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Relative Superiority of the Interaction Potential Models for Lattice Energy Calculation of Alkali Metal Halide Crystals

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The non-coulombic nature of the repulsive energy term $\psi(r)$ in the total potential energy function $\phi(r)$ for a diatomic ionic crystal has been of much interest for the last nine decades. Various workers have proposed it either as the inverse power function, exponential function or logarithmic function. A critical review of the potential energy functions proposed earlier has been presented. It was found that no potential model can be claimed as a universal model. However, the relative superiority of these potential models in the calculation of lattice energy of 20 alkali metal halide crystals has been reported.

Key Words: Interaction potential energy function, Coulomb interaction, Short-range repulsive interaction, van der Waals' interaction, Zero-point energy, Lattice energy.

In an interaction potential energy function the principal interactions are : (i) charge-charge interaction called Coulomb interaction, (ii) A short-range repulsive interaction, (iii) van der Waals' interaction, *i.e.*, dipole-dipole and dipole-quadrupole interactions and (iv) zero-point energy. With the inclusion of various interactions, the interaction potential energy function is expressed as:

$$\phi(r) = \psi_e + \psi_r + \psi_{vd} + \varepsilon_0 \tag{1}$$

$$\phi(r) = -\frac{AZ_1Z_2e^2}{r} + \psi_R - \frac{C}{r^6} - \frac{D}{r^8} + \varepsilon_0 \tag{2}$$

where A is Madelung constant, e is the electronic charge, Z_1, Z_2 the ionic charges, r the internuclear distance, C the dipole-dipole, D the dipole-quadrupole interacting terms and ε_0 is the zero-point energy. The non-Coulombic part of the repulsive energy term $\psi(r)$, in the total potential energy function $\phi(r)$ for a diatomic ionic crystal leaves scope for further investigation due to its uncertain nature.

Various forms of short range repulsive interaction $\psi(r)$ proposed by various workers may be represented in their general form as follows:

Born-Lande Br^{-n}, Born-Mayer $P_1 \exp[-\lambda_1 r]$, Hellmann $P_2 r^{-1} \exp[-\lambda_2 r]$, Wasastjerna $P_3 r^{-7} \exp[-\lambda_3 r]$, Varshni and Shukla[1,2] $P_4 \exp[-\lambda_4 r^2]$, Patel, Gohel and Trivedi[3] $P_5 \exp[-\lambda_5 r^{3/2}]$, Prakash Behari[4] $P_6 \log[1 + \lambda_6 r^{-9}]$, Thakur and Pandey[5] $P_7 \log[1 + \lambda_7 r^{-4}]$, Thakur and Pandey[6] $P_8 \log[2 + \lambda_8 r^{-2}]$, Thakur and Pandey[7] $P_9 \log[4 + \lambda_9 r^{-1}]$, Thakur[8] $P_{10} \log[1 + \lambda_{10} r^{-6}]$ and Sadwar, Sinha and Thakur[9,10] $P_{11} \log[1 + \lambda_{11} r^{-12}]$

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where P_1 and λ_i are adjustable potential parameters whose values are derived by applying the well known crystal stability and compressibility conditions.

At the equilibrium interionic distance $r = r_0$, the following conditions are imposed:

$$\phi(r_0) = -U_L \tag{3}$$

$$\phi'(r_0) = 0 \tag{4}$$

$$\phi''(r_0) = 9kr_0/\beta \tag{5}$$

where $\phi(r_0)$ is the total potential energy of 1 g-mol of the crystal with each other and with the rest of the lattice and the primes denote the first and second derivatives of $\phi(r_0)$; k is the structure dependent parameter defined by molar volume $V = kr_0^3$ and β is the compressibility of the crystal.

In Redington's potential[11] simply a number of empirical terms in the Born-Mayer expression has been introduced. The short-range repulsive term in the three term Woodcock potential[12] which includes both the inverse power function due to Born and Lande and the exponential function due to Born and Mayer is represented as:

$$\psi_R = \frac{A}{r^m} \exp[-B(r^n - 1)] \tag{6}$$

$$\psi_R = \frac{A}{r^m} \exp[B] \exp[-Br^n] \tag{7}$$

$$\psi_R = \frac{P}{r^m} \exp[-Br^n] \quad [\text{where } P = A \exp B] \tag{8}$$

It may be treated as the general exponential form of the repulsive part. In other words, all the exponential forms suggested so far may be treated as the special case of Woodcock form of the interaction potential. For $m = n = 1$, we get the repulsive part of Hellmann potential $\psi_R = \frac{P}{r} \exp[-\lambda r]$. The exponential forms of the interaction potentials, only Born-Mayer and Hellmann forms have quantum mechanical justification.

The following three conditions must be fulfilled[13] for the suitability of interaction potentials for diatomic ionic crystals:

(i) when $r \to \infty$, $\psi(r) \to 0$,
(ii) when $r \to r_0$, $\psi(r) \to \infty$, and
(iii) at $r = r_0$, $\phi(r)$ should be minimum.

On an examination of the exponential forms of the repulsive energy terms suggested by Born and Mayer it appears to yield a finite value as $r \to 0$ and is thus unphysical.

Dobbs and Jones[14] raised serious doubts about the validity of the exponential forms of repulsive functions with the remarks: *The exponential form for the repulsive potential makes calculation of the lattice properties rather complicated and, in any case, is perhaps not valid in the region near the minimum of the total potential which is of course the essential part in considering the properties of the lattices.* Ree and Halt[15] have shown that the exponential forms of pair potential are too soft and require a dipper minima. Brumer and Karplus[16] have concluded from the perturbation calculations that the use of an exponential form for the overlap repulsion is an inadequate representation. Woodcock[12] exponential function to get an improved result was also without much success.

The exponential form for the repulsive energy term was further tested and critically evaluated on the basis of potential energy and force curves by Thakur[8]. Sandwar and Thakur[10] have reexamined the critical evaluation of Thakur[8] on the ground that they do not yield acceptable nature of potential energy and force curves. They[10] concluded that for a given potential energy function, the potential energy curve in the region 0 to r_x should not be the deciding factor and the criticism levied has little merit. It is only the minima which a given potential function should correctly predict at the equilibrium internuclear distance.

The above discussion suggests that the exponential form for the repulsive energy term is an inadequate approximation and cannot represent the total manifestation demanded by ionic crystals. It was also realised that until the complete quantum mechanical treatment of ions in close contact was available, the overall effect of the short-range repulsive forces can only be represented by an empirical term in any model of the potential energy function.

As an alternative, logarithmic forms of repulsive potential energy functions have been suggested by several authors,[4–10] which may be represented in the general form $\psi(r) = P_i \log (a + \lambda_i r^{-n})$ where P_i and λ_i are again the two adjustable parameters whose values are derived by applying the same crystal stability and compressibility conditions as mentioned earlier. a and n are constants whose values have been selected arbitrarily by different authors in order to arrive at a closer agreement with the experimental observations. But out of these forms the type $\psi(r) = P_i \log (1 + \lambda_i r^{-n})$ only fulfils all the three conditions mentioned above and the rest with a is not equal to 1 are unphysical because $r \rightarrow \infty$, $\psi(r) = -P_i \log a$ (finite) and not zero.

The choice of the constant n also varies widely. The Born-Lande form of the inverse power repulsive energy term Br^{-n} in its simplest form uses a mean value of $n = 9$. Prakash-Behari[4] have used a value $n = 9$ in their logarithmic form. Thakur and Pandey[5–8] have used a value of $n = 1, 2, 4, 6$ in their logarithm model. Sinha, Sandwar and Thakur[9, 10] have also used a value of $n = 12$ in their logarithim form.

The lattice energy of 1 g-mole of an ionic crystal at 298 K is given by:

$$U_L = -[N\phi(r_0) + nRT + U_P]$$

where N is Avogadro's number, the term nRT is the PV correction to bring the value of U_L from 0 to 298 K and U_P is the ionic polarizability due to mutual distortion of the electronic charge density around an ion which Wen and Sho[17] have calculated for a large number of ionic crystals.

The average percentage error of the lattice energy values of the alkali halide crystals calculated with the help of repulsive function of the type inverse power and exponential power functions are:

BL[18] 1.5, BM[18] 1.3, VS[18] 1.8, PGT[19] 2.6, Was[20] 1.6, Hell[21] 1.2.

Thakur and Sandwar[10] recalculated the lattice energy values of alkali metal halide crystals from the reported logarithmic models along with their own model and compared with the experimental values. They have found the average percentage error as:

Thakur[8] 7.0 instead of 0.9 as reported, Thakur[8] 11.0 instead of 7.4, Prakash-Behari 4.0, and Thakur and Sandwar 1.3.

After a critical review of the previous potential models as suggested earlier, we may conclude that no potential model can be termed as *Universal Interaction Potential Model*. However, the relative superiority of the two main categories of repulsive interaction potential models, *i.e.*, exponential and logarithmic forms for the calculation of lattice energy of alkali-metal halide crystals may be sumarized as:

Hell > BM > BL > Was > VS > PGT (Inverse and exponential form)

Sandwar and Thakur > Prakash-Behari > Thakur,(Logarithmic forms)

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