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Contributions of Three-body Overlap Effects to the Force Fields in CaF_2-type Shell-model Lattices

Ø. RA

Institute of Physical Chemistry, The Technical University of Norway, Trondheim

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Due to the exclusion principle the distribution of electronic charge in an ionic crystal differs from a superposition of free-ion charge densities even in the simple Heitler-London picture. This charge density deformation engenders three-body long-range forces the influence of which on lattice vibrations is not accounted for by the usual Kellermann matrix. To obtain a better separation of long-range from short-range forces in CaF_2, SrF_2, and BaF_2, i. e. to avoid absorbing long-range interactions in an adjustable short-range force field, explicit formulae are derived for three-body contributions to the shell-model equations of motion. The additional dynamical matrices pertain to arbitrary wavelengths. In adding to the force field terms which are not purely volume dependent the present descirption of three-body forces is somewhat at variance with recent work on alkali halide dynamics. The deviation from pure volume dependence originates in overlap charges residing in internuclear regions.

I. Introduction

This report [hereafter called III] is part of a continuing effort to relate the dynamical properties of CaF_2, SrF_2, and BaF_2 to the force field predicted by a semi-empirical Heitler-London model. The reasons for choosing the ionic extreme as a point of departure for lattice dynamics studies have been summarized on a previous occasion and need not be repeated here[1]. We have thus far presented in

I) a detailed symmetry analysis of lattice waves and CaF_2-type Fourier-transformed dynamical matrices for all wave vectors the groups of which have translations as a proper subgroup[2]; and in

II) an adjustment of potentials describing such short-range forces which can, at least approximately, be studied without allowing for [dipole] polarization of the ions[1]. This adaptation of potentials was conducted on the basis of free-ion SCF functions.

Reprint requests to Dr. Ø. RA, Institute of Physical Chemistry Technical University of Norway, *Trondheim* Norwegen.

It was found that charge density deformations stemming from first neighbour $M^{2+}—F^-$ overlap and from second neighbour $F^-—F^-$ overlap induce forces which contribute significantly to the compressibility and, although to a lesser degree, quite appreciably to $\frac{1}{2}(c_{11} - c_{12})$. As regards the shear modulus this result differs from the findings of VERMA and DAYAL[3] concerning alkali halide crystals. These authors concluded that $\frac{1}{2}(c_{11} - c_{12})$ remains unaffected by many-body forces; the long-ranged three-body part of which was therefore described as a purely volume dependent force. This characterization, it would seem, does not extend to CaF_2, SrF_2, and BaF_2. As a general comment on II it may be stated that the trend in these calculations parallels the increase in cation „size" and $M^{2+}—F^-$ overlap charge, and the decrease in $F^-—F^-$ overlap charge, through the sequence CaF_2, SrF_2, and BaF_2.

It follows from the results in II that even a fully ionic picture is incompatible with a central force description. For restricted purposes it may, of

course, be useful to lump in with short-ranged forces even long-ranged interactions which transcend Coulomb forces between ions carrying point charges. This has been done by AXE[4] who found that a shell-model[5] with Born-Mayer shell-shell couplings reproduces reasonably well experimental long-wave properties of the three alkaline-earth fluorides. Axe's model, with some adjustment, has quite successfully been applied also in calculations of third-order elastic moduli[6-7]. Moreover the parameter values of the model are, in the CaF_2 case, not drastically different from results obtained by ELCOMBE and PRYOR[8] on fitting their experimental phonon dispersion curves with a shell-model based on point-charge ions and axially symmetric forces between low-order neighbours. Nevertheless, as indicated in II and as will be more fully discussed in a forthcoming paper[9], an Axe-type two-body model does not provide an entirely satisfactory picture of harmonic lattice dynamics of alkaline-earth fluorides. Nor does it lead to temperature variations of effective Grüneisen constants which are in quantitative agreement with deductions made from thermal expansion measurements[9]. These shortcomings do not become rectified by adding breathing effects or by accounting for the finite extension of shells[9]. Otherwise stated, there are interactions which cannot, for general purposes, be adequately represented when averaged into central force potentials. Hence it seems justified to extend the previous work on restoring forces activated by homogeneous deformations[1] to effects of three-body interactions on lattice waves of arbitrary wavelengths. After reviewing briefly in section II the origin of overlap charge, this extension will be undertaken in section III of this paper; numerical calculations, however, being deferred to a future publication. In section IV a comparison will be made with the works of LUNDQUIST[10-12], DICK and OVERHAUSER[13], and VERMA and coworkers[3,14-15] on overlap charge forces in alkali halides. However, before closing the present section, we outline the geometry of a fluorite lattice. In units of the cubic cell edge there is a cation ($\varkappa = 1$) at (0, 0, 0), fluorine ions ($\varkappa = 2, 3$) at (1/4, 1/4, 1/4), (3/4, 3/4, 3/4) plus f.c.c. translations.

II. Origin and Description of Overlap Charge

For convenience we summarize briefly the OC-model as applied to a static array of ions. Let $\boldsymbol{\rho}$ denote the superposition of first-order free-ion density matrices, and let $\boldsymbol{\Phi}$ denote the row $(\varphi_1, \ldots, \varphi_N)$ composed of free-ion one-electron wave functions. Then $\boldsymbol{\rho} = \boldsymbol{\Phi}\boldsymbol{\Phi}^\dagger$. Let furthermore $\bar{\boldsymbol{\rho}}$ stand for the first-order density in the Heitler-London lattice, i.e.

$$\bar{\boldsymbol{\rho}} = \boldsymbol{\Phi}\boldsymbol{\Delta}^{-1}\boldsymbol{\Phi}^\dagger, \quad \boldsymbol{\Delta} = \boldsymbol{\Phi}^\dagger\boldsymbol{\Phi} = 1 + \boldsymbol{S}. \tag{II.1}$$

The overlap charge is a result of the exclusion principle and can be identified with a sum over spins performed on the diagonal elements of the matrix $\Delta\boldsymbol{\rho} = \bar{\boldsymbol{\rho}} - \boldsymbol{\rho}$. Denoting overlap charge by $q_s(\boldsymbol{r})$ and applying the $\boldsymbol{S}^2$-approximation[16] we have

$$\begin{aligned}\Delta\boldsymbol{\rho} &= \boldsymbol{\Phi}[\boldsymbol{\Delta}^{-1} - 1]\boldsymbol{\Phi}^\dagger \\ &= \boldsymbol{\Phi}\{-\boldsymbol{S} + \mathrm{diag}[S^2(\boldsymbol{x}, \boldsymbol{x}), S^2(\boldsymbol{x}', \boldsymbol{x}'), \ldots]\}\boldsymbol{\Phi}^\dagger\end{aligned} \tag{II.2}$$

and

$$\begin{aligned}&\Delta\varrho(\boldsymbol{x}, \boldsymbol{x}) \\ &\quad = \sum_k \varphi_k^*(\boldsymbol{x})\,\varphi_k(\boldsymbol{x}) \sum_i S_{ki}^2 - \sum_{kl} \varphi_k(\boldsymbol{x})\,\varphi_l^*(\boldsymbol{x})\,S_{kl}\end{aligned} \tag{II.3}$$

whence follows

$$\begin{aligned}q_s(\boldsymbol{r}) &= \sum_{(fg)} q(\boldsymbol{r})_{s\,(fg)} \\ &= |e| \sum_{(fg)} \{q_f(\boldsymbol{r}) + q_g(\boldsymbol{r}) + q_{fg}(\boldsymbol{r})\}\end{aligned} \tag{II.4}$$

where

$$q_f(\boldsymbol{r}) = -2\sum_{\nu\mu} S_{\nu\mu}^2\,\varphi_\nu(\boldsymbol{r})\,\varphi_\nu^*(\boldsymbol{r}), \tag{II.5a}$$

$$q_g(\boldsymbol{r}) = -2\sum_{\nu\mu} S_{\mu\nu}^2\,\varphi_\mu(\boldsymbol{r})\,\varphi_\mu^*(\boldsymbol{r}), \tag{II.5b}$$

$$q_{fg}(\boldsymbol{r}) = 4\sum_{\nu\mu} S_{\nu\mu}\,\varphi_\mu(\boldsymbol{r})\,\varphi_\nu^*(\boldsymbol{r}). \tag{II.5c}$$

In the above expressions $\boldsymbol{x}$ signifies a space-spin coordinate, $\boldsymbol{r}$ refers to a space coordinate, and $\nu(\mu)$ designates an orbital centered on an ion f(g). In the point charge approximation the three-body interaction [more-body interactions involving the self-energy of overlap charge do not appear in the $\boldsymbol{S}^2$-approximation] of $q(\boldsymbol{r})_{s\,(fg)}$ with the lattice reads

$$\begin{aligned}E_s^3(f\,g) = |e|^2 \sum_{p \neq f,g} \varepsilon(p)\,&(q_{fg}/R_{fg,p} \\ &+ q_f/R_{fp} + q_g/R_{gp})\end{aligned} \tag{II.6}$$

with

$$q_{fg} = 4\sum_{\nu\mu} S_{\nu\mu} \int \varphi_\mu(\boldsymbol{r})\,\varphi_\nu^*(\boldsymbol{r})\,\mathrm{d}^3\boldsymbol{r} = 4S_{fg}^2, \tag{II.7a}$$

$$q_f = -2S_{fg}^2, \tag{II.7b}$$

$$q_g = -2S_{fg}^2 \tag{II.7c}$$

the first of which relations define S^2_{fg}. Here $\varepsilon(p)$ is the formal charge on p, $R_{fg,p}$ is the distance from the electrical center of gravity of $q_{fg}(r)$ to p, R_{fp} is the distance from f to p, and, similarly, R_{gp} is the distance from g to p. Justified by previous work[1] we express the dependence of q_{fg}, q_f, q_g on the internuclear distance R_{fg} by writing

$$S^2_{fg} = C_{fg}\, R_{fg} \exp[-R_{fg}/\varrho_{fg}]. \qquad \text{(II.8)}$$

For reasons previously detailed[1] we restrict the interest to first-neighbour $M^{2+}-F^-$ and second-neighbour $F^- - F^-$ pairs. Accordingly, we may use without ambiguity the alternative notation C_{+-}, C_{--}, ϱ_{+-}, ϱ_{--}. An account of the wave functions and procedures employed in evaluating the foregoing quantities for CaF_2, SrF_2, and BaF_2 can be found in II. This then completes the outline of the static lattice OC-model.

III. Effects of Three-body Interactions on the Dynamical Matrix

Focusing attention on a subspace of displacements spanned by lattice waves of fixed $\boldsymbol{k}$ the amplitude of the $\varkappa$-th core in the l-th cell can be written as $\boldsymbol{U}(l\varkappa) = \boldsymbol{U}(\varkappa)\exp[i\boldsymbol{k}\cdot\boldsymbol{x}(l)]$. Similarly we write for the displacement of the $(l\varkappa)$-shell away from its associated core $\boldsymbol{W}(l\varkappa) = \boldsymbol{W}(\varkappa)\exp[i\boldsymbol{k}\cdot\boldsymbol{x}(l)]$. We now assume that ion pair $(l\varkappa l'\varkappa')$ of the distorted lattice contributes three overlap point charges given by relations analogous to Eq. (II.7a, b, c), where this time $S^2(l\varkappa l'\varkappa')$ is to be approximated by

$$S^2(l\varkappa l'\varkappa') = C(l\varkappa l'\varkappa') R(l\varkappa l'\varkappa') \times \exp[-R(l\varkappa l'\varkappa')/\varrho(l\varkappa l'\varkappa')] \qquad \text{(III.1)}$$

with

$$R(l\varkappa l'\varkappa') = |\boldsymbol{x}(l\varkappa) - \boldsymbol{x}(l'\varkappa') + \boldsymbol{V}(l\varkappa) - \boldsymbol{V}(l'\varkappa')| \qquad \text{(III.2)}$$

and

$$\boldsymbol{V}(l\varkappa) = \boldsymbol{U}(l\varkappa) + \boldsymbol{W}(l\varkappa), \qquad \text{(III.3)}$$

and where $C(l\varkappa l'\varkappa')$, $\varrho(l\varkappa l'\varkappa')$ equal C_{+-}, ϱ_{+-} or C_{--}, ϱ_{--}. $\boldsymbol{x}(l\varkappa)$ is the equilibrium position of the $\varkappa$-th ion in the l-th unit cell. By analogy with Eq. (II.6), we furthermore assume the existence of a three-body energy term which can be approximated by

$$E^3_s(l\varkappa l'\varkappa') = |e|^2 \sum_{(l''\varkappa'')\neq(l\varkappa),(l'\varkappa')} \{q(l\varkappa l'\varkappa')(x(\varkappa'')/R^u(l\varkappa l'\varkappa', l''\varkappa'') + y(\varkappa'')/R^w(l\varkappa l'\varkappa', l''\varkappa'')) + q(l\varkappa)(x(\varkappa'')/R^u(l\varkappa, l''\varkappa'') + y(\varkappa'')/R^w(l\varkappa, l''\varkappa'')) + q(l'\varkappa')(x(\varkappa'')/R^u(l'\varkappa', l''\varkappa'') + y(\varkappa'')/R^w(l'\varkappa', l''\varkappa''))\} \qquad \text{(III.4)}$$

where $|e|\,x(\varkappa'')$ ($|e|\,y(\varkappa'')$) denotes a core (shell) charge, and where

$$R^u(l\varkappa l'\varkappa', l''\varkappa'') = |\boldsymbol{x}(l''\varkappa'') + \boldsymbol{U}(l''\varkappa'') - \{\boldsymbol{x}(l\varkappa) + \boldsymbol{V}(l\varkappa) + \mathcal{X}(l\varkappa l'\varkappa') \times [\boldsymbol{x}(l'\varkappa') + \boldsymbol{V}(l'\varkappa') - \boldsymbol{x}(l\varkappa) - \boldsymbol{V}(l\varkappa)]\}|, \qquad \text{(III.4a)}$$

$$R^w(l\varkappa l'\varkappa', l''\varkappa'') = |\boldsymbol{x}(l''\varkappa'') + \boldsymbol{V}(l''\varkappa'') - \{\boldsymbol{x}(l\varkappa) + \boldsymbol{V}(l\varkappa) + \mathcal{X}(l\varkappa l'\varkappa') \times [\boldsymbol{x}(l'\varkappa') + \boldsymbol{V}(l'\varkappa') - \boldsymbol{x}(l\varkappa) - \boldsymbol{V}(l\varkappa)]\}|, \qquad \text{(III.4b)}$$

$$R^u(l\varkappa, l''\varkappa'') = |\boldsymbol{x}(l''\varkappa'') + \boldsymbol{U}(l''\varkappa'') - \boldsymbol{x}(l\varkappa) - \boldsymbol{V}(l\varkappa)| \qquad \text{(III.4c)}$$

$$R^w(l\varkappa, l''\varkappa'') = |\boldsymbol{x}(l''\varkappa'') + \boldsymbol{V}(''\varkappa'') - \boldsymbol{x}(l\varkappa) - \boldsymbol{V}(l\varkappa)| \qquad \text{(III.4d)}$$

with $\mathcal{X}(l\varkappa l'\varkappa')$ given by

$$\mathcal{X}(l\varkappa l'\varkappa') = \{\sum_{\nu\mu} S_{\nu\mu} \int \varphi^*_\nu(\boldsymbol{r})\,\varphi_\mu(\boldsymbol{r})\,(\boldsymbol{r}\cdot[\boldsymbol{x}(l'\varkappa') - \boldsymbol{x}(l\varkappa)]\,d\tau\}/\{S^2(l\varkappa l'\varkappa')\,|\,\boldsymbol{x}(l'\varkappa') - \boldsymbol{x}(l\varkappa)|\}. \qquad \text{(III.4e)}$$

Since by construction $\mathcal{X}(l\varkappa l'\varkappa') = \frac{1}{2}$ for $F^- - F^-$ pairs, we shall in what follows suppress $(l\varkappa l'\varkappa')$ and write only $\mathcal{X}$ while reserving this symbol for $M^{2+}-F^-$ pairs. Clearly, Eqs. (III.1–4) make the $q(l\varkappa)$ and $q(l'\varkappa')$ point charges „follow" the shells and, in addition, impose „proportional" motion for the point charge $q(l\varkappa l'\varkappa')$. For convenience we defer comments on the adequacy of the above assumptions to Section IV.

In the remainder of this section we take up the modifications brought about by E^3_s in the equations of motion. For verbal simplicity we shall refer to the assembly of cores and shells as the CS-lattice(s). The distribution of overlap point charge

throughout the model crystal will be called the OC-lattice(s). Our task then is to develop to second order in $\boldsymbol{U}$ and $\boldsymbol{W}$ the interaction between the OC and the CS lattices. In so doing we shall consider separately the two OC-sublattices originating in M^{2+}—F^- and F^-—F^- overlap. The two corresponding contributions to E_s^3 will be denoted E_s^{+-} and E_s^{--}, respectively.

Effects of M^{2+}-F^- Overlap. A.

Allotting to a unit cell those eight OC distributions which arise from the overlap of one M^{2+} ion with its eight nearest F^- neighbours we find to second order in core and shell amplitudes

i) at M^{2+} sites $\boldsymbol{x}(l) + \boldsymbol{V}(l\,1)$ an OC charge which equals

$$-\tfrac{1}{2}|e|\sum_{\sigma\in I[1]} Q(+-,l,\sigma)$$

where $I[1] = \{1,\ldots,8\}$; where $Q = Q_0 + Q_1 + Q_2$ with

$$Q(+-,l,\sigma)_0 = 4S^2_{+-,0}, \tag{III.5a}$$

$$\begin{aligned} Q(+-,l,\sigma)_1 &= (4/\sqrt{3})\,S^2_{+-,1} \\ &\times \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\sum_\alpha t[\sigma]_\alpha \\ &\times \{V(\varkappa[\sigma])_\alpha \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] - V(1)_\alpha\}, \end{aligned} \tag{III.5b}$$

$$\begin{aligned} Q(+-,l,\sigma)_2 &= (4/3)\exp[2i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)] \\ &\times \sum_\alpha\sum_\beta \{(\sqrt{3}\,S^2_{+-,1}/r_0) \\ &\times (\delta_{\alpha\beta} - (1/3)\,t[\sigma]_\alpha t[\sigma]_\beta) + S^2_{+-,2}\,t[\sigma]_\alpha t[\sigma]_\beta\} \\ &\times \{V(\varkappa[\sigma])_\alpha \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] - V(1)_\alpha\} \\ &\times \{V(\varkappa[\sigma])_\beta \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] - V(1)_\beta\}; \end{aligned} \tag{III.5c}$$

and where

$$\begin{aligned} S^2_{+-,0} &= C_{+-}(r_0\sqrt{3}/2)\exp(-r_0\sqrt{3}/[2\varrho_{+-}]), \\ S^2_{+-,1} &= S^2_{+-,0}[2/(r_0\sqrt{3}) - 1/\varrho_{+-}], \\ S^2_{+-,2} &= S^2_{+-,0}[r_0\sqrt{3}\,\varrho_{+-}]^{-1}[r_0\sqrt{3}/(2\varrho_{+-}) - 2]; \end{aligned} \tag{III.5d}$$

$$\begin{aligned} \boldsymbol{t}[1] &= (1,1,1), & \boldsymbol{t}[2] &= (\bar1,1,1), \\ \boldsymbol{t}[3] &= (\bar1,\bar1,1), & \boldsymbol{t}[4] &= (1,\bar1,1), \\ \boldsymbol{t}[5] &= (1,1,\bar1), & \boldsymbol{t}[6] &= (\bar1,1,\bar1), \\ \boldsymbol{t}[7] &= (\bar1,\bar1,\bar1), & \boldsymbol{t}[8] &= (1,\bar1,\bar1); \end{aligned} \tag{III.5e}$$

$$\begin{aligned} \varkappa[\sigma] &= 2 \quad \text{for} \quad \sigma\in I[2] = \{1,3,6,8\}, \\ \varkappa[\sigma] &= 3 \quad \text{for} \quad \sigma\in I[3] = \{2,4,5,7\}, \end{aligned} \tag{III.5f}$$

$$\begin{aligned} \boldsymbol{x}(l[\sigma]) &= (r_0/2)\,\boldsymbol{t}[\sigma] - \boldsymbol{x}(\varkappa); \\ &\sigma\in I[\varkappa], \quad \varkappa = 2,3. \end{aligned} \tag{III.5g}$$

ii) at the eight F^- positions

$$\begin{aligned} &\boldsymbol{x}(l) + (r_0/2)\,\boldsymbol{t}[\sigma] + \boldsymbol{V}(\varkappa[\sigma]) \\ &\quad\times \exp[i\,\boldsymbol{k}\cdot\{\boldsymbol{x}(l) + \boldsymbol{x}(l[\sigma])\}], \end{aligned}$$

$\sigma\in I[1]$ point charges $-\tfrac{1}{2}|e|\,Q(+-,l,\sigma)$.

iii) at the eight bond charge positions

$$\begin{aligned} &\boldsymbol{x}(l) + \boldsymbol{z}[\sigma] + \{\mathscr{X}\boldsymbol{V}(\varkappa[\sigma])\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] \\ &\qquad + (1-\mathscr{X})\,\boldsymbol{V}(1)\}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)], \end{aligned}$$

where

$$\boldsymbol{z}[\sigma] = (r_0/2)\,t[\sigma]\mathscr{X},$$

point charges $|e|\,Q(+-,l,\sigma)$.

Above the symbol r_0 has been given to one half the cubic cell edge. E_s^{+-} can be regarded as the sum of three terms,

$$E_s^{+-} = E_s^{+-}(1) + E_s^{+-}(2) + E_s^{+-}(3),$$

the first of which comes about because of the change of OC location in the course of a lattice vibration. The second originates from the change in OC magnitude, while the third relates to changes in position as well as in magnitudes of overlap charges.

The E_s^{+-} (1) Contribution to the Force Field

$E_s^{+-}(1)$ is conveniently broken into two parts: $E_s^{+-}(11)$ and $E_s^{+-}(12)$. $E_s^{+-}(11)$ represents the interaction between an undistorted CS-lattice and quadrupoles

$$\begin{aligned} &|e|\,[4S^2_{+-,0}]\{\mathscr{X}V(\varkappa[\sigma])_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] \\ &\quad + (1-\mathscr{X})\,V(1)_\alpha\}\{\mathscr{X}V(\varkappa[\sigma])_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] \\ &\quad + (1-\mathscr{X})\,V(1)_\beta\}\exp[2i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)] \end{aligned}$$

situated at $\boldsymbol{x}(l) + \boldsymbol{z}[\sigma]$. The corresponding forces exerted on the contents of the zeroth cell [choosing the zeroth cell is merely a convenience and entails no loss of generality] can be obtained from

$$\begin{aligned} -\partial E_s^{+-}(11)/\partial U(0\,\varkappa)_\alpha &= -\partial E_s^{+-}(11)/\partial W(o\,\varkappa)_\alpha \\ &= \sum_{\varkappa'}\sum_\beta E_s^{+-}(11\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta \end{aligned} \tag{III.6}$$

$$\begin{aligned} &E_s^{+-}(11\,|\,\boldsymbol{k}\,|\,1\alpha\varkappa'\beta) \\ &\quad = -[|e|^2\,4S^2_{+-,0}](1-\delta_{1\varkappa'})\mathscr{X}[1-\mathscr{X}] \\ &\quad\times\sum_{\sigma\in I[\varkappa']}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\,\psi(\alpha\beta\,|\,\boldsymbol{z}[\sigma]) \end{aligned} \tag{III.6a}$$

$$\begin{aligned} &E_s^{+-}(11\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) \\ &\quad = -[|e|^2\,4S^2_{+-,0}]\,\delta_{1\varkappa'}\mathscr{X}[1-\mathscr{X}] \\ &\quad\times\sum_{\sigma\in I[\varkappa]}\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\,\psi(\alpha\beta\,|\,\boldsymbol{z}[\sigma]); \\ &\qquad\qquad \varkappa = 2,3 \end{aligned} \tag{III.6b}$$

where

$$\psi(\alpha\beta\,|\,\boldsymbol{z}[\sigma]) \qquad \text{(III.6c)}$$
$$= (\partial^2/\partial x_\alpha\,\partial x_\beta)\Big(\sum_{l\varkappa'}\varepsilon(\varkappa')\,|\,\boldsymbol{x}-\boldsymbol{x}(l\varkappa)\,|^{-1}\Big)_{\boldsymbol{x}=\boldsymbol{z}[\sigma]}$$
$$+(1-\delta_{\alpha\beta})\,4\varepsilon(1)\,t[\sigma]_\alpha\,t[\sigma]_\beta$$
$$\times[\mathscr{X}^3-2(1-\mathscr{X})^3][\sqrt{3}r_0\mathscr{X}(1-\mathscr{X})]^{-3}.$$

Eqs. (III.6), which clearly will add a Hermitian form to the dynamical matrix of the rigid-shell model, follow in a straightforward manner from the standard recipe for the energy of a quadrupole in the potential due to a fixed charge distribution, from the translational invariance of the undistorted CS-lattice, and from the fact that the interaction of a charge q_{fg} with the formal charges on ions f and g already is contained in the M^{2+}—F^- two-body repulsive potential. The evaluation of the sum appearing in Eq. (III.6c) can be handled by a standard technique. Owing to the site symmetries in the CS-lattice [$\mathscr{O}_h$ and $\mathscr{T}_h$], force field contributions from similar OC-quadrupoles located at the $\boldsymbol{x}(l\varkappa)$'s vanish identically. In writing Eqs. (III.6a, b) use has been made of the fact that

$$\sum_{\sigma\in I[\varkappa]}\psi(\alpha\beta\,|\,\boldsymbol{z}[\sigma])=0$$

for all pairs (α,β) and for all three $\varkappa$-values 1, 2, 3.

Turning to $E_s^{+-}(12)$, which term accounts for the interaction of OC-dipoles

$$-|e|\,[16S^2_{+-,0}]\,\boldsymbol{V}(1)\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)] \quad \text{at} \quad \boldsymbol{x}(l\,1)=\boldsymbol{x}(l),$$
$$-|e|\,[8S^2_{+-,0}]\,\boldsymbol{V}(\varkappa)\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)] \quad \text{at} \quad \boldsymbol{x}(l\varkappa);\qquad \varkappa=2,3,$$

and

$$|e|\,[4S^2_{+-,0}]\{\mathscr{X}\boldsymbol{V}(\varkappa[\sigma])\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]+(1-\mathscr{X})\,\boldsymbol{V}(1)\}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)] \quad \text{at} \quad \boldsymbol{x}(l)+\boldsymbol{z}[\sigma],$$

with CS-dipoles, we find

$$-\partial E_s^{+-}(12)/\partial U(o\varkappa)_\alpha=-\partial E_s^{+-}(121)/\partial U(o\varkappa)_\alpha-\partial E_s^{+-}(122)/\partial U(o\varkappa)_\alpha$$
$$-\partial E_s^{+-}(123)/\partial U(o\varkappa)_\alpha-\partial E_s^{+-}(124)/\partial U(o\varkappa)_\alpha, \qquad \text{(III.7a)}$$

$$-\partial E_s^{+-}(12)/\partial W(o\varkappa)_\alpha=-\partial E_s^{+-}(121/\partial W(o\varkappa)_\alpha-\partial E_s^{+-}(122)/\partial W(o\varkappa)_\alpha$$
$$-\partial E_s^{+-}(123)/\partial W(o\varkappa)_\alpha-\partial E_s^{+-}(124)/\partial W(o\varkappa)_\alpha, \qquad \text{(III.7b)}$$

$$-\varepsilon(\varkappa)^{-1}\,\partial E_s^{+-}(121)/\partial U(o\varkappa)_\alpha=-y(\varkappa)^{-1}\,\partial E_s^{+-}(121)/\partial W(o\varkappa)_\alpha=\sum_{\varkappa'\beta}\sum E_s^{+-}(121\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta, \qquad \text{(III.7c)}$$

$$E_s^{+-}(121\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)=[|e|^2S^2_{+-,0}]\{-(1+\delta_{1\varkappa'})\,24\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,\alpha\beta\,|\,5)$$
$$+\delta_{\alpha\beta}(1+\delta_{1\varkappa'})\,8\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,3) \qquad \text{(III.7d)}$$
$$+(\delta_{1\varkappa'}[1-\mathscr{X}]+(1-\delta_{1\varkappa'})\,\mathscr{X})\,4\sum_{\sigma\in I[\varkappa']}[3\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}[\sigma]\,|\,\alpha\beta\,|\,5)-$$
$$-\delta_{\alpha\beta}\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}[\sigma]\,|\,3)][\delta_{1\varkappa'}+(1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]\},$$

$$-\varepsilon(\varkappa)^{-1}\,\partial E_s^{+-}(122)/\partial U(o\varkappa)_\alpha=-y(\varkappa)^{-1}\,\partial E_s^{+-}(122)/\partial W(o\varkappa)_\alpha=\sum_{\varkappa'}\sum_{\beta}E_s^{+-}(122\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa'\beta), \qquad \text{(III.7e)}$$

$$E_s^{+-}(122\,|\,\boldsymbol{k}\,|\,1\alpha\varkappa'\beta)=-[|e|^2S^2_{+-,0}]\,(32[\mathscr{X}^{-2}-\tfrac{1}{2}][r_0\sqrt{3}]^{-3})(1-\delta_{1\varkappa'})(1-\delta_{\alpha\beta})$$
$$\times\sum_{\sigma\in I[\varkappa']}t[\sigma]_\alpha\,t[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])], \qquad \text{(III.7f)}$$

$$E_s^{+-}(122\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)=-[|e|^2S^2_{+-,0}]\,(32[(1-\mathscr{X})^{-2}-\tfrac{1}{2}][r_0\sqrt{3}]^{-3})\,\delta_{1\varkappa'}(1-\delta_{\alpha\beta})$$
$$\times\sum_{\sigma\in I[\varkappa]}t[\sigma]_\alpha\,t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])];\qquad \varkappa=2,3, \qquad \text{(III.7g)}$$

$$-\partial E_s^{+-}(123)/\partial U(o\varkappa)_\alpha=-\partial E_s^{+-}(123)/\partial W(o\varkappa)_\alpha$$
$$=\sum_{\varkappa'}\sum_{\beta}E_s^{+-}(123\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)[U(\varkappa')_\beta\,\varepsilon(\varkappa')+W(\varkappa')_\beta\,y(\varkappa')], \qquad \text{(III.7h)}$$

$$E_s^{+-}(123\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)=[|e|^2S^2_{+-,0}]\{-24(1+\delta_{1\varkappa})\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,\alpha\beta\,|\,5)$$
$$+\delta_{\alpha\beta}(1+\delta_{1\varkappa})\,8\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,3)+ \qquad \text{(III.7i)}$$
$$+[\delta_{1\varkappa}[1-\mathscr{X}]+(1-\delta_{1\varkappa})\,\mathscr{X}]\,4\sum_{\sigma\in I[\varkappa]}[3\mathscr{S}^*(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa')\,\boldsymbol{z}[\sigma]\,|\,\alpha\beta\,|\,5)$$
$$-\delta_{\alpha\beta}\,\mathscr{S}^*(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa')\,\boldsymbol{z}[\sigma]\,|\,3)][\delta_{1\varkappa}+(1-\delta_{1\varkappa})\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]\},$$

$$-\partial E_s^{+-}(124)/\partial U(o\varkappa)_\alpha = -\partial E_s^{+-}(124)/\partial W(o\varkappa)_\alpha = \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(124\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,[\varepsilon(\varkappa')\,U(\varkappa')_\beta + y(\varkappa')\,W(\varkappa')_\beta], \tag{III.7j}$$

$$E_s^{+-}(124\,|\,\boldsymbol{k}\,|\,1\alpha\varkappa'\beta) = -[|e|^2 S^2_{+-,0}](32\,[(1-\mathscr{X})^{-2} - \tfrac{1}{2}]\,[r_0\sqrt{3}]^{-3})\,(1-\delta_{1\varkappa'})\,(1-\delta_{\alpha\beta}) \times \sum_{\sigma\in I[\varkappa']} t[\sigma]_\alpha\, t[\sigma]_\beta \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])], \tag{III.7k}$$

$$E_s^{+-}(124\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = -[|e|^2 S^2_{+-,0}](32\,[\mathscr{X}^{-2} - \tfrac{1}{2}]\,[r_0\sqrt{3}]^{-3})\,\delta_{1\varkappa'}(1-\delta_{\alpha\beta}) \times \sum_{\sigma\in I[\varkappa]} t[\sigma]_\alpha\, t[\sigma]_\beta \exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])];\ \varkappa = 2,3, \tag{III.7l}$$

$$\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}\boldsymbol{x}'\,|\,\alpha^\mu\beta^\nu\gamma^\eta\,|\,n) = \sum_l{}' [x_\alpha - x'_\alpha - x(l)_\alpha]^\mu \times [x_\beta - x'_\beta - x(l)_\beta]^\nu [x_\gamma - x'_\gamma - x(l)_\gamma]^\eta \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]/|\boldsymbol{x} - \boldsymbol{x}' - \boldsymbol{x}(l)|^n \tag{III.7m}$$

The prime over the summation in Eq. (III.7m) indicates that the $l = 0$ term is to be omitted for $\boldsymbol{x} = \boldsymbol{x}'$. The numerical treatment of the sums in question is dealt with in a forthcoming paper. In the foregoing formulae the $E_s^{+-}(121)$ and $E_s^{+-}(122)$ terms represent the forces which OC-dipole arrays exert on the CS-dipoles in the zeroth cell. Conversely, $E_s^{+-}(123)$ and $E_s^{+-}(124)$ come about because the zeroth cell CS-displacements themselves are responsible for some OC-dipoles which interact with CS-dipole lattices; the generating CS-dipoles having been left out when working out the interaction energy.

The E_s^{+-} (2) Contribution to the Force Field

Next we discuss the effect of charges which remain at fixed positions but fluctuate in magnitude during lattice vibrations. We separate $E_s^{+-}(2)$ into two parts: $E_s^{+-}(21)$ and $E_s^{+-}(22)$. $E_s^{+-}(21)$ refers to the interaction between a fictitious static CS-lattice and changes in overlap charges which are of second order in $\boldsymbol{U}$ and $\boldsymbol{W}$. $E_s^{+-}(22)$ stands for the potential energy of CS-dipoles in a distribution of first-order OC-fluctuations. There is no difficulty in showing that

$$-\partial E_s^{+-}(21)/\partial U(o\varkappa)_\alpha = -\partial E_s^{+-}(21)/\partial W(o\varkappa)_\alpha = \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(21\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta, \tag{III.8a}$$

$$E_s^{+-}(21\,|\,\boldsymbol{k}\,|\,1\alpha\varkappa'\beta) = -|e|^2(4/3)\left[\psi(\boldsymbol{x}(1)=\boldsymbol{0}) + \frac{\varepsilon(1)}{r_0\sqrt{3}}\left\{\frac{\mathscr{X}^2 - 7\mathscr{X} + 4}{\mathscr{X}[1-\mathscr{X}]}\right\} - 2\psi(\boldsymbol{x}[1]) + \psi(\boldsymbol{x}(2))\right] \times \sum_{\sigma\in I[\varkappa']} [(\sqrt{3}\,S^2_{+-,1}/r_0)(\delta_{\alpha\beta} - (1/3)\,t[\sigma]_\alpha\, t[\sigma]_\beta) + S^2_{+-,2}\,t[\sigma]_\alpha\, t[\sigma]_\beta]\,[-\delta_{1\varkappa'} + (1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]], \tag{III.8b}$$

$$E_s^{+-}(21\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = -|e|^2(4/3)\left[\psi(\boldsymbol{x}(1)=\boldsymbol{0}) + \frac{\varepsilon(1)}{r_0\sqrt{3}}\left\{\frac{\mathscr{X}^2 - 7\mathscr{X} + 4}{\mathscr{X}[1-\mathscr{X}]}\right\} - 2\psi(\boldsymbol{x}[1]) + \psi(\boldsymbol{x}(2))\right] \times (\delta_{\varkappa\varkappa'} + \delta_{1\varkappa'})\sum_{\sigma\in I[\varkappa]} [(\sqrt{3}\,S^2_{+-,1}/r_0)(\delta_{\alpha\beta} - (1/3)\,t[\sigma]_\alpha\, t[\sigma]_\beta) + S^2_{+-,2}\,t[\sigma]_\alpha\, t[\sigma]_\beta]\,[\delta_{1\varkappa'}\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] - (1-\delta_{1\varkappa'})];\qquad \varkappa = 2,3. \tag{III.8c}$$

In keeping with the notation introduced in Eq. (III.6c) ψ is defined by

$$\psi(\boldsymbol{x}) = \sum_{l\varkappa}{}' \varepsilon(\varkappa)\,|\boldsymbol{x} - \boldsymbol{x}(l\varkappa)|^{-1} \tag{III.8d}$$

where the prime excludes summands with a zero denominator. In arriving at Eqs. (III.8b, c) trivial use has been made of lattice symmetry.

As for $E_s^{+-}(22)$ we get

$$-\partial E_s^{+-}(22)/\partial U(o\varkappa)_\alpha = -\sum_{j=1}^{4} \partial E_s^{+-}(22j)/\partial U(o\varkappa)_\alpha, \tag{III.9a}$$

$$-\partial E_s^{+-}(22)/\partial W(o\varkappa)_\alpha = -\sum_{j=1}^{4} \partial E_s^{+-}(22j)/\partial W(o\varkappa)_\alpha \tag{III.9b}$$

where

$$-\partial E_s^{+-}(221)/\partial U(o\varkappa)_\alpha = -\sum_{j=1}^{2}\partial E_s^{+-}(211\,j)/\partial U(o\varkappa)_\alpha, \tag{III.9c}$$

$$-\partial E_s^{+-}(221)/\partial W(o\varkappa)_\alpha = -\sum_{j=1}^{2}\partial E_s^{+-}(221\,j)/\partial W(o\varkappa)_\alpha, \tag{III.9d}$$

$$-\partial E_s^{+-}(223)/\partial U(o\varkappa)_\alpha = -\sum_{j=1}^{2}\partial E_s^{+-}(223\,j)/\partial U(o\varkappa)_\alpha, \tag{III.9e}$$

$$-\partial E_s^{+-}(223)/\partial W(o\varkappa)_\alpha = -\sum_{j=1}^{2}\partial E_s^{+-}(223\,j)/\partial W(o\varkappa)_\alpha \tag{III.9f}$$

and where

$$-\varepsilon(\varkappa)^{-1}\,\partial E_s^{+-}(2211)/\partial U(o\varkappa)_\alpha = -y(\varkappa)^{-1}\,\partial E_s^{+-}(2211)/\partial W(o\varkappa)_\alpha$$
$$= \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(2211\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta \tag{III.9g}$$

$$E_s^{+-}(2211\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = [2\,|e|^2\,S^2_{+-,1}/\sqrt{3}]\,[(\delta_{1\varkappa'}-1)\,\bar{\mathscr{P}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(1)\,|\,\alpha\,|\,3)$$
$$\times\Big(\sum_{\sigma\in I[\varkappa']} t[\sigma]_\beta \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big) + \delta_{1\varkappa'}\sum_{\varkappa''}(1-\delta_{1\varkappa''})\,\bar{\mathscr{P}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa'')\,|\,\alpha\,|\,3) \tag{III.9h}$$
$$\times\Big(\sum_{\sigma\in I[\varkappa'']} t[\sigma]_\beta \exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big) + 2\sum_{\sigma\in I[1]}(\delta_{1\varkappa'}+\delta_{\varkappa[\sigma]\varkappa'})$$
$$\times\,\bar{\mathscr{P}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}[\sigma]\,|\,\alpha\,|\,3)\,t[\sigma]_\beta\,[-\delta_{1\varkappa'}+(1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]],$$

$$-\varepsilon(\varkappa)^{-1}\,\partial E_s^{+-}(2212)/\partial U(o\varkappa)_\alpha = -y(\varkappa)^{-1}\,\partial E_s^{+-}(2212)/\partial W(o\varkappa)_\alpha$$
$$= \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(2212\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta \tag{III.9i}$$

$$E_s^{+-}(2212\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = i[2\,|e|^2\,S^2_{+-,1}/\sqrt{3}]\,(4\pi/v)\,|\,\boldsymbol{k}\,|^{-2}\,k_\alpha$$
$$\times\exp[i\,\boldsymbol{k}\cdot\{\boldsymbol{x}(\varkappa)+i\,\boldsymbol{k}[4\tau]^{-1}\}]\,\Big[(1-\delta_{1\varkappa'})\Big(\sum_{\sigma\in I[\varkappa']} t[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big)$$
$$-\delta_{1\varkappa'}\sum_{\varkappa''}(1-\delta_{1\varkappa''})\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(\varkappa'')] \tag{III.9j}$$
$$\times\Big(\sum_{\sigma\in I[\varkappa'']} t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big) - 2\sum_{\sigma\in I[1]}(\delta_{1\varkappa'}+\delta_{\varkappa[\sigma]\varkappa'})$$
$$\times\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{z}[\sigma]]\,t[\sigma]_\beta\,[-\delta_{1\varkappa'}+(1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]],$$

$$-\varepsilon(\varkappa)^{-1}\,\partial E_s^{+-}(222)/\partial U(o\varkappa)_\alpha = -y(\varkappa)^{-1}\,\partial E_s^{+-}(222)/\partial W(o\varkappa)_\alpha = \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(222\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,V(\varkappa')_\beta, \tag{III.9k}$$

$$E_s^{+-}(222\,|\,\boldsymbol{k}\,|\,1\alpha\varkappa'\beta) = [16\,|e|^2\,S^2_{+-,1}/(9r_0^2)]\,[\mathscr{X}^{-2}-\tfrac{1}{2}]$$
$$\times\sum_{\sigma\in I[\varkappa']}(-\delta_{1\varkappa'}\,\delta_{\alpha\beta}+(1-\delta_{1\varkappa'})\,t[\sigma]_\alpha\,t[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]), \tag{III.9l}$$

$$E_s^{+-}(222\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = [16\,|e|^2\,S^2_{+-,1}/(9r_0^2)]\,([1-\mathscr{X}]^{-2}-\tfrac{1}{2})$$
$$\times\sum_{\sigma\in I[\varkappa]}(\delta_{1\varkappa'}\,t[\sigma]_\alpha\,t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]-\delta_{\varkappa\varkappa'}\,\delta_{\alpha\beta});\quad \varkappa=2,3, \tag{III.9m}$$

$$-\partial E_s^{+-}(2231)/\partial U(o\varkappa)_\alpha = -\partial E_s^{+-}(2231)/\partial W(o\varkappa)_\alpha$$
$$= \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(2231\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)\,[\varepsilon(\varkappa')\,U(\varkappa')_\beta + y(\varkappa')\,W(\varkappa')_\beta], \tag{III.9n}$$

$$E_s^{+-}(2231\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = [2\,|e|^2\,S^2_{+-,1}/\sqrt{3}]\,\Big[(1-\delta_{1\varkappa})\,\bar{\mathscr{P}}(\boldsymbol{k}\,|\,\boldsymbol{x}(1)\,\boldsymbol{x}(\varkappa')\,|\,\beta\,|\,3)$$
$$\times\Big(\sum_{\sigma\in I[\varkappa]} t[\sigma]_\alpha\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big) - \delta_{1\varkappa}\sum_{\varkappa''}(1-\delta_{1\varkappa''})\,\bar{\mathscr{P}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa'')\,\boldsymbol{x}(\varkappa')\,|\,\beta\,|\,3) \tag{III.9o}$$
$$\times\Big(\sum_{\sigma\in I[\varkappa']} t[\sigma]_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\Big) + 2\sum_{\sigma\in I[1]}(\delta_{1\varkappa}+\delta_{\varkappa[\sigma]\varkappa})\,\bar{\mathscr{P}}^*(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa')\,\boldsymbol{z}[\sigma]\,|\,\beta\,|\,3)$$
$$\times\,t[\sigma]_\alpha\,[-\delta_{1\varkappa}+(1-\delta_{1\varkappa})\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]],$$

$$-\delta E_s^{+-}(2232)/\partial U(o\varkappa)_\alpha = -\partial E_s^{+-}(2232)/\partial W(o\varkappa)_\alpha$$
$$= \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(2232\,|\,\boldsymbol{k}|\,\varkappa\alpha\varkappa'\beta)[\varepsilon(\varkappa')\,U(\varkappa')_\beta + y(\varkappa')\,W(\varkappa')_\beta], \tag{III.9p}$$

$$E_s^{+-}(2\,232\,|\,\boldsymbol{k}|\,\varkappa\alpha\varkappa'\beta) = i[2\,|e|^2\,S^2_{+-,1}/\sqrt{3}](4\pi/v)\,|\boldsymbol{k}|^{-2}\,k_\beta \exp[-i\,\boldsymbol{k}\cdot\{\boldsymbol{x}(\varkappa') - i\,\boldsymbol{k}[4\tau]^{-1}\}]$$
$$\times\,[-(1-\delta_{1\varkappa})(\sum_{\sigma\in I[\varkappa]} t[\sigma]_\alpha \exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]) + \delta_{1\varkappa}\sum_{\varkappa''}(1-\delta_{1\varkappa''})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(\varkappa'')] \tag{III.9q}$$
$$\times\,(\sum_{\sigma\in I[\varkappa'']} t[\sigma]_\alpha \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]) + 2\sum_{\sigma\in I[1]}(\delta_{1\varkappa}+\delta_{\varkappa[\sigma]\varkappa})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{z}[\sigma]]$$
$$\times\,t[\sigma]_\alpha[-\delta_{1\varkappa} + (1-\delta_{1\varkappa})\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]],$$

$$-\partial E_s^{+-}(224)/\partial U(o\varkappa)_\alpha = -\partial E_s^{+-}(224)/\partial W(o\varkappa)_\alpha$$
$$= \sum_{\varkappa'}\sum_{\beta} E_s^{+-}(224\,|\,\boldsymbol{k}|\,\varkappa\alpha\varkappa'\beta)[\varepsilon(\varkappa')\,U(\varkappa')_\beta + y(\varkappa')\,W(\varkappa')_\beta], \tag{III.9r}$$

$$E_s^{+-}(224\,|\,\boldsymbol{k}|\,1\alpha\varkappa'\beta) = [16\,|e|^2\,S^2_{+-,1}/(9r_0^2)]$$
$$\sum_{\sigma\in I[\varkappa']}(-\delta_{1\varkappa'}\,\delta_{\alpha\beta}[\mathscr{X}^{-2} - \tfrac{1}{2}] + (1-\delta_{1\varkappa'})\,t[\sigma]_\alpha\,t[\sigma]_\beta([1-\mathscr{X}]^{-2} - \tfrac{1}{2})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]), \tag{III.9s}$$

$$E_s^{+-}(224\,|\,\boldsymbol{k}|\,\varkappa\alpha\varkappa'\beta) = [16\,|e|^2\,S^2_{+-,1}/(9r_0^2)]\,(\delta_{1\varkappa'}+\delta_{\varkappa\varkappa'})$$
$$\times\sum_{\sigma\in I[\varkappa]}(\delta_{1\varkappa'}[\mathscr{X}^{-2} - \tfrac{1}{2}]\,t[\sigma]_\alpha\,t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])] - \delta_{\varkappa\varkappa'}\,\delta_{\alpha\beta}([1-\mathscr{X}]^{-2} - \tfrac{1}{2})); \quad \varkappa = 2,3. \tag{III.9t}$$

$$\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}\boldsymbol{x}'\,|\,\alpha\,|\,3) = \mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}\boldsymbol{x}'\,|\,\alpha\,|\,3) + i(4\pi/v)\,|\boldsymbol{k}|^{-2}\,k_\alpha\exp[i\,\boldsymbol{k}\cdot\{\boldsymbol{x}-\boldsymbol{x}'+i\,\boldsymbol{k}[4\tau]^{-1}\}]. \tag{III.9u}$$

Here τ [later to be identified with the separation parameter typical of „incomplete gamma function—theta function transformation" recipees] is a quantity the units of which are cm^{-2} and the magnitude of which is nonzero but otherwise arbitrary. The symbol v stands for the volume [$v = 2r_0^3$] of a direct lattice rhombohedral unit cell. Above, $E_s^{+-}(221)$ and $E_s^{+-}(222)$ represent the interaction energy of zeroth cell CS-dipoles and first-order OC fluctuations throughout the lattice. Equations (III.9g—m) follow from placing charges given by

$$-\tfrac{1}{2}\,|e|\sum_{\sigma\in I[1]} Q(+-,l,\sigma)_1$$
$$= -[2\,|e|\,S^2_{+-,1}/\sqrt{3}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\sum_{\varkappa'}(1-\delta_{1\varkappa'})\sum_\beta\{\sum_{\sigma\in I[\varkappa']} t[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\}\,V(\varkappa')_\beta \tag{i}$$

at $\varkappa = 1$ sites, charges given by

$$-\tfrac{1}{2}\,|e|\sum_{\sigma\in I[\varkappa]} Q(+-,l-l[\sigma],\sigma)_1$$
$$= [2\,|e|\,S^2_{+-,1}/\sqrt{3}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\sum_{\varkappa'}\delta_{1\varkappa'}\sum_\beta\{\sum_{\sigma\in I[\varkappa]} t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\}\,V(\varkappa')_\beta \tag{ii}$$

at $\varkappa = 2, 3$ sites, charges given by

$$|e|\,Q(+-,l,\sigma)_1 = [4\,|e|\,S^2_{+-,1}/\sqrt{3}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\sum_{\varkappa'}(\delta_{1\varkappa'}+\delta_{\varkappa[\sigma]\varkappa'})$$
$$\times\sum_\beta\{t[\sigma]_\beta[-\delta_{1\varkappa'} + (1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]\} \tag{iii}$$

in $\boldsymbol{z}[\sigma]$ positions, and from differentiating the attendent potentials separately, summing over l, and subsequently removing terms which are implicit in two-body repulsions. The $E_s^{+-}(2211)$ terms are regular functions of $\boldsymbol{k}$ in the entire BZ. The remaining part of any $E_s^{+-}(221)$ term is only piecewise continuous at $\boldsymbol{k} = 0$ and has been written as a distinct contribution, $E_s^{+-}(2212\,|\,\boldsymbol{k}|\,\varkappa\alpha\varkappa'\beta)$. Since Eq. (III.9j) is based on the result obtained by differentiating a monopole sum *once* it is, perhaps, not immediately clear that when $\boldsymbol{k}\to\boldsymbol{0}$, $E_s^{+-}(2212)$ contributions become part of interactions involving the macroscopic field. [It will be recalled that one often singles out from a dipole wave sum that part which is non-regular in neighbourhoods of the origin by starting with the outcome of a double differentiation performed on a monopole sum[17].] However, by expanding exponentials in powers of $\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])$, or $\boldsymbol{k}\cdot\boldsymbol{x}(\varkappa)$, or $\boldsymbol{k}\cdot\boldsymbol{t}[\sigma]$ as required,

by using the lattice symmetry, and by noting that a charge of type (i) or (ii) as well as a $\sum_{\sigma\in I[1]}$-sum over type (iii) charges vanishes as $\boldsymbol{k}\to\boldsymbol{0}$, it follows that

$$\sum_{\varkappa'}\sum_{\beta}E_{\mathrm{s}}^{+-}(2212\,|\,\boldsymbol{k}\,|\,\varkappa\,\alpha\,\varkappa'\,\beta)\,V(\varkappa')_{\beta}=-\,|e|^{2}(4\pi/v)\,|\,\boldsymbol{k}\,|^{-2}\,k_{\alpha}\sum_{\beta}k_{\beta}\sum_{\varkappa'}D^{+-}(\boldsymbol{0}\,|\,\beta\,|\,\varkappa'\,\beta)\,V(\varkappa')_{\beta}+O(|\,\boldsymbol{k}\,|)\quad\text{(III.10)}$$

where

$$D^{+-}(\boldsymbol{0}\,|\,\beta\,|\,\varkappa'\,\gamma)=\delta_{\beta\gamma}\,8r_{0}[\mathscr{X}-\tfrac{1}{2}]\,S_{+-,1}^{2}(1-3\delta_{1\varkappa'})/\sqrt{3}\quad\text{(III.11)}$$

is a $\boldsymbol{k}=\boldsymbol{0}$ element of a rectangular matrix $\boldsymbol{D}^{+-}(\boldsymbol{k})$ given by

$$\begin{aligned}D^{+-}(\boldsymbol{k}\,|\,\beta\,|\,\varkappa'\,\gamma)=(2r_{0}[\mathscr{X}-\tfrac{1}{2}]\,S_{+-,1}^{2}(1-2\delta_{1\varkappa'})/\sqrt{3})\\ \times\sum_{\sigma\in I[\varkappa']}[t[\sigma]_{\beta}\,t[\sigma]_{\gamma}(1-\delta_{1\varkappa'})+\delta_{1\varkappa'}\,\delta_{\beta\gamma}][\delta_{1\varkappa'}+(1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]]\,.\end{aligned}\quad\text{(III.12)}$$

$\boldsymbol{D}^{+-}(\boldsymbol{k})$ determines the dipole moment $\boldsymbol{d}^{+-}(\boldsymbol{k}\,l)$ of the charge cluster comprising first order changes in the electrically neutral assembly of overlap charges previously attributed to the l-th unit cell, viz.

$$\boldsymbol{d}^{+-}(\boldsymbol{k}\,l)=|e|\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\,\boldsymbol{D}^{+-}(\boldsymbol{k})\,\boldsymbol{V}.\quad\text{(III.13)}$$

Thus, by virtue of the fact that an operator which projects out of a vector field the irrotational part is linear we are, in the long-wave limit, justified in lumping in $E_{\mathrm{s}}^{+-}(2212)$ terms with interactions to be expressed by means of the macroscopic field.

$E_{\mathrm{s}}^{+-}(223)$ along with $E_{\mathrm{s}}^{+-}(224)$ account for the energy accompanying zeroth cell CS generated OC fluctuations when taking place in the potential produced by CS-dipole arrays. Of the two parts making up $-\,\partial E_{\mathrm{s}}^{+-}(223)/\partial U(o\varkappa)_{\alpha}$ only $-\,\partial E_{\mathrm{s}}^{+-}(2231)/\partial U(o\varkappa)_{\alpha}$ is well-behaved at $\boldsymbol{k}=\boldsymbol{0}$. The role of

$$-\,\partial E_{\mathrm{s}}^{+-}(2232)/\partial U(o\,\varkappa)_{\alpha}$$

is analogous to that of $-\,\partial E_{\mathrm{s}}^{+-}(2212)/\partial U(o\,\varkappa)_{\alpha}$. For $|\,\boldsymbol{k}\,|$ small, it is convenient to expand the exponentials in Eq. (III.9q) to find

$$\begin{aligned}&\sum_{\varkappa'}\sum_{\beta}E_{\mathrm{s}}^{+-}(2232\,|\,\boldsymbol{k}\,|\,\varkappa\,\alpha\,\varkappa'\,\beta)\,[\varepsilon(\varkappa')\,U(\varkappa')_{\beta}+y(\varkappa')\,W(\varkappa')_{\beta}]\\ &\quad=-\,|e|^{2}\,D^{+-}(\boldsymbol{0}\,|\,\alpha\,|\,\varkappa\,\alpha)(4\pi/v)\,|\,\boldsymbol{k}\,|^{-2}\,k_{\alpha}\sum_{\beta}k_{\beta}\sum_{\varkappa'}[\varepsilon(\varkappa')\,U(\varkappa')_{\beta}+y(\varkappa')\,W(\varkappa')_{\beta}]+O(|\,\boldsymbol{k}\,|)\,.\end{aligned}\quad\text{(III.14)}$$

Hence we see that when $\boldsymbol{k}$ tends to zero $-\,\partial E_{\mathrm{s}}^{+-}(2232)/\partial U(o\varkappa)_{\alpha}$ [and $-\,\partial E_{\mathrm{s}}^{+-}(2232)/\partial W(o\varkappa)_{\alpha}$] can be taken to originate in the interaction of $\boldsymbol{d}^{+-}(\boldsymbol{0}\,\boldsymbol{0})$ with the CS-dipole contribution to the macroscopic field.

The E_{s}^{+-} (3) Contribution to the Force Field

$E_{\mathrm{s}}^{+-}(3)$ depending upon simultaneous alteration of both position and magnitude of OC, the influence of $E_{\mathrm{s}}^{+-}(3)$ on harmonic dynamics is governed by the scalar products of dipoles

$$\begin{aligned}&|e|\,Q(+-,l,\sigma)_{1}\{\mathscr{X}\boldsymbol{V}(\varkappa[\sigma])\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]+[1-\mathscr{X}]\,\boldsymbol{V}(1)\}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\quad\text{at}\quad\boldsymbol{x}(l)+\boldsymbol{z}[\sigma],\\ &|e|\,Q(+-,l,\sigma)_{1}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l+l[\sigma])]\,\boldsymbol{V}(\varkappa[\sigma])\quad\text{at}\quad\boldsymbol{x}(l+l[\sigma])+\boldsymbol{x}(\varkappa[\sigma]),\\ &|e|\,Q(+-,l,\sigma)_{1}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\,\boldsymbol{V}(1)\quad\text{at}\quad\boldsymbol{x}(l)\end{aligned}$$

with the field strength in a static CS-point charge lattice; in each case removing the field contribution of the engendering ion pair. One finds easily

$$-\,\partial E_{\mathrm{s}}^{+-}(3)/\partial U(o\,\varkappa)_{\alpha}=-\,\partial E_{\mathrm{s}}^{+-}(3)/\partial W(o\,\varkappa)_{\alpha}=\sum_{\varkappa'}\sum_{\beta}E_{\mathrm{s}}^{+-}(3\,|\,\boldsymbol{k}\,|\,\varkappa\,\alpha\,\varkappa'\,\beta)\,V(\varkappa')_{\beta}\quad\text{(III.15a)}$$

$$\begin{aligned}E_{\mathrm{s}}^{+-}(3\,|\,\boldsymbol{k}\,|\,1\,\alpha\,\varkappa'\,\beta)=[4\,|\,e\,|^{2}\,S_{+-,1}^{2}/\sqrt{3}]\,\{[\sum_{\sigma\in I[\varkappa']}(\delta_{1\varkappa'}[1-\mathscr{X}]\,t[\sigma]_{\beta}\,\psi(\alpha\,|\,\boldsymbol{z}[\sigma])+t[\sigma]_{\alpha}\,\psi(\beta\,|\,\boldsymbol{z}[\sigma])]\\ -(1-\delta_{1\varkappa'})\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]\,[t[\sigma]_{\beta}\,\psi(\alpha\,|\,\boldsymbol{z}[\sigma])\,[1-\mathscr{X}]-t[\sigma]_{\alpha}\,\psi(\beta\,|\,\boldsymbol{z}[\sigma])\,\mathscr{X}])]+(2\,\varepsilon(2)/[3\sqrt{3}r_{0}^{2}])\\ \times\sum_{\sigma\in I[\varkappa^{-}]}(2\,\delta_{\alpha\beta}\,\delta_{1\varkappa'}+(1-\delta_{1\varkappa'})\,t[\sigma]_{\alpha}\,t[\sigma]_{\beta}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])])\}\end{aligned}\quad\text{(III.15b)}$$

$$E_s^{+-}(3\,|\,\boldsymbol{k}|\,\varkappa\alpha\,\varkappa'\beta) = [4\,|e|^2 S^2_{+-,1}/\sqrt{3}]\{(\delta_{1\varkappa'}+\delta_{\varkappa\varkappa'})[\sum_{\sigma\in I[\varkappa]}(\delta_{1\varkappa'}\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])]$$
$$\times[\mathscr{X}\,t[\sigma]_\beta\,\psi(\alpha\,|\,\boldsymbol{z}[\sigma]) - [1-\mathscr{X}]\,t[\sigma]_\alpha\,\psi(\beta\,|\,\boldsymbol{z}[\sigma])] - \delta_{\varkappa\varkappa'}\mathscr{X}[t[\sigma]_\beta\,\psi(\alpha\,|\,\boldsymbol{z}[\sigma]) + t[\sigma]_\alpha\,\psi(\beta\,|\,\boldsymbol{z}[\sigma])])]$$
$$+(2\,\varepsilon(2)/[3\sqrt{3}r_0^2])(1-2\delta_{\varkappa\varkappa'})\sum_{\sigma\in I[\varkappa]}(4\delta_{\alpha\beta}\,\delta_{\varkappa\varkappa'}+\delta_{1\varkappa'}\,t[\sigma]_\alpha\,t[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(l[\sigma])])\}, \qquad \text{(III.15c)}$$

$$\psi(\alpha\,|\,\boldsymbol{z}[\sigma]) = (\partial/\partial x_\alpha)\,(\sum_{l\varkappa'}\varepsilon(\varkappa')/|\,\boldsymbol{x}-\boldsymbol{x}(l\,\varkappa)|)\,|_{\boldsymbol{x}=\boldsymbol{z}[\sigma]} + \varepsilon(1)\,(2t[\sigma]_\alpha/[3\sqrt{3}r_0^2])\,(2\mathscr{X}^{-2}+[1-\mathscr{X}]^{-2}). \qquad \text{(III.15d)}$$

Effects of F^--F^- Overlap. B

Below, every "− −" term has received a name analogous to the one given to its "+ −" counterpart. This time we consider

i) at each $\varkappa = 2$ − F^- site $\boldsymbol{x}(l)+\boldsymbol{x}(2)+\boldsymbol{V}(l\,2)$ a total OC equal to $-\frac{1}{2}|e|\sum_{\sigma\in J}Q(--,l,\sigma)$ where $J=\{1,\ldots,6\}$; where $Q=Q_0+Q_1+Q_2$ with

$$Q(--,l,\sigma)_0 = 4S^2_{--,0}, \qquad \text{(III.16a)}$$

$$Q(--,l,\sigma)_1 = [4S^2_{--,1}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\sum_\alpha p[\sigma]_\alpha\{V(3)_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]-V(2)_\alpha\}, \qquad \text{(III. 16b)}$$

$$Q(--,l,\sigma)_2 = [4S^2_{--,2}]\exp[2i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)][\sum_\alpha p[\sigma]_\alpha\{V(3)_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(\mathrm{m}[\sigma])]-V(2)_\alpha\}]^2$$
$$+\tfrac{1}{2}[4S^2_{--,1}/r_0]\sum_\alpha[1-\mathrm{p}[\sigma]^2_\alpha]\{V(3)_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(\mathrm{m}[\sigma])]-V(2)_\alpha\}^2. \qquad \text{(III.16c)}$$

and where

$$S^2_{--,0} = C_{---}\,r_0\exp[-r_0/\varrho_{--}], \qquad S^2_{--,1} = S^2_{--,0}\,r_0^{-1}[1-r_0/\varrho_{--}], \qquad \text{(III.16d)}$$
$$S^2_{--,2} = S^2_{--,0}[2r_0\,\varrho_{--}]^{-1}[r_0/\varrho_{--}-2];$$

$$\boldsymbol{p}[1]=(1,0,0), \quad \boldsymbol{p}[2]=(0,1,0), \quad \boldsymbol{p}[3]=(\bar{1},0,0),$$
$$\boldsymbol{p}[4]=(0,\bar{1},0) \quad \boldsymbol{p}[5]=(0,0,1), \quad \boldsymbol{p}[6]=(0,0,\bar{1}), \qquad \text{(III.16e)}$$

$$\boldsymbol{x}(m[\sigma]) = r_0\,\boldsymbol{p}[\sigma]+\boldsymbol{x}(2)-\boldsymbol{x}(3), \quad \sigma\in J. \qquad \text{(III.16f)}$$

ii) at each $\varkappa = 3$ − F^- site $\boldsymbol{x}(l)+\boldsymbol{x}(3)+\boldsymbol{V}(l\,3)$ a total OC equal to $-\frac{1}{2}|e|\sum_{\sigma\in J}Q(--,l-m[\sigma],\sigma)$.

iii) at each F^-—F^- bond charge position

$$\boldsymbol{x}(l)+\boldsymbol{z}'[\sigma]+\tfrac{1}{2}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\{\boldsymbol{V}(3)\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]+V(2)\},$$

where $\boldsymbol{z}'[\sigma]=\boldsymbol{x}(2)+\frac{1}{2}r_0\,\boldsymbol{p}[\sigma]$, an OC equal to $|e|\,Q(--,l,\sigma)$.

Transcribing a convention adopted in Section III.A we split E_s^{--} according to:

$$E_s^{--}(1)+E_s^{--}(2)+E_s^{--}(3).$$

The E_s^{--} (1) Contribution to the Force Field

With quadrupole components

$$[|e|\,S^2_{--,0}]\{V(3)_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]+V(2)_\alpha\}\{V(3)_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]+V(2)_\beta\}\exp[2i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]$$

and dipole components

$$[2\,|e|\,S^2_{--,0}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\{V(3)_\alpha\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]+V(2)_\alpha\}$$

at $\boldsymbol{x}(l)+\boldsymbol{z}'[\sigma]$; $\sigma\in J$; with dipole components

$$-[12\,|e|\,S^2_{--,0}]\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l)]\,V(\varkappa)_\alpha$$

at $\boldsymbol{x}(l)+\boldsymbol{x}(\varkappa)$; $\varkappa=2,3$; and with allowance for Laplace's equation [in the form

$$\sum_\alpha(\partial^2/\partial x_\alpha^2)(\sum_{l\varkappa}\varepsilon(\varkappa)\,|\,\boldsymbol{x}-\boldsymbol{x}(l\,\varkappa)|^{-1})|_{\boldsymbol{x}=\boldsymbol{z}'[\sigma]}=0]$$

and the point symmetry $[\mathscr{D}_{2h}]$ at $\boldsymbol{z}'[\sigma]$, it readily follows that

$$E_s^{--}(11\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)$$
$$= -(1-\delta_{1\varkappa})(1-\delta_{\varkappa\varkappa'})(1-\delta_{1\varkappa'})[|e|^2 S^2_{--,0}]\sum_{\sigma\in J}\exp[(1-2\delta_{2\varkappa'})\,i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\,\psi(\alpha\beta\,|\,\boldsymbol{z}'[\sigma]), \quad \text{(III.17a)}$$

$$E_s^{--}(121\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta)$$
$$= (1-\delta_{1\varkappa'})[2\,|e|^2 S^2_{--,0}]\{-18\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,\alpha\beta\,|\,5)+6\,\delta_{\alpha\beta}\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(\varkappa')\,|\,3) \quad \text{(III.17b)}$$
$$+\sum_{\sigma\in J}[(\delta_{2\varkappa'}+\delta_{3\varkappa'}\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])])(3\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}'[\sigma]\,|\,\alpha\beta\,|\,5)-\delta_{\alpha\beta}\,\mathscr{S}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}'[\sigma]\,|\,3))]\},$$

$$E_s^{--}(122\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) \quad \text{(III.17c)}$$
$$= (1-\delta_{1\varkappa})(1-\delta_{1\varkappa'})(1-\delta_{\varkappa\varkappa'})\,\delta_{\alpha\beta}[14\,|e|^2 S^2_{--,0}/r_0^3]\sum_{\sigma\in J}\{(1-3p[\sigma]^2_\alpha)\exp[(1-2\delta_{2\varkappa'})\,i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\},$$

$$E_s^{--}(123\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = E_s^{--*}(121\,|\,\boldsymbol{k}\,|\,\varkappa'\beta\varkappa\alpha), \quad \text{(III.17d)}$$

$$E_s^{--}(124\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = E_s^{--}(122\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) \quad \text{(III.17e)}$$

where

$$\psi(\alpha\beta\,|\,\boldsymbol{z}'[\sigma]) = (\partial^2/\partial x_\alpha\,\partial x_\beta)\Big(\sum_{l\varkappa}\varepsilon(\varkappa)\,|\,\boldsymbol{x}-\boldsymbol{x}(l\varkappa)\,|^{-1}\Big)\Big|_{\boldsymbol{x}=\boldsymbol{z}'[\sigma]} - 8\,\delta_{\alpha\beta}\,\varepsilon(1)\,r_0^{-3}\{1-3p[\sigma]^2_\alpha\}. \quad \text{(III.17f)}$$

The E_s^{--} (2) Contribution to the Force Field

Restoring forces which are related to the propagation of F⁻—F⁻ OC magnitude fluctuations can be described in terms of

$$E_s^{--}(21\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = -\delta_{\alpha\beta}(1-\delta_{1\varkappa})(1-\delta_{1\varkappa'})\,8\,|e|^2\sum_\sigma[([S^2_{--,2}]\,p[\sigma]^2_\alpha+\tfrac{1}{2}[S^2_{--,1}/r_0][1-p[\sigma]^2_\alpha])$$
$$\times(\delta_{\varkappa\varkappa'}-(1-\delta_{\varkappa\varkappa'})\exp[(1-2\delta_{2\varkappa'})\,i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])])](\psi(\boldsymbol{z}'[1])-\psi(\boldsymbol{x}(2))-3\,\varepsilon(2)\,r_0^{-1}), \quad \text{(III.18a)}$$

$$E_s^{--}(2211\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = [2\,|e|^2 S^2_{--,1}](1-\delta_{1\varkappa'})[\delta_{2\varkappa'}\,\overline{\mathscr{S}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(3)\,|\,\alpha\,|\,3)$$
$$\times\sum_{\sigma\in J}p[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]-\delta_{3\varkappa'}\,\overline{\mathscr{S}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{x}(2)\,|\,\alpha\,|\,3)\sum_{\sigma\in J}p[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])] \quad \text{(III.18b)}$$
$$+2\sum_{\sigma\in J}(\overline{\mathscr{S}}(\boldsymbol{k}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}'[\sigma]\,|\,\alpha\,|\,3)\,p[\sigma]_\beta[-\delta_{2\varkappa'}+\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\,\delta_{3\varkappa'}])],$$

$$E_s^{--}(2212\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = i[2\,|e|^2 S^2_{--,1}](4\pi/v)\,|\,\boldsymbol{k}\,|^{-2}\,k_\alpha\exp[i\,\boldsymbol{k}\cdot\{\boldsymbol{x}(\varkappa)+i\,\boldsymbol{k}[4\tau]^{-1}\}](1-\delta_{1\varkappa'})$$
$$[-\delta_{2\varkappa'}\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(3)]\sum_{\sigma\in J}p[\sigma]_\beta\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])] \quad \text{(III.18c)}$$
$$+\delta_{3\varkappa'}\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{x}(2)]\sum_{\sigma\in J}p[\sigma]_\beta\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]$$
$$-2\sum_{\sigma\in J}(\exp[-i\,\boldsymbol{k}\cdot\boldsymbol{z}'[\sigma]]\,p[\sigma]_\beta[-\delta_{2\varkappa'}+\exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\,\delta_{3\varkappa'}])],$$

$$E_s^{--}(222\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) \quad \text{(III.18d)}$$
$$= (1-\delta_{1\varkappa})(1-\delta_{1\varkappa'})\,\delta_{\alpha\beta}[14\,|e|^2 S^2_{--,1}/r_0^2]\{-2\delta_{\varkappa\varkappa'}+(1-\delta_{\varkappa\varkappa'})\sum_{\sigma\in J}p[\sigma]^2_\alpha\exp[(1-2\delta_{2\varkappa'})\,i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\},$$

$$E_s^{--}(2231\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = E_s^{--*}(2211\,|\,\boldsymbol{k}\,|\,\varkappa'\beta\varkappa\alpha), \quad \text{(III.18e)}$$

$$E_s^{--}(2232\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = E_s^{--*}(2212\,|\,\boldsymbol{k}\,|\,\varkappa'\beta\varkappa\alpha), \quad \text{(III.18f)}$$

$$E_s^{--}(224\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta) = E_s^{--}(222\,|\,\boldsymbol{k}\,|\,\varkappa\alpha\varkappa'\beta). \quad \text{(III.18g)}$$

It is to be noted that $\boldsymbol{E}_s^{--}(2212\,|\,\boldsymbol{k})\to 0$, and also that $\boldsymbol{E}_s^{--}(2232\,|\,\boldsymbol{k})\to 0$, when $\boldsymbol{k}\to\boldsymbol{0}$. In this respect these two terms differ from their "+ −" analogs which, it will be recalled, contribute to the macroscopic field in the long-wave limit. This difference corresponds to the lack of any dipole moment being induced by first order fluctuations in F⁻—F⁻ OC magnitude.

The E_s^{--} (3) Contribution to the Force Field

Owing to the lattice symmetry a second order bond charge dipole experiences no static CS-lattice field in the $F^- — F^-$ case. Subtracting from the total [and incidentally vanishing] CS field at F^- sites the contribution of the engendering ion pair, the second order dipoles at the fluorine sites are, however, found to induce force constants according to

$$E_s^{--}(3\,|\,\mathbf{0}|\,\varkappa\alpha\varkappa'\beta) = \delta_{\alpha\beta}(1-\delta_{1\varkappa})(1-\delta_{1\varkappa'})(2\delta_{\varkappa\varkappa'}-1)[4\,|\,e\,|^2 S^2_{--,1}\,\varepsilon(2)\,r_0^{-2}] \times \sum_{\sigma\in J} p[\sigma]^2_\alpha \{\delta_{\varkappa\varkappa'} + (1-\delta_{\varkappa\varkappa'})\exp[(1-2\delta_{2\varkappa'})\,i\,\boldsymbol{k}\cdot\boldsymbol{x}(m[\sigma])]\}\,. \tag{III.19}$$

The Extended Shell-Model Equations of Motion. C

The physical arguments underlying the shell-model equations

$$\omega^2 \boldsymbol{M}\,\boldsymbol{U} = \boldsymbol{\Phi}(\boldsymbol{k})^{cc}\,\boldsymbol{U} + \boldsymbol{\Phi}(\boldsymbol{k})^{cs}\,\boldsymbol{W}, \tag{III.20a}$$

$$\mathbf{0} = \boldsymbol{\Phi}(\boldsymbol{k})^{sc}\,\boldsymbol{U} + \boldsymbol{\Phi}(\boldsymbol{k})^{ss}\,\boldsymbol{W} \tag{III.20b}$$

have been very adequately expounded by several authors[5,13,18] and will be briefly rehearsed in Sect. IV so we do not want to belabor this point here. Also, the symbols appearing in Eqs. (20) are standard enough to need no elaboration. We now add the foregoing relations pertaining to three-body OC effects to find a set of modified time-independent equations, viz.

$$\begin{aligned}\omega^2 \boldsymbol{M}\,\boldsymbol{U} = {} & \{\boldsymbol{\Phi}(\boldsymbol{k})^{cc} + \boldsymbol{\Phi}_{+-}(1\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(1\,|\,\boldsymbol{k}) + \boldsymbol{\epsilon}[\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{+-}(3\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})] \\ & + [\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k})^\dagger + \boldsymbol{\Phi}_{+-}(4\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})^\dagger]\,\boldsymbol{\epsilon}\}\,\boldsymbol{U} + \{\boldsymbol{\Phi}(\boldsymbol{k})^{cs} + \boldsymbol{\Phi}_{+-}(1\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(1\,|\,\boldsymbol{k}) \\ & + \boldsymbol{\epsilon}[\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{+-}(3\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})] + [\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k})^\dagger + \boldsymbol{\Phi}_{+-}(4\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})^\dagger]\,\boldsymbol{y}\}\,\boldsymbol{W},\end{aligned} \tag{III.20c}$$

$$\begin{aligned}\mathbf{0} = {} & \{\boldsymbol{\Phi}(\boldsymbol{k})^{sc} + \boldsymbol{\Phi}_{+-}(1\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(1\,|\,\boldsymbol{k}) + \boldsymbol{y}[\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{+-}(3\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})] \\ & + [\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k})^\dagger + \boldsymbol{\Phi}_{+-}(4\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})^\dagger]\,\boldsymbol{\epsilon}\}\,\boldsymbol{U} + \{\boldsymbol{\Phi}(\boldsymbol{k})^{ss} + \boldsymbol{\Phi}_{+-}(1\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(1\,|\,\boldsymbol{k}) \\ & + \boldsymbol{y}[\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{+-}(3\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})] + [\boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k})^\dagger + \boldsymbol{\Phi}_{+-}(4\,|\,\boldsymbol{k}) + \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k})^\dagger]\,\boldsymbol{y}\}\,\boldsymbol{W}\end{aligned} \tag{III.20d}$$

where

$$\begin{aligned}\boldsymbol{\Phi}_{+-}(1\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{+-}(11\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(21\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(3\,|\,\boldsymbol{k}), \\ \boldsymbol{\Phi}_{+-}(2\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{+-}(121\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(2211\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(2212\,|\,\boldsymbol{k}), \\ \boldsymbol{\Phi}_{+-}(3\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{+-}(122\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(222\,|\,\boldsymbol{k}), \\ \boldsymbol{\Phi}_{+-}(4\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{+-}(124\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{+-}(224\,|\,\boldsymbol{k}), \\ \boldsymbol{\Phi}_{--}(1\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{--}(11\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(21\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(3\,|\,\boldsymbol{k}), \\ \boldsymbol{\Phi}_{--}(2\,|\,\boldsymbol{k}) &= -\boldsymbol{E}_s^{--}(222\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(121\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(122\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(2211\,|\,\boldsymbol{k}) - \boldsymbol{E}_s^{--}(2212\,|\,\boldsymbol{k})\end{aligned} \tag{III.20e}$$

and where now $\boldsymbol{\Phi}(\boldsymbol{k})^{cc}$, $\boldsymbol{\Phi}(\boldsymbol{k})^{cs}$, $\boldsymbol{\Phi}(\boldsymbol{k})^{sc} = \boldsymbol{\Phi}(\boldsymbol{k})^{cs\dagger}$, and $\boldsymbol{\Phi}(\boldsymbol{k})^{ss}$ consist of (space) Fourier transforms of *two-body* force tensor components; the central forces in mind comprising short-ranged repulsive, comparatively short-ranged dispersive, and long-ranged Coulombic interactions. Adopting also the quite common procedure of letting overlap and Van der Waals forces operate through the shells we have

$$\begin{aligned}&\boldsymbol{\Phi}(\boldsymbol{k})^{cc} = \boldsymbol{R}(\boldsymbol{k}) + \boldsymbol{\epsilon}\boldsymbol{C}\boldsymbol{\epsilon}, \quad \boldsymbol{\Phi}(\boldsymbol{k})^{cs} = \boldsymbol{R}(\boldsymbol{k}) + \boldsymbol{\epsilon}\boldsymbol{C}\boldsymbol{y}, \\ &\boldsymbol{\Phi}(\boldsymbol{k})^{sc} = \boldsymbol{R}(\boldsymbol{k}) + \boldsymbol{y}\boldsymbol{C}\boldsymbol{\epsilon}, \quad \boldsymbol{\Phi}(\boldsymbol{k})^{ss} = \boldsymbol{R}(\boldsymbol{k}) + \boldsymbol{d} + \boldsymbol{y}\boldsymbol{C}\boldsymbol{y}\end{aligned} \tag{III.20f}$$

where $\boldsymbol{d}$ is a diagonal matrix the elements of which, $d(\varkappa\alpha\varkappa'\beta) = \delta_{\varkappa\varkappa'}\delta_{\alpha\beta}\,d(\varkappa)$, are the spring constants responsible for the assumed isotropic and harmonic coupling of a shell to its associated core, where $\boldsymbol{C}$ is the usual „Kellermann-matrix" in the electrostatic approximation, and where $\boldsymbol{R}$ is given by

$$\begin{aligned}\boldsymbol{R}(\varkappa\alpha\varkappa'\beta) = {} & -(e^2/[2v])\sum_{l'} \{\delta_{\alpha\beta}\,B_{0\varkappa l'\varkappa'} \\ & + [x(O\varkappa)_\alpha - x(l'\varkappa')_\alpha][x(O\varkappa)_\beta + x(l'\varkappa')_\beta] \\ & \times |\,\boldsymbol{x}(l'\varkappa') - \boldsymbol{x}(\varkappa)\,|^{-2}(A_{0\varkappa l'\varkappa'} - B_{0\varkappa l'\varkappa'})\} \\ & \times \exp[i\,\boldsymbol{k}\cdot\boldsymbol{x}(l')]\end{aligned} \tag{III.20g}$$

with

$$B_{l\varkappa l'\varkappa'} = (2v/[r\,e^2])\,(\mathrm{d}/\mathrm{d}r)\,W_{l\varkappa l'\varkappa'}(r)_{r=|\,\boldsymbol{x}(l'\varkappa')-\boldsymbol{x}(l\varkappa)\,|} \tag{III.20h}$$

$$A_{l\varkappa l'\varkappa'} = (2v/e^2)\,(\mathrm{d}^2/\mathrm{d}r^2)\,W_{l\varkappa l'\varkappa'}(r)_{r=|\,\boldsymbol{x}(l'\varkappa')-\boldsymbol{x}(l\varkappa)\,|}$$

provided that $W_{l\varkappa l'\varkappa'}(r)$ is taken to designate what remains after subtraction of the electrostatic term

from the central-force part of the $(l\varkappa) - (l'\varkappa')$ interaction. In a following paper we shall retain W-type forces represented by i) $A_{+-}(r_0\sqrt{3}/2)$ and $B_{+-}(r_0\sqrt{3}/2)$ corresponding to first neighbour repulsions; ii) $A_{--}(r_0)$ and $B_{--}(r_0)$ corresponding to second neighbour interactions; iii) $A_{--}(r_0\sqrt{2})$, $B_{--}(r_0\sqrt{2})$, $A_{++}(r_0\sqrt{2})$, and $B_{++}(r_0\sqrt{2})$ corresponding to third neighbour interactions. Here a symbol followed by (r_0) represents forces acting between the two different F^- sublattices. The round bracket $(r_0\sqrt{2})$, on the other hand, is typical of force constants associated with two ions belonging to the same f.c.c. sublattice. For typographic simplicity we henceforth suppress the brackets when referring to a „+ −" or a „+ +" force constant. Furthermore we adopt the abbreviation $A_{--}(r_0) = A^1_{--}$, and $A_{--}(r_0\sqrt{2}) = A^2_{--}$ with a similar convention for the B's. Further W-contributions are likely to be be negligible as has been made plausible on a previous occasion[1]. It is easy to verify that Eqs. (20) comply with the general invariance relations decreed by Born- von Kármán theory once it is noted that

$$\bar{s}(\boldsymbol{x}(1)\,|\varkappa|\,\alpha\,\alpha) - \tfrac{1}{2}(1+\delta_{1\varkappa})\,\bar{s}(\boldsymbol{x}(2)\,|1|\,\alpha\,\alpha) - 2(1+\delta_{1\varkappa})(\partial/\partial X_\alpha)\,\psi(\boldsymbol{x})|_{\boldsymbol{x}=\mathscr{T}\boldsymbol{x}(2)} = 0 \quad \text{(III.21)}$$

where

$$\bar{s}(\boldsymbol{x}(\varkappa)\,|\varkappa'|\,\alpha\,\alpha) = \sum_{\sigma\in I[\varkappa']} \bar{\mathscr{S}}(\boldsymbol{O}\,|\,\boldsymbol{x}(\varkappa)\,\boldsymbol{z}[\sigma]\,|\,\alpha\,|\,3)\,t[\sigma]_\alpha \quad \text{(III.22)}$$

IV. Concluding Remarks

At this point it is well to keep in mind the ideas involved in Cowley's generalization[5] of the Dick-Overhauser[13] shell-model. Cowley divides the crystal space into „subcells", each subcell „belonging" to a particular nucleus. Such a definition of constituents is obviously feasible, though not unique. To get at the restoring forces being activated by a lattice wave, Cowley adopts the adiabatic, harmonic, and electrostatic approximations and assumes, furthermore, the perturbation in the Hamiltonian to be expandable in multipoles. This leads to a hierarchy of models, each one corresponding to a certain number of multipoles being retained. If truncation takes place immediately after the dipole term, the shell-model emerges. For any realistic number of multipoles there will be a range of intersubcell distances in which this number does not adequately account for intercell forces. Thus, a remainder is called for. The range and the structure of this remainder obviously depend on the order of the highest multipole included. Since an *ab initio* implementation of Cowley's approach is, as yet, numerically insuperable, becourse must had to empirical or semi-empirical treatments. Hitherto, most of the work devoted to the adjustment of remainders relates to the dipole shell-model. In this approximation all interactions beyond normally only a few neighbours originate in point charges. This way, the existence of long-range interactions which are inadequately accounted for by point charge shells and cores tends to make elusive the physical contents of fitted short-range fields. If the adjustable model is flexible enough this deficiency may be of no or little consequence when the construction of an interpolation formula in $\boldsymbol{k}$-space is the main object of the calculation. However, it may severely hamper efficient use of the results in situations where some understanding of the force field is of importance. To remedy this shortcoming one may, in principle, invoke one of the more refined models in the multipole hierarchy. Only, on the practical level this tends to create more problems than it eliminates because of the excessive number of parameters coming into play. The preceding section contains expressions accounting explicitly for long-range forces of a type which is likely to be of some importance in CaF_2, SrF_2, and BaF_2. The interactions between point cores, point shells and overlap charge distributions of finite extension have been incorporated in a manner which avoids adding new adjustable parameters to the ones comprising the simple shell-model. Admittedly, this end has been achieved by invoking some rather strong assumptions; in particular as regards the possibility of evaluating short-range repulsions, as well as overlap charge magnitudes and locations, by replacing interacting deformed ions by undeformed ones interacting according to Heitler-London theory at „effective" distances uniquely determined by artificially breaking electronic dipole moments into displacements $\boldsymbol{W}$ and charges $\boldsymbol{y}$. Suitable ways of somewhat relaxing these assumptions without destroying tractability and ease of picturization will be left for further contemplation.

Finally, it is in order to compare the foregoing formulae with similar work on alkali halides after which this paper has largely been modelled. The papers referred to are all based on the assumption

of negligible overlap between next nearest neighbours [as regards next nearest neighbour effects in alkali halides see, however, comments in a recent paper by CASTMAN et al.[19]]. Accordingly, the comparison will be limited to the „+ −" parts of our preceding formulae. Using Löwdin's work[16] as a starting point, LUNDQUIST[10-11] was apparently the first to consider nonorthogonality effects in a lattice dynamics context. He worked with a rigid ion model* in which free-ion wave functions move rigidly with the nuclei and was, accordingly, not able to arrive at results in accord with experimental facts. However, his work showed clearly that overlap charge polarization contributes appreciably to the difference between formal and effective [in the sense of LYDDANE, SACHS, and TELLER[20]] ionic charge. Moreover the papers in question formed the point of departure for VERMA and collaborators (see [3,14-15]) who undertook to combine Lundquist's approach with the shell-model. With seven adjustable parameters their modified shell-model can be fitted to the dispersion curves of KBr and KI with a goodness which calls for eleven to fourteen fitting variables when obtained from existing shell-model versions, each of which depicts long-ranged forces in terms of an ordinary „Kellermann"-matrix[15]. In particular, the need for incorporation of breathing is apparently disposed of. On comparing the papers of VERMA et al. with the present work, some differences in approach emerge. In view of the behaviour of three-body energy terms at large interaction distances Lundquist simplified these terms to a point where they reduce to a comparatively simple modification of the usual Coulomb interaction. VERMA and SINGH[14] claim to have relaxed this assumption to find „exact" three-body coupling coefficients which are in the nature of volume dependent forces. Not only is $\frac{1}{2}(c_{11} - c_{12})$ determined by two-body** potentials alone, as follows also from Lundquist's original formulation. In addition, the refined three-body force field does not influence the long-wave transverse optical mode because the contributions of overlap charge to the polarization now drops out of the Lorentz field. However, it seems to the present author that pure volume dependence of three-body forces comes about in the theory of VERMA et al. not as a fundamental characteristic of such interactions. Rather, pure volume dependence is achieved by implicitly using a simplified overlap charge distribution. To be explicit, they retain a feature of Lundquist's approximation which, in effect, relegates all the overlap charge to lattice sites. In our notation, their procedure is tantamount to splitting each $q_{fg}(\boldsymbol{r})$ [see Eq. (II.5c)] into two parts and letting one part condense on ion f and the other on g. Because of this, and in view of the vanishing of static lattice electric fields at positions of $\mathcal{O}_h$ symmetry, the coupling matrices of Verma et al. lack a $\boldsymbol{E}_s^{+-}(3\,|\,\boldsymbol{k})$ counterpart. However, although the electrostatic potentials at the NaCl-structure cation and anion sites are of equal magnitude and opposite sign, it is not clear to the present author why a term corresponding to $\boldsymbol{E}_s^{+-}(21\,|\,\boldsymbol{k})$ should not be included. Consider say a nearest neighbour $K^+—I^-$ pair in KI. Now let there be a small change δ in the interionic distance, as a consequence of which alterations of overlap charge develop. Letting $q_2(K^+)$ and $q_2(I^-)$ designate those parts of the alterations which are of second order in δ, there will be an energy contribution $\{q_2(K^+) - q_2(I^-)\}\,\psi\,(K^+)$, where $\psi\,(K^+)$ is the static lattice potential at a K^+ site. It is difficult to see why this term should not be manifest in the equations of motion for a vibrating KI lattice, unless such a contribution be proved negligible. That it is, in fact, negligible is not obvious. It is perhaps not irrelevant to point out that $\boldsymbol{E}_s^{+-}(21\,|\,\boldsymbol{k})$ is quite important in the cases of CaF_2, SrF_2, and BaF_2.[9] On injecting $\boldsymbol{E}_s^{+-}(21\,|\,\boldsymbol{k})$ and $\boldsymbol{E}_s^{+-}(3\,|\,\boldsymbol{k})$-like terms into the theory of Verma et al., coupling matrices appear which are not in the nature of a pure volume dependence. On the other hand, such contributions could formally be considered part of their adjustable short-range force field. It is of interest, therefore, to inquire whether the removal of charge from internuclear regions affects other interactions than those involving a fictitious static lattice. This is easily seen to be the case. VERMA et al. account for three-body forces exerted directly on the moving ions with matrices which correspond to what remains of $\boldsymbol{E}_s^{+-}(2211\,|\,\boldsymbol{k})$ and $\boldsymbol{E}_s^{+-}(2231\,|\,\boldsymbol{k})$

*This remark pertains to theory implemented numerically. In a later discussion[12] ideas were advanced which, theoretically, augment the Heitler-London treatment sufficiently to make the elabotated version encompass polarization effects.

** This is perhaps a slight abuse of language. At this point the author adheres to the terminology of VERMA et al. who regard as "three-body" those forces that depend explicitly on the derivate of overlap integrals with respect to a distance parameter.

upon suppression of the $\sum_{\sigma \in I[1]}$-summations occurring in Eq. (III.9h) and Eq. (III.9o). Both remainders tend to zero when $\boldsymbol{k} \to \boldsymbol{O}$, since first-order fluctuations in sums over the [according to the S^2-approximation] spherically symmetric charge distributions $q_f(\boldsymbol{r})$ and $q_g(\boldsymbol{r})$ vanish in the long-wave limit. [Those $q_f(\boldsymbol{r})$ and $q_g(\boldsymbol{r})$ charges which reside at the faces of a finite crystal give rise to nonzero fluctuations. However, this surface charge polarization contributes only to the macroscopic field and not to local forces.] This is why Verma et al. find first-order fluctuations in overlap charge to contribute nothing to locally conditioned forces governing the Γ_{15} transverse optical mode. However, on transferring charge back into the internuclear regions, counterparts of the $\sum_{\sigma \in I[1]}$-summations will materialize. This introduces additional forces which do not vanish as $\boldsymbol{k} \to \boldsymbol{O}$. As regards the resultant effect on the Γ_{15} transverse mode in fluorite-structures, it may be stated that the $\sum_{\sigma \in I[1]}$ terms induce fields which at lattice points of $\mathcal{O}_h$ symmetry can be well approximated by augmenting the Lorentz field[9]. The reinforcement in question is obtained on including in $(4\pi/3)\boldsymbol{P}$ that part of overlap charge polarization which takes place in internuclear regions. This statement probably applies to rock salt-structures as well. The discrepancies between Lundquist's formulae and those of Verma et al. stem from the fact that Lundquist [erroneously] included all the overlap charge polarization in $\boldsymbol{P}$, whereas Verma et al. discard this source of polarization entirely. Although explicit consideration of the here mentioned interactions may be of little consequence in an empirical approach to alkali halide dynamics, it seems safe to assert that the alleged pure volume dependence is an artifact of a simplified charge distribution. Admittedly, the here adopted point charges, which generate the same potentials as the continuous bond charge distributions $q_{fg}(\boldsymbol{r})$ only up to two terms in a multipole expansion, also represent an oversimplification. However, the picture is of service in bringing out some aspects of extended overlap charge. This point charge distribution is essentially the one suggested in the decisive paper of Dick and Overhauser[13] on dielectric properties of alkali halides; the only difference being our replacement of their ,,ionic radii rule'' with the ,,electrical center of gravity recipe'' Eq. (III.4e). Nevertheless, the Dick-Overhauser treatment of overlap charge polarization comes closer to that of Lundquist than to the $\boldsymbol{k} = \boldsymbol{O}$ results obtainable from our present expressions. This is because, as they state, ,,the exchange [= overlap] polarization is to be incorporated exactly as the usual dipoles are; that is, it is assumed that they contribute to and experience the same local field as they would if they were point dipoles at the lattice sites''. This treatment must be somewhat inaccurate. It is possible to calculate long-wave overlap charge polarization in NaCl-type structures from the dipole moment of an electrically neutral charge aggregate, replicas of which are assigned to all unit cells. This leads to the same result as obtained by Dick and Overhauser on considering concurrently all the charges in a finite crystal. If all forces are evaluated in the dipole approximation, the Dick-Overhauser formulae result. However, higher multipoles of the neutral charge clusters cannot be entirely negligible since their collective contribution annihilates precisely the macroscopic part [unintentionally] included. By the macroscopic part we refer to contributions of spherically symmetric $q_f(\boldsymbol{r})$-like distributions. Needless to say, this minor objection doe not detract from the importance of the Dick-Overhauser paper.

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