

# CHEM 26100 (Quantum Mechanics) Problem Sets

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# 1 Blackbodies and the Photoelectric Effect

- 10/6: 1. The intensity (or emissive power) of solar radiation at the surface of the earth is  $1.4 \times 10^3 \text{ W/m}^2$ , the distance from the center of the sun to the sun's surface is  $7 \times 10^8 \text{ m}$ , and the distance from the center of the sun to the earth is  $1.5 \times 10^{11} \text{ m}$ .

- (a) Assuming that the sun is a black body, calculate the temperature at the surface of the sun in Kelvin. (Hint: The surface area of a sphere of radius  $r$  is  $4\pi r^2$ .)

*Answer.* Let

$$I = 1400 \frac{\text{W}}{\text{m}^2} \quad r_1 = 7 \times 10^8 \text{ m} \quad r_2 = 1.5 \times 10^{11} \text{ m}$$

and let  $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2}$  be Stefan's constant. If  $P$  is the total power radiated by the sun, we have from physics that

$$I = \frac{P}{4\pi r_2^2}$$

$$P = 4\pi r_2^2 I$$

and from quantum that

$$P = R \cdot 4\pi r_1^2$$

$$= \sigma T^4 \cdot 4\pi r_1^2$$

Thus, setting these two quantities equal to each other, we obtain

$$4\pi r_2^2 I = \sigma T^4 \cdot 4\pi r_1^2$$

$$r_2^2 I = \sigma T^4 r_1^2$$

$$T = \sqrt[4]{\frac{r_2^2 I}{\sigma r_1^2}}$$

$T = 5803 \text{ K}$

□

- (b) Secondly, compute the wavelength at which the emissive power at the sun's surface has its maximum. In which region of the radiation spectrum does this wavelength lie, i.e., infrared (IR), visible, or ultraviolet (UV)?

*Answer.* If  $b = 2.898 \times 10^{-3} \text{ m K}$  is Wien's displacement constant and we plug in the temperature value  $T$  from part (a), then Wien's first law gives us

$$\lambda_{\max} T = b$$

$$\lambda_{\max} = \frac{b}{T}$$

$\lambda_{\max} = 4.99 \times 10^{-7} \text{ m}$

This wavelength lies in the visible spectrum.

□

2. (a) Using Planck's formula for the energy density  $\rho(\lambda, T)$ , prove that the total energy density  $\rho(T)$  is given by  $\rho(T) = aT^4$ , where  $a = 8\pi^5 k^4 / (15h^3 c^3)$ . (Hint: Use the integral  $\int_0^\infty x^3 / (e^x - 1) dx = \pi^4/15$ .)

*Proof.* Planck's formula for the energy density is

$$d\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

Thus, if we use the change of variables  $x = hc/(\lambda kT)$  (also implying  $\lambda = hc/(xkT)$  and  $d\lambda = -hc/(x^2 kT) dx$ ), we have that

$$\begin{aligned} \int_0^\infty d\rho(\lambda, T) &= \int_{\lambda=0}^\infty \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{hc/\lambda kT} - 1} \\ \int_0^\infty \rho_\lambda(T) d\lambda &= \int_{x=\infty}^0 \frac{8\pi hc}{\left(\frac{hc}{xkT}\right)^5} \cdot \frac{1}{e^x - 1} \cdot -\frac{hc}{x^2 kT} dx \\ \rho(T) &= \int_{x=\infty}^0 -\frac{8\pi (hc)^2 (kT)^5 x^5}{(hc)^5 (e^x - 1)(x^2)(kT)} \\ &= \int_{x=0}^\infty \frac{8\pi (kT)^4 x^3}{(hc)^3 (e^x - 1)} \\ &= \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \\ &= \frac{8\pi (kT)^4}{(hc)^3} \cdot \frac{\pi^4}{15} \\ &= \frac{8\pi^5 k^4}{15h^3 c^3} T^4 \\ &= aT^4 \end{aligned}$$

as desired. □

- (b) Does this agree with the Stefan-Boltzmann law for the total emissive power?

*Answer.* Yes — we are given the conversion factor  $\rho(\lambda, T) = 4/c \cdot R(\lambda, T)$ , so from the above, we should have

$$\begin{aligned} R(T) &= \frac{c}{4} \cdot R(\lambda, T) \\ &= \frac{c}{4} \cdot \frac{8\pi^5 k^4}{15h^3 c^3} T^4 \\ &= \frac{2\pi^5 k^4}{15h^3 c^2} T^4 \end{aligned}$$

But by plugging in the appropriate values, we can determine that

$$\frac{2\pi^5 k^4}{15h^3 c^2} = \sigma$$

where  $\sigma$  is Stefan's constant, giving us

$$R(T) = \sigma T^4$$

as desired. □

3. The photoelectric work function for lithium is 2.3 eV.

- (a) Find the threshold frequency  $\nu_t$  and the corresponding  $\lambda_t$ .

*Answer.* From Einstein's annus mirabilis papers, we have that

$$\nu_t = \frac{W}{h} \qquad \lambda_t = \frac{c}{\nu_t} = \frac{ch}{W}$$

Plugging in  $W = 3.685 \times 10^{-19} \text{ J}$  and  $h = 6.626 \times 10^{-34} \text{ J s}$ , we have that

$$\nu_t = 5.56 \times 10^{14} \text{ Hz}$$

$$\lambda_t = 5.39 \times 10^{-7} \text{ m}$$

□

- (b) If UV light of wavelength  $\lambda = 3000 \text{ \AA}$  is incident on the Li surface, calculate the maximum kinetic energy of the electrons.

*Answer.* From Einstein's annus mirabilis papers, we have that

$$\begin{aligned} KE_{\max} &= h\nu - W \\ &= \frac{hc}{\lambda} - W \end{aligned}$$

$$KE_{\max} = 2.941 \times 10^{-19} \text{ J}$$

□

4. (a) Using the Bohr model, compute the ionization energies for  $\text{He}^+$  and  $\text{Li}^{2+}$ .

*Answer.* From the Bohr model, we have that

$$\begin{aligned} IE &= E_{\infty} - E_1 \\ &= -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{\infty^2} + \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \cdot \frac{1}{1^2} \\ &= \frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2} \end{aligned}$$

It follows since  $Z = 2$  for  $\text{He}^+$  and  $Z = 3$  for  $\text{Li}^{2+}$  that

$$IE(\text{He}^+) = 8.72 \times 10^{-18}$$

$$IE(\text{Li}^{2+}) = 1.962 \times 10^{-19}$$

in units of Joules per electron.

□

- (b) Can the Bohr model be employed to compute the first ionization energy for He and Li? Explain briefly.

*Answer.* No — the Bohr model is only valid for single electron systems as it does not take into account electron-electron interactions.

□

5. (a) An electron is confined within a region of atomic dimensions on the order of  $1 \times 10^{-10} \text{ m}$ . Compute the uncertainty in its momentum.

*Answer.* From the Heisenberg uncertainty principle, we have that

$$\begin{aligned} \Delta x \cdot \Delta p &\geq \frac{h}{4\pi} \\ \Delta p &\geq \frac{h}{4\pi \Delta x} \end{aligned}$$

$$\Delta p \geq 5.273 \times 10^{-25} \frac{\text{kg m}}{\text{s}}$$

□

- (b) Repeat the calculation for a proton confined to a region of nuclear dimensions on the order of  $1 \times 10^{-14} \text{ m}$ .

*Answer.* From the Heisenberg uncertainty principle, we have that

$$\Delta p \geq \frac{h}{4\pi\Delta x}$$

$$\Delta p \geq 5.273 \times 10^{-21} \frac{\text{kg m}}{\text{s}}$$

□

6. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet “Blackbody Radiation” on Canvas and answer the following questions.

- (a) Using the interactive graph of the spectral energy density  $\rho(\nu, T)$  as a function of the frequency  $\nu$  and temperature  $T$ , determine the frequency in Hz at which the spectral energy density peaks at a temperature of 700 K.

*Answer.*

$$5 \times 10^{13} \text{ Hz}$$

□

- (b) The cosmic background radiation, discovered in 1964 by Penzias and Wilson, can be explained by treating the universe as a blackbody. Using the interactive plot, determine the frequency (in Hz) and wavelength (in m) at which the cosmic background radiation peaks.

*Answer.*

$$\nu = 2 \times 10^{11} \text{ Hz}$$

$$\lambda = \frac{c}{\nu}$$

$$\lambda = 1.5 \times 10^{-3} \text{ m}$$

□

- (c) In which region of the electromagnetic spectrum does the peak cosmic background radiation lie?

*Answer.* In the microwave region.

□

7. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet “Photoelectric Effect” on Canvas and answer the following questions.

- (a) Copy and complete Table 1 of the worksheet.

*Answer.*

□

	Au	Mg	Pb	Na	Average value of $h$ :
Threshold frequency ( $\nu_0$ )	$1.084 \times 10^{15} \text{ Hz}$	$8.793 \times 10^{14} \text{ Hz}$	$1.034 \times 10^{15} \text{ Hz}$	$5.684 \times 10^{14} \text{ Hz}$	
Planck's constant ( $h$ )	$6.681 \times 10^{-34} \text{ J s}$	$6.553 \times 10^{-34} \text{ J s}$	$6.717 \times 10^{-34} \text{ J s}$	$6.522 \times 10^{-34} \text{ J s}$	$6.618 \times 10^{-34} \text{ J s}$

Table 1: Photoelectric data for Au, Mg, Pb, and Na.

- (b) What is the computed average value of Planck's constant, and how does this value compare to its experimental value?

*Answer.* The computed average value of Planck's constant is  $6.618 \times 10^{-34} \text{ J s}$ . It is 0.12% off from the true value of  $6.626 \times 10^{-34} \text{ J s}$ .

□

- (c) For which element is it *least* difficult to eject an electron?

*Answer.* Sodium — lowest threshold frequency means least energy required to excite an electron to the infinite energy level.

□

## 2 ???

- 10/13:
- Imagine the particle in the infinite square well bouncing back and forth against the walls classically. In the absence of friction, the particle will continue to bounce back and forth with a constant speed. What is the probability  $P(x)$  of finding this classical particle as a function of its position in the box?
    - Secondly, consider the particle to be in the quantum ground state. What is the probability  $P(x)$  of finding this quantum particle as a function of its position in the box? Give a sketch.
    - Thirdly, consider the particle to be in the quantum state  $n = 2$ . What is the probability  $P(x)$  of finding this quantum particle as a function of its position in the box? Give a sketch.
    - As the quantum state  $n$  of the particle approaches infinity, the energy and frequency of the particle become very large. What happens to the probability  $P(x)$  of finding this quantum particle as a function of its position in the box?
  - The spread or uncertainty in position and momentum may be computed by a mathematical measure of the deviation from the average position

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \quad (1)$$

and

$$\Delta p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2} \quad (2)$$

where the notation  $\langle \rangle$  was developed by Dirac to denote the expectation value. The text evaluates these uncertainties for a particle in the ground state of an infinite square well.

- Do they satisfy the Heisenberg uncertainty relation?
  - Evaluate these uncertainties for a particle in the second- and fourth-excited states (the first and second even excited states) of an infinite square well. Do they satisfy the Heisenberg uncertainty relation?
  - Compare the uncertainties in the position and momentum for the ground, second-excited, and fourth-excited states. What would you expect to happen to the uncertainties as the state  $n$  approaches infinity?
- Consider a particle in a one-dimensional infinite square well where the infinite walls are located and  $-b$  and  $+b$ . Give the time-dependent form of the ground and the first-excited states.
  - We have been examining a one-dimensional infinite square well where the infinite walls are located at  $-b$  and  $+b$ . The energy levels in this quantum system are non-degenerate, that is, for each energy, there is only one wave function. Let us place an infinite potential step between  $-b/2$  and  $+b/2$ .
    - Is the particle more likely to be in the left or the right infinite square well?
    - What are the new energy levels and wave functions of this modified system? (Hint: How are they related to the infinite square well?)
    - Are the energy levels degenerate, and if so, what is the degeneracy?
    - Are the new energies higher or lower than the box without the infinite step?
  - Consider an electron of energy  $E$  incident on the potential step where

$$V(x) = \begin{cases} 0 \text{ eV} & x < 0 \\ 8 \text{ eV} & x > 0 \end{cases}$$

Calculate the reflection coefficient  $R$  and the transmission coefficient  $T$

- When  $E = 4 \text{ eV}$ ;
- When  $E = 16 \text{ eV}$ ;

- (c) When  $E = 8 \text{ eV}$ .
6. Use the Quantum Chemistry Toolbox in Maple to complete the worksheet "Particle in a Box" on Canvas and answer the following questions.
- (a) Based on the interactive plot, does the wave function become more classical as the quantum number  $n$  increases?
  - (b) Does the energy spacing between states become more or less classical as  $n$  increases?
  - (c) Sketch the  $n = 3$  state of the particle in a box and the third molecular orbital of the hydrogen chain.
  - (d) What do you observe about the nodal patterns in part (c)?
  - (e) Based on parts (c) and (d), are the particle-in-a-box wave functions a good model for the wave functions of the hydrogen chain?