# LATTICE DYNAMICS OF SIMPLE HARMONIC AND ANHARMONIC SHELL MODELS 

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## Summary

The lattice dynamics of harmonic and anharmonic shell models are reviewed. It is shown that the various dynamical equations for the shell model can be expressed in the same form as those for the rigid ion model, but with modified force constants. The anharmonic shell model leads to higher order contributions to the dipole moment, quadratic and cubic in the normal coordinates, for which explicit expressions are obtained.

## I. Introduction

In the harmonic approximation the Hamiltonian of a crystal lattice can be written (e.g. Born and Huang 1954; Cochran 1963)

$$
\begin{equation*}
H_{0}=\sum_{l \kappa \alpha}\left(2 m_{\kappa}\right)^{-1}\left\{p_{\alpha}(l \kappa)\right\}^{2}+\Phi_{0}+\frac{1}{2} \sum_{\substack{l \kappa \alpha \\ l^{\prime} \kappa^{\prime} \beta}} \Phi_{\alpha \beta}\left(l \kappa, l^{\prime} \kappa^{\prime}\right) u_{\alpha}\left(l_{\kappa}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right), \tag{1.1}
\end{equation*}
$$

where $u_{\alpha}\left(l_{\kappa}\right)$ is the $\alpha$-component of the displacement from equilibrium of the $\kappa$ th atom in the $l$ th unit cell, and $p_{\alpha}\left(l_{\kappa}\right)$ is the corresponding component of momentum.

In ionic crystals the potential energy can be split up into a part due to the long-range Coulomb forces and a part due to the short-range repulsive forces, which are, in the main, due to overlap of electron distributions on near-neighbour atoms. Thus the force constant $\Phi_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)$ can be written as

$$
\begin{equation*}
\Phi_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)=\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right), \tag{1.2}
\end{equation*}
$$

$Z_{\kappa} e$ being the charge on the type $\kappa$ ions.
The equations of motion for a harmonic crystal are then

$$
\begin{equation*}
m_{\kappa} \ddot{u}_{\alpha}\left(l_{\kappa}\right)=-\sum_{l^{\prime} \kappa^{\prime} \beta} \Phi_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) . \tag{1.3}
\end{equation*}
$$

If we consider an ionic crystal of NaCl structure with $N$ unit cells, (1.3) is a set of $6 N$ linear coupled differential equations. Writing the displacement as a plane wave of the form
gives

$$
\begin{equation*}
u_{\alpha}\left(l_{\kappa}\right)=U_{\alpha}(\kappa \mathbf{q}) \exp \left\{2 \pi \mathrm{i} \mathbf{q} \cdot \mathbf{r}\left(l_{\kappa}\right)-\mathrm{i} \omega(\mathbf{q}) t\right\} \tag{1.4}
\end{equation*}
$$

$$
\begin{equation*}
m_{\kappa} \omega^{2}(\mathbf{q}) U_{\alpha}(\kappa \mathbf{q})=\sum_{\kappa \beta^{\prime}} M_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right) U_{\beta}\left(\kappa^{\prime} \mathbf{q}\right), \tag{1.5}
\end{equation*}
$$

where

$$
\begin{equation*}
M_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=\sum_{l} \Phi_{\alpha \beta}\left(0 \kappa, l \kappa^{\prime}\right) \exp \left[2 \pi \mathrm{i} \mathbf{q} \cdot\left\{\mathbf{r}\left(l \kappa^{\prime}\right)-\mathbf{r}(0 \kappa)\right\}\right] . \tag{1.6}
\end{equation*}
$$

[^0]Thus the set of $6 N$ equations (1.3) has been reduced to sets of six equations for each of the $N$ allowed values of $\mathbf{q}$. This reduction is possible because of the translation symmetry of the lattice.

Equation (1.5) can be written concisely in matrix notation as

$$
\begin{equation*}
\boldsymbol{M} \mathbf{U}=\boldsymbol{m} \omega^{2} \mathbf{U} \tag{1.7}
\end{equation*}
$$

where $\boldsymbol{M}$ is a $6 \times 6$ matrix, the dynamical matrix, and $\mathbf{U}$ is a six-dimensional column vector. It is convenient to define a related matrix, the mass-dependent dynamical matrix $\boldsymbol{D}$, by

$$
D_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=\left(m_{\kappa} m_{\kappa^{\prime}}\right)^{-\frac{1}{2}} M_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)
$$

Then for any $\mathbf{q}$ the allowed frequencies are given as the square roots of the eigenvalues of $\boldsymbol{D}$. This leads to six frequencies $\omega(\mathbf{q} j), j=1,2, \ldots 6$.

The Hamiltonian (1.1) is that of an interacting $N$-body system, since the displacements of the different atoms are coupled in the potential energy term. By transforming to normal coordinates $Q(\mathbf{q} j)$ and $P(\mathbf{q} j)$ defined by

$$
\left.\begin{array}{l}
u_{\alpha}(l \kappa)=\left(N m_{\kappa}\right)^{-\frac{1}{2}} \sum_{\mathbf{q}_{j}} e_{\alpha}(\kappa \mid \mathbf{q} j) Q(\mathbf{q} j) \exp \{2 \pi \mathbf{i} \mathbf{q} \cdot \mathbf{r}(l \kappa)\}  \tag{1.8}\\
p_{\alpha}(l \kappa)=\left(m_{\kappa} / N\right)^{\frac{1}{2}} \sum_{\mathbf{q}_{j}} e_{\alpha}^{*}(\kappa \mid \mathbf{q} j) P(\mathbf{q} j) \exp \{-2 \pi \mathbf{i} \mathbf{q} \cdot \mathbf{r}(l \kappa)\}
\end{array}\right\}
$$

where $e_{\alpha}(\kappa \mid \mathbf{q} j)$ are the components of the normalized eigenvectors of the dynamical $\operatorname{matrix} \boldsymbol{D}$, the Hamiltonian reduces to

$$
\begin{equation*}
H_{0}=\frac{1}{2} \sum_{\mathbf{q}_{j}}\left\{P^{*}(\mathbf{q} j) P(\mathbf{q} j)+\omega^{2}(\mathbf{q} j) Q^{*}(\mathbf{q} j) Q(\mathbf{q} j)\right\} \tag{1.9}
\end{equation*}
$$

where * denotes the Hermitian conjugate.
The Hamiltonian has thus been reduced to one of $6 N$ non-interacting linear harmonic oscillators. This transformation essentially solves the problem, for once the frequencies have been determined from (1.7) any thermodynamic function of the crystal is given by the sum over all modes of the corresponding function of a harmonic oscillator.

The Hamiltonian (1.1) is essentially that of a rigid ion model, since electron coordinates do not appear. It is true that the repulsive potential energy originates from overlap of electron distributions, but in practice a semi-empirical potential is always used and distortions of the electron cloud during lattice vibrations are not allowed for. The above model fails both in predicting many details of observed dispersion curves (Woods, Cochran, and Brockhouse 1960) and in the theory of dielectric constants (Szigeti 1949, 1950).

Dick and Overhauser (1958) realized that the main defect of the above model was its inability to take account of the so-called "short-range polarization". As the ions vibrate the overlap between electron distributions will change, and this will cause a distortion of the electron clouds thus inducing a dipole moment on the ions, in addition to the dipole moment due to the electric field. In order to take account of this short-range polarization, Dick and Overhauser introduced the shell model of ionic crystals, in which each ion is represented by a rigid spherical massless shell, representing
the loosely bound outer electrons, coupled by a spring to a rigid spherical core, representing the nucleus and inner electrons. Thus in lattice vibrations the shell and core can move relative to each other, resulting in dipole moments on the ions. This model, although only a first approximation to real deformable ions, contains most of the features of a real crystal, and gives much better agreement with experiment than the rigid ion model (Woods, Cochran, and Brockhouse 1960).

## II. A Simple Harmonic Shell Model

We consider the model illustrated in Figure 1, and take the only short-range force as that acting between the shells of nearest-neighbour atoms. Although more complex models with many different short-range force constants have been used


Fig. 1.-Simple shell model showing equilibrium configuration above and displaced configuration below.
(Cowley et al. 1963, models I-VI), this is only at the expense of more and more adjustable parameters. The simple model has all the essential features of the more complex models and gives quite good agreement with experiment.

The potential energy of the displaced configuration, in the harmonic approximation, can be written as

$$
\begin{align*}
\Phi_{\mathrm{h}}= & \frac{1}{2} \sum_{l / \kappa \alpha} \Phi_{\alpha \beta}^{\mathrm{l}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\left\{u_{\alpha}(l \kappa)+w_{\alpha}(l \kappa)\right\}\left\{u_{\beta}\left(l^{\prime} \kappa^{\prime}\right)+w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right\} \\
& +\frac{1}{2} \sum_{l \kappa \alpha}\left[k_{\kappa} w_{\alpha}^{2}(l \kappa)-e\left\{Z_{\kappa} u_{\alpha}(l \kappa)+Y_{\kappa} w_{\alpha}\left(l_{\kappa}\right)\right\} E_{\alpha}\left(l_{\kappa}\right)\right] \tag{2.1}
\end{align*}
$$

where $u_{\alpha}\left(l_{\kappa}\right)$ is the $\alpha$-component of the displacement of the core of atom $\left(l_{\kappa}\right), w_{\alpha}\left(l_{\kappa}\right)$ is the $\alpha$-component of the core-shell displacement of atom $\left(l_{\kappa}\right)$, and $E_{\alpha}\left(l_{\kappa}\right)$ is the effective field at site ( $l_{k}$ ).

If there is no external field, the effective field is (Cochran 1963)

$$
\begin{equation*}
E_{\alpha}(l \kappa)=-e^{-1} \sum_{l^{\prime} \kappa^{\prime} \beta} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l \kappa, l^{\prime} \kappa^{\prime}\right)\left\{Z_{\kappa^{\prime}} u_{\beta}\left(l^{\prime} \kappa^{\prime}\right)+Y_{\kappa^{\prime}} w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right\} \tag{2.2}
\end{equation*}
$$

The equations of motion are (Mashkevich and Tolpygo 1957)

$$
\begin{align*}
m_{\kappa} \ddot{u}_{\alpha}\left(l_{\kappa}\right) & =-\partial \Phi_{\mathrm{h}} / \partial u_{\alpha}\left(l_{\kappa}\right)  \tag{2.3}\\
0 & =\partial \Phi_{\mathrm{h}} / \partial w_{\alpha}\left(l_{\kappa}\right) \tag{2.4}
\end{align*}
$$

Equation (2.4) expresses the adiabatic approximation, namely, that the shell displacements instantaneously take up a position to minimize the potential energy. Using (2.4) we can, at least in principle, eliminate the shell displacements from (2.1).

Using (2.1) and (2.2) the equations of motion become

$$
\begin{align*}
& m_{\kappa} \ddot{u}_{\alpha}(l \kappa)=-\sum_{l^{\prime} \kappa^{\prime} \beta}\left[\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} u_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right. \\
&\left.+\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right]  \tag{2.5}\\
& 0=\sum_{l^{\prime} \kappa^{\prime} \beta}[ \left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Y_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) \\
&\left.+\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+k_{\kappa} \delta_{\alpha \beta} \delta_{l l^{\prime}} \delta_{\kappa \kappa^{\prime}}+Y_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right] . \tag{2.6}
\end{align*}
$$

These equations can be written in matrix notation as

$$
\begin{align*}
m \ddot{u} & =-(r+z c z) \mathbf{u}-(r+z c y) \mathbf{w}  \tag{2.7}\\
0 & =(r+y c z) \mathbf{u}+(r+k+y c y) \mathbf{w} \tag{2.8}
\end{align*}
$$

where $\boldsymbol{m}, \boldsymbol{r}, \boldsymbol{c}, \boldsymbol{k}, \boldsymbol{z}$, and $\boldsymbol{y}$ are $6 N \times 6 N$ matrices and $\mathbf{u}$ and $\mathbf{w}$ are $6 N$-dimensional column vectors.

Eliminating w from (2.7) and (2.8) gives
where

$$
\begin{equation*}
m \ddot{\mathbf{u}}=-\psi \mathbf{u} \tag{2.9}
\end{equation*}
$$

$$
\begin{equation*}
\psi=(r+z c z)-(r+z c y)(r+k+y c y)^{-1}(r+y c z) \tag{2.10}
\end{equation*}
$$

Using (2.2) the potential energy (2.1) is given by

$$
\begin{align*}
\Phi_{\mathrm{h}}=\frac{1}{2} \sum_{l \kappa \alpha}[ & {\left[\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, \bar{l}^{\prime} \kappa^{\prime}\right)\right\} u_{\alpha}\left(l_{\kappa}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) } \\
& +\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l \kappa, l^{\prime} \kappa^{\prime}\right)\right\} u_{\alpha}\left(l_{\kappa}\right) w_{\beta}\left(l^{\prime} \kappa^{\prime}\right) \\
& +\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Y_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} w_{\alpha}\left(l_{\kappa}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) \\
& \left.+\left\{\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+k_{\kappa} \delta_{\alpha \beta} \delta_{l l^{\prime}} \delta_{\kappa \kappa^{\prime}}+Y_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)\right\} w_{\alpha}\left(l_{\kappa}\right) w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right] \tag{2.11}
\end{align*}
$$

which can be written in matrix notation as

$$
\begin{align*}
& \Phi_{\mathrm{h}}=\frac{1}{2}\left\{\mathbf{u}^{\mathrm{T}}(\boldsymbol{r}+\boldsymbol{z c z}) \mathbf{u}+\mathbf{u}^{\mathrm{T}}(\boldsymbol{r}+\boldsymbol{z} \boldsymbol{c} \boldsymbol{y}) \mathbf{w}\right. \\
&\left.+\mathbf{w}^{\mathrm{T}}(\boldsymbol{r}+\boldsymbol{y c z}) \mathbf{u}+\mathbf{w}^{\mathrm{T}}(\boldsymbol{r}+\boldsymbol{k}+\boldsymbol{y} \boldsymbol{c} \boldsymbol{y}) \mathbf{w}\right\} \tag{2.12}
\end{align*}
$$

Using (2.8) and (2.10) this becomes

$$
\begin{equation*}
\Phi_{\mathrm{h}}=\frac{1}{2} \mathbf{u}^{\mathrm{T}} \boldsymbol{\psi} \mathbf{u} \tag{2.13}
\end{equation*}
$$

Writing (2.9) and (2.13) in terms of components we have

$$
\begin{equation*}
\Phi_{\mathrm{h}}=\frac{1}{2} \sum_{\substack{l \kappa \alpha \\ l^{\prime} \kappa^{\prime} \beta}} \psi_{\chi \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right) u_{\alpha}\left(l_{\kappa}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) \tag{2.14}
\end{equation*}
$$

and

$$
\begin{equation*}
m_{\kappa} \ddot{u}_{\alpha}(l \kappa)=-\sum_{l^{\prime} \kappa^{\prime} \beta} \psi_{\alpha \beta}\left(l \kappa, l^{\prime} \kappa^{\prime}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) \tag{2.15}
\end{equation*}
$$

These are of the same form as the equations (1.1) and (1.3) for the rigid ion model, but with "effective force constants" given by the elements of the matrix (2.10).

Introducing the plane wave solution (1.4) as before, we obtain the result that the allowed frequencies are again given by the solutions of the equation (1.7), the elements of the dynamical matrix being given by

$$
\begin{equation*}
M_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=\sum_{l} \psi_{\alpha \beta}\left(0 \kappa, l \kappa^{\prime}\right) \exp \left[2 \pi \mathbf{i} \mathbf{q} \cdot\left\{\mathbf{r}\left(l \kappa^{\prime}\right)-\mathbf{r}(0 \kappa)\right\}\right] . \tag{2.16}
\end{equation*}
$$

Taking matrix elements of (2.10) and substituting in (2.16), it can be shown that the dynamical matrix is given by

$$
\begin{equation*}
M=(R+Z C Z)-(R+Z C Y)(R+K+\boldsymbol{Y} C \boldsymbol{Y})^{-1}(R+\boldsymbol{Y} C \mathbf{Z}), \tag{2.17}
\end{equation*}
$$

where the elements of the various $6 \times 6$ matrices are given by

$$
\left.\begin{array}{l}
R_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=\sum_{l} \Phi_{\alpha \beta}^{\mathrm{R}}\left(0 \kappa, l \kappa^{\prime}\right) \exp \left[2 \pi \mathrm{i} \mathbf{q} \cdot\left\{\mathbf{r}\left(l_{\kappa^{\prime}}\right)-\mathbf{r}(0 \kappa)\right\}\right] \\
C_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=\sum_{l} \Phi_{\alpha \beta}^{\mathrm{C}}\left(0 \kappa, l \kappa^{\prime}\right) \exp \left[2 \pi \mathrm{i} \mathbf{q} \cdot\left\{\mathbf{r}\left(l \kappa^{\prime}\right)-\mathbf{r}(0 \kappa)\right\}\right] \\
Z_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=Z_{\kappa} \delta_{\alpha \beta} \delta_{\kappa \kappa^{\prime}},  \tag{2.20}\\
Y_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=Y_{\kappa} \delta_{\alpha \beta} \delta_{\kappa \kappa^{\prime}}, \\
K_{\alpha \beta}\left(\kappa \kappa^{\prime}, \mathbf{q}\right)=k_{\kappa} \delta_{\alpha \beta} \delta_{\kappa \kappa^{\prime}}
\end{array}\right\}
$$

Using (2.14) the Hamiltonian is

$$
\begin{equation*}
H_{0}=\sum_{l \kappa \alpha}\left(2 m_{\kappa}\right)^{-1}\left\{p_{\alpha}(l \kappa)\right\}^{2}+\frac{1}{2} \sum_{\substack{l \kappa \alpha \\ l^{\prime} \kappa^{\prime} \beta}} \psi_{\alpha \beta}\left(l \kappa, l^{\prime} \kappa^{\prime}\right) u_{\alpha}(l \kappa) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right) . \tag{2.21}
\end{equation*}
$$

This can be transformed into normal coordinates, as in the rigid ion case, by using the transformation (1.8), which gives the same result (1.9), and all the thermodynamic properties can be worked out as before.

## III. A Simple Anharmonic Shell Model

It is well known that some properties of real crystals cannot be explained by purely harmonic theory, whether for a rigid ion model or a shell model, e.g. thermal expansion. Thus it is sometimes necessary to include higher order terms in the potential energy expansion. This procedure is well known for the rigid ion model (e.g. Maradudin, Flinn, and Coldwell-Horsfall 1961), but little has been published regarding the extension of the harmonic shell model to include anharmonic terms.

Another phenomenon that emphasizes the need to include anharmonic terms in the dynamics of the shell model is infrared lattice absorption. For a harmonic
crystal, which has a dipole moment depending linearly on the normal coordinates, the predicted absorption consists of an infinitely sharp line (i.e. a $\delta$-function) at the infrared absorption frequency $\omega_{0}$, which is the frequency of the transverse optic mode of zero wave-vector. However, the experimentally measured spectra of alkali halides show a broad absorption band in the infrared together with one or more subsidiary maxima. This discrepancy has been attributed by Blackman (1933), Born and Blackman (1933), and Barnes, Brattain, and Seitz (1935) to anharmonicity that couples the harmonic modes and provides for the absorption of a photon by the creation of two or more phonons. It has also been attributed by Burstein, Oberly, and Plyler (1948) and Lax and Burstein (1955) to the presence of a lattice dipole moment containing terms that are quadratic, cubic, etc. in the normal coordinates. This phenomenon, due to deformation of the ions by the motion of those nearby, also permits multiphonon absorption of a photon. Born has concluded that the widening of the main band is due to the third-order potential while the side bands are probably due to the second-order dipole moment (e.g. Born and Huang 1954).

It has been shown by Keating and Rupprecht (1965) that a harmonic crystal has no higher order dipole moments. Thus to obtain such dipole moments, anharmonic terms must be included in the shell model. These dipole moments will be evaluated in Section IV.

We shall now develop the theory of a simple anharmonic shell model. The potential energy (2.11) of the harmonic shell model was written in the form

$$
\begin{align*}
& \Phi_{\mathrm{h}}=\frac{1}{2} \sum_{l \kappa \alpha}\left\{a_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right) u_{\alpha}(l \kappa) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right)+b_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right) u_{\alpha}\left(l_{\kappa}\right) w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right. \\
& l^{\prime} \kappa^{\prime} \beta  \tag{3.1}\\
&\left.+b_{\beta \alpha}\left(l^{\prime} \kappa^{\prime}, l_{\kappa}\right) w_{\alpha}\left(l_{\kappa}\right) u_{\beta}\left(l^{\prime} \kappa^{\prime}\right)+c_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right) w_{\alpha}(l \kappa) w_{\beta}\left(l^{\prime} \kappa^{\prime}\right)\right\}
\end{align*}
$$

where

$$
\left.\begin{array}{l}
a_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)=\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Z_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)  \tag{3.2}\\
b_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)=\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+Z_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l \kappa, l^{\prime} \kappa^{\prime}\right) \\
c_{\alpha \beta}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)=\Phi_{\alpha \beta}^{\mathrm{R}}\left(l_{\kappa}, l^{\prime} \kappa^{\prime}\right)+k_{\kappa} \delta_{\alpha \beta} \delta_{l l^{\prime}} \delta_{\kappa \kappa^{\prime}}+Y_{\kappa} Y_{\kappa^{\prime}} \Phi_{\alpha \beta}^{\mathrm{C}}\left(l \kappa, l^{\prime} \kappa^{\prime}\right)
\end{array}\right\}
$$

In general the potential function (3.1) will also contain cubic and higher order terms in the coordinates $u_{\alpha}\left(l_{\kappa}\right)$ and $w_{\alpha}\left(l_{\kappa}\right)$.

We shall include anharmonic Coulomb terms between rigid ions and anharmonic repulsive terms between shells of nearest neighbours. Replacing for convenience the triple index ( $l_{\kappa \alpha}$ ) by a single index $(\lambda)$, the potential function can be written as

$$
\begin{align*}
\Phi= & \frac{1}{2} \sum_{\lambda_{1} \lambda_{2}}\left\{a\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} u_{\lambda_{2}}+b\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} w_{\lambda_{2}}+b\left(\lambda_{2} \lambda_{1}\right) w_{\lambda_{1}} u_{\lambda_{2}}+c\left(\lambda_{1} \lambda_{2}\right) w_{\lambda_{1}} w_{\lambda_{2}}\right\} \\
& +\frac{1}{6} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi^{\mathrm{C}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}}+\frac{1}{24} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi^{\mathrm{C}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} \\
& +\frac{1}{6} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)\left(u_{\lambda_{1}}+w_{\lambda_{1}}\right)\left(u_{\lambda_{2}}+w_{\lambda_{2}}\right)\left(u_{\lambda_{3}}+w_{\lambda_{3}}\right) \\
& +\frac{1}{24} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)\left(u_{\lambda_{1}}+w_{\lambda_{1}}\right)\left(u_{\lambda_{2}}+w_{\lambda_{2}}\right)\left(u_{\lambda_{3}}+w_{\lambda_{3}}\right)\left(u_{\lambda_{4}}+w_{\lambda_{4}}\right), \tag{3.3}
\end{align*}
$$

where $\Phi^{\mathrm{C}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right), \Phi^{\mathrm{C}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right), \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)$, and $\Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)$ are respectively
the third- and fourth-order derivatives of the Coulomb and repulsive potential energies with respect to the ionic displacements, and $\gamma$ is the usual order parameter.

We now make an approximation. We expand the last two terms in (3.3) and retain only those terms linear in $w_{\lambda}$. Since the rigid ion model has fairly good quantitative success, it is expected that the core-shell displacements will be less than the displacements of the cores from equilibrium. Making this approximation, (3.3) becomes

$$
\begin{align*}
\Phi= & \frac{1}{2} \sum_{\lambda_{1} \lambda_{2}}\left\{a\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} u_{\lambda_{2}}+b\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} w_{\lambda_{2}}+b\left(\lambda_{2} \lambda_{1}\right) w_{\lambda_{1}} u_{\lambda_{2}}+c\left(\lambda_{1} \lambda_{2}\right) w_{\lambda_{1}} w_{\lambda_{2}}\right\} \\
& +\frac{1}{6} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}}+\frac{1}{24} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} \\
& +\frac{1}{2} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) w_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}}+\frac{1}{6} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) w_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}}, \tag{3.4}
\end{align*}
$$

where $\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)$ and $\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)$ are the total anharmonic coefficients given by

$$
\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)=\Phi^{\mathrm{C}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)+\Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right),
$$

and so on.
The equations of motion to be used in conjunction with (3.4) are

$$
\left.\begin{array}{rl}
m_{\lambda} \ddot{u}_{\lambda} & =-\partial \Phi / \partial u_{\lambda}  \tag{3.5}\\
0 & =\partial \Phi / \partial w_{\lambda}
\end{array}\right\}
$$

The second equation of motion gives

$$
\begin{align*}
0= & \sum_{\lambda_{2}}\left\{b\left(\lambda_{2} \lambda_{1}\right) u_{\lambda_{2}}+c\left(\lambda_{1} \lambda_{2}\right) w_{\lambda_{2}}\right\}+\frac{1}{2} \gamma \sum_{\lambda_{2} \lambda_{3}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{2}} u_{\lambda_{3}} \\
& +\frac{1}{6} \gamma^{2} \sum_{\lambda_{2} \lambda_{3} \lambda_{4}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} . \tag{3.6}
\end{align*}
$$

This equation embodies the adiabatic principle. It expresses the core-shell displacements uniquely in terms of the nuclear displacements. Using (3.6) we can eliminate the $w_{\lambda}$ 's from (3.4) and thus express the potential function in terms of core displacements only.

Multiplying (3.6) by $\frac{1}{2} w_{\lambda_{1}}$, summing over $\lambda_{1}$, and subtracting the result from (3.4) gives

$$
\begin{align*}
\Phi= & \frac{1}{2} \sum_{\lambda_{1} \lambda_{2}}\left\{a\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} u_{\lambda_{2}}+b\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} w_{\lambda_{2}}\right\} \\
& +\frac{1}{6} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}}+\frac{1}{24} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} \\
& +\frac{1}{4} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) w_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}}+\frac{1}{12} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) w_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} . \tag{3.7}
\end{align*}
$$

Defining quantities $d\left(\lambda_{i} \lambda_{j}\right)$ by

$$
\begin{equation*}
\sum_{\lambda_{k}} d\left(\lambda_{i} \lambda_{k}\right) c\left(\lambda_{k} \lambda_{j}\right)=\delta_{\lambda_{i} \lambda_{j}}, \tag{3.8}
\end{equation*}
$$

gives from (3.6)

$$
\begin{align*}
w_{\lambda_{5}}= & -\sum_{\lambda_{1} \lambda_{2}} d\left(\lambda_{5} \lambda_{1}\right) b\left(\lambda_{2} \lambda_{1}\right) u_{\lambda_{2}}-\frac{1}{2} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} d\left(\lambda_{5} \lambda_{1}\right) \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{2}} u_{\lambda_{3}} \\
& -\frac{1}{6} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} d\left(\lambda_{5} \lambda_{1}\right) \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}} . \tag{3.9}
\end{align*}
$$

Eliminating the $w_{\lambda}$ 's from (3.7) by using (3.9) gives for the potential energy

$$
\begin{align*}
\Phi= & \frac{1}{2} \sum_{\lambda_{1} \lambda_{2}} \psi\left(\lambda_{1} \lambda_{2}\right) u_{\lambda_{1}} u_{\lambda_{2}}+\frac{1}{6} \gamma \sum_{\lambda_{1} \lambda_{2} \lambda_{3}} \psi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} \\
& +\frac{1}{24} \gamma^{2} \sum_{\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}} \psi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right) u_{\lambda_{1}} u_{\lambda_{2}} u_{\lambda_{3}} u_{\lambda_{4}}, \tag{3.10}
\end{align*}
$$

where

$$
\begin{equation*}
\psi\left(\lambda_{1} \lambda_{2}\right)=a\left(\lambda_{1} \lambda_{2}\right)-\sum_{\lambda_{3} \lambda_{4}} b\left(\lambda_{1} \lambda_{3}\right) d\left(\lambda_{3} \lambda_{4}\right) b\left(\lambda_{2} \lambda_{4}\right) \tag{3.11}
\end{equation*}
$$

which is the same as the result (2.10) for the harmonic shell model.
The cubic and quartic coefficients are given by

$$
\begin{equation*}
\psi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)=\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)-3 \sum_{\lambda_{4} \lambda_{5}} b\left(\lambda_{1} \lambda_{4}\right) d\left(\lambda_{4} \lambda_{5}\right) \Phi^{\mathrm{R}}\left(\lambda_{5} \lambda_{2} \lambda_{3}\right) \tag{3.12}
\end{equation*}
$$

and

$$
\begin{align*}
\psi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)= & \Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)-4 \sum_{\lambda_{5} \lambda_{6}} b\left(\lambda_{1} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{2} \lambda_{3} \lambda_{4}\right) \\
& -3 \sum_{\lambda_{5} \lambda_{6}} \Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{3} \lambda_{4} \lambda_{6}\right) \tag{3.13}
\end{align*}
$$

From (3.10) the force constants $\psi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)$ and $\psi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)$ should be symmetrical in the $\lambda$ 's. However, the expressions (3.12) and (3.13) are not symmetrical. We therefore replace these by the symmetrized force constants

$$
\begin{align*}
& \psi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)=\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)-\sum_{\lambda_{4} \lambda_{5}}\{ \left\{\left(\lambda_{1} \lambda_{4}\right) d\left(\lambda_{4} \lambda_{5}\right) \Phi^{\mathrm{R}}\left(\lambda_{5} \lambda_{2} \lambda_{3}\right)\right. \\
&+b\left(\lambda_{2} \lambda_{4}\right) d\left(\lambda_{4} \lambda_{5}\right) \Phi^{\mathrm{R}}\left(\lambda_{5} \lambda_{3} \lambda_{1}\right) \\
&\left.+b\left(\lambda_{3} \lambda_{4}\right) d\left(\lambda_{4} \lambda_{5}\right) \Phi^{\mathrm{R}}\left(\lambda_{5} \lambda_{1} \lambda_{2}\right)\right\}  \tag{3.14}\\
& \psi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)=\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)-\sum_{\lambda_{5} \lambda_{6}}\{ \left\{b\left(\lambda_{1} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{2} \lambda_{3} \lambda_{4}\right)\right. \\
&+b\left(\lambda_{2} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{3} \lambda_{4} \lambda_{1}\right) \\
&+b\left(\lambda_{3} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{4} \lambda_{1} \lambda_{2}\right) \\
&\left.+b\left(\lambda_{4} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{1} \lambda_{2} \lambda_{3}\right)\right\} \\
&-\sum_{\lambda_{5} \lambda_{6}}\left\{\Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{2} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{3} \lambda_{4}\right)\right. \\
&+\Phi^{\mathrm{R}}\left(\lambda_{2} \lambda_{3} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{4} \lambda_{1}\right) \\
&\left.+\Phi^{\mathrm{R}}\left(\lambda_{1} \lambda_{3} \lambda_{5}\right) d\left(\lambda_{5} \lambda_{6}\right) \Phi^{\mathrm{R}}\left(\lambda_{6} \lambda_{2} \lambda_{4}\right)\right\} \tag{3.15}
\end{align*}
$$

Thus we see that the cubic and quartic anharmonic force constants for the shell model $\psi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)$ and $\psi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)$ differ from the corresponding quantities $\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3}\right)$ and $\Phi\left(\lambda_{1} \lambda_{2} \lambda_{3} \lambda_{4}\right)$ for the rigid ion model. This has not been pointed out by Cowley
(1963), although Szigeti (1959) has pointed out that higher order dipole moments make an appreciable contribution to the anharmonic potential energy.

The new anharmonic force constants still satisfy the invariance relations due to translation symmetry, namely,

$$
\left.\begin{array}{rl}
\psi_{\alpha \beta \gamma}\left(l \kappa, l^{\prime} \kappa^{\prime}, l^{\prime \prime} \kappa^{\prime \prime}\right) & =\psi_{\alpha \beta \gamma}\left(0 \kappa,\left(l^{\prime}-l\right) \kappa^{\prime},\left(l^{\prime \prime}-l\right) \kappa^{\prime \prime}\right)  \tag{3.16}\\
\psi_{\alpha \beta \gamma \delta}\left(l \kappa, l^{\prime} \kappa^{\prime}, l^{\prime \prime} \kappa^{\prime \prime}, l^{\prime \prime \prime} \kappa^{\prime \prime \prime}\right) & =\psi_{\alpha \beta \gamma \delta}\left(0 \kappa,\left(l^{\prime}-l\right) \kappa^{\prime},\left(l^{\prime \prime}-l\right) \kappa^{\prime \prime},\left(l^{\prime \prime \prime}-l\right) \kappa^{\prime \prime \prime}\right)
\end{array}\right\}
$$

Transforming the potential energy (3.10) into normal coordinates according to (1.8) and using the fact that the kinetic energy of this model is the same as that for the rigid ion model, the Hamiltonian becomes

$$
\begin{equation*}
H=H_{0}+\gamma H_{3}+\gamma^{2} H_{4} \tag{3.17}
\end{equation*}
$$

where $H_{0}$ is the harmonic Hamiltonian

$$
\begin{equation*}
H_{0}=\frac{1}{2} \sum_{\mathbf{q}_{j}}\left\{P^{*}(\mathbf{q} j) P(\mathbf{q} j)+\omega^{2}(\mathbf{q} j) Q^{*}(\mathbf{q} j) Q(\mathbf{q} j)\right\} \tag{3.18}
\end{equation*}
$$

and the cubic and quartic terms are

$$
\begin{gather*}
H_{3}=\frac{1}{6} N^{-\frac{1}{2}} \sum_{\substack{\mathbf{q}_{1} \mathbf{q}_{2} \mathbf{q}_{3} \\
j_{1} j_{2} j_{3}}}^{\sum} \Delta\left(\mathbf{q}_{1}+\mathbf{q}_{2}+\mathbf{q}_{3}\right) \Psi\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3}\right) Q\left(\mathbf{q}_{1} j_{1}\right) Q\left(\mathbf{q}_{2} j_{2}\right) Q\left(\mathbf{q}_{3} j_{3}\right),(3.19) \\
H_{4}=\frac{1}{24} N^{-1} \sum_{\substack{\mathbf{q}_{1} \mathbf{q}_{2} \mathbf{q}_{3} \mathbf{q}_{4} \\
j_{1} j_{2} j_{3}}} \Delta\left(\mathbf{q}_{1}+\mathbf{q}_{2}+\mathbf{q}_{3}+\mathbf{q}_{4}\right) \Psi\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3} ; \mathbf{q}_{4} j_{4}\right) \\
 \tag{3.20}\\
\times Q\left(\mathbf{q}_{1} j_{1}\right) Q\left(\mathbf{q}_{2} j_{2}\right) Q\left(\mathbf{q}_{3} j_{3}\right) Q\left(\mathbf{q}_{4} j_{4}\right),
\end{gather*}
$$

where the $\Psi$ coefficients are given by

$$
\begin{align*}
& \Psi\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3}\right)=\sum_{\substack{\kappa \alpha \\
l^{\prime} \kappa^{\prime} \beta \\
l^{\prime \prime} \kappa^{\prime \prime} \gamma}}\left(m_{\kappa} m_{\kappa^{\prime}} m_{\kappa^{\prime \prime}}\right)^{-\frac{1}{2}} \psi_{\alpha \beta \gamma \gamma}\left(0 \kappa, l^{\prime} \kappa^{\prime}, l^{\prime \prime} \kappa^{\prime \prime}\right) \\
& \times e_{\alpha}\left(\kappa \mid \mathbf{q}_{1} j_{1}\right) e_{\beta}\left(\kappa^{\prime} \mid \mathbf{q}_{2} j_{2}\right) e_{\gamma}\left(\kappa^{\prime \prime} \mid \mathbf{q}_{3} j_{3}\right) \\
& \times \exp \left[2 \pi \mathrm{i}\left\{\mathbf{q}_{1} \cdot \mathbf{r}(0 \kappa)+\mathbf{q}_{2} \cdot \mathbf{r}\left(l^{\prime} \kappa^{\prime}\right)+\mathbf{q}_{3} \cdot \mathbf{r}\left(l^{\prime \prime} \kappa^{\prime \prime}\right)\right\}\right], \tag{3.21}
\end{align*}
$$

$$
\begin{align*}
& \Psi\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3} ; \mathbf{q}_{4} j_{4}\right)=\sum_{\substack{\kappa^{\prime} \alpha \\
l^{\prime} \kappa^{\prime}, l^{\prime \prime}, \kappa^{\prime \prime}, l^{\prime \prime \prime} \kappa^{\prime \prime \prime} \delta}}\left(m_{\kappa} m_{\kappa^{\prime}} m_{\kappa^{\prime \prime}} m_{\kappa^{\prime \prime}}\right)^{-\frac{1}{2}} \psi_{\alpha \beta \gamma \delta}\left(0 \kappa, l^{\prime} \kappa^{\prime}, l^{\prime \prime} \kappa^{\prime \prime}, l^{\prime \prime \prime} \kappa^{\prime \prime \prime}\right) \\
& \times e_{\alpha}\left(\kappa \mid \mathbf{q}_{1} j_{1}\right) e_{\beta}\left(\kappa^{\prime} \mid \mathbf{q}_{2} j_{2}\right) e_{\gamma}\left(\kappa^{\prime \prime} \mid \mathbf{q}_{3} j_{3}\right) e_{\delta}\left(\kappa^{\prime \prime \prime} \mid \mathbf{q}_{4} j_{4}\right) \\
& \times \exp \left[2 \pi \mathrm { i } \left\{\mathbf{q}_{1} \cdot \mathbf{r}(0 \kappa)+\mathbf{q}_{2} \cdot \mathbf{r}\left(l^{\prime} \kappa^{\prime}\right)+\mathbf{q}_{3} \cdot \mathbf{r}\left(l^{\prime \prime} \kappa^{\prime \prime}\right)\right.\right. \\
& \left.\left.+\mathbf{q}_{4} \cdot \mathbf{r}\left(l^{\prime \prime \prime} \kappa^{\prime \prime \prime}\right)\right\}\right] . \tag{3.22}
\end{align*}
$$

These equations (3.17)-(3.22) are all of the same form as for the anharmonic rigid ion model (e.g. Maradudin, Flinn, and Coldwell-Horsfall 1961), but it must be remembered that the force constants (3.11)-(3.13) are different.

Thus the same methods of evaluating thermodynamic properties as have been used for the anharmonic rigid ion model can be used for the anharmonic shell model.

## IV. The Dipole Moment

To calculate properties that are due to the interaction of a crystal with either a static or a time-dependent electric field it is necessary to express the dipole moment of the crystal in terms of the normal coordinates. In terms of core and core-shell displacements, the $x$ component of the dipole moment is

$$
\begin{equation*}
\mathscr{M}=\sum_{l \kappa}\left\{Z_{\kappa} u_{x}\left(l_{\kappa}\right)+Y_{\kappa} w_{x}\left(l_{\kappa}\right)\right\} \tag{4.1}
\end{equation*}
$$

Substituting for $w_{x}\left(l_{\kappa}\right)$ from (3.9) gives

$$
\begin{gather*}
\mathscr{M}=\sum_{l_{1} \kappa_{1}} Z_{\kappa_{1}} u_{x}\left(l_{1} \kappa_{1}\right)+\sum_{l_{1} \kappa_{1}} Y_{\kappa_{1}}\left\{-\sum_{\substack{l_{2} \kappa_{2} \alpha \\
l_{3} \kappa_{3} \beta}} d_{x \alpha}\left(l_{1} \kappa_{1}, l_{2} \kappa_{2}\right) b_{\beta \alpha}\left(l_{3} \kappa_{3}, l_{2} \kappa_{2}\right) u_{\beta}\left(l_{3} \kappa_{3}\right)\right. \\
-\frac{1}{2} \gamma \sum_{\substack{l_{2} \kappa_{2} \alpha \\
l_{3} \alpha \\
l_{4} \kappa_{3} \beta \\
l_{4}}} d_{x \alpha}\left(l_{1} \kappa_{1}, l_{2} \kappa_{2}\right) \Phi_{\alpha \beta \gamma}^{\mathrm{R}}\left(l_{2} \kappa_{2}, l_{3} \kappa_{3}, l_{4} \kappa_{4}\right) u_{\beta}\left(l_{3} \kappa_{3}\right) u_{\gamma}\left(l_{4} \kappa_{4}\right) \\
-\frac{1}{6} \gamma^{2} \sum_{\substack{l_{2} \ldots l_{5} \\
\kappa_{2} \ldots \ldots \kappa_{5} \\
\alpha \ldots \delta}} d_{x \alpha}\left(l_{1} \kappa_{1}, l_{2} \kappa_{2}\right) \Phi_{\alpha \beta \gamma \delta}^{\mathrm{R}}\left(l_{2} \kappa_{2}, l_{3} \kappa_{3}, l_{4} \kappa_{4}, l_{5} \kappa_{5}\right) \\
\left.\times u_{\beta}\left(l_{3} \kappa_{3}\right) u_{\gamma}\left(l_{4} \kappa_{4}\right) u_{\delta}\left(l_{5} \kappa_{5}\right)\right\} \tag{4.2}
\end{gather*}
$$

Transforming to normal coordinates, according to (1.8), gives

$$
\begin{align*}
\mathscr{M}= & N^{\frac{1}{2}} \sum_{j} M(0 j) Q(0 j)+\frac{1}{2} \gamma \sum_{\substack{\mathbf{q}_{1} j_{1} \\
\mathbf{q}_{2} j_{2}}} \Delta\left(\mathbf{q}_{1}+\mathbf{q}_{2}\right) M\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2}\right) Q\left(\mathbf{q}_{1} j_{1}\right) Q\left(\mathbf{q}_{2} j_{2}\right) \\
& +\frac{1}{6} \gamma^{2} N^{-\frac{1}{2}} \sum_{\substack{\mathbf{q}_{1} \mathbf{q}_{2} \mathbf{q}_{3} \\
j_{1} j_{2} j_{3}}} \Delta\left(\mathbf{q}_{1}+\mathbf{q}_{2}+\mathbf{q}_{3}\right) M\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3}\right) Q\left(\mathbf{q}_{1} j_{1}\right) Q\left(\mathbf{q}_{2} j_{2}\right) Q\left(\mathbf{q}_{3} j_{3}\right) \tag{4.3}
\end{align*}
$$

The first-order dipole moment coefficient is

$$
\begin{align*}
M(0 j)= & \sum_{\kappa} m_{\kappa}^{-\frac{1}{2}} Z_{\kappa} e_{x}(\kappa \mid 0 j) \\
& -\sum_{\substack{\kappa \kappa^{\prime} \kappa^{\prime \prime} \\
\alpha \beta}} m_{\kappa^{\prime \prime}}^{-\frac{1}{\prime \prime}} Y_{\kappa} e_{\beta}\left(\kappa^{\prime \prime} \mid 0 j\right) D_{x \alpha}\left(\kappa \kappa^{\prime}, 0\right) B_{\beta \alpha}\left(\kappa^{\prime \prime} \kappa^{\prime}, 0\right) \tag{4.4}
\end{align*}
$$

the coefficients $D$ and $B$ being defined as in (2.18).
The second- and third-order coefficients are

$$
\begin{align*}
M\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2}\right)=-\sum_{\substack{l_{3} l_{4} \\
\kappa_{1} \kappa_{2} \kappa_{4} \kappa_{3} \kappa_{4} \\
\alpha \beta \gamma}} & \left(m_{\kappa_{3}} m_{\kappa_{4}}\right)^{-\frac{1}{2}} Y_{\kappa_{1}} e_{\beta}\left(\kappa_{3} \mid \mathbf{q}_{1} j_{1}\right) e_{\gamma}\left(\kappa_{4} \mid \mathbf{q}_{2} j_{2}\right) \\
& \times D_{x \alpha}\left(\kappa_{1} \kappa_{2}, 0\right) \Phi_{\alpha \beta \gamma}^{\mathrm{R}}\left(0 \kappa_{2}, l_{3} \kappa_{3}, l_{4} \kappa_{4}\right) \\
& \times \exp \left[2 \pi \mathrm{i}\left\{\mathbf{q}_{1} \cdot \mathbf{r}\left(l_{3} \kappa_{3}\right)+\mathbf{q}_{2} \cdot \mathbf{r}\left(l_{4} \kappa_{4}\right)\right\}\right] \tag{4.5}
\end{align*}
$$

$$
\begin{align*}
& M\left(\mathbf{q}_{1} j_{1} ; \mathbf{q}_{2} j_{2} ; \mathbf{q}_{3} j_{3}\right)=-\sum_{\substack{l_{3} l_{4} l_{5} \\
\kappa_{1} \kappa_{2} \kappa_{3} \kappa_{4} \kappa_{5} \\
\alpha \beta \gamma \delta}}\left(m_{\kappa_{3}} m_{\kappa_{4}} m_{\kappa_{5}}\right)^{-\frac{1}{2}} Y_{\kappa_{1}} e_{\beta}\left(\kappa_{3} \mid \mathbf{q}_{1} j_{1}\right) e_{\gamma}\left(\kappa_{4} \mid \mathbf{q}_{2} j_{2}\right) e_{\delta}\left(\kappa_{5} \mid \mathbf{q}_{3} j_{3}\right) \\
& \times D_{x \alpha}\left(\kappa_{1} \kappa_{2}, 0\right) \Phi_{\alpha \beta \gamma \delta}\left(0 \kappa_{2}, l_{3} \kappa_{3}, l_{4} \kappa_{4}, l_{5} \kappa_{5}\right) \\
& \times \exp \left[2 \pi \mathrm{i}\left\{\mathbf{q}_{1} \cdot \mathbf{r}\left(l_{3} \kappa_{3}\right)+\mathbf{q}_{2} \cdot \mathbf{r}\left(l_{4} \kappa_{4}\right)+\mathbf{q}_{3} \cdot \mathbf{r}\left(l_{5} \kappa_{5}\right)\right\}\right] . \tag{4.6}
\end{align*}
$$

The first term in (4.4) is the only term that contributes to the dipole moment of a harmonic or anharmonic rigid ion model. The second term in (4.4) is the additional contribution from a harmonic shell model. The higher order moments appear only in the anharmonic shell model.

## V. Conclusions

The lattice dynamics of simple harmonic and anharmonic shell models have been reviewed. It has been shown that the theory can be expressed in the same form as the better-known theory of the rigid ion model, but with modified harmonic and anharmonic force constants.

The shell model is the simplest model that allows for distortion of the electron clouds during lattice vibrations. This is especially significant in optic modes in which the two atoms of a unit cell vibrate in opposite directions, and the shell model gives good agreement with experimental dispersion curves for these modes.

It is also seen that it is possible to have deformable ions without the appearance of higher order dipole moments, e.g. in the harmonic shell model. Inclusion of anharmonic terms leads to the appearance of higher order dipole moments.

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