C343 Experiment III

Tunneling Splitting in Ammonia

1 Potential Energy Curve - Ammonia Inversion

Ammonia,in its ground state, exhibits a pyramidal geometry, with the nitrogen atom at the apex and the three hydrogen atoms forming the base of the pyramid. The inversion process involves the "umbrella-like" motion of the hydrogen atoms, where they move from one side of the nitrogen atom to the other, causing the molecule to temporarily adopt a planar geometry before reverting back to its original pyramidal structure.

The potential energy surface (PES) for the ammonia inversion process can be described by a symmetric double-well. At the minima(s) of this potential energy curve is the equilibrium geometry corresponding to the pyramidal structure of ammonia. As the hydrogen atoms move away from this equilibrium position, the potential energy increases, forming two symmetric potential wells on either side of the equilibrium. These potential wells represent the stable conformations of ammonia with the hydrogen atoms on one side or the other of the nitrogen atom. The barrier height between the two potential wells corresponds to the energy required for the hydrogen atoms to pass over the apex of the pyramid during inversion. This height is known as **Barrier for Inversion**.

The Energy for various geometries of NH_3 was calculated using ab-initio method : MP2/6-31G**. The degree of freedom that was varied was the angle between H-N-X; where X is a dummy atom along axis of N perpendicular to H_3 plane. The equilibrium geometries(C_{3v}) occur at 67.298° and 112.702° , the transition state has a planar geometry(D_{3h}) and occurs at 90°. The inversion coordinate is set by defining transition state at 0° and calculating relative to transition state. Also the Energy of Reactant has been set to 0 and all other geometries are relative to it. The obtained points were fitted to a polynomial of type $V(x) = a + bx^2 + cx^4$.The fitted parameters are :

$$\boldsymbol{a = 0.0105567, b = -3.5627 * 10^{-5}, c = 3.12338 * 10^{-8}}$$

Hence, the potential for inversion is:

$$\boldsymbol{V(x) = 0.0105567 - 3.5627 * 10^{-5}x^2 + 3.12338 * 10^{-8}x^4}$$

The Barrier for inversion = 0.0111 Hartree = **29.032** kJ/mol

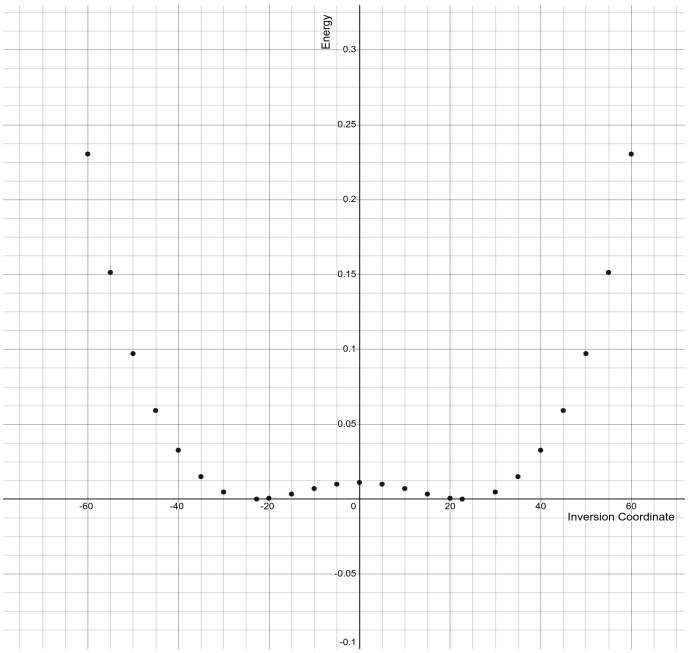


Figure 1: Plot of Energy for various geometries vs Inversion Coordinate

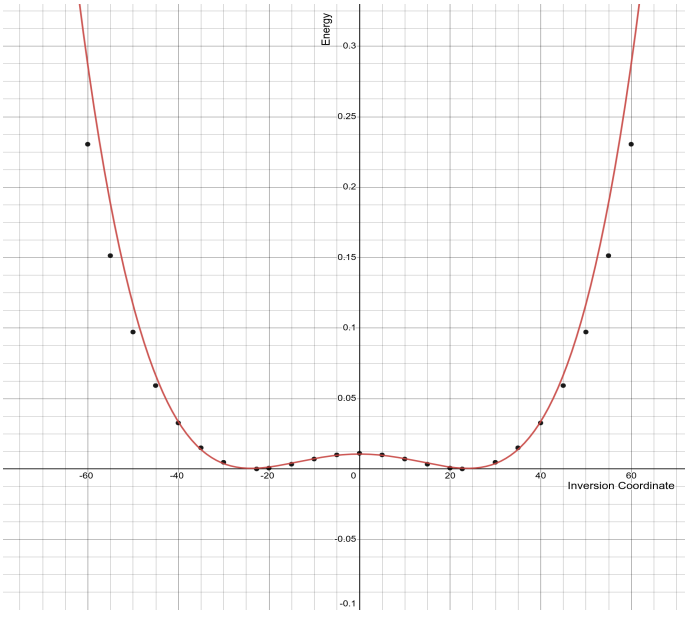


Figure 2: Plot showing the points along with fitted Polynomial(Red)

2 Eigenstates of SHO

The first 5 eigenstates of SHO ($\boldsymbol{V(x) = 0.5 * x^2}$) were calculated using Numerov Method. In Numerov Method the Schrodinger equation is solved by a trial and error method. We guess a Energy eigenvalue and generate the wavefunction for it. Now if the wavefunction is well behaved we are closer to the actual energy. So by choosing different initial energies and our intuition of the wavefunction, we try to find out the correct energy and wavefunction.

Their **Energy eigenvalues are 0.5, 1.5, 2.5, 3.5, 4.5.** In the plot all wavefunctions are adjusted with 10 times their Energy. As we can see the symmetry of the eigenstate keeps oscillating.

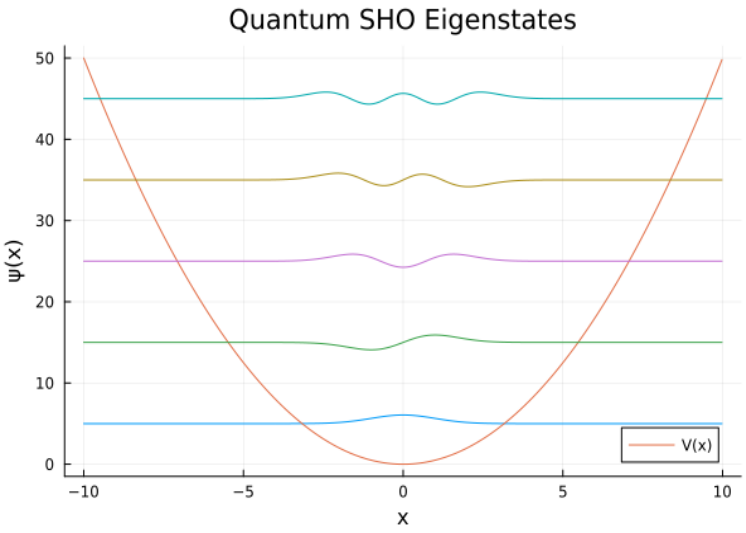


Figure 3: First 5 eigenstates of Quantum SHO

3 Eigenstates of Ammonia Inversion

The first two eigenstates of Ammonia inversion - double well potential was found using the Numerov method. Tunneling Splitting is the energy difference between two levels. This occurs due to superposition of eigenstates of Separated harmonic well potentials. When two such wells are superimposed, they create two levels very close to each other having almost same Probability amplitude but differ by parity. The Energy difference between these two closely split levels is **Tunneling Splitting**.

The Energy eigenvalue of the first two states are:

- v=0 : E = 0.005549934245 Hartree
- v=1 : E = 0.006095308051 Hartree

Thus , Tunneling Splitting = 0.000545374 Hartree = 1.4318 kJ/mol

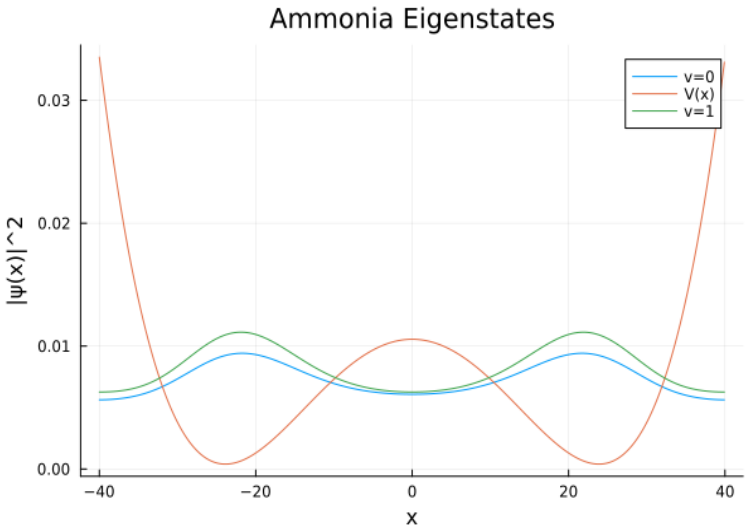
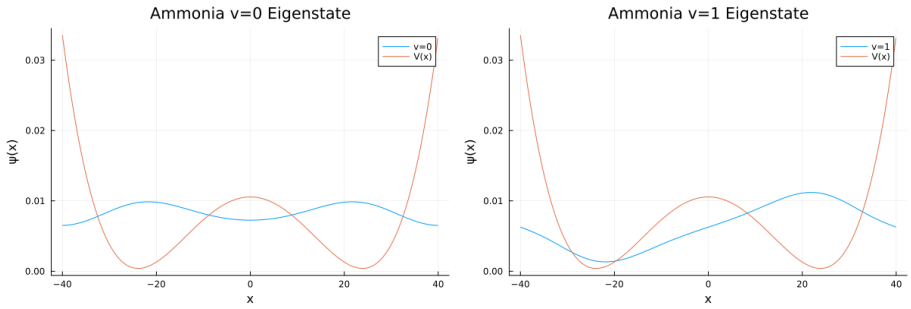


Figure 4: Probability Amplitude of first two Eigenstates

As we can observe the two levels are very close to each other and the Probability amplitudes are also similar.They differ by the sign of wave function ie, the ground state is symmetric and first excited state is anti symmetric.



(a) v=0 (b) v=1

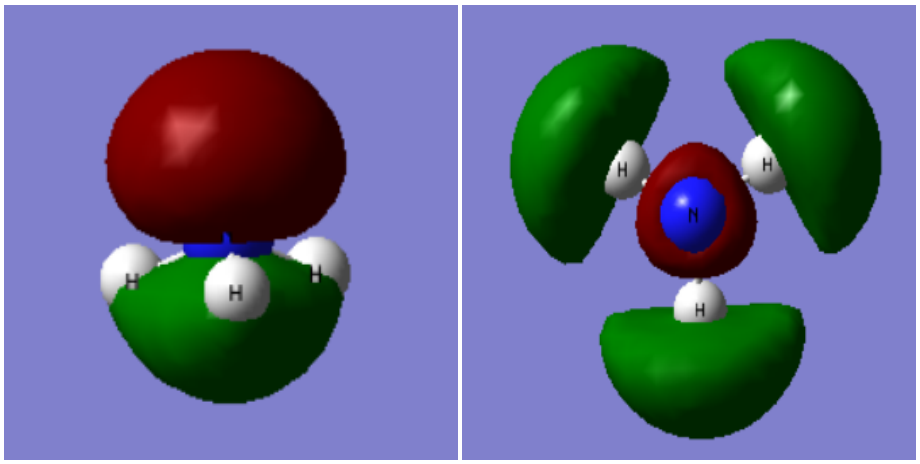
Figure 5: First two eigenstates of Ammonia Inversion

4 Vertical Transition Energies

The Vertical transition energy for ammonia was calculated using TD-DFT Method and 6-31G* basis set. The MO's of NH_3 were visualised and the transition Energy from HOMO (non-bonding MO) to LUMO (anti-bonding sigma MO) was found to be **7.5485 eV** with an oscillator strength of **0.0356**. The oscillator strength is not zero meaning the transition is allowed.

The vertical Transition Energy = 7.5485eV

It corresponds to a transition from n$\rightarrow\boldsymbol{\sigma}^*$, which is a allowed transition.



(a) non-bonding MO (n) (b) antibonding sigma MO ($\boldsymbol{\sigma}^*$)

Figure 6: HOMO and LUMO of NH_3