QUESTION 1:

Write down what have you understood (in your own language) about the Born-Mayer potential of a 1:1 ionic compound.

SOLUTION:

The Born-Mayer potential is based on the assumption that an ionic crystal is an aggregate of oppositely charged ions, essentially hard spheres with center of charge at the nucleus.

$$U = -\frac{AZ_1Z_2e^2}{4\pi\varepsilon_0 r} + b\exp -r/\rho \tag{1}$$

The potential(1) has two terms, the first term accounts for a net attractive energy which is the conventional coulombic energy multiplied by a geometric factor based on the crystal structure, called the Madelung constant(A). The repulsive term is considered on the basis of Pauli repulsion from quantum mechanics, which indicates that the electron density falls off exponentially with distance from the nucleus giving rise to the term $b\exp -r/\rho$. ρ has a value close to 0.3 A for most such salts, is determinable from the compressibility of the crystal.

Considering NaCl(1:1 ionic compound),

Z_1 (integral charge on anion)=1 Z_2 (integral charge on cation)=1

Madelung constant(A) is calculated as follows. We consider the Na+ in NaCl. It has 6 first neighbour's Cl– at a distance $r_1 = r$; then there are 12 second Na+ as second neighbours at a distance $r_1 = \sqrt{2}r$; 8 third neighbours Cl– at a distance $r_1 = \sqrt{3}r$ and so on. This is gives rise to infinite series which converges to a constant(A).

$$A = +6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - .... \tag{2}$$

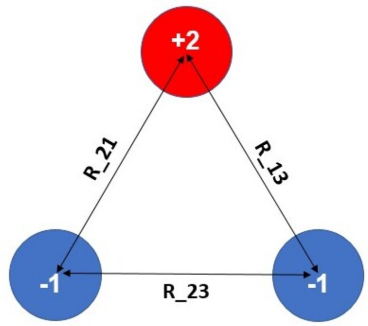
A has a value of 1.763 and ρ has a value close to 0.3 A for most such salts, is determinable from the compressibility of the crystal.

QUESTION 2:

Write how this potential may change for 1:2 ionic compound.

SOLUTION:

Assuming a 1:2 unit cell of a crystal in 1 Dimension. The Born Mayer potential will have 3 Coloumbic interaction terms and 3 Repulsive terms in contrast to the 2 terms in 1:1 ionic



compounds.The total energy of the 1D Unit cell is given by $U = U_{12} + U_{13} + U_{23} + R_{12} + R_{13} + R_{23}$. The system will arrange itself in a state with minimum total energy (U_0).

$$U_{12} = \frac{2e^2}{r_{12}} + b_{12}e^{-r_{12}/\rho}, U_{13} = \frac{2e^2}{r_{13}} + b_{13}e^{-r_{13}/\rho}, U_{23} = -\frac{e^2}{r_{23}} + b_{23}e^{-r_{23}/\rho} \tag{3}$$

the constants(b_{ij}) depends on the electronic density around the ions. The electronic interaction between cation and two anions being equal, $b_{12} = b_{13} = b$. The potential is minimum at infinity when considering only the 2 -vely charged ions. So the system is likely to attain a configuration such that the distance between the anions will be maximum and the distance between cation and anions will be same.(in a linear form Anion-Cation-Anion) $r_{12} = r_{13}$, r_{23} maximum is possible in such a configuration. [In actual cases, this unit cell will be repeated periodically forming the lattice in 3 Dimensions.]

QUESTION 3:

Explain (either by using this method or by any other method) that solving problem through graphical method can be very useful particularly in a situation when analytical solution of a given problem becomes very difficult to obtain.

SOLUTION:

Consider the equation

$$e^x - 1 = 2x \tag{4}$$

Analytical Method

Consider the function $y(x) = \exp x2x1$, its inverse x(y), and the Taylor expansion of the x(y):

$$\frac{dx}{dy} = \frac{1}{\frac{dy}{dx}} = \frac{1}{e^x - 2}, \tag{5}$$

Applying chain rule of differentiation, we get

$$\frac{d^2x}{dy^2} = -\frac{e^x}{(e^x - 2)^2}\frac{dx}{dy} = -\frac{e^x}{(e^x - 2)^3}, \tag{6}$$

$$\frac{d^3x}{dy^3} = \Big(-\frac{e^x}{(e^x-2)^3} + \frac{3e^{2x}}{(e^x-2)^4}\Big)\frac{dx}{dy} = -\frac{e^x}{(e^x-2)^4} + \frac{3e^{2x}}{(e^x-2)^5}, \tag{7}$$

We then obtain a close approximation of the root, $x_0 = \frac{5}{4}, y_0 = e^{x_0} - 2x_0 - 1$, giving

$$x(y) = x_0 + \frac{1}{e^{x_0}-2}(y-y_0) - \frac{e^{x_0}}{(e^{x_0}-2)^3}\frac{1}{2}(y-y_0)^2 + \Big(-\frac{e^{x_0}}{(e^{x_0}-2)^4} + \frac{3e^{2x_0}}{(e^{x_0}-2)^5}\Big)\frac{1}{6}(y-y_0)^3 + ... \tag{8}$$

The solution as

$$x(0) = x_0 - \frac{1}{e^{x_0}-2}y_0 - \frac{e^{x_0}}{(e^{x_0}-2)^3}\frac{1}{2}y_0^2 - \Big(-\frac{e^{x_0}}{(e^{x_0}-2)^4} + \frac{3e^{2x_0}}{(e^{x_0}-2)^5}\Big)\frac{1}{6}y_0^3 + ... \tag{9}$$

$$\approx 1.25 + 0.00647974514175 - 4.91663237447\cdot 10^{-5} - 6.39922963124\cdot 10^{-7} - 1.02964389462\cdot 10^{-8} \tag{10}$$

$$= 1.2564299286 \tag{11}$$

Other solution is obtained by taking $x_0 = 0 => y_0 = 0$, leading to the trivial solution $x = 0$.

Graphical Method We define a variable y and set it equal to the left and then the right side of the original equation. This will give us the following system of equations.

We then plot the graph the equations, and find their intersection point which will give their solution.

$$y = e^x - 1 \tag{12}$$

$$y = 2x \tag{13}$$

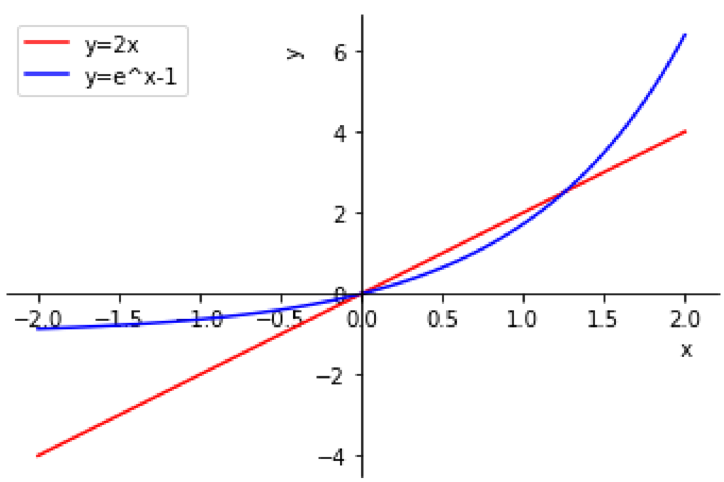


Figure 1: Graphical Method of Solution

We find that the two intersection points(from the graph) are

$$x = 0 \qquad\qquad x = 1.2564$$

This example clearly shows, how graphical method can be employed as a fast and efficient method of solution, when the analytical method of solution(as we saw in this case) is hard to obtain.