1. Consider a particle of mass \( m \) constrained to be in a box between \( x = 0 \) and \( x = a \), where the potential energy is assumed to vanish. At time \( t = 0 \) the wave function is given by \( \Psi(x, 0) = \frac{30}{a^2} x(a - x) \).

Questions:

a) Show that the function \( \Psi(x, 0) \) is normalized.

b) Draw the wave function \( \Psi(x, 0) \). Does it satisfy the boundary conditions?

c) Compute the expectation value of \( \langle \hat{X}^2 \rangle \) for the normalized function at \( t=0 \).

d) If the energy would be measured at \( t=0 \) for a sample described by the wave function \( \Psi(x,0) \), what would be the possible values that can in principle be measured? Calculate the average value of the energy that would be measured in this experiment. Briefly explain how this average would be obtained in the actual experiment, i.e. describe the basic features of the “quantum” experiment for this case.

e) Is the wavefunction at \( t = 0 \) an eigenfunction of the Hamiltonian? Why or why not?
2) The 6 \( \pi \) electrons in benzene can be described by a particle on the ring model, with a Hamiltonian \( \hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\phi^2} \), where \( R \) is the radius of the ring while \( \phi \) denotes the angular coordinate. Take the C-C bondlength in benzene (a regular hexagon) to be 1.4 Å.

Questions:

a) What is the boundary condition for the particle on the ring?

b) What are a suitable set of orthogonal eigenfunctions of the Hamiltonian for the particle on the ring? Clearly indicate the energies, the wave functions and their degeneracies. Show that your wave functions satisfy the boundary condition, and satisfy the time-independent Schrödinger equation. Also show explicitly that your wavefunctions are orthogonal if they have the same energy.

c) Taking the radius as implied by the C-C bondlength, calculate the energies of the lowest 4 energy levels in eV. What is the excitation energy for the HOMO-LUMO excitation in benzene? Express the excitation energy both in eV and calculate the corresponding wavelength in nm.

3. You are given a Hamiltonian \( \hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \) and a time-dependent wave function
\[
\Psi(x,t) = \cos(\pi x)e^{-\frac{\hbar\pi^2}{2m}t} + \sin(2\pi x)e^{-\frac{2\hbar\pi^2}{m}t}
\]

a. Show that \( \Psi(x,t) \) satisfies the time-dependent Schrödinger equation
\[
i\hbar \frac{\partial \Psi(x,t)}{\partial t} = \hat{H} \Psi(x,t).
\]
Is the wave function at time \( t = 0 \) an eigenfunction of \( \hat{H} \)? Why or why not?

b. Sketch the wavefunction over the interval \(-\frac{1}{2} \leq x \leq \frac{1}{2}\) at times \( t = 0 \) and at time
\[
t = \frac{2m}{\pi \hbar}.
\] Also sketch the probability \( |\Psi(x,t)|^2 \) for these times. Is \( \Psi(x,t) \) a stationary state? Why or why not?
4 a) In the Bohr model, the motion of an electron about the nucleus is circular in the xy plane. The radius is $R$ and the angular momentum $Rp$ about the z axis is quantized in units of $\hbar$. Newton's law gives \(-mv^2 / R = F = -Ze^2 / 4\pi\varepsilon_0 R^2\) for nuclear charge $Ze$. Derive that $R$ is quantized when $Rp = n\hbar$ and give an expression for $R$. Simply use the Bohr formula for the energy levels without derivation and find the wavelength (in Å) of photons that are emitted when an electron falls from the first excited level to the lowest level for $Z = 29$ (copper). In practice an electron is first ionized from the 1s orbital, and subsequently an electron in the 2p orbital falls back into the 1s hole and emits a photon. Make an orbital level picture and sketch the entire process. This process is the source of 1.54 Å X-rays in spectrometers. The answer you get for the wavelength using the Bohr model is not very accurate. Which way would you expect your answer to differ from the experimental result and why?

1 b) Wavelengths in the Angstrom range are needed to determine atomic spacing by electron or neutron diffraction. Find the wavelength of thermal (~500 K) neutrons with kinetic energy 0.05 eV.

5 (a) The energy levels of a rigid rotator are $E_J = \hbar^2 J(J+1)/2I$. Show and label the first four levels, indicate their degeneracy, and sketch the microwave spectrum of a polar diatomic that involves these lines. The observed spacing between the microwave lines of H$^{35}$Cl is $6.350 \times 10^{11}$ Hz ($21.18$ cm$^{-1}$). Find the bond length and predict the microwave spectrum of D$^{35}$Cl.

(b) The far infrared spectrum of $^{39}$K$^{35}$Cl has an intense line at 278.0 cm$^{-1}$. In the harmonic oscillator approximation, find the force constant and the period of vibration of $^{39}$K$^{35}$Cl.
6. Consider a particle that is moving on the surface of a cylinder described by the coordinates \((x, y, z) = (R \cos \varphi, R \sin \varphi, z)\) where \(R\) is the radius of the cylinder. The \(z\) coordinate is constrained to lie between 0 and \(a\), where \(a\) is the length of the cylinder.

On the surface of the cylinder the potential is zero, and the Hamiltonian is given by
\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2mR^2} \frac{\partial^2}{\partial \varphi^2}.
\]
Questions:

a.) Try as a solution for the time-independent Schrödinger equation the product function \(\Psi(\varphi, z) = f(\varphi)g(z)\), and derive differential equations for the functions \(f\) and \(g\).

b.) What are the boundary conditions associated with the differential equations under a)? Show that the functions \(\sin\left(\frac{n \pi z}{a}\right) e^{i k \varphi}\) satisfy the time-independent Schrödinger equation. For what values of \(n\) and \(k\) are the boundary conditions satisfied? What are the energy levels for the allowed values of \(n\) and \(k\)?

c.) Consider the special case that \(2 \pi R = 2a\), i.e. the circumference of the circle is precisely the length to travel back and forth on the \(z\)-axis of the cylinder. Draw a energy level diagram of the energy levels up to and including \(10\hbar^2 / (2mR^2)\). For each energy level indicate the possible associated values of \(n\) and \(k\), and indicate the degeneracy of the energy level.