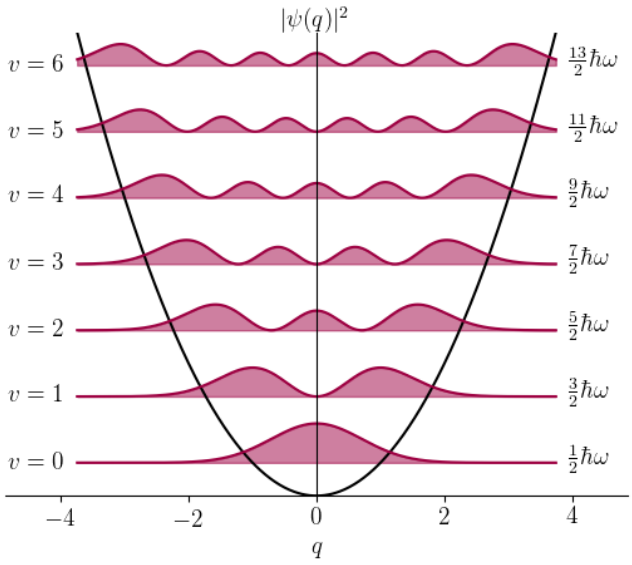
# Homework #4

## Thermodynamic properties

1. We solved the particle in a box in Homework 1. In the class, we saw that it is used to represent the quantum states of nuclear translational motions. Another simple but useful model system that approximates the vibrational degree of freedom is the harmonic oscillators. In the following question set, we are going to discuss the simplest case: 1-D harmonic oscillator.




   (a) Please write down the Schrödinger equation of this 1-D harmonic oscillator.

   (b) Following Q1(a), please solve this equation. (*Hint: you may try the power series method.*)

   (c) If you do everything correctly in (b), you'll find that the energy of this system is $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$. Please evaluate the energy gap between two successive states for $\tilde{\nu} = 3000\,cm^{-1}$ (This is a typical vibrational frequency for C-H bond).

   (d) You may notice that when $n = 0$, the energy of 1-D harmonic oscillator does not go to zero. What does this imply?

2. The reaction $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ has become very popular recently in

the literatures since the huge attention in the community has been paid into the related catalytic reaction. This includes oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER).

(a) Perform frequency computations (and of course, optimize them first) for three molecules in this reaction. Make figures of their vibrational modes (specified their frequencies as well). Please also check if the number of normal modes is reasonable.

(b) Compare their vibrational frequencies with those computes using higher level of theory (DFT, MP2 or CCSD). How much do they differ? Please specify the reference (where you get the data).

(c) Compute the $\Delta G$ at 298.15K and 1 atm for this reaction and compare it with the experimental value and simulated ones obtained with higher level of theory. Please specify the reference (where you get the data).

(d) Following Q2(c), how large is the difference between xTB and exp. values? Please list at least three possible origins of this discrepancy and justify them (as much as you could).