Beyond the Rigid-Ion Approximation with Spherically Symmetric Ions

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Ab initio calculations show that a spherically symmetric charge relaxation of ions in a crystal, in response to the long-range electrostatic potential, is important for understanding the splitting between longitudinal- and transverse-optic-mode frequencies, and the violation of the Cauchy relations among elastic constants.

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There are two major deficiencies of the lattice dynamics of ionic solids based on the rigid-ion approximation: (1) The splitting between the longitudinal optic (LO) and transverse optic (TO) mode frequencies is too large; and (2) the Cauchy relations between elastic constants, which follow from the rigid-ion approximation, are usually not satisfied experimentally. While lattice-dynamical models involving dipolar (or higher-order) charge relaxation are capable of removing these deficiencies, we point out in this Letter another form of charge relaxation which is also important in this regard. What previous models of lattice dynamics have not taken into account is the fact that the ions are free to change their radial charge distribution, i.e., undergo a spherically symmetric breathing motion, in response to changes in the long-range electrostatic potential. We refer to this as a potential-induced breathing (PIB). Variations of the shell model which incorporate breathing[1,2] are basically different from PIB in that their breathing motions are not directly coupled to the Madelung potential. As such, they have no direct effect on the splitting of the LO- and TO-mode frequencies.

The charge density of an anion in a crystal is more localized about the nucleus than it is in vacuum. This is because the electrostatic potential in the region of an anion site lowers the potential energy of the electrons in this region, which draws them closer to the nucleus. This effect can be approximated in an atomic calculation by imposing an external potential[3]

$$V_k(r)=\begin{cases}-eV_k \text{ for } r<z_k/(-eV_k),\\ ez_k/r \text{ for } r>z_k/(-eV_k),\end{cases} \tag{1}$$

where e is the electronic charge, V_k is the electrostatic potential at the site of the kth ion due to the rest of the ions in the crystal, and z_k is the charge of the kth ion. A value for V_k is readily obtained by application of the Ewald method with the assumption that the rest of the ions are point charges. For the rock-salt structure

$$V_k=-3.495\,129z_k/a \tag{2}$$

in atomic units with energy in hartrees, where a is the lattice constant.

Once realistic charge densities have been determined by this or some other method, reasonably good predictions for phonon frequencies are obtained from pair potentials derived by the assumptions that (a) the charge densities of the ions do not change as the ions move (rigid-ion approximation) and (b) the electronic energy is related to density as though it were locally a free electron gas.[4-6] In such a calculation, however, one finds that the frequencies of the LO modes are predicted to be significantly larger [26% for NaCl (Ref. 5) and ~51% for MgO (Ref. 6)] than the corresponding experimental values.

If we go beyond the rigid-ion approximation, but still require the ions to be spherically symmetric, the total energy of the crystal takes the form

$$\Phi=\frac{1}{2}\sum_{\substack{ll'\\kk'}}\frac{z_kz_{k'}}{|\mathbf{r}(^l_k)-\mathbf{r}(^{l'}_{k'})|}+\sum_{lk}S_k(P(^l_k))+\frac{1}{2}\sum_{\substack{ll'\\kk'}}{}'\phi_{kk'}(P(^l_k),P(^{l'}_{k'}),|\mathbf{r}(^l_k)-\mathbf{r}(^{l'}_{k'})|); \tag{3}$$

the first term is the long-range Coulomb interaction expressed in terms of the ionic charges and the positions of the ions [$\mathbf{r}(^l_k)$ is the position of the kth ion in the lth unit cell]; the second term is the contribution from the self-energies S_k of the ions, which are functions of the potential

$$P(^l_k)=\sum_{l'k'}{}' z_{k'}/|\mathbf{r}(^l_k)-\mathbf{r}(^{l'}_{k'})|, \tag{4}$$

at the (^l_k) site; and the third term represents the rest of the energy, expressed as a sum over pairwise contributions. The self-energy of an ion is its total energy, which we calculate from its charge density as described below. The prime on the summation signs indicate that the $(l'k')=(lk)$ terms are omitted. The pairwise interactions now depend upon the electrostatic potential at the sites of the ions as well as their separations. In spite of their dependence on electrostatic potential the contribution of these pair interactions to the dynamical matrix is short range in nature (i.e., does not contribute to the LO-TO splitting) because it originates from the overlap of charge densities which fall off exponentially with large distance from the nucleus.

Differentiating the second term with respect to Cartesian components of the position vectors $\mathbf{r}(^l_k)$, we have

$$\frac{\partial^2}{\partial r_\alpha(^m_j)\partial r_\beta(^{m'}_{j'})}\sum_{lk}S_k(P(^l_k))=\sum_{lk}\left\{S_k'(P(^l_k))\frac{\partial^2 P(^l_k)}{\partial r_\alpha(^m_j)\partial r_\beta(^{m'}_{j'})}+S_k''(P(^l_k))\frac{\partial P(^l_k)}{\partial r_\alpha(^m_j)}\frac{\partial P(^l_k)}{\partial r_\beta(^{m'}_{j'})}\right\}. \tag{5}$$

The last term does not contribute to the LO-TO splitting (see Appendix) and so we give it no further consideration here. Writing S_k, or one of its derivatives, with the argument omitted indicates that it is evaluated at the potential at the kth site of the undistorted crystal. Substituting $P(^l_k)$ from Eq. (4) we have

$$\frac{\partial^2}{\partial r_\alpha(^m_j)\partial r_\beta(^{m'}_{j'})}\sum_{lk}S_k(P(^l_k))=\frac{\partial^2}{\partial r_\alpha(^m_j)\partial r_\beta(^{m'}_{j'})}\sum_{\substack{ll'\\kk'}}{}'\frac{S_k'z_{k'}}{|\mathbf{r}(^l_k)-\mathbf{r}(^{l'}_{k'})|}=\frac{\partial^2}{\partial r_\alpha(^m_j)\partial r_\beta(^{m'}_{j'})}\frac{1}{2}\sum_{\substack{ll'\\kk'}}{}'\frac{f_{kk'}}{|\mathbf{r}(^l_k)-\mathbf{r}(^{l'}_{k'})|} \tag{6}$$

where

$$f_{kk'}=S_k'z_{k'}+S_{k'}'z_k. \tag{7}$$

Thus, that portion of the dynamical matrix which comes from the first and second terms of Eq. (3) is the same as that from the first term alone, but with $z_kz_{k'}$ replaced by $z_kz_{k'}+f_{kk'}$.

For compounds with the rock-salt structure the LO-TO splitting is given by

$$\omega_{\rm LO}^2-\omega_{\rm TO}^2=4\pi e^2Y_2/\mu v, \tag{8}$$

where μ is the reduced mass, v is the volume per unit cell, and Y^2 is an effective charge factor. In the rigid-ion approximation $Y^2=z^2=1$ (4) for alkali halides (alkaline-earth oxides). When the self-energy term is included Y^2 becomes

$$Y^2=z^2-z_1S_2'-z_2S_1' \tag{9}$$

where the subscripts 1 and 2 refer to positive and negative ions, respectively.

Charge densities for the ions under consideration were calculated as a function of V_k [Eq. (1)] with use of a suitably modified version of the program of Liberman, Cromer, and Waber.[7] These calculations were carried out with use of the local-density exchange-correlation functional of Hedin and Lundqvist[8] with self-interaction corrections[9] included explicitly. Next, the self-energies S_k were determined by integration of the same expressions for exchange and correlation energy density, while the Thomas-Fermi form was used for the kinetic-energy contribution. We use the Thomas-Fermi form for kinetic energy to be consistent with the calculation of the short-range pairwise energies [third term of Eq. (3)]. (The pairwise energies are derived following the work of Gordon and Kim[4] which uses the Thomas-Fermi form.) The derivatives of the self-energies, $S_k'=dS_k/dV_k$, were then evaluated numerically at values of V_k corresponding to the lattice constants of the various ionic compounds under consideration [Eq. (2)]. The values for S_k' for the positive ions ($k=1$) are relatively small compared to those for the negative ions. The values obtained for S_2' are listed in Table I along with the corresponding effective charge factors calculated from Eq. (9) with $S_1'=0$. For comparison, empirical values for Y^2 obtained from experimental values[10] for $\omega_{\rm LO}$ and $\omega_{\rm TO}$ using Eq. (8) are also listed in Table I.

From the results in Table I we see that much of the reduction in LO-TO splitting from the rigid-ion value can be accounted for by a spherically symmetric breathing of the ions in response to changes in the electrostatic potential at their sites. Previous lattice-dynamical models attribute the entire reduction in LO-TO splitting to dipolar effects.

We have calculated the elastic constants of MgO[11] by evaluating the total energy [from Eq. (3)] as a func-

TABLE I. Self-energy derivatives $S_k' = dS_k/dV_k$ for the negative ions ($k=2$) of the alkali halides and alkaline-earth oxides along with calculated [Eq. (9)] and empirical [Eq. (8) with experimental frequencies taken from Ref. 10] effective charge factors Y.

Compound	Lattice constant (Å)	S_2'	Y_{calc}	Y_{emp}
NaF	4.63	0.51	0.70	0.80
NaCl	5.64	0.20	0.89	0.70
NaBr	5.98	0.32	0.82	0.70
NaI	6.47	0.20	0.89	0.63
KF	5.35	0.34	0.81	0.87
KCl	6.29	0.20	0.89	0.74
KBr	6.60	0.26	0.84	0.73
KI	7.07	0.18	0.91	0.71
RbF	5.63	0.29	0.84	0.85
RbCl	6.58	0.19	0.90	0.72
RbBr	6.89	0.24	0.87	0.73
RbI	7.34	0.17	0.91	0.62
MgO	4.21	0.94	1.46	1.15
CaO	4.81	0.88	1.50	1.26
SrO	5.16	0.72	1.60	1.40
BaO	5.52	0.68	1.62	1.43

tion of lattice strains, with the long-range Coulomb interactions and the potential at the ion sites computed by the Ewald method. The results are shown in Table II along with corresponding results in the rigid-ion approximation and experimental values. The better agreement obtained for the lattice constant of MgO in the rigid-ion approximation is fortuitous. Typically one finds discrepancies of a few percent in the lattice constant using either rigid ions or PIB ions, with no clear trend in the discrepancies. In the rigid-ion approximation the lattice constant is determined by a balance between the positive pressure due to the Madelung energy and the negative pressure due to the overlap of the ions. With PIB included the anions inhale as the lattice contracts, which reduces the overlap forces as it increases the self-energy of the anions, thus transferring some of the negative overlap pressure to that arising from the anion self-energy. When the ions are allowed to breathe and the lattice allowed to relax to a new energy minimum the energy of the crystal is obviously lowered, but the new lattice constant can be either larger or smaller than the rigid-ion value. On the other hand, a clear improvement is seen in the calculated elastic constants when PIB is introduced. We see that the rigid-ion elastic constants are much too large and of course the Cauchy relation, $C_{12} = C_{44}$, is contrary to experiment. If the ions are allowed to breathe in response to the electrostatic potential we obtain much better agreement with experiment.

We have also begun to calculate transition pressures

TABLE II. Comparison of calculated results for the elastic constants of MgO in the rigid-ion and breathing-ion approximations with the corresponding experimental values.

	a (Å)	C_{11} (Mbar)	C_{12} (Mbar)	C_{44} (Mbar)
Rigid ion	4.23	4.28	1.87	1.87
Breathing ion	4.30	2.67	0.70	1.36
Expt.	4.21	2.88	0.88	1.55

for the rock salt to CsCl structure with PIB ions. Here we find modest improvement, but still substantial discrepancies exist. For example, for NaCl PIB raises the transition pressure from its rigid-ion value of ~ 50 to ~ 150 kbar, but still much short of the ~ 300 kbar experimental value. Recently Hemley and Gordon[12] have included PIB in the calculation of transition pressures for alkali halides and find a value of 191 kbar for NaCl. In their calculation the charge densities were derived by the Hartree-Fock method.

We have shown that a potential-induced breathing of ions, which has not been previously considered in model calculations, plays a major role in the lattice dynamics of ionic solids. However, as can be seen by the results in Table I, substantial discrepancies still exist within the spherical-ion approximation. Notice that the discrepancies between Y_{calc} and Y_{emp} increase as one goes to the heavier halide systems, which is consistent with the notion that the heavier halides are more polarizable.

In conclusion, we stress that our results imply that PIB is *not* a minor, subtle effect compared to charge-relaxation effects treated by earlier lattice-dynamical models.[13] The strategy employed in the development of these earlier models was (a) to formally express changes in energy as perturbations (or variations) from an assumed ground state and (b) to test various parametrized models of these expressions for accuracy in reproducing measured phonon dispersion curves. While the models which evolved are capable of accurately fitting phonon-dispersion curves, they require typically a half-dozen or more parameters, and as such, their success in this arena does not prove their physical validity. On the other hand, our results came from an effort to derive the ground state of the system from first principles. While our approach is relatively simple, we believe that it is reasonably accurate at this zero-order level.

We emphasize that PIB is a zero-order effect coming as it does from the response of the negative ions to the Madelung potential. Other charge-relaxation effects arising from overlap, or electric field, which are treated in various ways by earlier models, can be included as perturbations on this new ground state of the system. It is important that one start with a proper zero-

order description of the system because perturbation theory can only be applied to a reasonably accurate ground state. Obviously this is essential for oxides because it is this zero-order effect which stabilizes the O^{2-} ion. In view of this it should not be too surprising that PIB would play a major role in the statics and dynamics of ionic systems.

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Appendix.—As long as either $\binom{m}{j}$ or $\binom{m'}{j'}$ is equal to $\binom{l}{k}$ the term involving S_k'' in Eq. (5) is zero for the rock-salt structure because $\partial P(\binom{l}{k})/\partial r_\alpha(\binom{l}{k})$ is the αth component of the electric field at the $\binom{l}{k}$ site, which is zero for crystals with ions at sites of inversion symmetry. Thus,

$$\sum_{lk} S_k'' \frac{\partial P(\binom{l}{k})}{\partial r_\alpha(\binom{m}{j})} \frac{\partial P(\binom{l}{k})}{\partial r_\beta(\binom{m'}{j'})}$$

$$= \sum_{lk}{}' S_k'' z_j z_{j'} \frac{(r_\alpha(\binom{l}{k}) - r_\alpha(\binom{m}{j}))(r_\beta(\binom{l}{k}) - r_\beta(\binom{m'}{j'}))}{|\mathbf{r}(\binom{l}{k}) - \mathbf{r}(\binom{m}{j})|^3 |\mathbf{r}(\binom{l}{k}) - \mathbf{r}(\binom{m'}{j'})|^3}.$$

This term converges absolutely, since it goes as $1/r^4$, and therefore does not contribute to the LO-TO splitting.

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