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Study of Interionic Potentails and Polarization Models

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Abstract – Formula for the energy of an ionic crystal with ions having complete electron shells have been derived in the Heitler –London approximation by Hylleraas and others [102].Hylleraas formulated the physics of the problem and derived the energy expression for the LiH crystal. Landshoff [160] introduced a convenient calculating device of using approximately orthonormalised one electron wave function, obtained as linear combination of the one electron wave functions of free ions .Later Lowdin derived a mathematically exactly energy expression in the Heitler-London approximation by using a mathematically exact method of orthonormalisation. In his calculation, however he used a series expansion in the overlap integrals defined below and considered the so called S^2 approximation better than that of Landshoff's analysis. The calculation of the cohesive energy is based on the realization that the free ion one electron wave functions of Hartree and Hartree Fock do not form an orthonormal set of wave functions when the ions come as close as they are in the solid.The correct value of the cohesive energy can be obtained as the lowest eigen value of the complete Hamiltonian of the solid.The evaluation of this value demands a knowledge of the true wave functions for the solids as a whole. These wave functions can be expressed as a linear combination of the free ion wave functions by imposing the condition of orthonormality of the linear combinations we can obtain the true wave functions corresponding to the solid.

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INTRODUCTION

Suppose ψ_μ represents the free ion wave functions. Let us define a function $S_{\mu\nu}$ by

$$S_{\mu\nu}=\int\psi^*_\mu\psi_\nu\, d\acute{\imath} - \delta_{\mu\nu} \qquad (3.1)$$

Where μand ν are the quantum numbers of the electron wave functions centered at various ions and $\delta_{\mu\nu}$ is known as kronecker symbol. Obviously $S_{\mu\nu}$ measures the deviation of the overlap integral of wave function $\varphi_\mu$from orthonormality. We shall, however, for convenience call $S_{\mu\nu}$ as the overlap integrals. Usually one considers overlap between nearest neighbours only hence ν and μ refers to electron wave functions centered at nearest neighbouring ions. It can now show that a linear combination of φ_μ is the form,

$$\varphi_\mu = \psi_\alpha\,(I+S)^{-1/2} \qquad (3.2)$$

Where I is the unit matrix of power order.φ_μ as given by equation (3.2) from an exactly orthonormal set. If we retain terms only up to the second degree in $S_{\mu\nu}$ this function will be

$$\varphi_\mu=\psi_\alpha\,(S_{\alpha\mu} - S_{\beta\mu}/2 + 3S_{\alpha\beta}S_{\beta\mu}/8) \qquad (3.3)$$

The wave functions, φ_μ lead to a cohesive energy expression which can be broadly divided in to three distinct parts,

$$\Phi = \Phi_c + \Phi_R + \Phi_T \qquad (3.4)$$

Φ_C is the classical electrostatic energy of the lattice, which is obtained by considering the ions as point charges.

$$\Phi_C = \frac{e^2}{2}\sum_{lk}\sum_{l'k'}{}' \frac{Z_k Z'_k}{r(lk,\, l'k')} \qquad (3.5)$$

Where l and k are respectively the cell and basis indices, $Z_k = \pm 1$ and ∑' denotes a summation, where the terms (lk) = (l'k') are omitted. Φ_R collects terms which depend only on the distance between two neighbouring nuclei and give the main contribution to the repulsive lattice potential.

$$\Phi_R = e^2 \sum_{lk}\sum_{l'k'}{}' V[\ r(lk,\, l'k')] \qquad (3.6)$$

Φ_T corresponds to a three body potential,

$$\Phi_T = e^2 \sum_{lk} \sum'_{l'k'} \sum''_{l''k''} Z_k P_\mu (\nu|\, G\, |\mu) \qquad (3.7)$$

The double prime over the third sigma indicates that the term (l''k'')=(lk) or (l'k') are omitted and G represents the composite index (lk).The matrix element (v| G |μ) are given by,

$$(\nu|\, G\, |\mu) = \frac{\int \psi^*_\nu \psi_\mu \, d_1\psi}{|X_\alpha - X_\alpha (lk)|} \qquad (3.8)$$

and in the S^2 approximation $P_{\mu v}$ is equal to

$$P_{\mu\nu} = S_{\mu\nu} - S_{\mu\alpha} S_{\alpha\mu} \qquad (3.9)$$

The expression (3.8) for three body potential has calculated by Lowndin as well as by Lundquvist [33]using different methods Lowdin expands the integral in spherical harmonics with the origin at lattice point of the positive ion based on the method which was first introduced by Landshoff[33-39]for NaCl.The expression coverage rapidly if the cation is small in size, but for large size cations the overlap product $\psi^*_v \psi_\mu$ will no longer be localized around the nucleus of the cations and for crystals with large cations the convergence of the expansion will be rather slow. Lundquist has proposed a modification according to which the integral is expanded in spherical harmonics with the origin at the centre of gravity of the overlap density,$\psi^*_v \psi_\mu$.For NaCl this expansion seems to converge rapidly and it is a good approximation to neglect the first term. However, the first term will be rather a complicated function of the relative coordinates of the three nuclei because each pair of overlapping orbitals has its own centre of gravity, the coordinates of which will appear in the formulae. In a later work of Lundqvist evaluate the matrix elements (v| G |μ)by evaluating them over the positive and negative ion spaces reported by arbitrary planes perpendicular to the lines joining these neighbouring ions. This approach simplifies the calculations considerably and reduces the three body potential to the form

Where f_k is a function related to $S_{\mu v}$ and Z''_k is the charge on the k'' ion in the free state.The cohesive energy φ becomes

$$\Phi_T = e^2 \sum_{lk} \sum'_{l'k'} \sum''_{l''k''} f_k[\, r(lk,l'k')] \frac{Z''_k}{r(\,l\,k,\, l''k'')} \qquad (3.10)$$

On simplifying expression (3.11), the binding energy Φ per unit cell is obtained as,

$$\Phi = \frac{e^2}{2} \sum_{lk} \sum'_{l'k'} \frac{Z_k Z'_k}{r(lk,\, l'k')} + e^2 \sum_{lk} \sum'_{l'k'} V[\; r(lk,\, l'k')] + e^2 \sum_{lk} \sum'_{l'k'} \sum''_{l''k''} f_k[\, r(lk,l'k')] \frac{Z''_k}{r(\,l\,k,\, l''k'')} \qquad (3.11)$$

$$\Phi = e^2[\alpha_m(1+6f)^2/r + 12\, V(\, r)] \qquad (3.12)$$

A classical interpretation of this energy has been given by Cohran [55] and by Verma [13], according to which the function *f*(r) determines the amount of charge transferred from negative to positive ion due to the overlap of electron clouds so that it can be considered as a charge transfer parameter.

Description of Shell Model:-

An ionic crystal was initially considered tom be composed of spherical non-polarizable point ions held together by long range attractive and short range repulsive forces. This picture of point ion or the rigid-ion model explains the cohesive properties of ionic crystals with considerable success but does not explain their dielectric behaviour. The rigid ion model predicts the electronic dielectric constant ε_∞ for all the ionic crystals equal to one, while the experimental values for the most of the ionic solids lie between 2 and 3.This situation demonstrates the invalidity of the rigid ion model. The electronic polarizability and the observed dielectric behaviour of ionic and partially covalent crystals can be described plausibly well with the help of the shell model. In the shell mode, ions are regarded as having an outer shell of loosely bound electrons and an inner core composed of the nucleus plus tightly bound inner electrons. The shell in an ideal sense is assumed to be spherical, mass –less, non-deformable and isotropically coupled with the core by a spring of force constant k . Thus, the shell charge Y and the force constant k are the only two parameters in terms of which this model can be defined.

Under the application of an electric field $E=E_0e^{i\omega t}$ the equation of motion of the shell with respect to the core can be written as,

$$YeE = kd - Ym\omega^2 \qquad (3.13)$$

Where'd' is the displacement between the centers of the core and the shell.m and e are the electronic mass and charge, respectively. An expression for the polarizability is now written in the form,

$$\alpha = \frac{P}{E} = \frac{Yed}{E} = \frac{(Ye)^2}{K} = [1-(\omega^2 mY/k)]^{-1} \qquad (3.14)$$

$$\alpha = \frac{P}{E} = \frac{Yed}{E} = \frac{(Ye)^2}{K} \qquad (3.15)$$

For the frequencies where $(\omega^2 mY/k) << 1$,then

This equation in fact, is valid for the ions in free state. Y and K can be calculated by knowing the free state polarizability and its dispersion. When the ions are considered in a crystalline form the equation of motion of ion shells can be written as,

$$Y_- \, e \, E_{eff} - k_- d_- + (\Delta - d_- + d_+) = 0 \qquad (3.16)$$

$$Y_+ e \, E_{eff} - k_+ d_+ - (\Delta - d_- + d_+) = 0 \qquad (3.17)$$

And for all the cores

$$-(Y_- - Z)eE_{eff} + k_- d_- = - M_- \omega^2 \Delta_- \qquad (3.18)$$

$$-(Y_+ + Z)eE_{eff} + k_+ d_+ = - M_+ \omega^2 \Delta_+ \qquad (3.19)$$

Where 'A' is the repulsive force constant between the shells per ion pair and $\Delta = \Delta_+ - \Delta_-$ is the relative displacement of ions of masses M_+ and M_- of the cores, and Z is the valency of the ions. With the help of equations (3.16) through we can write,

$$\mu\omega^2\Delta = Z \, e \, E_{eff} + A \, (\Delta - d_- + d_+) \qquad (3.20)$$

Where μ is the reduced mass per ion pair. The dipole moment per ion pair is

$$p = - Z \, e\Delta + Y_- e \, d_- + Y_+ e \, d_+ \qquad (3.21)$$

For polarizability per ion pair one can obtain from equations (3.16),(3.17),(3.20) and

$$\frac{\alpha}{e^2} = \frac{(Y_+ + Z)^2/K_+ + (Y_- - Z)^2/K_- + Z^2/A}{[1-\mu\omega^2(1/A-1/k_+ + 1/k_-)]} + \frac{\mu\omega^2[(Y_+^{\,2}/AK_+) + (Y_-^{\,2}/AK_-) + (Y_+ + Y_-^{\,2}/k_-K_+)]}{[1-\mu\omega^2(1/A+1/k_+ + 1/k_-)]} \qquad (3.22)$$

In the limit ω→∞, equation (3.22) will yield the following expression for electronic polarizability (Lorentz-Lorentz relation),

$$\alpha = \frac{(\varepsilon_\infty - 1)\,3V}{(\varepsilon_\infty + 2)4\pi} = \frac{(Y_+ + Z)^2 e^2}{k_+} + \frac{(Y_+ + Z)^2 e^2}{k_-} + \frac{z^2 e^2}{A} \qquad (3.24)$$

The infrared absorption frequency ω_t occurs when there is a definite polarization without application of a field. For transverse wave there is no depolarizing field and so we have,

$$E = 4\pi P/3 \text{ or } \alpha_t = 3/4\pi N$$

Now equation(3.22) yields, with the use of equations (3.23)and (3.24) ,the relation

$$\mu \; \omega^2_{\,t} = \frac{(\varepsilon_\infty + 2)}{(\varepsilon_0 + 2)} \frac{1}{(1/A + 1/k_+ + 1/k_-)} \qquad (3.25)$$

Equation (3.23) to (3.25) lead to the following relation for the effective charge parameter.

$$\frac{e^*}{e} - 1 = \left[\frac{Y_+}{K_+} - \frac{Y_-}{K_-}\right] \Bigg/ Z\left(\frac{1}{A} + \frac{1}{K_+} + \frac{1}{K_-}\right) \qquad (3.26)$$

Values of (e*/e) obtained from (3.26) using the shell model parameters have been found to present closer agreement with experimental data.

Three Body Force Shell Model:-

The simple shell model as described in earlier section does not go beyond the rigid ion model as far as the elastic constants are concerned .It should be emphasized that the shell model as well as rigid ion model ion both consider the interactions in terms of two body or pair wise potentials. However, the consideration of two body potentials is not satisfactory for explaining the breakdown of the Cauchy's relation between the constants (C_{12}=C_{44}).It is therefore to induce three body interactions within the framework of the shell model in order to develop a more sophisticated model which is satisfactory from explaining the dielectric as well as elastic properties of crystals.

Verma and Singh [183] have developed a three body force shell model (TSM) based on Lindquist's expression for the lattice potential. The model uses a function *f*(a)of the nearest neighbour separation connected with the overlap integrals of electron wave functions and its space derivative (d*f*/da) as parameters, in addition to the usual parameters of the simple shell model [112-156].On classical considerations one can show that the TSM takes account of the charge transfer between neighbouring ions in addition to the dipoles included on the ion sites, while the simple shell model accounts only for the induced dipoles .An error in the formulation of the TSM has been pointed out by Agrawal and Verma[184] which concerned the definition of shell and core charges. By redefining the shell and core charges suitably, it is still possible to obtain the basic equations of the model as they have been described before but the meaning of the electrical and distortion Polarizabilities become somewhat different. It is therefore necessary to reformulate the model correctly and to investigate the extent to which this correction affects the results obtained earlier in various lattice dynamical studies [156].

Cochran [55] has shown that the TSM is equivalent to another variation of the shell model [113].A simple classical derivation of the Lundqvisite's expression for the lattice potential of ionic solids and a proof of the equivalence of the TSM and BSM have been obtained by Verma [182] by reinterpreting an analysis of the breathing motion of the shells in the BSM presented by Basu and Sengupta [41].This interpretation leads to charge transfer implied in Lundqvist's lattice potential and is in agreement with Cochran's analysis of the TSM.Let us designate the ions in an ionic lattice structure with two atoms per unit cell by the usual symbol(l,k), where the cell index l is the integral triplet(l_1,l_2, l_3) and the basis index k=1,2.The charge densitydistribution ρ_{lk} around an ion can be expressed as a function of position relative to corresponding nucleus,

$$\rho_{lk} = \rho_{lk} (\bar{r}) \qquad (3.27)$$

In view of the translation symmetry,ρ_{lk}(r) will be independent of l in the ideal undistributed state of the lattice and may be considered as a function of the scalar distance from the corresponding nucleus,

$$P^{0}_{lk}(\bar{r}) = \rho^{0}_{k} (r) \qquad (3.28)$$

In the state of vibration, the ions move out of their equilibrium configurations causing a change in the charge density function which can now be expressed as a series in spherical harmonics. Thus,

$$\delta\rho_{lk}(r) = \rho_{lk}(r) - \rho^{0}_{lk}(r) = f_0(r) + \sum f_{1m}(r)^{m} Y_{1m} + \sum f_{2m}(r)^{m} Y_{2m} + \ldots.. \qquad (3.29)$$

The first term represents an isotropic scalar deformation of the charge cloud, the second a dipole deformation, and so on. The simple shell model accounts for only the second term in the expansion. If we retain only the first two terms in the equation (3.29) and assume that the charge on the ion remains unaltered during the vibrations, we obtain

Equation (3.30)is identically satisfied by a simple function

$$\int_0^{\infty} 4\pi r^2 f_0 (r)\, dr = 0 \qquad (3.30)$$

$$f_0(r) = (1+a_{lk})^3\, g\, (r+a_{lk}r) - g(r) \qquad (3.31)$$

Where g (r) is an arbitrary function and a_{lk} is a parameter.

By choosing g (r)= ρ^{0}_{k} (r), we obtains,

$$4\pi r^2\, dr\, \rho_{lk}(r) = 4\pi r^2\, dr' \rho^{0}_{lk}(r') \qquad (3.32)$$

Where r'=r+a_{lk}(r), Equation (3.32) represents the breathing motion implied in the breathing shell model.

This interpretation of the breathing motion of the shells depend entirely on the result(3.30),which is valid only if the upper limit of integration on the charge density distribution is extended to infinity. In a solid the ions (or atoms) are fairly close together and the total space can be divided among various ions by suitably drawn dividing surfaces. In an ionic solid where the charge density distribution is to a large extent spherically symmetric around each nucleus, the positive and negative ions spaces can be conveniently divided in spheres of ionic radii r_k centered at the corresponding lattice points. The charge belonging to k type ions will therefore be determined by,

$$\int_0^{k} [\rho^{0}_{k}(r) + f_0 (r)] 4\pi r^2 dr \qquad (3.33)$$

Where the upper limit is mow r_k instead of ∞.Even in a static lattice the proximity of the ions will cause a deformation of a charge clouds owing to the overlap of electron wave functions. It is this deformation that that been considered by Lundqvist and is thus implied in the TSM. Let us define the original charge on the ion in absence of the deformation f_0(r) to be Z_k;

$$\int_0^{k} [\rho^{0}_{k}(r) + f_0 (r)] 4\pi r^2 dr = Z_k \qquad (3.34)$$

Substituting in equation in (3.33)in the expression (3.31) with g(r)=ρ^{0}_{k} and assuming a_{lk} to be small, we obtain for the charge on a k-type ion,

$$\int_0^{\infty} (1+a_{lk})^3 \rho^{0}_{k}(r+a_{lk}) 4\pi r^2\, dr - Z_k + \bar{a}_{lk} Z_k \qquad (3.35)$$

Where

$$\bar{a}_{lk} = 4\pi r^{3}_{k} \rho_k(r_k) a_{lk}/Z_k$$

The charge neutrality over the unit cell demands

$$\sum (Z_k + \bar{a}_{lk} Z_k) = 0 \qquad (3.36)$$

Since a_{lk} is a parameter which will vary with the proximity of neighbouring ions, equation (3.36) implies

$$Z_1 = -Z_2 \text{ and } \bar{a}_{11} = \bar{a}_{12}$$

It appears as through a charge $a_{lk}Z_1$ is transferred from the negative ion to the positive ion of the same cell. In effect, each ion will have a charge transferred to it from all its neighbours so that a_{lk}can be supposed to be the sum of such transfer. If we neglect overlap between ions farther than the first, a_{lk} will not have not any contribution from second and higher neighbours. In the static lattice we can therefore consider this parameter to be independent not only of k but also of l. Denoting the charge on the positive ion by Z(=|Z_k|),we can write the charge on the ions as ±Z[1+a(r)].

The coulomb energy per unit cell of this modified charge system will be

$$- \alpha_m e^2 Z^2 \, [1+\overline{a}(r)]^2/r \qquad (3.37)$$

And if we neglect the square of a (r) we can write the energy per unit cell of the ionic solid as,

$$\Phi = - \alpha_m e^2 \, Z \, [\, Z + 12 \, f(r)]/r + 12 \, V(r) \qquad (3.38)$$

Where V(r)is the overlap potential and Z a (r)=6f(r) to obtain the expression given by Lundqvist for Φ. The coulomb pair potential coupling two ions at (l m k) and (l' m k') will be,

$$C\phi \underset{(kk')}{\overset{(l\,l')}{=}} Z_k Z'_k [1+6f(r)]^2 \quad r \Big/ \underset{(kk')}{\overset{(l\,l')}{=}} \sim \frac{Z_k Z'_K}{r \underset{(kk')}{\overset{(l\,l')}{}}} + \frac{12f(r)\, Z_k Z'_K}{r \underset{(kk')}{\overset{(l\,l')}{}}} \qquad (3.39)$$

The first term is a central two-body potential identical with the conventional coulomb potential of the rigid ion model. The second term is also of the same type but its magnitude depends on f (r) which in turn depends on the proximity of neighbouring ions. Thus this potential contains the coordinates of atoms at (l,k) ,(l'k') ,and all the nearest –neighbouring states of (l,k).In view of the dependence of this potential on the coordinates of three different ions of the solids, it is termed a three body potential.Clearly, the three body potential derived quantum mechanically by Lundqvist[33] implies a charge transfer between neighbouring ions.

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