C343 Lab Report 4

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4 March 2021

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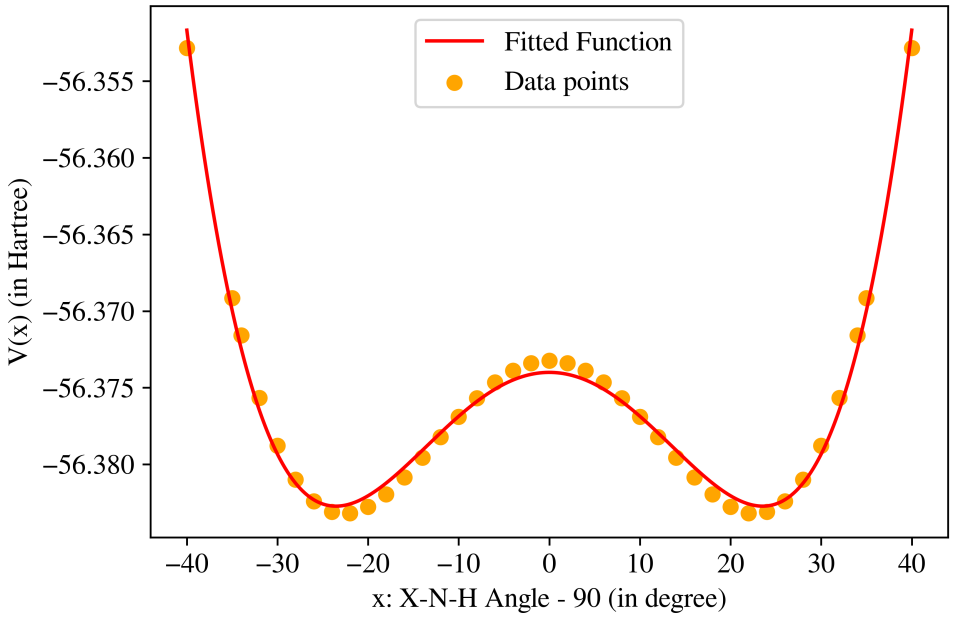

Figuur 1: Potential energy profile for Ammonia inversion from MP2/6-31G** energies

$$\text{Fitting Equation: } V_{fit}(x) = a + bx^2 + cx^4 \tag{1}$$

Parameters ⟶	a	b	c
Value after Fitting	-56.374	-3.14882e-05	2.84015e-08
Asymptotic Standard Error	+/- 0.0001885	+/- 7.13e-07	+/- 4.956e-10

- **Chi-Square Goodness of Fit Test:** performed using python code

$$\begin{aligned}\text{Chi-squared Test Statistic} &= \sum_{x=-40}^{40} \frac{(V_{data}(x) - V_{fit}(x))^2}{V_{fit}(x)} \\ &= \text{-3.61146581e-06}\end{aligned} \tag{2}$$

- **Barrier for Inversion:** 0.0093509 Hartree = 5.86768975 kcal/mol

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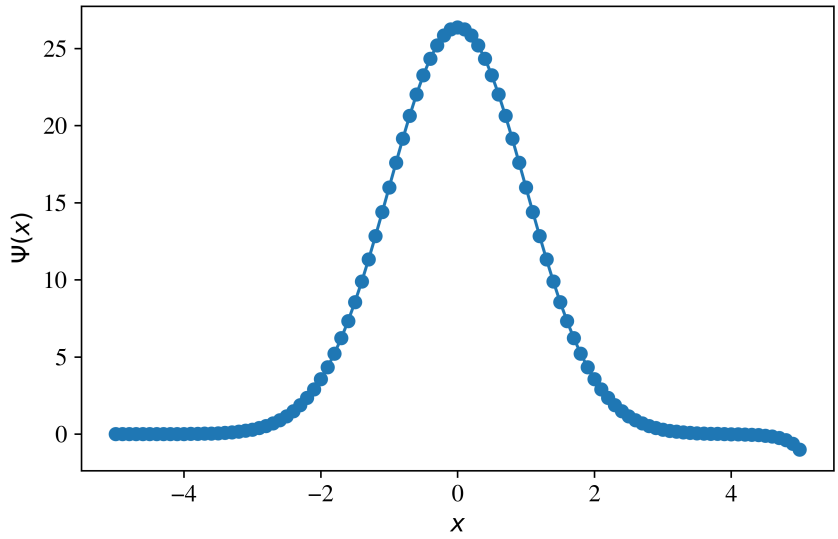
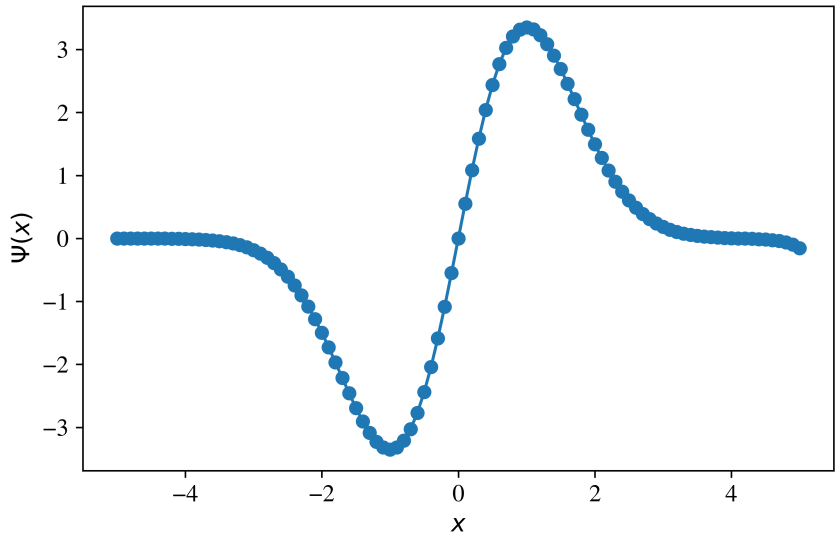
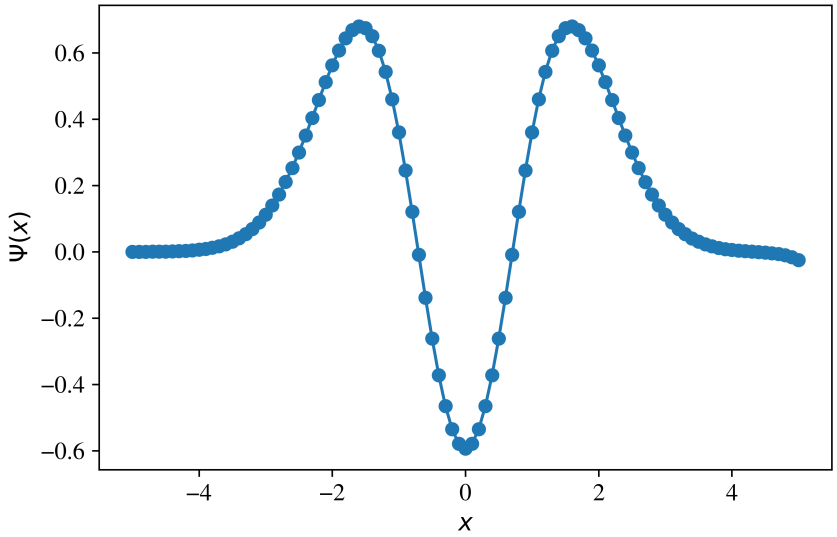
Initial Values : $\Psi(-5.0) = 0$, $\Psi(-4.9) = 0.001$, when no of nodes is odd and $\Psi(-4.9) = -0.001$, when no of nodes is even.
(Code implementing the Numerov's method can be found at the end of the report)



Figuur 2: Energy eigenvalue: 0.5 Hartree, Number of Nodes: 0



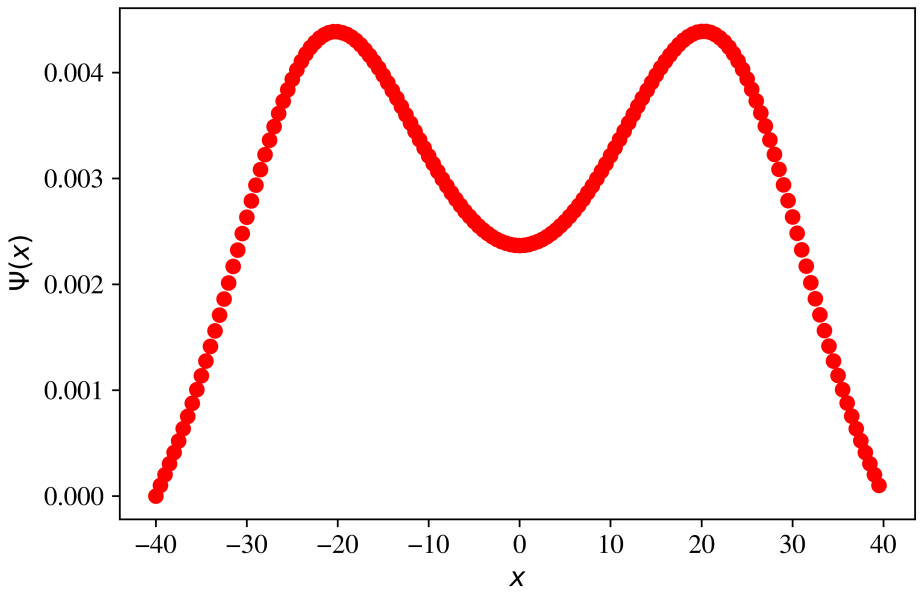
Figuur 3: Energy eigenvalue: 1.5 Hartree, Number of Nodes: 1



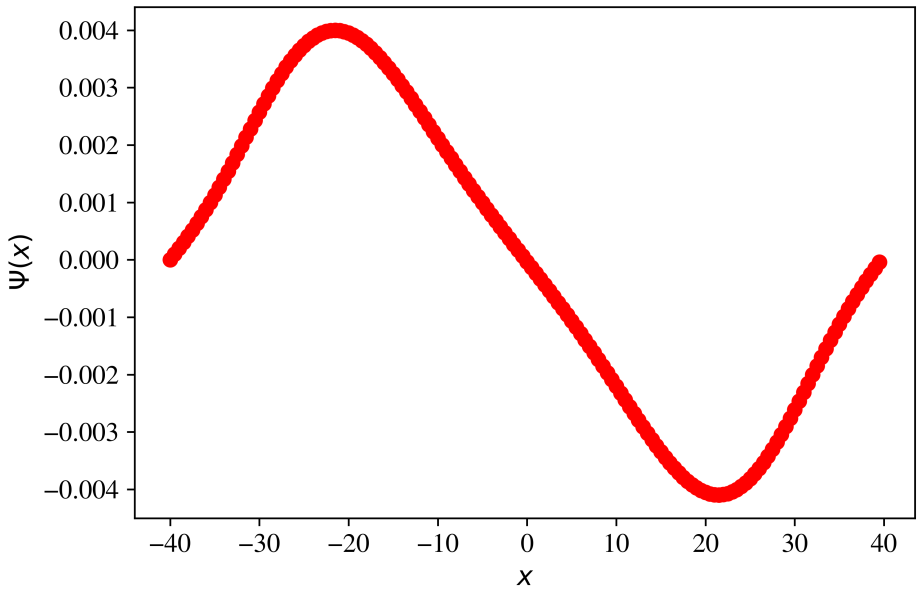
Figuur 4: Energy eigenvalue: 2.5 Hartree, Number of Nodes: 2

3

Initial Values : $\Psi(-40.0) = 0$, $\Psi(-39.9) = 0.001$, when no of nodes is odd and $\Psi(-39.9) = -0.001$, when no of nodes is even.
(Code implementing the Numerov's method can be found at the end of the report)



Figuur 5: Energy eigenvalue: -56.377784611 Ha, Number of Nodes: 0



Figuur 6: Energy eigenvalue: -56.377090847 Ha, Number of Nodes: 1

$$\begin{aligned} \text{Tunelling Splitting Energy} &= \text{Difference in Energy between 0th and 1st Energy Level} \\ &= 0.000641278 \text{ Hartree} \\ &= 140.744 \text{ cm}^{-1} (\text{Experimental Value: } 0.793 \text{ cm}^{-1}) \end{aligned} \tag{3}$$

Sources of Error:

- Fitting : We have approximated the Potential to be of form **Eqn 1**. It underestimates the barrier height. Instead using an expotential term with quadratic gives a better fit.
- Numerov : The wavefunctions computed using this numerical methods of solving differential equations are accurate within their cutoff
- Experiment: There will be a limit of accuracy of the instruments and it will involve other conditions too.

Reference for Experimental Tunelling Splitting Value:

Papoušek, D. (1983). The story of the ammonia molecule: Ten years of investigation of molecular inversion. **Journal of Molecular Structure**, 100, 179-198.

Codes for Lab 4: `https://github.com/aniruddha-seal/C343-Computational-Ch tree/main/Lab%204`