EN-204 – Materials for Energy Applications
Problem Set – Fundamental Quantum Mechanics

1. (a) Set up the Schrödinger equation for a particle in a one-dimensional box. Show that the solution of Schrodinger equation leads to the quantization of translational motion and hence derive the energy expression $E = n^2 (h^2 / 8ml^2)$
(b) What are the permitted values of quantum number *n*? Explain why a value of zero is not permitted.
(c) Show hat for a free particle moving in an unbounded region of space, the translational energy is virtually unquantized. Show that the above statement is also true for a larger mass moving in a box of ordinary dimensions.
(d) Obtain the normalized wave function for the particle in a one-dimensional box. Plot the various wave functions and the corresponding probability density curves and thus show that the results for a very large value of *n* justify the Bohr's correspondence principle.
(e) Show how the model of particle in a box can be applied to calculate the energy spectra of polyenes.
(f) Set up the Schrodinger equation for the particle in a three-dimensional box. Solve it for the various allowed energies and the wave functions.

2. A particle of mass *m* is confined a one-dimensional box with the origin at the center of the box. The box extends from $-l/2$ to $+l/2$. The potential energy is
$V(x) = 0;\ -l/2 < x < l/2$
$\quad = \infty;\ |x| \geq l/2$
(a) Write the Schrodinger equation for the system showing separate equations for the inside and the outside of the box.
(b) Assume a solution (inside the box) of the form

$$\Psi(x) = A \sin(\alpha x) + B \cos(\alpha x)$$

Find out its correct form by making use of boundary conditions.
(c) Derive the energy expression of the particle.

3. If ψ_1 and ψ_2 are wave functions for a degenerate state of energy E, prove that any linear combination $c_1 \psi_1 + c_2 \psi_2$ is also a wave function.

4. Consider a particle with quantum number **n** moving in a one-dimensional box of length **l.**(a) Determine the probability of finding the particle in the left quarter of the box. (b) For what value of **n** is this probability a maximum. (c) What is the limit of this probability for $\mathbf{n} \to \infty$. (d) What is principle is illustrated in (c).

5. The ground state translational energy of a particle in a one-dimensional box of 300 pm length is about 4 eV. Suppose that the same particle is moving in a three-dimensional cubic box of 100 pm on the side. Estimate the ground-state energy of the particle in the three-dimensional box.

6. Consider an electron in a one dimensional box of length 2.000 $\dot{A}$ with the left end of the box at x = 0. (a) Suppose we have one million of these systems, each in the n=1 state, and we measure the x coordinate of the electron in each system. About how many times will the electron be found between 0.600 $\dot{A}$ to 0.601 $\dot{A}$ consider the interval to be infinitesimal. (Hint : Check whether you have set your calculator to degrees or radians). (b) Suppose we have a large number of these

systems, each in the n = 1 state, and we measure the x coordinate of the electron in each system and the find the electron between 0.7 $\dot{A}$ and 0.701 $\dot{A}$ in 126 of the measurement. In about how many measurements will the electron be found between 1 $\dot{A}$ and 1.001 $\dot{A}$.

7. An extremely crude picture of an electron in an atom or molecule treats it as a particle in a one-dimensional box whose length is on the order of the size of atoms and molecules. (a) For an electron in a one-dimensional box of length 1 $\dot{A}$, calculate the separation between the two energy levels. (b) Calculate the wavelength of a photon corresponding to a transition between these two levels. (c) In what portion of the electromagnetic spectrum is this wavelength.

8. When a particle of mass 9.1×10^{-28} gm in a certain one-dimensional box goes from n=5 to n=2 level, it emits a photon of frequency 6×10^{14} sec^{-1}. Find the length of the box.

9. An electro confined to a one-dimensional box of length 0.14 nm has a ground-state energy corresponding to the radiation of wavelength about 70 nm. Benzene, as a rough approximation, may be considered to be a two-dimensional box that encompasses the regular hexagonal shape. The C-C bond length in benzene is 0.14 nm, so that side of the box would be about 0.28 nm. Estimate wavelength for transition from ground state to first excited state of benzene, assuming that it is π-bonding electrons that are involved.

10. When an electron in a certain excited energy level in a one-dimensional box of length 2 $\dot{A}$ makes a transition to the ground state, a photon of wavelength 8.79 nm is emitted. find the quantum number of the initial state.

11. An electron in a stationery state of a one dimensional box of length 0.3 nm emits a photon of frequency 5.05×10^{15} sec^{-1}, find the initial and final quantum numbers for this transition.

12. A crude treatment of the pi electrons of a conjugated molecule regards these electrons as moving in the particle in a box of fig 1, where the box length is somewhat more than the length of the conjugated chain. The Poly exclusion principle allows no more than two electrons to occupy each box level. For butadiene take the box length as 7 $\dot{A}$ and use this model to estimate the wavelength of light absorbed when a pi electron is excited from the highest occupied to the lowest level. The experimental value is 217 nm.

13. A cubic box of edge-length 1.2 nm contains 10 electrons. Applying he simple particle-in-a-box theory, calculate the value of ΔE for the first excited state of this system.

14. The particle in a box time independent Schrödinger equation contains the constants h and m, and the boundary conditions involved the box length l. We therefore expect the stationery state energies to be function of h, m and l. [$E = \left(\frac{n^2}{8}\right)\left(\frac{h^2}{ml^2}\right)$]. Prove that the only value of a, b and c that give the product $h^a m^b l^c$ the dimension of energy are a = 2, b = -1, c = -2.
15. The average kinetic energy of a gas molecule is (3/2)kT, where k is the Boltzmann constant. What will have to be the average value of ($n_x^2 + n_y^2 + n_z^2$) in order that an atom of He may possess a temperature of 30 K when confined in a cubical box of 10 nm of edge?

16. Determine the energy required for a transition from the $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ state for

(a) An argon atom (molar mass = 39.95 g mol^{-1}) in a cubic container with a 1.0 cm side
(b) An electron (m_e = 9.11 x 10^{-28} g) in a cubic hole of a crystal with 10^{-8} cm edge-length.

17. True or false
a) The particle in a box ground state has quantum number n=0
b) The particle in a box stationary state wave functions are discontinuous at certain points.
c) The 1st derivative of each particle in a box stationary state wave functions is discontinuous at certain points.
d) The max. probability density for every particle ina box stationary state is at the centre of the box.
e) For the particle in a box n=2 stationary state, the probability of finding the particle in the left quarter of box is same as that of finding it in right corner. (No need of integrals)
f) For the particle in a box n=1 stationary state, the probability of finding the particle in the left third of box is same as that of finding it in middle third. (No need of integrals)
g) The wavelength of the particle in a box absorption transition from quantum number n to n+1 decreases as the value of n increases.