

## Perturbation-theoretic-model approach to the study of alkali halides

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Starting from the Hartree-Fock wave functions of the free ions a method is suggested to make a comprehensive calculation of the lattice static and dynamic properties of alkali halides. This is achieved through the intermediary of a model, the parameters of which are extracted from a first-principles calculation. It may be mentioned here that until now no calculation of lattice dynamics of alkali halides, without using any experimental input, has been reported. In the present calculation for the KCl crystal neither any measured property of the solid is used nor any parameter is varied arbitrarily to fit experiment. The calculated properties are found to agree quite satisfactorily with the measured ones.

### I. INTRODUCTION

The group of ionic solids known as alkali halides is characterized by electron distributions which form closed shells round each ion. Being saturated structures, their electron distributions are not radically altered when the free ions are brought together to form the solid. The response of the electron system may, therefore, be adequately treated by perturbation theory. The electron distributions round isolated ions are well known from the accurate Hartree-Fock calculation of the wave functions for the free ions.<sup>1</sup> It would be highly desirable, if one could make a comprehensive calculation of the static and dynamic properties of alkali halides from a knowledge of the Hartree-Fock wave functions of the corresponding free ions.

A first-principles calculation of the above type of some of the static properties of alkali halides was initially attempted by Lowdin,<sup>2</sup> Lundqvist,<sup>3</sup> and Landshoff.<sup>4</sup> The main purpose of these authors was to calculate the cohesive energy, the equilibrium lattice constant, and the elastic constants. Recently, Gordon and Kim<sup>5,6</sup> have used the Clementi wave functions<sup>1</sup> to calculate some of the static properties. The result of their calculations is very encouraging. They, indeed, prove the basic correctness of the approach. The major difficulty of their method is that every property involves lengthy and tedious numerical computations. Further, for some properties these become prohibitively unwieldy. Because of this limitation, the calculation of even the static properties of a crystal in all its entirety has not been done. The more serious limitation, however, is the difficulty of extending the method to calculate the lattice dynamics.

The first-principles calculation of the lattice-dynamical spectra of alkali halides presents many

problems. Particularly difficult is the inclusion of the effect of short range and electrical polarizability. An initial attempt by Lundqvist<sup>7</sup> in this direction was not very successful. During the last few years there have been several attempts<sup>8-11</sup> to formulate a microscopic theory for the lattice dynamics of alkali halides. The most persistent attempt to tackle the problem has been made by Sinha<sup>11,12</sup> in a series of papers. He has recently been successful in reducing his equations to a form which makes the numerical calculation of dispersion curves possible. However, several drastic approximations had to be made to carry out the calculation and four parameters were introduced. Two of these were related to the lattice constant by *ad hoc* assumptions and the remaining two were treated as adjustable. This procedure somewhat detracts from the spirit of a first-principles calculation. Wakabayashi and Sinha's final result for<sup>12</sup> KCl and KBr is similar to that of a simple shell model.<sup>13</sup>

It is clear from the above discussion that a comprehensive first-principles calculation of the properties of alkali halides is still a far cry. On the other hand, using a suitable effective-potential function within the framework of the shell model several authors<sup>14-16</sup> have shown that it is possible to obtain best-fit values of the parameters of the model which give a fairly good representation of the lattice mechanics of alkali halides. Such a calculation has been done for AgCl by Sarkar and Roy<sup>14</sup> and for NaF by Ghosh *et al.*<sup>15</sup> Earlier Sarkar and Sengupta<sup>16</sup> did a similar calculation of the static properties of six potassium and rubidium halides. From the over-all success of these calculations one can conclude that within certain limitations this model describes the actual situation and the model is considered to be empirically verified. The question, therefore, naturally arises, if the parameters of the model can

be calculated from the free-ion wave functions. If this can be done, it is possible to predict the properties of a crystal from a knowledge of the wave functions of the constituent free ions alone. This method which we call a perturbation theoretic-model calculation combines the advantages of a model approach with the essence of a first-principles calculation. Moreover the utility and simplicity of the approach are all of the more impressive. We propose to do a calculation of the above type for the KCl crystal.

## II. METHOD OF CALCULATION

We consider only the dominant part of the static interaction, namely, the Coulomb interaction between the ions and the overlap repulsive interaction represented by  $V(r) = be^{-r/\rho}$ . As a first approximation we neglect the van der Waals and the many-body interaction which are much weaker. From the Clementi wave functions<sup>1</sup> for  $K^+$  and  $Cl^-$  and using the well-known expression for the zero-point, exchange, and correlation energy, the overlap potential for  $K^+$  and  $Cl^-$  can be calculated in a straightforward manner (for details see Ref. 5) for several values of  $r$ , the interionic separation. Using these energies we plot  $\ln V$  against  $r$ , which is found to be an accurate straight line in the region of  $r$  which is significant for the crystal properties. From this curve are derived the values of  $b$  and  $\rho$ .

Next, to take account of the electrical and short-range polarization of the ions in the lattice spectrum we make use of the polarizable one-ion shell model<sup>13</sup> in which the overlap interaction is assumed to act entirely through the shells. The negative-ion polarizable shell model introduces two new parameters, one is  $-Y$ , the shell charge, and the other is  $K$ , the core-shell spring constant. The electrical polarizability of the negative ion is given by<sup>13</sup>

$$\alpha = Y^2/K. \quad (1)$$

Now, a quantum-mechanical calculation of  $\alpha$  for an ion can be done in a straightforward manner using the coupled Hartree-Fock equations in presence of a perturbing electric field.<sup>17</sup> Such a calculation for several ions have been done by Lahiri and Mukherjee.<sup>17</sup> But in order to get the values of  $Y$  and  $K$  separately we require another first-principles calculation of a property of the ion which depends on  $Y$  and/or  $K$ . To achieve this we use the fact pointed out by Sarkar and Sengupta<sup>18</sup> that the shell model implies a modification of the overlap interaction between the two ions, when one of them has a dipole moment. Since we assume that the overlap interaction acts entirely through the shells, the overlap interaction between nearest neighbors is given by

$$V = b e^{-r/\rho_{1s}} = V(r_{1s}), \quad (2)$$

where  $\vec{r}_{1s}$  is the separation between the center of the rigid positive-ion and the center of the negative-ion shell. If  $-Y$  is the shell charge and  $\vec{\xi}_s$  the core-shell separation of the negative ion, and  $\vec{r}_{12}$  is the separation vector for the positive and the negative ions then

$$\vec{r}_{12} = \vec{r}_{1s} - \vec{\xi}_s, \quad (3)$$

and the dipole moment of the negative ion is

$$\vec{d} = -Y\vec{\xi}_s. \quad (4)$$

From these relations we get

$$\vec{r}_{1s} = \vec{r}_{12} - \vec{d}/Y. \quad (5)$$

Hence, we can write the overlap interaction between the two ions, when one of them has a dipole moment  $\vec{d}$ , as

$$V = V(r_{12}) + [V(|\vec{r}_{12} - \vec{d}/Y|) - V(r_{12})], \quad (6)$$

where the first term is the usual interaction for rigid ions and the second term is the correction due to the polarization of one of the ions. The parameter  $Y$  or  $d_0 = Y\rho$  can be found by considering the special case when  $\vec{d}$  and  $\vec{r}_{12}$  are in the same direction. For this case the correction reduces to

$$\Delta V \approx V(r_{12}) d/d_0. \quad (7)$$

Here,  $\Delta V$  is the change in overlap energy between a chlorine and a potassium ion, separated by a distance  $\vec{r}_{12}$ , when the chlorine ion develops a dipole moment  $\vec{d}$  along  $\vec{r}_{12}$ .  $d_0$  may be regarded as a characteristic constant of the chlorine ion which determines its short-range polarizability. Further it may be mentioned that both the electrical polarizability  $\alpha$  and the short-range polarizability parameter  $d_0$  have direct physical significance.

Our problem, therefore, reduces to a first-principles calculation of  $d_0$  from the Hartree-Fock wave functions of the free potassium and chlorine ions and the perturbed wave functions of the chlorine ion. We proceed in the following way. Let the chlorine ion be polarized by an arbitrary external electric field,  $E_{ex}$  along the  $Z$  direction. The dipole moment developed in the chlorine ion is also in the  $Z$  direction and its magnitude is  $d = \alpha E_{ex}$ , where  $\alpha$  is the polarizability of the free ion already computed.<sup>17</sup> The perturbed wave functions upto first order in  $E_{ex}$  for the chlorine ion with dipole moment  $d$  are now known. Next we place a potassium ion on the  $Z$  axis at a distance  $\vec{r}_{12}$  from the chlorine ion. In the present calculation the potassium ion is considered to be rigid and hence its wave functions are the same as those of a free ion. However, a similar but not exactly identical calculation may be performed

TABLE I. Parameters and calculated crystal properties. All properties refer to harmonic values.

Parameters	Lattice constant		Cohesive energy		Bulk modulus		Static dielectric constant		High-frequency dielectric constant	
	Exp <sup>t</sup> <sup>a</sup>	Calc.	Exp <sup>t</sup> <sup>a</sup>	Calc.	Exp <sup>t</sup> <sup>a</sup>	Calc.	Exp <sup>t</sup> <sup>a</sup>	Calc.	Exp <sup>t</sup> <sup>b</sup>	Calc.
$b = 6.998 \times 10^{-9}$ erg	$\text{\AA}$		(kcal/mole)		( $10^{11}$ dyn/cm <sup>2</sup> )		$\epsilon_0$		$\epsilon_\infty$	
$\rho = 0.298$ $\text{\AA}^3$										
$\alpha = 3.74$ $\text{\AA}^3$										
$d_0/e = 0.887$ $\text{\AA}$	6.216	6.214	169.2	168.93	2.09	2.03	4.49	4.67	2.2	2.1

<sup>a</sup>See Ref. 16.<sup>b</sup>See Ref. 21.

to include the effect of the deviation of the positive ion from being rigid. We now compute the overlap interaction between the polarized chlorine ion and the unpolarized potassium ion using the well-known equations given in detail in Ref. 5. As mentioned earlier in this section, we have also computed, using the same procedure, the overlap energy between the two ions, when the perturbation  $E_{\text{ex}}$  on the chlorine ion is absent. The difference gives us  $\Delta V$  as a first-order quantity in  $E_{\text{ex}}$ . Let us put the computed energy in the form

$$\Delta V_{\text{computed}} = A E_{\text{ex}}, \quad (8)$$

where  $A$  is the numerical factor. Equation (7) may now be written in the form

$$A E_{\text{ex}} = V(r_{12}) \alpha E_{\text{ex}} / d_0 \quad (9)$$

or

$$d_0 = V(r_{12}) \alpha / A. \quad (10)$$

Since all the quantities on the right-hand side are computed using the free-ion Hartree-Fock wave functions of the ions, we get the value of  $d_0$  without using any solid-state property.

Thus all the four parameter  $b$ ,  $\rho$ ,  $\alpha$  and  $d_0$  are obtained from the free-ion wave functions. The values for  $\alpha$  and  $d_0$  may be used to get the shell-model parameters, namely,  $Y$  and  $K$ . The values of  $Y$  and  $K$  determined from the negative-ion polarizable-shell-model calculation for KCl by Basu and Sengupta,<sup>19</sup> by fitting the crystal properties, are found to compare favorably with those obtained from  $\alpha$  and  $d_0$ .

Now, using these parameters, some of the crystal properties, namely, the harmonic lattice constant, the harmonic cohesive energy, the harmonic bulk modulus, the static and high-frequency dielectric constants, and the dispersion of phonons in the symmetry directions have been calculated. The detailed equations for all these properties are given in Refs. 15, 19, and 20. All the calculations have been done on an IBM 1130 com-

puter. In Table I and Fig. 1, the calculated properties are compared with experiment.

### III. RESULTS AND DISCUSSION

It is clear from the results that the agreement with experiment is quite satisfactory. However, Fig. 1 shows that there are some small discrepancies specially in the [111]LO, [111]LA branches as also in the TO branches in all three directions. It is interesting to note that these discrepancies may be understood in terms of the interactions neglected in the present calculation. It is well known that the discrepancy in the LO and LA [111] branches is specifically due to the type of many-body interaction arising out of the deformation of the shell<sup>20</sup> and which is not included here. Similarly it is presumed that the neglect of the van der Waals interaction might be responsible for the discrepancies in the TO branches. Apart from the specific discrepancies mentioned above, the over-all small remaining discrepancy may be partly due to the neglect of the positive-ion polarizability. It is to be further noted that the electrical polarizability of the negative ion in the present case is somewhat larger than the correspond-

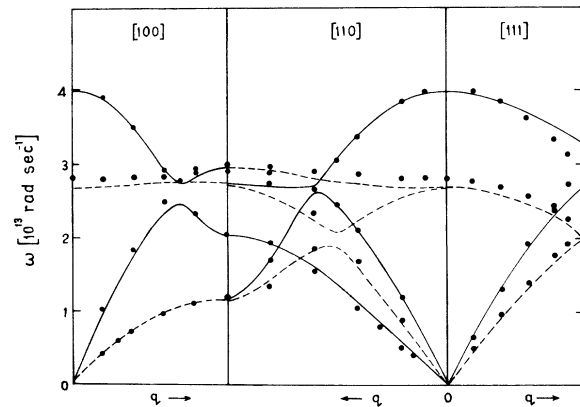


FIG. 1. Phonon dispersion curves for KCl crystal at 80°K. Solid and dashed lines represent the theoretical calculation for longitudinal and transverse modes, respectively. Experimental points are taken from Ref. 22.

ing value of Tessen-Kahn-Shockley polarizability. It appears that in a more rigorous calculation, the polarizability of the positive ion should also be included. Nevertheless, considering the simplicity of the approach it appears that the present method is adequate enough to describe the basic features of both the static and dynamic aspects of alkali

halides, without the knowledge, whatsoever, of any of the measured properties of the solid.

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