Anharmonic oscillation is defined as the deviation of a system from harmonic oscillation, or an oscillator not oscillating in simple harmonic motion.

**Introduction**

A harmonic oscillator obeys Hooke's Law and is an idealized expression that assumes that a system displaced from equilibrium responds with a restoring force whose magnitude is proportional to the displacement. In nature, idealized situations break down and fails to describe linear equations of motion. Anharmonic oscillation is described as the restoring force is no longer proportional to the displacement. Two forms of nonlinearity are used to describe real-world situations:

1. elastic anharmonicity
2. damping anharmonicity

Anharmonic oscillators can be approximated to a harmonic oscillator and the anharmonicity can be calculated using perturbation theory.

**Figure 1:** The HCl molecule as an anharmonic oscillator vibrating at energy level \(E_3\). \(D_0\) is dissociation energy here, \(r_0\) bond length, \(U\) potential energy. Energy is expressed in wavenumbers. The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve. Figure used with permission from Wikipedia.

Figure 1 shows the ground state potential well and is calculated using the energy levels of a harmonic oscillator with the first anharmonic correction. \(D_0\) is the dissociation energy, which is different from the well depth \(D_e\). The vibrational energy levels of this plot are calculated using the harmonic oscillator model:
\[ E_v = \left(v + \frac{1}{2}\right) v_e - \left(v + \frac{1}{2}\right)^2 v_e x_e + \left(v + \frac{1}{2}\right)^3 v_e y_e + \text{higher terms} \]

where \( v \) is the vibrational quantum number and \( x_e \) and \( y_e \) are the first and second anharmonicity constants, respectively. The \( v = 0 \) level is the vibrational ground state.

The lines in the first figure represent overtones correspond to the transitions of the quantum number \( v \) which terminate at the top line \( v = v_{\text{max}} \). Because this line is less confining than a parabola, the energy levels become less widely spaced at high excitation. These overtones are present because the selection rule is derived from the properties of harmonic oscillator wavefunctions, which are only approximately valid in the presence of anharmonicity.

References