "best" set of form factors consistent with the approximate factorized representation of the true $\epsilon(\vec{q}+\vec{G}, \vec{Q}+\vec{G}')$ may not be consistent with Eqs. (2.52) and (2.53).

We recall that $(Z_\kappa e)$ corresponds to the total charge assumed to be moving rigidly with the κth ion, and hence corresponds to the "core charge" in the shell-model language, while from Eqs. (2.49) and (2.50), it is obvious that Y_κ corresponds to the "shell charge." Their relative magnitude depends on the choice of the volumes $V_0(\kappa)$. The model splits the electron-density perturbation due to the lattice displacements into a rigid part and a deformation part, and then approximates the calculation for the latter. Obviously, there is an optimum choice for $V_0(\kappa)$ where this approximation is most likely to be valid. We recall that in the shell models too, the core charge and shell charge are often taken as adjustable parameters.

To obtain the exact correspondence of Eqs. (2.24) with the shell model equations, we recall that the "shell" dipole moment developed in the latter is represented by the motion of the "shell" of charge $Y_\kappa|e|$ with an amplitude $\vec{w}_\kappa^{SM}$ of the relative core-shell motion. In our model the same dipole amplitude is given by $-|e|\vec{w}_\kappa$. Thus, we have

$$-w_\alpha(\kappa) = Y_\kappa[u_\alpha(\kappa) + w_\alpha^{SM}(\kappa)] \quad . \tag{2.54}$$

Using Eqs. (2.50) it may be shown that the shell model equations corresponding to Eqs. (2.24) are

$$\omega^2 \underline{M}\,\underline{u} = \underline{A}\,\underline{u} + \underline{B}\,\underline{w}^{SM} \quad , \quad 0 = \underline{B}^{+}\underline{u} + \underline{G}\,\underline{w}^{SM}, \tag{2.55}$$

where

$$\underline{A} = \underline{Z}\,\underline{C}\,\underline{Z} + \underline{R}' + \underline{J}\,\underline{a}^{-1}\underline{J}^{\dagger} + \underline{D}^{(0)} - \underline{W}\,\underline{Y} - \underline{J}\,\underline{a}^{-1}\underline{Y}$$

$$-\underline{Y}\,\underline{W}^{\dagger} - \underline{Y}\,\underline{a}^{-1}\underline{J}^{\dagger} + \underline{Y}(\underline{V}+\underline{a}^{-1})\underline{Y} = \underline{Z}\,\underline{C}\,\underline{Z}+\underline{R}'$$

$$+\underline{J}\,\underline{a}^{-1}\underline{J}^{\dagger} - \underline{W}'\underline{Y} - \underline{Y}\,\underline{W}'^{\dagger} + \underline{Y}(\underline{V}+\underline{a}^{-1})\underline{Y}+\underline{D}^{(0)} \quad , \tag{2.56}$$

$$\underline{B} = -\underline{W}\,\underline{Y} - \underline{J}\,\underline{a}^{-1}\underline{Y} + \underline{Y}(\underline{V}+\underline{a}^{-1})\underline{Y}$$

$$= -\underline{W}'\underline{Y} + \underline{Y}(\underline{V}+\underline{a}^{-1})\underline{Y}, \tag{2.57}$$

$$\underline{G} = \underline{Y}(\underline{V}+\underline{a}^{-1})\underline{Y} \quad , \tag{2.58}$$

where $\underline{w}^{SM}$ is the $3r$-element column matrix $\underline{w}_{\alpha}^{SM}(\kappa)$, and $\underline{Y}$ is the diagonal matrix $\underline{Y}_{\kappa}\delta_{\alpha\beta}\delta_{\kappa\kappa'}$, with Y_{κ} defined by Eq. (2.50).

Let us define an "ionic charge" by

$$Z_i(\kappa) = Y_{\kappa} + Z_{\kappa} \tag{2.59}$$

$\{Z_i(\kappa)$ would be the actual ionic charge if the sum rule [Eq. (2.52)] were satisfied$\}$. By Eq. (2.50), the acoustic sum rule is equivalent to the condition for total ionic charge neutrality in the unit cell. We may then rewrite Eqs. (2.56)–(2.58) in the conventional shell model form

$$\underline{A} = \underline{Z}\,\underline{C}\,\underline{Z}_i + \underline{R} \quad , \tag{2.60}$$

$$\underline{B} = \underline{Z}_i\underline{C}\,\underline{Y} + \underline{T} \quad , \tag{2.61}$$

$$\underline{G} = \underline{Y}\,\underline{C}\,\underline{Y} + \underline{U} + \underline{k} \tag{2.62}$$

[$\underline{k}$ assumed to be independent of $\vec{q}$ and of the form $\bar{k}(\kappa)d_{\kappa\kappa'}$ for cubic crystals], where

$$\underline{R} = -\underline{Y}\,\underline{C}\,\underline{Z}_i - \underline{Z}_i\underline{C}\,\underline{Y} - \underline{W}'\underline{Y} - \underline{Y}\,\underline{W}'^{\dagger}$$

$$+\underline{Y}\,\underline{C}\,\underline{Y} + \underline{Y}\,\underline{S}^{-1}\underline{Y} + \underline{R}' + \underline{J}\,\underline{a}^{-1}\underline{J}^{\dagger} + \underline{D}^{(0)}, \tag{2.63}$$

$$\underline{T} = -\underline{Z}_i\underline{C}\,\underline{Y} - \underline{W}'\underline{Y} + \underline{Y}(\underline{S}^{-1})\underline{Y} \quad , \tag{2.64}$$

$$\underline{U} + \underline{k} = -\underline{Y}\,\underline{C}\,\underline{Y} + \underline{Y}\,\underline{S}^{-1}\underline{Y} \quad . \tag{2.65}$$

(Note that in the shell model the matrix $\underline{U}$ is usually called $\underline{S}$, but here it must be distinguished from our matrix $\underline{S}$.) The long-range (Coulombic) parts of the matrices $\underline{W}'$ and $\underline{S}^{-1}$ are, by Eqs. (2.4) and (2.23), equal to $-\underline{Z}\,\underline{C}$ and $\underline{C}$, respectively. Using this result and Eq. (2.59) it may be shown that $\underline{R}$, $\underline{T}$, $\underline{U}+\underline{k}$ have no long-range Coulombic components and hence are regular as $\vec{q} \to 0$. Also, by Eq. (2.32a) and the definition of $\underline{D}^{(0)}$, it may be seen that $\underline{D}^{(0)}$ is given by

$$D_{\alpha\beta}^{(0)\kappa\kappa'} = -\delta_{\kappa\kappa'}\sum_{\kappa''}\left(\underline{Z}\,\underline{\bar{C}}\,\underline{Z} + \underline{\bar{R}}' + \underline{\bar{J}}\,\underline{\bar{a}}^{-1}\underline{\bar{J}}^{\dagger} - \underline{\bar{W}}'\underline{\bar{S}}\,\underline{\bar{W}}'^{\dagger}\right) \quad . \tag{2.66}$$

Using Eqs. (2.59) and (2.66), and the microscopic definition of the "shell charge" Y_{κ} given by Eq. (2.50), it may be shown after a little manipulation that

$$\sum_{\kappa'} \bar{R}_{\alpha\beta}^{\kappa\kappa'} = 0 \tag{2.67}$$

(where $\underline{\bar{R}}$ denotes the value at $\vec{q}=0$), and also that

$$\sum_{\kappa} \bar{T}_{\alpha\beta}^{\kappa\kappa'} = 0 \quad . \tag{2.68}$$

Equations (2.67) and (2.68) are the usual invariance conditions imposed in the shell model to satisfy the conditions of vanishing frequencies and dipole moments for a uniform lattice translation. They are seen here to arise as a result of the way the microscopic theory defines the shell charge, and the acoustic sum rule. If we further impose the usual shell model invariance condition on the matrix $\underline{U}$, i.e.,

$$\sum_{\kappa'} \bar{U}_{\alpha\beta}^{\kappa\kappa'} = 0 \quad , \tag{2.69}$$

then by Eq. (2.65),

$$k(\kappa) = \sum_{\kappa'}\left(-\underline{Y}\,\underline{\bar{C}}\,\underline{Y} + \underline{Y}\,\underline{S}^{-1}\underline{Y}\right)_{\alpha\beta}^{\kappa\kappa'}$$

$$= \sum_{\kappa'}\left(-Y_{\kappa}\bar{C}_{\kappa\kappa'}Y_{\kappa'} + Y_{\kappa}\bar{W}_{\kappa\kappa'}'^{\dagger}\right) \quad . \tag{2.69}$$

We note that the coupling coefficients $\underline{R}$, $\underline{T}$, and $\underline{U}+\underline{k}$ contain short-range interactions that arise both from the "mechanical-overlap" matrices $\underline{R}'$ and $\underline{J}$, and from the "dipole overlap" or short-range corrections to the Lorentz fields in the matrices $\underline{W}$ and $\underline{V}$. In addition, there may be a further short-range contribution from possible $\vec{q}$ dependence of $\underline{a}$. Let us suppose that the mechanical-overlap matrices $\underline{R}'$ and $\underline{J}$ vanish. In addition let us suppose that the pseudo potential $W_{\kappa}(\vec{Q})$ is such that it is pure Coulomb-like for interaction between a core and the dipole distributions on neighboring ions but is a constant for interaction between a core and its own dipole distribution, as would for instance be the case for $W_{\kappa}(\vec{Q})$ given by Eq. (2.15) if $r_s(\kappa)$ were greater than the diameter of the dipole distributions on the site κ. In such a case $\underline{W}'$ becomes equal to $-\underline{Z}\,\underline{C}$, and it may be easily verified that the $k(\kappa)$ given by Eq. (2.69) vanish, and that further by Eqs. (2.63)–(2.65), $\underline{R}=\underline{T}=\underline{U}$, which is a commonly used assumption in practical applications of the shell model. In general, however these short-range coupling coefficients will not be equal. Equation (2.69), in conjunction with Eq. (2.50), represents a microscopic expression for the force constant between an ion core and its own "shell," and it is not surprising that it vanishes in the case that the pseudopotential removes all self-interaction at an ion site.

The "electronic polarizability" matrix for the ions in the shell model is given by[1]

$$(\alpha_e)_{\kappa\kappa'} = (e^2/\Omega)\left[\underline{Y}(\underline{\bar{U}}+\underline{\bar{k}})^{-1}\underline{Y}\right]_{\kappa\kappa'} \quad .$$

In the above microscopic interpretation of the shell model, using Eq. (2.65), this matrix is given by

$$(\alpha_e)_{\kappa\kappa'} = (e^2/\Omega)\,(\overline{V} - \overline{C} + \overline{a}^{-1})^{-1}_{\kappa\kappa'}, \qquad (2.70)$$

and would be $(e^2/\Omega)a_{\kappa\kappa'}$, if the coupling coefficient $\underline{V}$ did not differ from the usual Coulomb-coupling coefficient $\underline{C}$ due to overlap, exchange and correlation effects. This is consistent with Eq. (2.8) which is the true microscopic expression for the polarizability.

III. CALCULATIONS FOR KCl AND KBr

A rigorous calculation of the phonon spectrum of ionic crystals within the framework of the formalism described in Sec. II, is an extremely difficult task. In principle, one has to calculate $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ in terms of the electronic band structure and from it obtain the "best" $a^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ and the $f^{\kappa}(\vec{Q})$. In addition, the task of calculating the overlap matrices $\underline{J}$ and $\underline{R}'$ from Eqs. (2.17), (2.20), and (2.21) is a formidable one. Finally, there is the question of exchange and correlation corrections to the effective electron-electron interaction. We therefore introduce at this stage some drastic simplifications so that a practicable calculation can be carried out. The first simplification is to assume that the alkali ions are nonpolarizable (i.e., behave like rigid cores) and there are neither cross-polarizability terms nor any $\vec{q}$-dependent contribution to $\underline{a}$. Then $\underline{a}$ simplifies to the form

$$a^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = a_2\delta_{\alpha\beta}\delta_{\kappa\kappa'}\delta_{\kappa 2}\ , \qquad (3.1)$$

where 2 denotes an anion site. $(e^2/\Omega)a_2$ is then the polarizability of the anion in the crystal. The form factor $f^{(1)}(\vec{Q})$ associated with the cation disappears from the equations. For the form factor $f^{(2)}(\vec{Q})$ we have chosen the form factor of the outer p electrons on a free halogen ion, as calculated from the Clementi[28] wave functions. The procedure has some justification from the discussion following Eq. (2.53) in Sec. II.

The second simplification is to totally neglect the overlap matrices $\underline{J}$ and $\underline{R}'$. This may be justified somewhat by remembering that $\underline{J}$ and $\underline{R}'$ depend on the choice of volumes $V_0(\kappa)$ chosen around each ion. [Their variation with $V_0(\kappa)$ being compensated for by a corresponding variation in the matrix $\underline{W}$.] The overlap matrices are discussed in more detail in Sec. IV. The most dominant overlap contributions will arise from overlap atomic orbitals centered on neighboring ions. It is shown in the next section that, under certain approximations, if we regard the alkali ion as being nonpolarizable (i.e., as a rigid core) then overlap can be neglected, provided there is no *occupied* halogen orbital inside the $V_0(1)$. (1 is the cation site).

Finally, the electron-electron interaction is approximated by the simple form given in Eq. (2.13), representing exchange and correlation effects in terms of a simple "cut-off radius" r_{xc}. The residual potential $W_\kappa(\vec{Q})$ is given by Eq. (2.15).

With these approximations it may be verified that the only nonvanishing components of the matrix $S^{\kappa\kappa'}_{\alpha\beta}(\vec{q})$ are for $\kappa=\kappa'=2$, and that $\overline{S}_{\kappa\kappa'}$ defined in Eq. (2.10) simplifies to

$$\overline{S}_{\kappa\kappa'} = [a_2/(1+\overline{V}_{22}a_2)]\delta_{\kappa\kappa'}\delta_{\kappa 2}\ , \qquad (3.2)$$

$$\epsilon_\infty = 1 + \frac{4\pi e^2}{\Omega}\,\frac{a_2}{1+\overline{V}_{22}a_2}\ . \qquad (3.3)$$

The formulas for the effective charges [Eq. (2.36)] reduce to

$$Z^{\mathrm{eff}}(1) = Z_1\left(1 + \overline{W}^{12}_r\,\frac{a_2}{1+\overline{V}_{22}a_2}\right)\ , \qquad (3.4a)$$

$$Z^{\mathrm{eff}}(2) = Z_2\left(1 + \overline{W}^{22}_r\,\frac{a_2}{1+\overline{V}_{22}a_2}\right)\ , \qquad (3.4b)$$

where we have written

$$\overline{W}^{\kappa\kappa'} = Z_\kappa\overline{W}^{22}_r\ , \qquad (3.5)$$

so that $W^{\kappa\kappa'}_r$ is independent of Z_κ. The effective-charge sum rule then becomes

$$\frac{a_2}{1+\overline{V}_{22}a_2}\,(Z_1\overline{W}^{12}_r + Z_2\overline{W}^{22}_r) = -(Z_1+Z_2)\ . \qquad (3.6)$$

Using Eq. (3.6), the shell charges given by Eq. (2.50) may be seen to be

$$Y_1 = 0\ ,\quad Y_2 = -(Z_1+Z_2)\ .$$

The dynamical matrix may be written

$$D^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) = Z_\kappa Z_{\kappa'}C^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) - (\underline{W}\ \underline{S}\ \underline{W}^{\dagger})^{\kappa\kappa'}_{\alpha\beta}(\vec{q}) + D^{(0)\kappa\kappa'}_{\alpha\beta}\ . \qquad (3.7)$$

The model is now physically similar to a simple shell model with only the halogen ion polarizable except for the difference that the point-dipole assumption is here generalized to include multipole corrections arising from the overlapping extended dipole distributions (approximated here by the free halogen-ion p-electron distribution). These multipole corrections give rise to the only short-range forces present in this model.

At our disposal are the radii r_1, r_2 of the volumes V_0 around the cation and anion, respectively. In order to carry out the calculations we also need to know the corresponding pseudoion or "core"charges Z_1, Z_2, the parameter a_2 and the value of r_{xc}. It is to be noted that r_{xc} (which enters into a calculation of $\overline{V}_{22}$) and a_2 determine the high-frequency dielectric constant ϵ_∞. In practice, it was found that the phonon-dispersion curves did not depend sensitively on the separate values of a_2 and r_{xc} but only on that combination which yielded a given ϵ_∞. Thus, r_x-was fixed at 0.10a (a is the lattice constant) and a_2 was left as an adjustable parameter, which was adjusted to fit reasonably well to the experimental ϵ_∞, as well as to give good agreement with the dispersion curves. For the radius r_1 around the cation it is sufficient to choose a value which is consistent with $V_0(1)$ containing *all* the core electrons. For both KCl and KBr r_1 was set at $a/\sqrt{8}$ [or the radius at which the spheres $V_0(1)$ centered on the cations touch] and Z_1 at $+1$. Z_2 is then determined by the effective-charge sum rule as given by Eq. (3.6). The radius r_2 was kept as an adjustable parameter, together with a_2 as discussed above. The calculations were quite sensitive to the choice of r_2. Figure 1 shows the resulting curves for KCl together with the experimental data of Copley *et al.*[29] The agreement with experiment is better than 10%. The value of a_2 chosen was 0.46×10^{-4} cm/dyn.

The value of ϵ_∞ calculated using a_2 is 2.13 in agreement with the experimental value.[30] The value chosen for r_2 was $0.132a$ in order to obtain reasonable agreement with the dispersion curves. The value for Z_2 calculated from the sum rule was 1.4 implying 3.6 $3p$ electrons inside the volume V_2. Estimates of the valence electron charge density on the Cl ion based on the Clementi wave functions used in the calculation indicate the number of $3p$ electrons inside the radius r_2 to be ~2.2 however, implying that the above simple model is not totally consistent with the static charge density in the crystal. It is to be emphasized that we are here referring to the distribution of all *six p* electrons belonging to the Cl ion.

Figure 2 shows the corresponding calculations for KBr together with the experimental data of Woods *et al.*[2] Agreement with experiment is in general better than 5%. However, there are large discrepancies at the zone boundary for the TA[001] and LO[111] branches. The discrepancy for the LO[111] branch is also present in the six-parameter simple shell-model analysis of Cowley *et al.*,[3] where they assume that the ionic charge is unity and the cation is nonpolarizable (i.e., we refer here to their model II). Physical arguments[3] suggest that this discrepancy is unlikely to be resolved by any model which assumes spherically symmetric dipole distributions on the anions only, as in the simple shell model or in the present model, whereas introduction of a breathing mode[8,9] or other "shell deformation" modes is known to be able to considerably reduce this discrepancy. The effect is also expected to be larger for the more polarizable anions, which may explain why KCl is fitted much better by our model. Another possible explanation is that the experimental measurements of the LO[111] branch in KBr are contaminated by interference with two-phonon scattering from the TA[111] branch, a circumstance that does not occur for KCl. The cause of the discrepancy in the TA[001] mode is not clear. The value of r_2 used was $0.15a$ and a_2 was chosen as 0.617×10^{-4} cm/dyn.

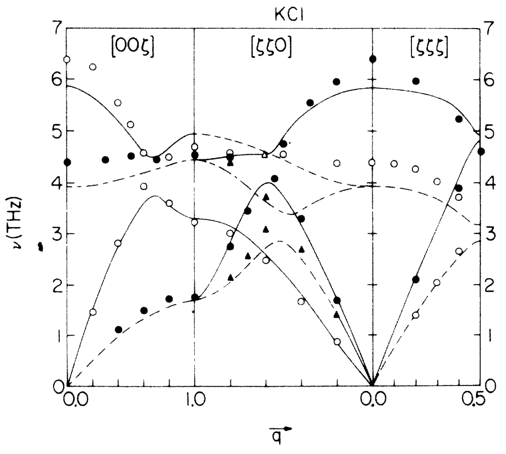

FIG. 1. Comparison of calculated phonon dispersion curves for KCl with the experimental results of Copley *et al.* (Ref. 29) at 115°K.

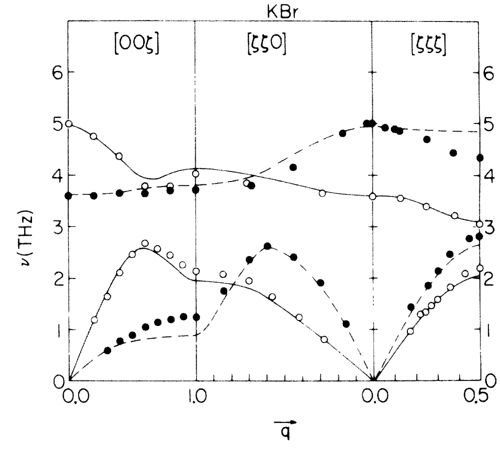

FIG. 2. Comparison of calculated phonon dispersion curves for KBr with the experimental results of Woods *et al.* (Ref. 2) at 90°K.

The calculated value of ϵ_∞ is 2.18 which is about 2% less than the experimental value.[30] This set of parameters also yield a value for Z_2, the charge on the Br pseudoion core of 0.725, and would thus imply that the number of $4p$ electrons inside the radius r_2 was 4.275, whereas the Clementi orbitals for the free bromine ion yield 2.35 electrons inside the radius r_2.

One of the essential approximations used in the present calculations is to use the form factor of the outermost p shell of the anion in place of $f^{(2)}(Q)$. In principle, a_2 and $f^{(2)}(\vec{Q})$ could be determined by $\epsilon(\vec{Q},\vec{Q})$ calculated from the valence electron energy bands and wave-functions. Such a calculation has been performed for the alkali halides by Lipari[31,32] using a tight-binding representation for the valence bands and a single orthogonalized plane wave representation for the conduction band. Lipari adjusts the parameters of his wavefunctions so that his calculated $\epsilon(\vec{Q},\vec{Q})$ at $\vec{Q}=0$ agrees with the experimental ϵ_∞, thereby completely ignoring the local-field corrections to ϵ_∞. This procedure is highly questionable and likely to be very inaccurate for ionic crystals. Thus the calculations of $\epsilon(\vec{Q},\vec{Q})$ using his method were repeated (after correcting some minor errors in some of his equations) in such a way that ϵ_∞ calculated using the correct expression (3.3) agreed with experiment. However, the $f(\vec{Q})$ thus obtained appears to decrease too rapidly as a function of $\vec{Q}$ and the calculated dispersion curves could not reproduce the experimental results very well, even if all parameters were adjusted. The use of the p-shell form factor may be partially justified by appealing to the sum rule given in Eq. (2.51) [see Eq. (2.53)], but even so the free-ion form factor may be changed in the crystal and no attempt is made here to account for this. The neglect of the overlap matrices $\underline{J}$ and $\underline{R}'$ while allowing for the overlap of the form factor on the anion onto the cation site is also, in principle, an inconsistent procedure. Nevertheless, considering the simplicity of the model it appears to be reasonably successful in explaining basic features of the phonon dispersion curves without invoking any highly unphysical parameters or arbitrary short-range force constants.

IV. DISCUSSION OF OVERLAP FORCES

In general, it is not always possible to neglect the "mechanical-overlap" forces, no matter what choice is made for the $V_0(\kappa)$. An example of an ionic crystal where such forces will always be important is AgCl. In general, the short-range "overlap" forces arise from two causes. The first is the exchange interaction between charge clouds on neighboring ions. Such interactions have been analyzed by Löwdin[33] and Lundqvist[34] for ionic crystals, and also by several other workers.[6,7,35–40] In addition to two-body forces, they also give rise to three-body and higher many-body forces. Within the context of the present formalism, the major part of such interactions are taken into account by including the exchange part of $W_\kappa(\vec{r})$, the electron-pseudoion interaction [for electrons *outside* $V_0(\kappa)$] in the nonlocal matrix element $M_{k'k}$, as discussed in Sec. II. The second type of overlap force arises from the distortion of the ionic wave functions as the ions change their relative distances. Within the framework of the harmonic and adiabatic approximations, such effects are included in the dynamics by directly calculating the effect of $M_{k'k}$ [as given by Eq. (2.16)] on the electronic state energies to second order in perturbation theory. This results in the "overlap" coupling coefficient R', defined in Eq. (2.20). Corresponding overlap coupling coefficients involving the dipole moments are $\underline{a}$ and $\underline{J}$ defined in Eqs. (2.6) and (2.21), respectively. In the present work, therefore, only the second contribution to the overlap forces has been explicitly discussed. While the exchange interactions are undoubtedly important for calculating the cohesive energy and stability of the *static* lattice, it is likely that the "distortion effect" plays a major role in determining the dynamics of the vibrating lattice, since the dynamics will involve the first effect only through second-order changes of the exchange interactions. This hypothesis is thus equivalent to stating that the contribution to $M_{k'k}$ given by Eq. (2.16) dominates over additional contributions introduced by the nonlocal exchange part of $W_\kappa(\vec{r})$.

Although, as mentioned, numerical evaluation of such forces is extremely difficult, we show in this section how the nature of such forces can be qualitatively analyzed in terms of the electronic structure. Such considerations may be useful for an economical parameterization of such forces, if necessary. We confine ourselves to crystals where each ion is at a center of symmetry. We thus examine the matrices $\underline{a}$, $\underline{R}'$, and $\underline{J}$ as defined in Eqs. (2.6), (2.20), and (2.21), respectively. Let us first consider the matrix $\underline{R}'$. The corresponding force constant between the ion at $(0,\kappa)$ and that at (l',κ') may be seen by Fourier analyzing Eq. (2.20) to be given by

$$\begin{aligned}\Phi^{R'}_{\alpha\beta}\binom{0l'}{\kappa\kappa'} = &-\frac{1}{N\Omega}\left(\frac{\hbar^2}{2m}\right)^2\sum_{kk'}\tfrac{1}{2}\{\exp[i(\vec{k}'-\vec{k})\circ(\vec{r}_{l'}+\vec{r}_{\kappa'}-\vec{r}_\kappa)]+\exp[-i(\vec{k}'-\vec{k})\cdot(\vec{r}_{l'}+\vec{r}_{\kappa'}-\vec{r}_\kappa)]\}\\ &\times\frac{n(k)-n(k')}{E_k-E_{k'}}\left[\int_{V_0(0,\kappa)}d\vec{r}\left(\nabla^2\varphi^\kappa_{k'}(\vec{r}-\vec{r}_\kappa)\frac{\partial}{\partial x_\alpha}\varphi^{*\kappa}_k(\vec{r}-\vec{r}_\kappa)-\varphi^\kappa_{k'}(\vec{r}-\vec{r}_\kappa)\nabla^2\frac{\partial}{\partial x_\alpha}\varphi^{*\kappa}_k(\vec{r}-\vec{r}_\kappa)\right)\right]\\ &\times\left[\int_{V_0(0,\kappa')}d\vec{r}\left(\nabla^2\varphi^{*\kappa'}_{k'}(\vec{r}-\vec{r}_{\kappa'})\frac{\partial}{\partial x_\beta}\varphi^{\kappa'}_k(\vec{r}-\vec{r}_{\kappa'})-\varphi^{*\kappa'}_{k'}(r-r_{\kappa'})\nabla^2\frac{\partial}{\partial x_\beta}\varphi^{\kappa'}_k(\vec{r}-\vec{r}_{\kappa'})\right)\right]\ ,\end{aligned}\qquad(4.1)$$

where we have transformed the surface integrals in Eq. (2.17) to volume integrals by the use of Green's theorem. The integrations are over the volumes $V_0(\kappa)$, $V_0(\kappa')$ in the origin unit cell.

Equation (4.1) shows that the force constant is a sum of contributions from various sets of interband transitions. [Since, for an insulator, we need only consider interband transitions, we may drop the prime over the summation in Eq. (4.1).] Let us consider the contribution to the above force constant from two bands λ, λ', which we shall assume for simplicity to be flat, i.e., we assume $\Delta_{\lambda\lambda'} \equiv (E_{\vec{k},\lambda} - E_{\vec{k}',\lambda'})$, independent of the Bloch wave vectors $\vec{k}$, $\vec{k}'$. In this tight-binding approximation, we may regard the functions $\varphi^{\kappa}_{\vec{k}\lambda}(\vec{r}-\vec{r}_\kappa)$ in the subcell $(0,\kappa)$ to be made up of atomic orbitals centered both on the ion at $(0,\kappa)$ and on neighboring ions, i.e., we write

$$\varphi^{\kappa}_{\vec{k}\lambda}(\vec{r}-\vec{r}_\kappa) = \sum_{\kappa_1 l_1} \exp[i\,\vec{k}\circ(\vec{r}_{l_1}+\vec{r}_{\kappa_1}-\vec{r}_\kappa)] \sum_t C_{\vec{k}\lambda}(\kappa_1 t)\,\chi_t(\vec{r}-\vec{r}_{l_1}-\vec{r}_{\kappa_1}) \quad , \tag{4.2}$$

where $\chi_t(\vec{r}-\vec{r}_{l_1}-\vec{r}_{\kappa_1})$ denotes an atomic orbital of type t centered on the ion at (l_1,κ_1). Consistent with our approximation of flat bands, we neglect the dependence of $C_{\vec{k}\lambda}(\kappa_1\ t)$ on k. Then the $\lambda \to \lambda'$ contribution to $\Phi^{R'}_{\alpha\beta}\binom{0l}{\kappa\kappa'}$ may be written

$$\begin{aligned}\Phi^{\lambda\lambda',R'}_{\alpha\beta}\begin{pmatrix}0l'\\ \kappa\kappa'\end{pmatrix} = &-\frac{1}{2N\Omega}\left(\frac{\hbar^2}{2m}\right)^2 \Delta^{-1}_{\lambda\lambda'} \sum_{\vec{k},\vec{k}'} \sum_{\substack{\kappa_1 l_1\\ \kappa_2 l_2}} \sum_{\substack{\kappa_3 l_3\\ \kappa_4 l_4}} \sum_{\substack{t_1 t_2\\ t_3 t_4}} C_{\lambda'}(\kappa_1 t_1) C^*_{\lambda}(\kappa_3 t_3) C_{\lambda'}(\kappa_2 t_2) C^*_{\lambda}(\kappa_4 t_4)\, \mu^*_\alpha\left(\begin{matrix} l_1\kappa_1 & l_3\kappa_3\\ t_1 & t_3\end{matrix}\,\middle|\, 0\kappa\right)\\ &\times \mu_\beta\left(\begin{matrix} l_2\kappa_2 & l_4\kappa_4\\ t_2 & t_4\end{matrix}\,\middle|\, 0\kappa'\right) \{\exp[i\,\vec{k}'\cdot(\vec{r}_{l'}+\vec{r}_{l_1}+\vec{r}_{\kappa_1}-\vec{r}_{l_2}-\vec{r}_{\kappa_2}+2\vec{r}_{\kappa'}-2\vec{r}_\kappa)]\\ &\times \exp[i\,\vec{k}\cdot(-\vec{r}_{l'}-\vec{r}_{l_3}-\vec{r}_{\kappa_3}+\vec{r}_{l_4}+\vec{r}_{\kappa_4}-2\vec{r}_{\kappa'}+2\vec{r}_\kappa)] + \exp[i\,\vec{k}'\circ(-\vec{r}_{l'}+\vec{r}_{l_1}+\vec{r}_{\kappa_1}-\vec{r}_{l_2}-\vec{r}_{\kappa_2})]\\ &\times \exp[i\,\vec{k}\cdot(\vec{r}_{l'}-\vec{r}_{l_3}-\vec{r}_{\kappa_3}+\vec{r}_{l_4}+\vec{r}_{\kappa_4})]\} \quad ,\end{aligned} \tag{4.3}$$

where

$$\mu_\alpha\left(\begin{matrix} l\kappa & l'\kappa'\\ t & t'\end{matrix}\,\middle|\, 0\kappa''\right) \equiv \int_{V_0(0,\kappa)} d\vec{r}\left(\nabla^2\chi^*_t(\vec{r}-\vec{r}_l-\vec{r}_\kappa)\frac{\partial}{\partial x_\alpha}\,\chi_{t'}(\vec{r}-\vec{r}_{l'}-\vec{r}_{\kappa'}) - \chi^*_t(r-r_l-r_\kappa)\nabla^2\frac{\partial}{\partial x_\alpha}\,\chi_{t'}(r-r_{l'}-r_{\kappa'})\right). \tag{4.4}$$

We now consider the case where band λ is made up only of orbitals centered on sites $\kappa=2$, of specific type λ, while band λ' is made up only of orbitals centered on sites $\kappa=1$ of type λ', i.e., we set

$$C_\lambda(\kappa t) = \delta_{t\lambda}\delta_{\kappa 2} \;\; ; \;\; C_{\lambda'}(\kappa t) = \delta_{t\kappa'}\delta_{\kappa 1} \quad .$$

Then Eq. (4.3) becomes

$$\begin{aligned}\Phi^{\lambda\lambda',R'}_{\alpha\beta}\begin{pmatrix}0l'\\ \kappa\kappa'\end{pmatrix} = &-\frac{1}{2N\Omega}\left(\frac{\hbar^2}{2m}\right)^2 \Delta^{-1}_{\lambda\lambda'} \sum_{l_1 l_2 l_3 l_4} \mu^*_\alpha\left(\begin{matrix} l_1 1 & l_3 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa\right) \mu_\beta\left(\begin{matrix} l_2 1 & l_4 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa'\right)\\ &\times\left(\sum_{\vec{k}} \exp[i\,\vec{k}\circ(\vec{r}_{l_4}-\vec{r}_{l_3}-\vec{r}_{l_1}+2\vec{r}_\kappa-2\vec{r}_{\kappa'})]\sum_{\vec{k}'}\exp[i\,\vec{k}'\cdot(\vec{r}_{l'}-\vec{r}_{l_2}+\vec{r}_{l_1}-2\vec{r}_\kappa+2\vec{r}_{\kappa'})]\right.\\ &\left.+\sum_{\vec{k}}\exp[i\,\vec{k}\cdot(\vec{r}_{l_4}-\vec{r}_{l_3}+\vec{r}_{l'})]\sum_{\vec{k}'}\exp[i\vec{k}'\circ(\vec{r}_{l_1}-\vec{r}_{l_2}-\vec{r}_{l'})]\right) \quad .\end{aligned} \tag{4.5}$$

For lattices with every ion at a center of symmetry $2(\vec{r}_{\kappa'}-\vec{r}_\kappa) \equiv \vec{L}(\kappa',\kappa)$ equals a lattice vector for all κ, κ' and the sums over $\vec{k}$, $\vec{k}'$ yield δ functions in terms of which l_2, l_4 can be eliminated. The result is

$$\begin{aligned}\Phi^{\lambda\lambda',R'}_{\alpha\beta}\begin{pmatrix}0l'\\ \kappa\kappa'\end{pmatrix} = &-\frac{1}{2}\left(\frac{\hbar^2}{2m}\right)^2 \Delta^{-1}_{\lambda\lambda'} \sum_{l_1 l_3} \left[\mu^*_\alpha\left(\begin{matrix} l_1 1 & l_3 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa\right) \mu_\beta\left(\begin{matrix} l_1 1 + L(\kappa'\kappa),1 & l_3+l'+L(\kappa'\kappa),2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa'\right)\right.\\ &\left.+\mu^*_\alpha\left(\begin{matrix} l_1 1 & l_3 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa\right) \mu_\beta\left(\begin{matrix} l_1 - l' 1 & l_3 - l' 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa'\right)\right] \quad ,\end{aligned} \tag{4.6}$$

where the notation

$$\mu_\alpha\left(\begin{matrix} l_1'+l_2'+\ldots,1 & l_1+l_2+\ldots,2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa\right)$$

stands for $\mu_\alpha\left(\begin{smallmatrix} l',1 & l\,2\\ \lambda' & \lambda\end{smallmatrix}\middle| 0\kappa\right)$, with

$$\vec{r}_{l'} = \vec{r}_{l_1'}+\vec{r}_{l_2'}+\ldots, \quad \vec{r}_l = \vec{r}_{l_1}+\vec{r}_{l_2}+\ldots,\text{etc.}$$

Now

$$\mu_\beta\left(\begin{matrix} l_1-l',1 & l_3-l',2\\ \lambda' & \lambda\end{matrix}\,\middle|\, 0\kappa'\right) = \mu_\beta\left(\begin{matrix} l_1 1 & l_3 2\\ \lambda' & \lambda\end{matrix}\,\middle|\, l'\kappa'\right) \tag{4.7}$$

upon shifting the origin of integration in Eq. (4.4).

Let us choose the unit cell origin to be at the κth ion. Then the inversion operation will take a general ion position $(r_{l'}+r_{\kappa'})$ to $[-r_{l'}-L(\kappa'\kappa)+r_{\kappa'}]$.

Let us symbolically represent this operation by $(l', \kappa') \rightarrow (-l' - \kappa')$. Then

$$\mu_\beta \left(\begin{matrix} l_1 + l' + L(\kappa'\kappa), 1 & l_3 + l' + L(\kappa'\kappa), 2 \\ \lambda' & \lambda \end{matrix} \middle| \, 0\kappa' \right)$$

$$= \mu_\beta \left(\begin{matrix} l_1 1 & l_3 2 \\ \lambda' & \end{matrix} \middle| \begin{matrix} -l' - \kappa' \\ \lambda \end{matrix} \right) . \tag{4.8}$$

On examination of Eq. (4.4) we also see that

$$\mu_\beta \left(\begin{matrix} -l_1 - 1 & -l_3 - 2 \\ \lambda' & \lambda \end{matrix} \middle| \, -l' - \kappa' \right) = - \mu_\beta \left(\begin{matrix} l_1 1 & l_3 2 \\ \lambda' & \lambda \end{matrix} \middle| \, l'\kappa' \right), \tag{4.9}$$

since the χ_t's have a definite parity. Since the sums run over all l_1, l_3 we see by performing the inversion operation on both μ^*_α and μ_β in the first term of Eq. (4.6) and making use of Eqs. (4.7) and (4.8) that the first term is identical to the second, and hence

$$\Phi^{\lambda\lambda', R'}_{\alpha\beta} \begin{pmatrix} 0l' \\ \kappa\kappa' \end{pmatrix} = - \left(\frac{\hbar^2}{2m} \right)^2 \Delta^{-1}_{\lambda\lambda'}$$

$$\times \sum_{l_1 l_3} \mu^*_\alpha \left(\begin{matrix} l_1 1 & l_3 2 \\ \lambda' & \lambda \end{matrix} \middle| \, 0\kappa \right) \mu_\beta \left(\begin{matrix} l_1 1 & l_3 2 \\ \lambda' & \lambda \end{matrix} \middle| \, l'\kappa' \right). \tag{4.10}$$

From Eq. (4.10), the physical meaning of the origin of the contribution $\Phi^{\lambda\lambda', R'}_{\alpha\beta}\binom{0l'}{\kappa\kappa'}$ becomes clear. It arises from a process where the displacement $u_\alpha(0\kappa)$ of the ion inside the volume $V_0(0, \kappa)$ causes a virtual excitation of an electron from an occupied orbital λ centered on the ion at $(l_3 2)$ to an unoccupied orbital λ' centered on the ion at $(l_1 1)$, due to overlap inside the volume $V_0(0, \kappa)$, while the virtual deexcitation between the same two orbitals occurs due to the displacement $u_\beta(l'\kappa')$ via the overlap in the volume $V_0(l'\kappa')$. Thus the most general kind of force of this type is a four-body force (see Fig. 3).

The restrictions on this kind of force are also obvious from Eq. (4.10). Both the occupied orbital λ centered on $(l_3, 2)$ and the unoccupied orbital λ' centered on $(l_1, 1)$ must have appreciable overlap in both volumes $V_0(0\kappa)$ and $V_0(l'\kappa')$ *simultaneously*, otherwise the ions at $(0, \kappa)$ and $(l'\kappa')$ will not be coupled via this mechanism. Thus in practice the most important such interactions are of the two-body type [where the pair $(l_1, 1)$ and $(l_3, 2)$ coincides with the pair $(0, \kappa)$ and (l', κ')] or of the three-body type [where *one* of $(l_1, 1)$ or $(l_3, 2)$ coincides with *one* of $(0, \kappa)$ or (l', κ')]. It may also be seen that if the occupied orbitals λ centered on the sites 2 do not overlap onto the volumes $V_0(l, 1)$ or $V_0(l, 2)$ of other cells, there is *no* overlap contribution as discussed in Sec. III. The next case to consider is that of both orbitals λ', λ overlapping only onto volumes $V_0(l, \kappa)$ centered on *neighboring* ions. In this case, it is obvious that second-neighbor ions cannot be coupled together, since such a pair of ions cannot simultaneously have a type-1 *and* a type-2 ion as nearest neighbors. On the other hand, nearest-neighbor interactions of the two-body type will be present. We now examine the nature of the forces when the atomic orbitals overlap onto volumes $V_0(l\kappa)$ centered on second-neighbor ions. Let us consider the case of an alkali halide of the NaCl structure as shown schematically in Fig. 4. The occupied orbitals λ are centered on the type 2 (anion) sites and we suppose these to overlap only with nearest neighbors. The excited state orbitals λ' are centered on the type-1 (cation) sites and we suppose that these can overlap second neighbor as well. Then it is obvious that there is still no second-neighbor anion-anion interaction, since there are no orbitals λ' common to *both* volumes V_0 on these sites, (see Fig. 4). On the other hand, cation-cation interactions now exist up to second *and* third neighbors. For example, the second neighbors A and D may interact via three-body forces involving the orbital λ on ion B and the excited state orbitals λ' on either A or D. The third neighbors A and C may interact via four-body forces involving the orbitals λ on B, and orbitals λ' on D or E, and so on. Figures 3 and 4 implicitly assume spherically symmetric or s-type orbitals on the ions. The case of p-type and d-type orbitals with directed lobes can also be considered and the presence or absence of specific interactions can be analyzed in a similar fashion.

We now show explicitly how the structure of the force constants is determined by the symmetry of

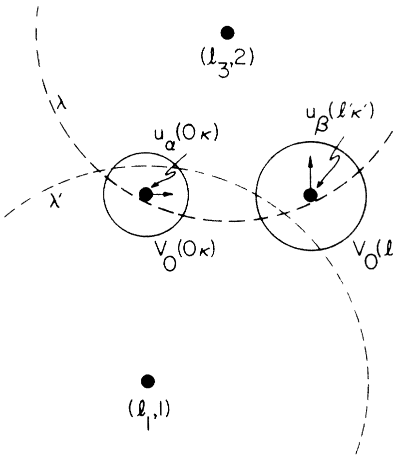

FIG. 3. Diagram indicating how the ionic displacements $u_\alpha(0, \kappa)$ and $u_\beta(l', \kappa')$ get coupled via the overlap of an occupied orbital (indicated by λ) and an excited state orbital (indicated by λ') centered on two different ions into *both* the volumes $V_0(0, \kappa)$ and $V_0(l'\kappa')$ surrounding the ions in question. For simplicity, the orbitals shown here are both spherically symmetric.

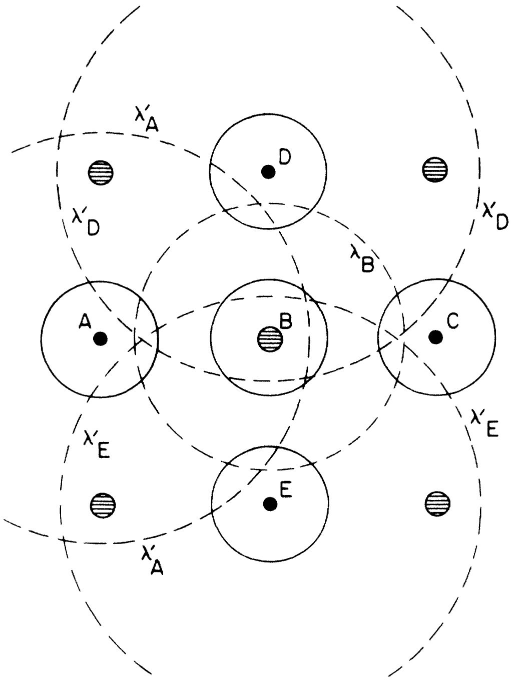

FIG. 4. Diagram indicating how ionic displacements get coupled by overlap interactions in the case that the occupied orbitals (indicated by λ) overlap only onto volumes V_0 centered on neighboring ions, whereas the excited state orbitals (indicated by λ') overlap on to volumes V_0 centered on ions out to second neighbors. The full circles indicate the volumes V_0 (chosen equal on both anion and cation sites for simplicity). The dashed circles indicate the orbitals (taken as spherically symmetric here for simplicity). A, C, D, E denote cation sites and B is an anion site. λ_B denotes an orbital centered on site B and so on. Note that A and C are coupled via $\lambda_B \rightarrow \lambda'_E$, and $\lambda_B \rightarrow \lambda'_D$ transitions; A and D are coupled via $\lambda_B \rightarrow \lambda'_A$ and $\lambda_B \rightarrow \lambda'_D$ transitions; and so on, while A and B are coupled via $\lambda_B \rightarrow \lambda'_A$, $\lambda_B \rightarrow \lambda'_D$ and $\lambda_B \rightarrow \lambda'_E$ transitions, etc.

the orbitals involved. Consider any unitary transformation $R_{\alpha\beta}$ (which includes rotations and reflections) under which $(l\kappa)$ is brought to $\underline{R}(l\kappa)$. (Note as yet we do not specify these to correspond to point group operations of the crystal lattice.) Under such a transformation the atomic orbitals are transformed according to

$$\chi_t(\underline{R}\vec{r}) = \sum_{t'} T_{tt'}(R)\,\chi_{t'}(\vec{r}) \ , \tag{4.11}$$

where the $\chi_{t'}$ are the set of atomic orbitals having the same angular momentum quantum number as χ_t. On examination of Eq. (4.4) we see that

$$\mu_\alpha\left(\begin{matrix}\underline{R}(l\kappa) & \underline{R}(l'\kappa') \\ t & t'\end{matrix}\,\middle|\, R(0\kappa'')\right) = \sum_{t''t'''\beta} T^*_{tt''}(R)$$

$$\times T_{t't'''}(R) R_{\alpha\beta}\, \mu_\beta\left(\begin{matrix}l\kappa & l'\kappa' \\ t'' & t'''\end{matrix}\,\middle|\, 0\kappa''\right) \ , \tag{4.12}$$

where the rotation is assumed to be performed about the point $(0\kappa'')$. Substituting in Eq. (4.10) we obtain

$$\Phi^{\lambda\lambda', R'}_{\alpha\beta}\begin{pmatrix}0l' \\ \kappa\kappa'\end{pmatrix} = -\left(\frac{\hbar^2}{2m}\right)\Delta^{-1}_{\lambda\lambda'} \sum_{\substack{\mu\mu' \\ \nu\nu'}} \sum_{\substack{\gamma\,\delta \\ l_1 l_3}} \times T_{\lambda'\mu'}(R)\, T^*_{\lambda'\nu'}(R)\, T^*_{\lambda\mu}(R)\, T_{\lambda\nu}(R) R_{\alpha\gamma} R_{\beta\delta}$$
$$\times \mu^*_\gamma\left(\begin{matrix}\underline{R}(l_1,1) & R(l_3,2) \\ \mu' & \mu\end{matrix}\,\middle|\, R(0\kappa)\right) \times \mu_\delta\left(\begin{matrix}\underline{R}(l_1,1) & \underline{R}(l_3,2) \\ \nu' & \nu\end{matrix}\,\middle|\, \underline{R}(l'\kappa')\right) \ . \tag{4.13}$$

In μ_γ, the rotation is performed about (0κ) and in μ_δ, it is performed about $(l'\kappa')$. Let us now suppose that we have two sets of bands p, p', with the occupied set p being a degenerate set formed out of orbitals λ which *completely* span the space of functions of a given angular momentum, and similarly for p'. Thus p, p' may be single s bands, or triply degenerate p bands, or fivefold degenerate d bands, and so on. The total contribution $\Phi^{pp', R'}_{\alpha\beta}\binom{0\,l'}{\kappa\kappa'}$ is obtained from Eq. (4.13) by summing over all λ, λ' orbitals belonging to bands p, p'. Using the unitary character of the $T_{tt'}(R)$, we obtain

$$\Phi^{pp', R'}_{\alpha\beta}\begin{pmatrix}0l' \\ \kappa\kappa'\end{pmatrix} = -\left(\frac{\hbar^2}{2m}\right)^2 \Delta^{-1}_{pp'} \sum_{\gamma\,\delta} R_{\alpha\gamma} R_{\beta\delta} \times \sum_{\mu,\mu'} \sum_{l_1 l_3} \mu^*_\gamma\left(\begin{matrix}\underline{R}(l_1,1) & \underline{R}(l_3,2) \\ \mu' & \mu\end{matrix}\,\middle|\, \underline{R}(0\kappa)\right)$$
$$\times \mu_\delta\left(\begin{matrix}\underline{R}(l_1,1) & \underline{R}(l_3,2) \\ \mu' & \mu\end{matrix}\,\middle|\, \underline{R}(l'\kappa')\right) \ , \tag{4.14}$$

where μ belongs to band p, and μ' to band p'. Let us further consider the case when only two-body contributions $[(l_1, 1), (l_3, 2)] = (0, \kappa)$, $(l'\kappa')$ are appreciable . So far there has been no restriction on the matrix $\underline{R}$. Let us now restrict it to those operations that leave $[\vec{r}(l'\kappa') - \vec{r}(0,\kappa)]$ unchanged. For such matrices, Eq. (4.14) yields (for the case of two-body forces only)

$$\Phi^{pp', R'}_{\alpha\beta}\begin{pmatrix}0l' \\ \kappa\kappa'\end{pmatrix} = \sum_{\gamma\,\delta} R_{\alpha\gamma} R_{\beta\delta}\, \Phi^{pp', R'}_{\gamma\delta}\begin{pmatrix}0l' \\ \kappa\kappa'\end{pmatrix} \ . \tag{4.15}$$

Consideration of all such operations leads to the result that the force constant must be of the form

$$\Phi^{pp', R'}_{\alpha\beta}\begin{pmatrix}0l' \\ \kappa\kappa'\end{pmatrix} = C\, X_\alpha\, X_\beta + D\, \delta_{\alpha\beta} \ , \tag{4.16}$$

where

$$\vec{X} = \vec{r}(l'\kappa') - \vec{r}(0\kappa) \ , \tag{4.17}$$

i.e., we have the result that the force-constant contribution arising from the transition from a completely occupied set of bands to a completely unoccupied set is of the axially symmetric kind. This result is of course intuitively obvious. In particular, $s \to s$ transitions always give rise only to central overlap forces in the two-body approximation. In the case that three-body forces are appreciable, or that crystal-field effects separate out a subset of orbital states for the bands p or p' (e.g., T_{2g} or E_g bands from the total set of d orbitals), $\underline{R}$ must be restricted to one of the point-group operations of the *crystal* itself, and Eq. (4.15) then reduces to the usual crystal symmetry restrictions on the tensor force constants. Equation (4.12) however can still be used to reduce the number of independent overlap (multi-center) integrals which go into a calculation of the force constant tensor. In addition, the number may be reduced further by recognizing that certain orbitals will have very little overlap with certain sets of neighbors.

Similar considerations hold for the force constants contained in the matrices $\underline{J}$ and $\underline{a}$. It is to be noted however that it is $\underline{a}^{-1}$ which enters the equations of motion for the lattice, and hence even nearest-neighbor force constants in $\underline{a}$ will give rise to rather complicated force constants between the constituent entities ("cores" and "shells") in the shell model interpretation of the equations of motion. Thus, in practice, it may be better to parametrize $\underline{a}$ directly in terms of "force constants" rather than to parametrize the interactions in the shell model where $\underline{a}^{-1}$ appears.

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