

Equation for Anharmonic Oscillator

$$E_v = \left(v + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right)^2 \omega_e x_e \text{ cm}^{-1}$$

$$v = 0, 1, 2, 3, \dots$$

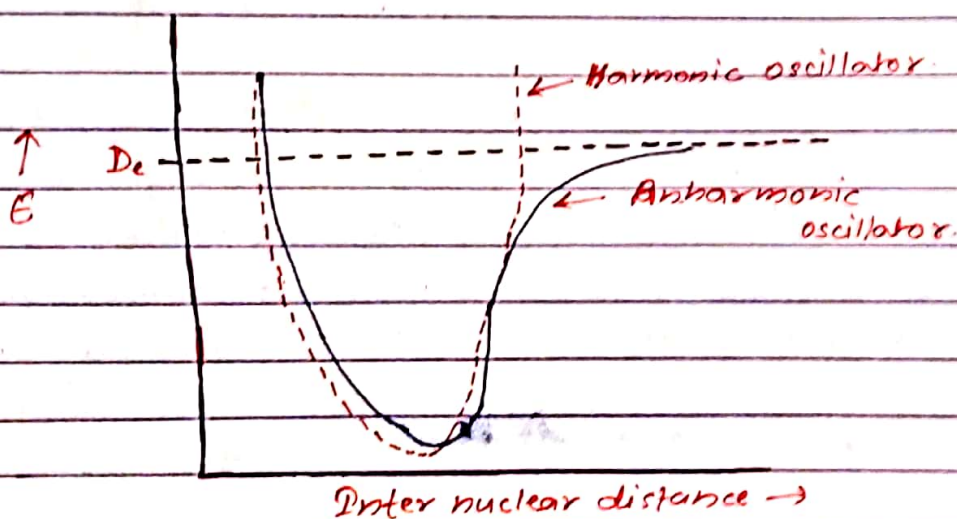
ω_e = Oscillation frequency (expressed in wave number)

x_e = Corresponding anharmonicity constant and is always same and positive (≈ 0.1)

So, vibrational levels crowd more closely together with increasing v .

$$\therefore E_v = \left[1 - x_e \left(v + \frac{1}{2}\right)\right] \left(v + \frac{1}{2}\right) \omega_e \quad \text{--- (2)}$$

for anharmonic oscillator.



We know that energy level of the harmonic oscillator is -

$$E_v = \left(v + \frac{1}{2}\right) \omega_{osc} \text{ cm}^{-1} \quad \text{--- (3)}$$

Now on comparing eq - (2) and eq - (3) we get -

$$\omega_{osc} = \omega_e \left[1 - x_e \left(v + \frac{1}{2}\right)\right]$$

Thus the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v .

If we consider the hypothetical energy states obtained by putting $v = -1/2$.

$$\bar{\omega}_{osc} = \bar{\omega}_e \left[1 - X_e \left(-\frac{1}{2} + \frac{1}{2} \right) \right]$$

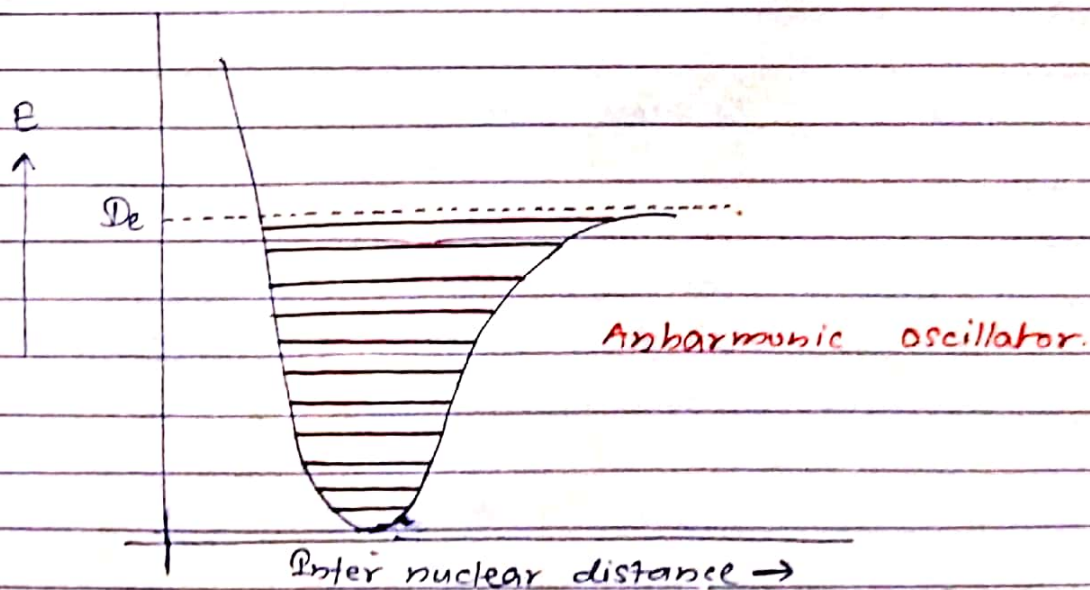
$$\bar{\omega}_{osc} = \bar{\omega}_e \left[1 - X_e (0) \right]$$

$$\therefore \boxed{\bar{\omega}_{osc} = \bar{\omega}_e}$$

i.e. The molecule would be at equilibrium point with zero vibrational energy.

Thus, ' $\bar{\omega}_e$ ' may be defined as the hypothetical equilibrium oscillator frequency of the anharmonic system. i.e. The frequency for infinitely small vibrations about the equilibrium point.

The vibrational energy levels for a diatomic molecule undergoing anharmonic oscillation may be shown below -



* Calculation of Zero point energy -

we know that -

$$\bar{\omega}_{osc} = \bar{\omega}_e \left[1 - x_e \left(v + \frac{1}{2} \right) \right]$$

for ground state -

$$v = 0$$

$$\therefore \bar{\omega}_{osc} = \bar{\omega}_e \left[1 - x_e \left(0 + \frac{1}{2} \right) \right] \text{ cm}^{-1}$$

$$\bar{\omega}_{osc} = \bar{\omega}_e \left[1 - \frac{1}{2} x_e \right] \text{ cm}^{-1}$$

$$\& E_v = \bar{\omega}_e \left[1 - \left(v + \frac{1}{2} \right) x_e \right] \left(v + \frac{1}{2} \right) \text{ cm}^{-1}$$

$$E_{0v} = \bar{\omega}_e \left[1 - \left(0 + \frac{1}{2} \right) x_e \right] \left(0 + \frac{1}{2} \right) \text{ cm}^{-1}$$

$$E_0 = \frac{1}{2} \bar{\omega}_e \left[1 - \frac{1}{2} x_e \right] \text{ cm}^{-1}$$

for anharmonic oscillator.

$$\text{and } E_0 = \frac{1}{2} \bar{\omega}_{osc} \text{ cm}^{-1}$$

for harmonic oscillator.

It means that The zero point energy (ZPE) of the harmonic oscillator slightly differ from that of anharmonic oscillator.

* Selection rules for the anharmonic oscillator:—

The selection rules for anharmonic oscillator are found to be—
 $\Delta v = \pm 1, \pm 2, \pm 3 \dots \dots \dots$

Thus, they are the same for the harmonic oscillator, with the additional ~~frequency~~ possibility of larger jumps. However, these are predicted by theory and observed in practice to be of rapidly decreasing probability and normally only the values of $\Delta v = \pm 1, \pm 2$ & ± 3 are the most have observable intensity.