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Shell model and the nature of the collective oscillations of shells

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The specific form of the change in overlap interaction between ions due to the presence of dipole polarizability implied by the shell model lacks any microscopic justification, while all other terms of the model have a sound quantum-mechanical basis. Recently we have shown that within the framework of the Heitler-London approach this modified overlap term of the shell model is microscopically justifiable. This calculation provides a method of evaluating the parameters of the model directly from the wave functions of the ions. Since the shell model has been successful in describing the different lattice-mechanical properties, it seems instructive to investigate how far it can reproduce the collective dynamics of the electrons in insulators. Starting from the Hartree-Fock wave function of the ions the calculation is presented for the dispersion relations of the collective oscillation of the shells in the shell model by relaxing the usual adiabatic condition for the two crystals: namely, KCl and NaCl. It is interesting to note that the $\vec{q}\rightarrow 0$ frequencies of these collective oscillations of shells of these two crystals together with those of the other fourteen crystals obtained phenomenologically are found to compare satisfactorily with the measured plasma frequencies.

I. INTRODUCTION

Evidence, both empirical and theoretical, is gradually increasing and is by now compelling enough to justify the objective validity of the crucial underlying assumption of the shell model,[1] i.e., the existence of a localized electronic dipole or more commonly that of a shell in the shell-model parlance. This model has been widely used to interpret the dielectric and the phonon data of various solids in general and the insulators in particular. On the theoretical side since the introduction of the idea of the shell model by Dick and Overhauser[2] several works have appeared to justify the model. Among the earlier works those of Tolpygo and co-workers[3] need special mention. During the last decade or so the works of Gliss *et al.*,[4] Zeyher,[5] Wakabayashi and Sinha,[6] and Nidermann and Wagner[7] have presented quantum-mechanical justification of the basic formalism of the shell model. Recently it has been demonstrated by Banerjee *et al.*[8] that under suitable approximations the specific form of the change in overlap interaction between ions due to the presence of the dipole polarizability implied by the shell model is derivable from the first-principles analysis.

The above-mentioned works indicate that the shell model may be looked upon as a simplified way of taking account of the very complicated collective response of the electron system in insulators to nuclear displacement and the external electric field. Moreover, the empirical success of the shell model shows that this treatment of the electron response describes fairly well the properties of insulators connected with nuclear displacement. It is therefore legitimate to ask if the same response mechanism can also describe the collective dynamics of the electron system, i.e., of the plasma oscillations in insulators. In fact, in this report we shall attempt to add a new dimension to the shell model by interpreting the collective oscillations of the shells in the shell model hitherto not considered as a meaningful physical quantity as the plasma oscillations in insulators. However, it is to be mentioned that the idea presented in this work is not altogether a new one. Slater[9] discussed a general scheme of obtaining the collective oscillations of ions and electrons in insulators from a unified point of view, although he did not actually use the idea of the shell model. Next, in the first international conference on lattice dynamics a somewhat analogous idea, of course not exactly similar to the present work, was advanced as a speculation by Lax[10] in which he called attention to a "shellon" the shell frequency. We shall try to substantiate our interpretation by presenting a parameter-free calculation of the dispersion relation of the collective shell oscillations for the two solids, namely, NaCl and KCl crystals. Next we shall present the phenomenological calculations for 14 other crystals. Finally, we shall compare these frequencies with the measured plasma oscillations.

II. THEORY AND METHOD OF CALCULATION

Before we proceed with the actual calculation let us briefly recall the shell model. In insulators it is assumed that the response of the electron system to an external electric field will in general continuously vary from the loosely bound valence-electron states to the rigidly held deep-lying core states of the ion, the perturbation being maximum for the outermost electron and vanishingly small for the innermost one. In the shell-model description this entire complicated process of response is approximated by assigning a fixed charge to the shell whose response is controlled by a spring of finite strength, while the rest of the electrons are held to the core with infinite strength. This assumption is seen to be justified from the following direct numerical calculation. Placing a Cl^- ion in an electric field a coupled Hartree-Fock calculation is performed to obtain the dipole polarizability. The perturbation-wise break up of the result is shown in Table I. The results clearly show that the perturbation of the 3*p* electrons alone contributes about 99% of the total dipole polarizability. In the shell model this entire process shown in Table I is approximated by assigning a fixed charge to the outermost valence orbital (3*p* shell in the present case) whose response is controlled by a spring of finite strength, while the rest of the electrons (i.e., 3*s*, 2*p*, 2*s*, and 1*s* orbitals) are held rigidly to the core. Retaining the full charge of each orbital a rough estimate from the values given in Table I shows that the spring constant of the next important orbital (3*s*) is approximately 60 times larger than that of the 3*p* orbital. This may be advanced as a justification of the mechanical spring shell picture envisaged by the shell model. But this simple picture should not be stretched too far. It must be emphasized here that after an ion is transferred to a lattice the shell charge is no longer an individual ion property: It is a joint property of the ion and its surroundings. What is important to note is that the relative response of the orbitals is assumed to remain more or less the same in the crystal, and the shell-model description is tenable. This point is further treated later. After these preliminaries our purpose in the present work is (1) to indicate that under suitable approximations the form of the change in the overlap interaction term due to the presence of dipole polarizability implied by the phenomenological shell model is derivable from the first-principles analysis (it may be noted here that all other terms in the shell model except this one have sound quantum-mechanical justification in the Heitler-London approach for an aggregate of ions), (2) to then calculate the relevant parameters from the Hartree-Fock wave functions of the ions when the ions are placed in a lattice, and (3) finally to solve the equations of motion in the shell-model formalism without invoking the adiabatic condition and to obtain the dispersion relations of the collective oscillation of the shells. For crystals other than NaCl and KCl only the $\vec{q}\rightarrow 0$ frequencies have been calculated by using the values of the parameters determined from the crystal properties.

Recently, in a series of works[8,11,12] we have presented a careful analysis of the energy expression for an assembly of ions within the s^2 approximation. We indicate, in brief, the part of the analysis related to our discussion. We make use of the Heitler-London method of construction of the wave functions first used by Paul *et al.*[13] for ionic solids. Denoting by the one-electron wave functions the ion at site G, where $\nu = G,i,\sigma$ (i and σ indicate the spatial and spin quantum numbers), we construct the antisymmetric wave function for the whole crystal. We associate with every lattice site G a positive nucleus of charge $z_G e$ and the electronic charge $n_G e$, and $\epsilon_G e = (z_G - n_G)e$ is the net ionic charge at G. With an even number of electrons the electronic states are occupied, including both spin states $\sigma = \pm 1$, and the normalized antisymmetric wave functions are given by

$$\Phi_G = A_G \prod_{\nu} \Phi_\nu , \tag{1}$$

where A_G is a normalized antisymmetric operator acting on the electrons of the G ion. The antisymmetric wave function for the entire solid is given by

$$\Psi_0 = A\Phi_0, \quad \Phi_0 = \prod_{G} \Phi_G \tag{2}$$

where A antisymmetrizes Φ_0 with respect to interchange of electrons belonging to different ions. With the use of the standard set for numbering of electrons the Hamiltonian of the solid is given by

$$H = H_0 + V, \quad V = \tfrac{1}{2} \sum_{G,G'} V_{GG'} \tag{3}$$

where H_0 is the Hamiltonian of the isolated ions and $V_{GG'}$ represents the interaction term. It is to be noted that this is not the total potential but represents only that part of the potential which results from the interaction between ions and is small compared to the energy of the isolated ions. Now in order to include the effect of perturbation the modified wave function is given by

$$\begin{aligned} \Phi_0' &= \Phi_0 + \sum_{\nu} C_\nu \Phi_\nu \\ &= \Phi_0 + \sum_{G} C_G \Phi(G\nu) + \sum_{G,G'} C_{GG'} \Phi(G\nu, G'\nu') , \end{aligned} \tag{4}$$

where the excited state is denoted by ν. In the above expression $\Phi(G\nu)$ and $\Phi(G\nu, G'\nu')$ are the excited states of the crystal in which only the G ion and the G and G' ions are excited, respectively. Since our major motivation is to derive the shell-model energy expression we are interested only in the dipolar deformation of the ions. Hence without any loss of generality we assume the individual ion excited state to be *p* states only. Antisymmetrizing the wave function (4), $\Psi_0' = A\Phi_0'$, the total energy of the solid may be written as

$$E = \frac{\int \Psi_0' H \Phi_0 d\tau}{\int \Psi_0' \Phi_0 d\tau} . \tag{5}$$

Next, making a multipole expansion of V and using the S^2 approximation, Eq. (5) may be split up in different orders of S^2 and V. The details of this derivation are discussed by Banerjee *et al.*[8] Of all the terms, we consider the one which is second order in V and first order in S^2 because this is the crucial term on which the shell model hinges. The other terms occurring in the shell model are quite well known and correspond to various terms in the expansion of Eq. (5). The dominant term of this second-order exchange interaction is given by

$$E_{21} \simeq 2 \sum C_\nu (V_{0\nu}^{\text{ex}} - V_{00} S_{0\nu}^2) , \tag{6}$$

where

TABLE I. Contribution to dipole polarizability from different orbitals of Cl^- in atomic units.

Perturbation	1*s*-*np*	2*s*-*np*	2*p*-*ns*	2*p*-*nd*	3*s*-*np*	3*p*-*ns*	3*p*-*nd*	Total
Polarizability	0.0001	0.0018	0.0011	0.0138	0.1059	4.5798	20.6712	25.3737

$$V_{0\nu}=\langle 0\,|\,V\,|\,\nu\rangle,\quad V_{0\nu}^{\rm ex}=\langle \nu\,|\,V(A-1)\,|\,0\rangle\ ,$$
$$S_{0\nu}^{2}=\langle 0\,|\,(A-1)\,|\,\nu\rangle\ .$$

If we compare this term with the term which is first order in V and first order in S^2, namely,

$$E_{11}=(S^2V_{00}-V_{00}^{\rm ex})\ , \tag{6a}$$

where

$$V_{00}=\langle 0\,|\,V\,|\,0\rangle,\quad V_{00}^{\rm ex}=\langle 0\,|\,V(A-1)\,|\,0\rangle\ ,$$
$$S^2=\langle 0\,|\,(A-1)\,|\,0\rangle\ ,$$

we may immediately note that Eq. (6) is a modification of Eq. (6a). Let us clarify the point; Eq. (6a) describes, along with the Coulomb overlap interaction, the usual short-range overlap interaction (see Paul *et al.*[13]) between ions which are spherically symmetrical, and their electron distribution is unperturbed by the field of other ions. The part of E_{21} given in Eq. (6) describes a modification of this short-range interaction [Eq. (6a)] due to the presence of the dipolar perturbation of the electron wave functions produced by the $C_\nu\Phi_\nu$ terms of Eq. (4). Basically this is also the essence of the shell-model approach where a specific form of this change in overlap interaction due to the presence of the dipole moments of the interacting ions has been phenomenologically suggested. We shall now show that under reasonable assumptions Eq. (6) leads to correction to the overlap interaction, which is identical to that envisaged in the shell model.

Let us consider two ions separated by a distance $R_{GG'}$. Taking the z axis along $R_{GG'}$ we assume that the dipole moments $\vec{m}_G$ and $\vec{m}_{G'}$ are also along this direction. We shall only consider those terms for which C_ν is C_G. In this case C_G reduces to a single component and Eq. (6) may be written completely in terms of the dipole moments,

$$E_{21}=-\left[\frac{\vec{m}_G\phi_{\nu 0}(G,G')}{2en_G\xi_G}+\frac{\vec{m}_{G'}\phi_{0\nu}(G,G')}{2en_{G'}\xi_{G'}}\right]\ , \tag{7}$$

where

$$\xi_G=\left\langle \Phi_G\,\left|\,\sum_i(\tau_i-R_G)_z\,\right|\Phi_{G\nu}\right\rangle$$

and

$$\vec{m}_G=-2eC_G\left\langle \Phi_G\,\left|\,\sum_i(\tau_i-R_G)\,\right|\Phi_{G\nu}\right\rangle\ ,$$

and $\phi_{\nu 0}(G,G')$ is the overlap interaction between G and G' ions when an electron of the G ion is in an excited state. We further assume that the overlap interaction does not substantially alter when only one of the electrons in the ions concerned is in an excited state. So, we may write

$$\phi_{\nu 0}(G,G')=\phi_{0\nu}(G,G')\simeq\phi(G,G')$$

when $\phi(G,G')$ is the total overlap interaction between the ions in their ground state. This is quite justified since the overlap interaction involves all the electrons of both the ions and the perturbation of a single electron will not significantly alter the total interaction energy. With this approximation Eq. (7) reduces to

$$E_{21}=-\left[\frac{\vec{m}_G}{\eta_G}+\frac{\vec{m}_{G'}}{\eta_{G'}}\right]\phi(G,G')\ , \tag{8}$$

where $\eta_G=2en_G\xi_G$. Again in the shell model the crucial assumption is that the overlap interaction between the two ions will alter when the ions have generated dipoles according to the following relation (see Refs. 14 and 15):

$$E=-\left[\frac{\vec{m}_G}{y_G\rho}+\frac{\vec{m}_{G'}}{y_{G'}\rho}\right]\phi(G,G')\ , \tag{9}$$

where $\phi(GG')=b\exp(-R_{GG'}/\rho)$ is the Born-Mayer (BM) form of the overlap interaction and $-y_G$ is the shell charge of the G ion. Equation (8) provides the justification of the specific form implied by the shell model (9).

Next we briefly discuss how to determine the shell parameters from the Hartree-Fock wave functions of the ions. Comparing Eqs. (8) and (9) we immediately obtain the expression for the shell charge

$$y_G=\eta_G/\rho\ , \tag{10}$$

which clearly shows that the shell charge of the G ion is no longer a property of the ion alone, in contrast to the simple arguments given earlier. Basu and Sengupta[16,17] have discussed in detail the method of evaluation of Eq. (8) by using the Clementi wave functions of the ions. In addition to the shell parameters the BM potential parameters, namely, b and ρ are also determined. The method essentially consists of evaluating the overlap energy between the ion with and without dipole perturbation of the wave functions. It is noted from a very exhaustive calculation that the magnitude of the shell charge slightly varies with the equilibrium separation between the ions.[16] Since we do not expect an exact reproduction of the plasma frequencies using only the free-ion wave functions we disregard this small variation and use the values corre-

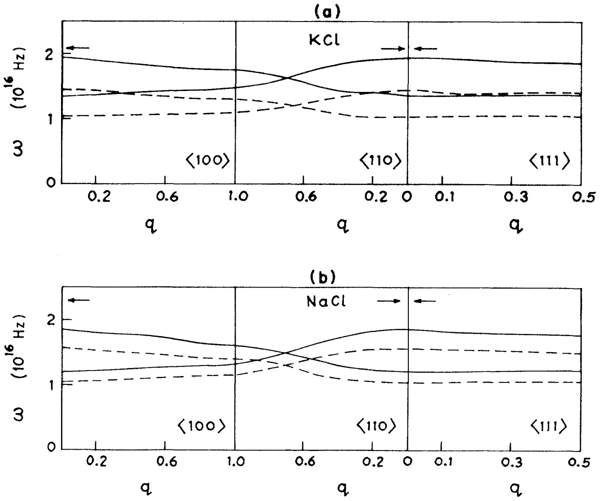

FIG. 1. Dispersion relation of collective oscillation of shells for (a) KCl crystal and (b) NaCl crystal. Dotted and solid curves refer to parameter-free and phenomenological calculations, respectively. The upper and lower branches indicate longitudinal and transverse modes. The arrow shows the observed plasma frequency.

TABLE II. Frequencies of collective shell oscillations ($\vec{q}\to 0$) in 10^{16} Hz.

Crystal	Calc.	Expt.[a]
KCl[b]	1.92 (1.49)	2.11
NaCl[b]	1.84 (1.55)	2.31
NaI	1.56	1.94
NaBr	1.60	2.10
NaF	3.20	2.62 (?)
KI	1.33	1.79
KBr	1.68	2.02
RbI	1.55	1.68
RbBr	1.83	1.85
RbCl	2.36	2.04
CsI	1.78	1.62
CsBr	2.32	1.72
CsCl	2.32	1.78
LiF	2.85	3.84
TlBr	1.67	1.78
MgO	2.80	3.39

[a] Reference 18.

[b] The values within parentheses for these two crystals refer to the parameter-free calculation.

sponding to the equilibrium separation. The perturbed wave functions used correspond to the values given in Table I. With the use of the results of the calculation for NaCl and KCl crystals[16] and the above equations the shell charges and the spring constants are evaluated. The values of the shell charges obtained are $1.826e$ and $1.639e$ for the NaCl and KCl crystals, respectively, the corresponding spring constants being 20.450 and 16.570 10^4 dyn/cm. We have consistently used the one-ion polarizable model in all the calculations. The variation in the value of the shell charge for the same ion (Cl^-) indicates the effect of different surroundings in the two crystals.

Having thus known the parameters we may now obtain the dispersion relations of the collective shell oscillations by solving the equations of motion of the shell model: In the usual vector notation the dynamical equations are given by (symbols are those of Ref. 1)

$$\begin{aligned}(R+ZCZ)U+(R-ZCY)W&=\omega^2 m_{\text{ion}}U\ ,\\ (R-YCZ)U+(K+R+ZCY)W&=\omega^2 m_{\text{shell}}W\ ,\end{aligned}\tag{11}$$

where m_{shell} is the mass of an electron multiplied by the shell charge. The other terms of the equations have their usual significance. The major difference of Eq. (11) from that of the conventional shell model is the absence of the adiabatic condition. In the usual application the shell mass in Eq. (11) is put equal to zero and the second equation of Eq. (11) reduces to the adiabatic condition. The solution of Eq. (11) will yield both the phonon and the plasma frequencies. In the symmetry directions the solution yields two branches, longitudinal and transverse, of the collective oscillations of the shells. We discuss the results in the next section.

III. DISCUSSION

Figures 1(a) and 1(b) and Table II show the results of the calculation and the experimental values. The $\vec{q}\to 0$ longitudinal frequency compares with the measured plasma frequency of the solid. It is seen from the figures that as expected the branches are more or less flat and it is found that the dispersion is produced by the underlying lattice structure. In all cases, without any exception, the correct order of magnitude is predicted. Even in the cases of the NaCl and KCl crystals where no crystal datum is used, the satisfactory agreement bears out the justification of the interpretation advanced in this work. Moreover, it may be mentioned that the same calculation also reproduces the different lattice-mechanical properties of these two crystals within reasonable limits.

However, it is found from Table II in general, including the two cases mentioned above, that the agreement with experiment improves when the parameters are obtained from the crystal data. The parameters for the crystals are directly taken from Refs. 19—22. It may be further pointed out that we have not tried to adjust the parameters for better agreement. The parameters used are also consistent with the other lattice properties of the crystals.

In conclusion, it may be noted that it has been possible to obtain a more or less satisfactory description of the plasma frequencies in insulators within the framework of the shell model. However, the verification of the dispersion relations awaits further observation.

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[1] A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. 119, 980 (1960); for a recent review see also, W. Cochran, Crit. Rev. Solid State Sci. 1, 1 (1971); J. R. Hardy, in *Dynamical Properties of Solids,* edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1, p. 157.

[2] B. G. Dick and A. W. Overhauser, Phys. Rev. 112, 90 (1958).

[3] K. B. Tolpygo, J. Exp. Theor. Phys. 20, 497 (1950); V. S. Mashkevich and K. B. Tolpygo, *ibid.* 5, 435 (1957).

[4] B. Gliss, R. Zeyher, and H. Bilz, Phys. Status Solidi B 44, 747 (1971).

[5] R. Zeyher, Phys. Rev. Lett. 35, 174 (1975).

[6] N. Wakabayashi and S. K. Sinha, Phys. Rev. B 10, 745 (1974).

[7] H. P. Niedermann and M. Wagner, Phys. Status Solidi B 78, 615 (1976).

[8] Lalit K. Banerjee, A. N. Basu, and S. Sengupta, Phys. Rev. B 26, 1018 (1982).

[9] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1967), Vol. 3, p. 196.

[10] M. Lax, in *Lattice Dynamics,* edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 184.

[11] S. Sengupta, D. Roy, and A. N. Basu, in *Current Trends in Lattice Dynamics,* edited by K. R. Rao (Indian Physics Association, Bombay, 1979), p. 63.

[12] S. Ghosh, A. N. Basu, and S. Sengupta, Phys. Rev. B 23, 1818 (1981).

[13] S. Paul, A. K. Sarkar, and S. Sengupta, Phys. Status Solidi B 54, 321 (1972).

[14] A. N. Basu and S. Sengupta, Phys. Rev. B 14, 2633 (1976).

[15] S. K. Sarkar and S. Sengupta, Indian J. Phys. 49, 836 (1975).

[16] A. N. Basu and S. Sengupta, Phys. Status Solidi B 102, 117 (1980).

[17] A. N. Basu and S. Sengupta, in *Lattice Dynamics,* edited by M. Balkanski (Flammarion, Paris, 1977), p. 65.

[18] A. B. Kunz, in *Elementary Excitations in Solids, Molecules and Atoms, Part B,* edited by A. B. Kunz and T. C. Collins (Plenum, New York, 1974).

[19] A. Ghosh and A. N. Basu, Phys. Rev. B 14, 4616 (1976); 17, 4558 (1978).

[20] A. Ghosh, A. N. Basu, and S. Sengupta, Proc. R. Soc. London, Ser. A 340, 199 (1974).

[21] A. Ghosh and A. N. Basu, J. Phys. C 9, 4616 (1976).

[22] Lalit K. Banerjee, A. N. Basu, and S. Sengupta, Phys. Rev. B 20, 1706 (1979).