Problem Set 2

Chemistry 675, Fall 2024

Due Date: September 20, 2024

Relevant Chapters: Excerpts of Levine Chapters 1,2, 3, and 7

1. Let the initial wavefunction be defined by

$$\Psi\left(x, t=0\right) = \frac{1}{\sqrt{2}}\left(\phi_1\left(x\right) - \phi_3\left(x\right)\right) \tag{1}$$

   where $\phi_i\left(x\right)$ is the i^{th} lowest-energy eigenstate of the particle in a box.

   (a) Give the analytic expression for the probability density.

   (b) Give the analytic expression for the expected evolution of the probability density.

   (c) Explain how the expected evolution of the probability density relates to the expected result for a nonstationary state.

   (d) Give the analytic expression for the average position as a function of time.

2. Let the initial wavefunction be defined as the Gaussian wavepacket

$$\Psi\left(x, t=0\right) = \mathcal{N}\mathrm{e}^{-a^2\left(x-L/2\right)^2/2} \tag{2}$$

   where $\mathcal{N}$ is the normalization coefficient, $L = 5$ Å, and $a = 4$ Å^{-1}.

   (a) Demonstrate analytically whether $\Psi\left(x, t=0\right)$ is a stationary state for a particle-in-a-box potential.

   (b) Using the accompanying Jupyter notebook:

      i. Explain what the function $f\left(N\right) = \sum_{i=1}^{N} c_i^{\star} c_i$ represents.

      ii. Plot $f\left(N\right)$ for the given expansion coefficients c_i.

      iii. Calculate $\lim_{N\to\infty} f\left(N\right)$.

      iv. Explain what $f\left(N\right)$ says about the number of expansion terms required to accurately simulate the wavefunction.

      v. Plot $\left|\Psi\left(x, t\right)\right|^2$ at several choices of t to show how the wavefunction changes in time.

      vi. Explain what $\left|\Psi\left(x, t\right)\right|^2$ tells us about the motion of a particle in a box.

      vii. Plot $\left\langle x\left(t\right)\right\rangle$ and $\left\langle \left(x - L/2\right)^2\left(t\right)\right\rangle$.

      viii. Explain the significance of $\left\langle x\left(t\right)\right\rangle$ and $\left\langle \left(x - L/2\right)^2\left(t\right)\right\rangle$ and their relationships to $\left|\Psi\left(x, t\right)\right|^2$.