Equation for Anharmonic Oscillator

$$E_v = \left(v+\tfrac{1}{2}\right)\bar{\omega_e} - \left(v+\tfrac{1}{2}\right)^2 \omega_e x_e \quad cm^{-1}$$

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

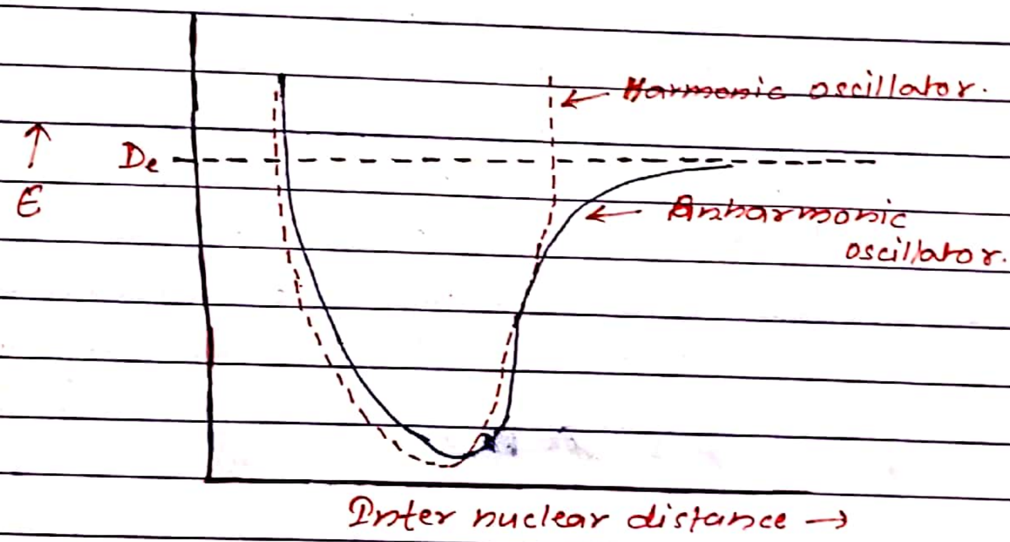
$\bar{\omega_e}$ = Oscillation frequency (expressed in wave number)

x_e = Corresponding anharmonicity constant and is always same and positive ($\simeq +0.1$)

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

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

for anharmonic oscillator.



We know that energy level of the harmonic oscillator is —

$$E_\vartheta = \vartheta + \tfrac{1}{2} \; \bar{\omega}_{osc} \; cm^{-1} \quad \text{———} \quad (3)$$

Now on comparing eqn – (2) and eqn – (3) we get —

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

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

If we consider the hypothetical energy states obtained by putting $\nu = -\frac{1}{2}$.

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

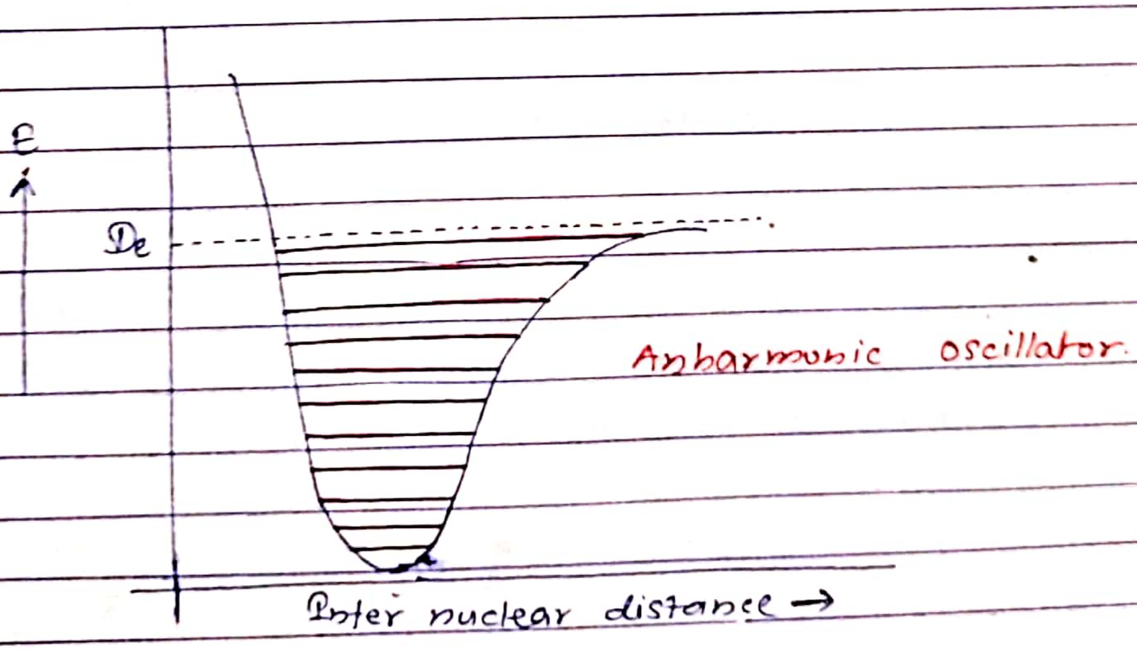
$$\bar{\omega}_{osc} = \bar{\omega}_e \left[1 - x_e(0)\right]$$

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

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

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

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



* Calculation of Zero point energy –

we know that –

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

for ground state –

$$v = 0$$

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

$$\bar{\omega}_{osc} = \bar{\omega}_e \left(1 - \tfrac{1}{2} x_e\right) \; cm^{-1}$$

&

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

$$E_v = \bar{\omega}_e \left[1 - \left(0 + \tfrac{1}{2}\right) x_e\right] \left[0 + \tfrac{1}{2}\right] \; cm^{-1}$$

$$\boxed{E_0 = \tfrac{1}{2} \bar{\omega}_e \left[1 - \tfrac{1}{2} x_e\right] \; cm^{-1}}$$

for anharmonic oscillator.

and $\boxed{E_0 = \tfrac{1}{2} \bar{\omega}_{osc} \; cm^{-1}}$

for harmonic oscillator.

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

* Selection rules for the anharmonic oscillator :—

The selection rules for anharmonic oscillator are found to be-

$$\Delta v = \pm 1, \pm 2, \pm 3 \ldots\ldots\ldots$$

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 pratice to be of rapidly disminst of probability and normally only the values of $\Delta v = \pm 1, \pm 2$ & ± 3 at the most has observable intensity.