# Solid State

## B. Sc. Part II

**Ankita Ojha**
**Department of Chemistry**
**Maharaja College, Arrah**

# Lattice Energy

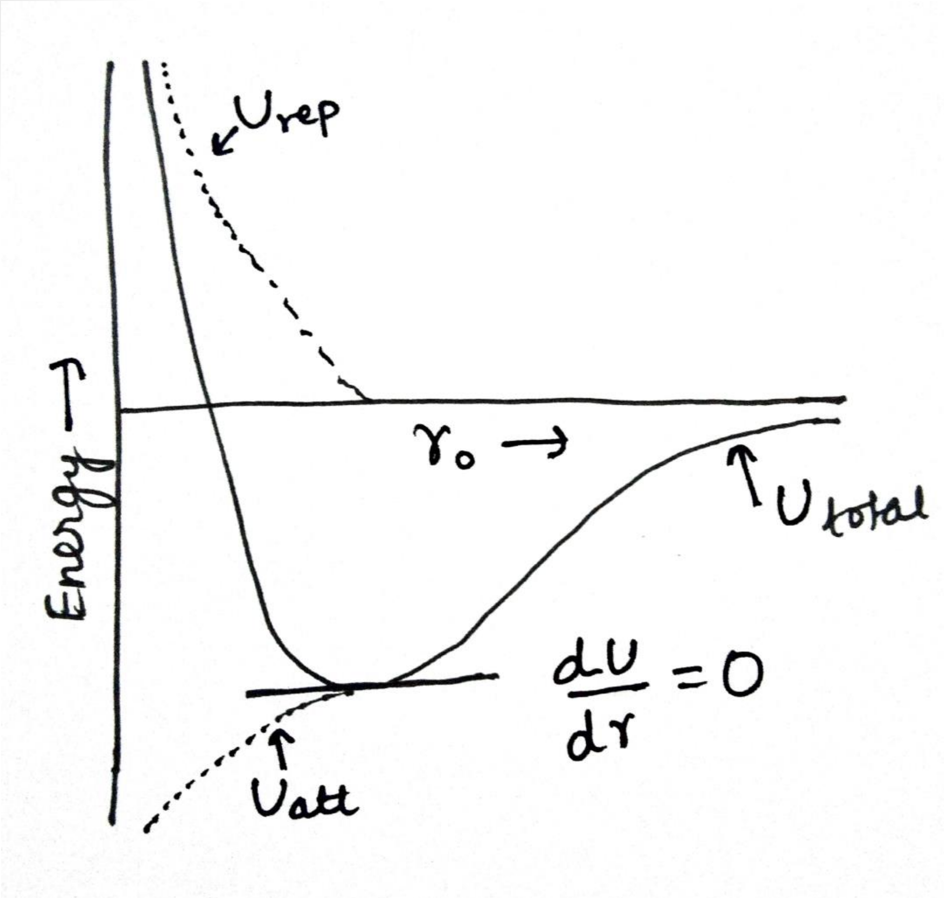
It is defined as the amount of energy released when cation and anions in their gaseous state are brought together from infinite separation to form a crystal.

$$M^{+}(g) + \ X^{-}\ (g) \rightarrow MX\ (s); U = lattice\ energy$$

The theoretical treatment of ionic lattice energy was given by M. Born and A. Lande.

Considering the potential energy of an ion pair $M^+$, $X^-$ separated by a distance *r*, thus the electrostatic force of attraction is given by:

$$\boldsymbol{U_{att}(r) = \frac{z_+ z_- e^2}{4\pi\epsilon_o r}}$$




**The summations of all the interactions between the ions is known as *Madelung Constant, M*. The energy of attraction can thus be given as**

$$U_{att}(r) = M\frac{z_+ z_- e^2}{4\pi\epsilon_o r}$$

- As the interionic distance decreases, the electrostatic energy becomes negative and as z- is negative and the electrostatic energy becomes increasingly negative (with respect to energy at infinite separation).
- The interaction between ions is more in crystal lattices as compared to the isolated ion-pair.
- For examples, in NaCl, each sodium atom is attracted by six chlorine atoms and repelled by next 12 sodium atoms.

- The value of Madelung Constant depends only on the geometry of the lattice and is completely independent of ionic radius and charge.
- A stable lattice results from the balance between repulsive energy along with attractive coulumbic energy.
- The attractive energy becomes infinite at infinitesimally small distances.
- Ions are not point charge but charge clouds which show repulsion at very close distances.
- The repulsions are very small at large distances but become more when the distance reduces.
- According to the Born, the repulsive energy is given by

$$U_{rep} = {}^{B}\!/_{r^n}$$

Where B is constant and the Born exponent *n*, is determined from the compressibility data which measures the resistance exhibited by the ions on forcing close to each other.

- For a crystal consisting of Avogadro's number of ions the total energy is given by:

$$U_{total}(r) = U_{att}(r) + U_{rep}(r)$$

$$= \frac{MN_A z_+ z_- e^2}{4\pi\epsilon_o r} + \frac{N_A B}{r^n}$$

- The graph mentioned earlier shows a solid line for the total energy where the minimum in the curve, corresponds to the equilibrium lattice configuration $(r = r_o)$ and hence

$$\left(\frac{dU}{dr}\right)_{r=r_o} = 0 = -\frac{MN_A z_+ z_- e^2}{4\pi\epsilon_o r} - n\frac{N_A B}{{r_o}^{n+1}}$$

- In this lattice configuration, the lattice force balances the repulsive forces.

$$B = \frac{MN_A z_+ z_- e^2}{4\pi\epsilon_o n} r_o^{n-1}$$

And

$$U = \frac{MN_A z_+ z_- e^2}{4\pi\epsilon_o r_o} - \frac{MN_A z_+ z_- e^2}{4\pi\epsilon_o r_o n}$$

$$= \frac{MN_A z_+ z_- e^2}{4\pi r_o \epsilon_o}\left(1 - \frac{1}{n}\right)$$

**Born Landes Equation**