Home Work # 6

Tinoco: 9.4  9.5  9.8

Engel:  14.6  14.9  14.19

Atkins: 9.21  9.23

House:  3.10

Blinder:  3.5


Additional extra 2

Total: 10 regular problems

Total: 6 extra problems
4. Consider a one-dimensional box of length $l$. For parts (a), (b), and (c), calculate the energy of the system in the ground state and the wavelength (in Å) of the first transition (longest wavelength).

(a) $l = 10$ Å, and the box contains one electron.
(b) $l = 20$ Å, and the box contains one electron.
(c) $l = 10$ Å, and the box contains two electrons (assume no interaction between the electrons).
(d) Write the complete Hamiltonian for the system described in part (c).
(e) What will happen to the answers in part (c) if the potential of interaction between the electrons is included in this Hamiltonian?

5. Consider a particle in a one-dimensional box.

(a) For a box of length 1 nm, what is the probability of finding the particle within 0.01 nm of the center of the box for the lowest-energy level?
(b) Answer part (a) for the first excited state.
(c) The longest-wavelength transition for a particle in a box [not the box in part (a)] is 200 nm. What is the wavelength if the mass of the particle is doubled? What is the wavelength if the charge of the particle is doubled? What is the wavelength if the length of the box is doubled?

P14.6 Calculate the probability that a particle in a one-dimensional box of length $a$ is found between $0.31a$ and $0.35a$ when it is described by the following wave functions:

a. $\sqrt{\frac{2}{a}} \sin \left( \frac{\pi x}{a} \right)$

b. $\sqrt{\frac{2}{a}} \sin \left( \frac{3\pi x}{a} \right)$

What would you expect for a classical particle? Compare your results in the two cases with the classical result.

8. Nitrogenase is an enzyme that converts $N_2$ to $NH_3$. Extraction procedures have shown that nitrogenase contains an iron–sulfur cluster, $Fe_4S_4$, where the atoms of each type are arranged alternately at the corners of a cube. We wish to attempt to model the bonding in this iron–sulfur cube with the wavefunctions derived for an electron in a cubical (three-dimensional) box whose edges have length $a$:

(a) Write the Hamiltonian for the electron in the box.
(b) Write general expressions for the energies (eigenvalues) and wavefunctions (eigenfunctions) for the electron in a three-dimensional cubical box as a function of the quantum numbers.
(c) Construct an energy-level diagram showing the relative ordering of the lowest 11 “molecular orbitals” of this cube. Label the levels in terms of their quantum numbers. Be alert for degeneracies.
(d) Assuming that the total number of valence electrons available is 20, show the electron configuration on the plot in part (c).
(e) If $a = 3$ Å, calculate the transition energy for excitation of an electron from the highest filled orbital to the lowest unfilled orbital. At what wavelength in nm should this transition occur?

P14.19 Generally, the quantization of translational motion is not significant for atoms because of their mass. However, this conclusion depends on the dimensions of the space to which they are confined. Zeolites are structures with small pores that we describe by a cube with edge length 1 nm.

Calculate the energy of a $H_2$ molecule with $n_x = n_y = n_z = 10$. Compare this energy to $kT$ at $T = 300$ K. Is a classical or a quantum description appropriate?

P14.9 The function $\psi(x) = Ax[1 - (x/a)]$ is an acceptable wave function for the particle in the one-dimensional infinite depth box of length $a$. Calculate the normalization constant $A$ and the average values $\langle x \rangle$ and $\langle x^2 \rangle$. 

8-5
9.23 The rate, \( v \), at which electrons tunnel through a potential barrier of height 2 eV, like that in a scanning tunneling microscope, and thickness \( d \) can be expressed as \( v = A e^{-d/\lambda} \), with \( A = 5 \times 10^{14} \text{s}^{-1} \text{ and } \lambda = 70 \text{ pm} \). (a) Calculate the rate at which electrons tunnel across a barrier of width 750 pm. (b) By what factor is the current reduced when the probe is moved away by a further 100 pm?

10. When sodium dissolves in liquid ammonia, some dissociation occurs.

\[
\text{Na} \rightarrow \text{Na}^+ (\text{solvated}) + e^- (\text{solvated}).
\]

The solvated electron can be treated as a particle in a three-dimensional box. Assume that the box is cubic with an edge length of \( 1.55 \times 10^{-7} \text{ cm} \) and suppose that excitation occurs in all directions simultaneously for the lowest state to the first excited state. What wavelength of radiation would the electron absorb? Would the solution be colored?

3.5. Consider the hypothetical reaction of two "cube-atoms" to form a "molybox":

Each cube-atom contains one electron. The interaction between electrons can be neglected. Determine the energy change in the above reaction.
6. The exact ground-state energy for a particle in a box is $0.125 \hbar^2/ma^2$; the exact wavefunction is $(\sqrt{2}/a) \sin(\pi nx/a)$. Consider an approximate wavefunction $\psi(x) = x(a - x)$.

(a) Show that the approximate wavefunction fits the boundary conditions for a particle in a box.

(b) Given this approximate wavefunction, $\psi(x) = x(a - x)$, the approximate energy $E'$ of the system can be calculated from

$$E' = \frac{\int_0^a \psi(x) |\psi(x)| dx}{\int_0^a \psi^2(x) dx}$$

This is called the variational method. Calculate the approximate energy $E'$.

(c) What is the percent error for the approximate energy?

(d) According to the variational theorem, the more closely the wavefunction used approximates the correct wavefunction, the lower will be the energy calculated according to part (b). The converse is also true. Propose another approximate wavefunction that could be used to calculate an approximate energy. How can you find out whether it is a better approximation?

7. The $\pi$ electrons of metal porphyrins, such as the iron-heme of hemoglobin or the magnesium-porphyrin of chlorophyll, can be visualized using a simple model of free electrons in a two-dimensional box.

(a) Obtain the energy levels of a free electron in a two-dimensional square box of length $a$.

(b) Sketch an energy-level diagram for this problem. Set $E_0 = \hbar^2/8ma^2$ and label the energy of each level in units of $E_0$.

(c) For a porphyrin-like hemin that contains 26 $\pi$ electrons, indicate the electron population of the filled or partly filled $\pi$ orbitals of the ground state of the molecule. (Note that orbitals that are degenerate in energy, $E_{12} = E_{21}$, can still hold two electrons each.)

(d) The porphyrin structure measures about 1 nm on a side ($a = 1$ nm). Calculate the longest-wavelength absorption band position for this molecule. (Experimentally these bands occur at about 600 nm.)

P14.18 This problem explores under what conditions the classical limit is reached for a macroscopic cubic box of edge length $a$. An argon atom of average translational energy $3/2 kT$ is confined in a cubic box of volume $V = 0.500$ m$^3$ at 298 K. Use the result obtained in Problem P14.15b for the dependence of the energy levels on $a$ and on the quantum numbers $n_x$, $n_y$, and $n_z$.

a. What is the value of the "reduced quantum number" $\alpha = \sqrt{n_x^2 + n_y^2 + n_z^2}$ for $T = 298$ K?

b. What is the energy separation between the levels $a$ and $a + 1$? (Hint: Subtract $E_{a+1}$ from $E_a$ before plugging in numbers.)

c. Calculate the ratio $E_{a+1} - E_a/kT$ and use your result to conclude whether a classical or quantum mechanical description is appropriate for the particle.

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Extra Problem

9.24 The wavefunctions and energies of a particle in a rectangular box are given by

$$\psi_{n_x,n_y}(x,y) = \frac{2}{(L_1L_2)^{1/2}} \sin\frac{n_x\pi x}{L_1} \sin\frac{n_y\pi y}{L_2}$$

$$0 \leq x \leq L_1, 0 \leq y \leq L_2$$

$$E_{n_x,n_y} = \frac{n_x^2}{L_1^2} + \frac{n_y^2}{L_2^2} \frac{\hbar^2}{8m}$$

where $L_1$ and $L_2$ are the lengths of the box along the $x$ and $y$ dimensions, respectively. We see that we require two quantum numbers, $n_x$ and $n_y$, to describe motion in two dimensions. (a) Use mathematical software or an electronic spreadsheet to plot the wavefunctions $\psi_{1,1}, \psi_{1,2}, \psi_{2,1}, \psi_{2,2}$, and the corresponding probability densities. (b) The particle in a two-dimensional box is a useful model for the motion of electrons around the indole ring (5), the conjugated cycle found in the side chain of tryptophan. We may regard indole as a rectangle with sides of length 280 pm and 450 pm, with 10 electrons in the conjugated system. As in Case study 9.1, we assume that in the ground state of the molecule each quantized level is occupied by two electrons. (c) Calculate the energy of an electron in the highest occupied level. (d) Calculate the frequency of radiation that can induce a transition between the highest occupied and lowest unoccupied levels.

4-5
2. Prof. Jansen studies Xe atoms in xonolites, these are porous functions that are commonly used for catalysis. If the xonolite cavity can be treated as a cube of 10Å = 1nm on a side, calculate the first 3 energy levels for Xe in the xonolite cavity. What happens to E-value if you substitute A?