

Quantum Mechanics and Spectroscopy

CHEM 3PA3

Assignment 14

Name: _____

1. Evaluate the commutator $[l_y, [l_y, l_z]]$ given that $[l_x, l_y] = i\hbar l_z$, $[l_y, l_z] = i\hbar l_x$, and $[l_z, l_x] = i\hbar l_y$.
2. Evaluate the commutators: (a) $[H, p_x]$, and (b) $[H, x]$, where $H = \frac{p_x^2}{2m} + V(x)$, with (i) a constant potential, $V(x) = V$, and (ii) $V(x) = \frac{kx^2}{2}$. Which observables can be measured simultaneously?
3. Calculate the variance $\sigma_A = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$, for position x and momentum p_x for the particle in a one-dimensional box. Remember that $\langle \hat{A} \rangle = \int \psi \hat{A} \psi d\tau$. Does the Heisenberg uncertainty principle apply for this system, $\sigma_x \sigma_{p_x} > \frac{\hbar}{2}$?
4. The eigenvalues of the simple oscillator are given by

$$E(\nu) = \hbar \left(\sqrt{\frac{k_e}{\mu}} \right) \left(\nu + \frac{1}{2} \right) \quad \nu = 0, 1, 2, \dots$$

where the reduced mass of the oscillator is simply related to the atomic masses by $\nu = (m_A m_B / (m_A + m_B))$. Here, k_e is the force constant of the oscillator and r_e denotes the equilibrium bond distance. The eigenfunctions of the two lowest energy states of the harmonic oscillator are given below

$$\psi_0(r) = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\frac{\alpha}{2}(r-r_e)^2} \quad \psi_1(r) = \left(\frac{\alpha}{\pi} \right)^{1/4} (\sqrt{2\alpha}) (r - r_e) e^{-\frac{\alpha}{2}(r-r_e)^2}$$

where

$$\alpha = \sqrt{\frac{k_e \mu}{\hbar^2}}$$

- (a) Write down the Harmonic-Oscillator Hamiltonian and show that $\psi_0(r)$ is an eigenfunction of it.
- (b) The lowest-energy vibrational excitation of the $^{12}\text{C}^{16}\text{O}$ (carbon monoxide) molecule is associated with absorbing photons with frequency 6.42×10^{13} Hz. The equilibrium bond length of CO is 1.128×10^{-10} m. Use the harmonic oscillator model to estimate the spread in bond lengths, $\sigma_r = \sqrt{\langle r^2 \rangle - \langle r \rangle^2}$, for the ground state of CO. It is easier to use Hellmann-Feynman theorem to evaluate the integrals.
- (c) Using your result from (b), obtain a lower bound for the kinetic energy for the ground vibrational state of the $^{12}\text{C}^{16}\text{O}$ molecule. First, calculate the the lower bound of the spread using the Heisenberg uncertainty principle and then find the value of $\langle \hat{p}^2 \rangle$. Remember that the momentum distribution is symmetric for the harmonic oscillator, so $\langle \hat{p} \rangle = 0$.