Although the harmonic oscillator proves useful at lower energy levels, like v=1, it fails at higher numbers of v, failing not only to properly model atomic bonds and dissociations, but also unable to match spectra showing additional lines than is accounted for in the harmonic oscillator model.

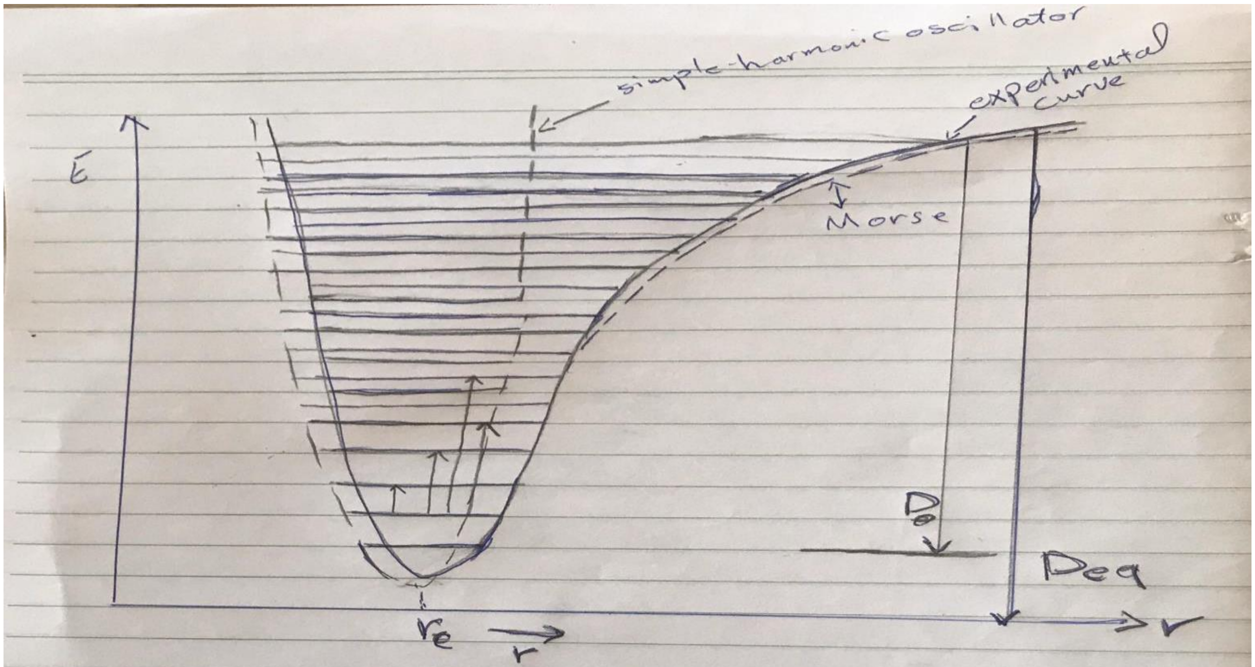
Until this point, we have been using the harmonic oscillator to describe the internuclear potential energy of the vibrational motion. Fundamental vibrational frequencies of a molecule corresponds to transition from $\Delta v=\pm 1$. While this is a decent approximation, bonds do not behave like they do in the Harmonic Oscillator approximation. For example, unlike the parabola given in the Harmonic Oscillator approximation, atoms that are too far apart will dissociate.

Quantum an harmonic oscillator

At high enough energy, bonds will of course break, this means that they are not true harmonic oscillator, as the figure shows, there is considerable similarity between the two models at low energy. At higher energy, the spacing between the levels decreases as the potential curve will get wider.

The practical consequence of anharmonicity is that instead of all absorption overlapping to give a single sharp peak, multiple peaks at slightly off-set energies occur, which is practice leads to line broadening always seen towards the low energy side of the absorption peak.

The vibration energy levels for diatomic molecules is shown in fiq. below.



The allowed vibrational energy Levels and some transitions between them for diatomic molecals undergoing anharmonic oscillation.

The potential energy function for harmonic oscillator model

$V(r) = \frac{1}{2}k(r - r_e)$ ----------------------16

The harmonic oscillation is a great approximation of a molecular vibration, but has key limitations:

- The harmonic oscillator does not predict bond dissociation; you cannot break it no matter how much energy is introduced.

- Due to equal spacing of energy, all transitions occur at the same frequency (i.e. single line spectrum). However experimentally many lines are often observed (called overtones).

A more powerful approach than just "patching up" the harmonic oscillator solution with anharmonic corrections is to adopt a different potential V(x). One such approach is the Morse potential, named after physicist Philip M. Morse, and a better approximation for the vibrational structure of the molecule than the harmonic oscillator because it explicitly includes the effects of bond breaking and accounts for the anharmonicity of real bonds.

The Morse potential is a good approximation to V(x) and is best when looking for a general formula for all x from 0 to ∞ , not just applicable for the local region around the x_0

$V_m = D_{eq.}\left[1 - exp\left\{a\left(r_{eq.} - r\right)\right\}\right]^2$ ------------------------17

where

V_m morse potential function

$D_{eq.}$ The dissociation energy for molecule

a constant value for each electronic state

From eqn. 17 → $V_m \approx D_{eq.}$ when r → ∞

This is similar to actual behavior of diatomic molecules for atoms.

when $r = r_{eq.}$

V_m has minimum value and similar for harmonic oscillator.

If we substitute the morse function potential energy (eqn. 17) in Schrodinger equation, we get the pattern of allowed vibrational energy levels is found to be

$$\varepsilon_v = \left(v + \tfrac{1}{2}\right)\bar{w}_e - \left(v + \tfrac{1}{2}\right)^2 \bar{w}_e x_e \qquad (\text{cm}^{-1}) \text{ -------------18}$$

where v=0, 1, 2, 3…..

$\bar{w}_e$ is oscillation frequency (expressed in wave number)

x_e= is the corresponding anharmonicity constant which for bond stretching vibrations is always small and positive (≈+0.01), so that the vibrational levels crowed more closely together with increasing (v).