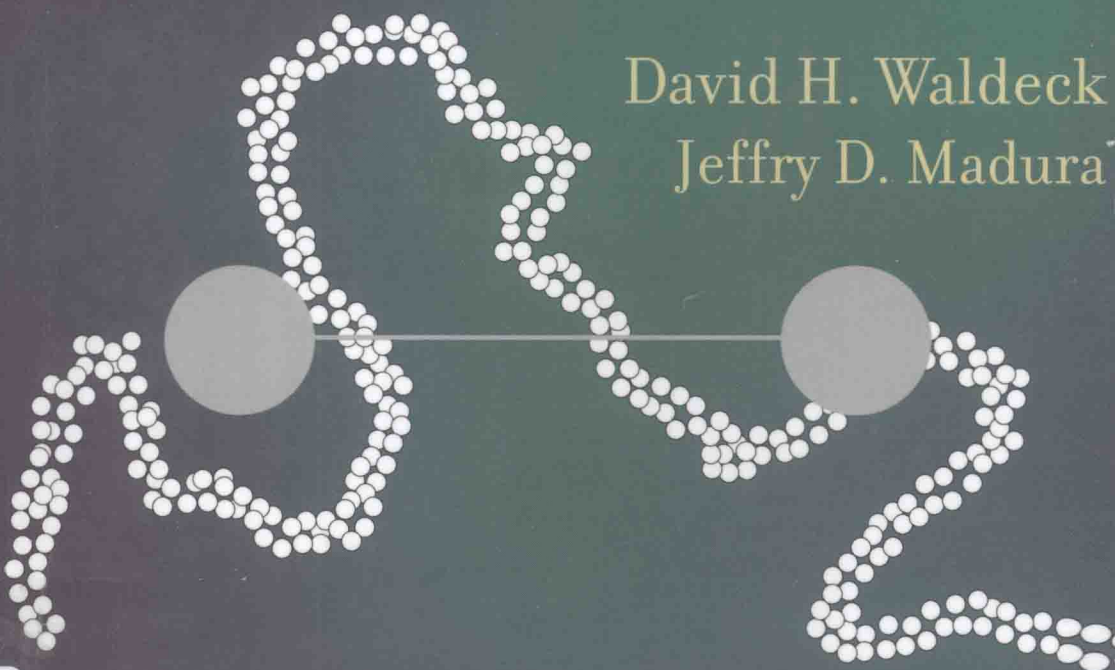


SOLUTIONS MANUAL FOR  
**PRINCIPLES  
OF PHYSICAL  
CHEMISTRY**

BY H. KUHN,  
H.D. FOERSTERLING,  
AND D.H. WALDECK

David H. Waldeck  
Jeffrey D. Madura



# **Solutions Manual for Principles of Physical Chemistry**

**by H. Kuhn, H. D. Foersterling, and D. H. Waldeck**

David H. Waldeck and Jeffry Madura



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***Library of Congress Cataloging-in-Publication Data is available.***

ISBN 978-0-470-56197-3

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

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# Chapter 1

## WAVE-PARTICLE DUALITY

### 1.1 Exercises

**E1.1)** Consider a microwave source that is generating 2.0 GHz electromagnetic radiation. Compute the wavelength of the microwaves. If this microwave source was used in an oven of width 30 cm, how many wavelengths of the microwave can be included across the oven's width.

Compute the energy per photon for the 2.0 GHz frequency. If a cup containing 250 mL of water is irradiated by this source, how many photons must be absorbed to raise the temperature of the water from 25 °C to 80 °C (a nice temperature for a cup of tea). For simplicity, assume that the water density is 1.0 g/mL, that the heat capacity is 4.184 J/(g degree), and that they do not change over the temperature range.

**Solution:** First we calculate the wavelength of a 2.0 GHz microwave and then compare it to the oven's width. The wavelength and frequency are related by  $\lambda(\text{cm}) = c(\text{cm} / \text{s}) / \nu (\text{s}^{-1})$  with  $c$  being the speed of light ( $2.998 \times 10^{10} \text{ cm s}^{-1}$ ), so

$$\begin{aligned}\lambda(\text{cm}) &= (2.998 \times 10^{10} \text{ cm s}^{-1}) / (2.0 \times 10^9 \text{ s}^{-1}) \\ &= 1.5 \times 10^1 \text{ cm} = 15 \text{ cm}\end{aligned}$$

. Hence, the oven is about  $2\lambda$  wide.

Here we calculate the energy in a 2.0 GHz photon and compare it to the energy needed to warm the water (assuming no extraneous losses). The energy and frequency are related by  $E = h\nu$ , so that the energy per photon is

$$E = (6.626 \times 10^{-34} \text{ J s})(2.0 \times 10^9 \text{ s}^{-1}) = 1.3 \times 10^{-24} \text{ J}$$

. The amount of energy the water must absorb is  $Q = mC \cdot \Delta T$ , where  $m$  is the mass of water (250. mL or 250. g),  $C$  is the heat capacity, and  $\Delta T$  is the

change in temperature  $(80 - 25)^\circ\text{C}$ . Thus  $Q = (250. \text{ g})(4.184 \text{ J / g}^\circ\text{C})(55^\circ\text{C}) = 57,530 \text{ J}$ , so that the number of 2.0 GHz photons will be

$$\frac{Q}{E} = \frac{57530 \text{ J}}{1.3 \times 10^{-24} \text{ J}} = 4.4 \times 10^{28}$$

Because we have ignored any extraneous losses (e.g., heat conduction to the container, convective cooling, etc.), this value is a lower bound.

**E1.2)** Consider an ultraviolet light source that generates 300 nm electromagnetic radiation. Compute the frequency of the ultraviolet light. If one photon of this light is absorbed by an organic molecule, how much energy does the molecule gain? Is this energy enough to break a carbon-carbon bond in the molecule? Use a 'typical' carbon-carbon bond energy of  $5.8 \times 10^{-19} \text{ J}$  for your comparison. Perform the same calculations for a photon of wavelength 600 nm and a photon of wavelength 1200 nm. Perform your comparisons using the energy units of J and of eV.

**Solution:** The wavelength and frequency are related by  $\nu = c_0/\lambda$  with  $c_0$  being the speed of light ( $2.998 \times 10^8 \text{ m s}^{-1}$ ), so  $\nu = (2.998 \times 10^8 \text{ m s}^{-1})/(300. \times 10^{-9} \text{ m}) = 9.96 \times 10^{14} \text{ s}^{-1}$ .

The energy and frequency are related by  $E = h\nu$ , so the energy per photon  $E = (6.626 \times 10^{-34} \text{ J s})(9.96 \times 10^{14} \text{ s}^{-1}) = 6.60 \times 10^{-19} \text{ J}$ .

This amount of energy is "just" sufficient to break a bond of  $5.8 \times 10^{-19} \text{ J}$ .

The corresponding energies for 600 nm and 1200 nm photons are  $6.60/2 \times 10^{-19} = 3.30 \times 10^{-19} \text{ J}$  and  $6.60/4 \times 10^{-19} = 1.65 \times 10^{-19} \text{ J}$ , neither of which is sufficient to break the typical carbon-carbon double bond.

The corresponding energies in eV ( $1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}$ ) are 4.12 eV (300 nm light), 2.06 eV (600 nm light), and 1.03 eV (1200 nm light).

**E1.3)** If a source of 58.5 nm wavelength photons (typical of that used in photoelectron spectroscopy) irradiates a sample of neutral hydrogen atoms, it is possible to eject electrons from the atoms and generate protons. The most stable hydrogen atoms (i.e., ground state hydrogen atoms) bind the electron with about 13.6 eV of energy. Convert the 13.6 eV binding energy into Joules. Determine the energy of the 58.5 nm photon. Use energy conservation to deduce the kinetic energy of the photo-ejected electron. If you were trying to measure the electron's kinetic energy in an apparatus analogous to that illustrated in Figure 1.2, what stopping voltage would you need to apply? Comment on why electron Volts (eV) might be a convenient energy unit for scientists doing photoelectron spectroscopy.

**Solution:** First we calculate the energy of a 58.5 nm photon and compare it to the binding energy of an electron in the H-atom. Using  $E = h\nu$  we find that

$$\begin{aligned}
 E &= h\nu = \frac{hc}{\lambda} \\
 &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m s}^{-1})}{58.5 \times 10^{-9} \text{ m}} \\
 &= 3.40 \times 10^{-18} \text{ J} \quad \text{for the photon energy.}
 \end{aligned}$$

The binding energy of the electron to the proton in the H-atom is

$$13.6 \text{ eV} \left( \frac{1.60 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right) = 2.18 \times 10^{-18} \text{ J}.$$

When the H-atom absorbs the light, the photon energy is converted into electronic energy, placing the electron above the ionization limit and it can escape from the atom. The kinetic energy of the photoejected electron is given by the difference between this absorbed energy and its initial state binding energy, hence the difference between these two energies or

$$(3.40 - 2.18) \times 10^{-18} \text{ J} = 1.22 \times 10^{-18} \text{ J}.$$

To stop the electrons, the applied potential must be made at least as large as the electron kinetic energy. The kinetic energy computed above corresponds to an energy of  $1.22 \times 10^{-18} \text{ J} \left( \frac{1 \text{ eV}}{1.60 \times 10^{-19} \text{ J}} \right) = 7.62 \text{ eV}$ . Hence the stopping potential would be 7.62 V.

The kinetic energies of the ejected electrons correspond to energies of 1 – 10 eV (a conveniently sized number because of its direct relation to the voltage difference used in detecting the photoelectrons).

**E1.4)** Consider the kinetic energy calculations in E1.3. Perform a similar calculation but use a photon wavelength of 23 nm. Perform a similar calculation but use a photon wavelength of 100 nm. Compare your three values of the kinetic energy and comment on them.

Assuming that the electron is bound by 13.6 eV, determine the largest wavelength that a photon may have if it is to eject an electron from a hydrogen atom.

**Solution:** For the 23 nm photon, we calculate

$$\begin{aligned}
 E &= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m s}^{-1})}{23. \times 10^{-9} \text{ m}} \\
 &= 8.6 \times 10^{-18} \text{ J} \quad \text{per photon}
 \end{aligned}$$

and for the 100 nm photon we find

$$\begin{aligned}
 E &= \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m s}^{-1})}{100. \times 10^{-9} \text{ m}} \\
 &= 1.99 \times 10^{-18} \text{ J}
 \end{aligned}$$



The kinetic energies of the photoejected electrons resulting from these wavelengths are  $-1.9 \times 10^{-19}$  J (100 nm) and  $6.4 \times 10^{-18}$  J (23 nm). The negative value indicates that an electron can not be ejected from a H atom by 100 nm light. The increase in kinetic energy with shorter wavelengths results because the shorter wavelength photons have a higher energy. The table shows how the photon energy and the kinetic energy of the electron increase with decreasing wavelength.

$\lambda / \text{nm}$	100	58.5	23
$E / 10^{-18} \text{J}$	1.99	3.40	8.6
kinetic energy / J	—	1.22	6.4

The longest wavelength photon that can photoionize an H-atom is that corresponding to a light energy of 13.6 eV, or

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m s}^{-1})}{(13.6 \text{ eV}) \left( \frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} \right)} = 91.2 \text{ nm}$$

**E1.5)** Consider an electron with a kinetic energy of 1.0 eV (i.e., it has been accelerated across a 1 Volt potential difference).

Compute the momentum of this electron. Compare this momentum to that of a 'typical'  $\text{N}_2$  gas molecule at room temperature (consider the gas molecule to have a speed of 500 m/s).

Compute this electron's speed. At what fraction of light speed ( $3.00 \times 10^8$  m/s) is the electron moving?

Compute this electron's wavelength. Compare this wavelength to the diameter of a hydrogen atom (*ca.* 128 pm). Perform this same calculation for a 10 eV electron and a 100 eV electron. Comment on the trends in your values. How many electron wavelengths can fit into a hydrogen atom at these different energies?

**Solution:** The momentum is related to the kinetic energy by  $E_{kin} = p^2/(2m)$ , so we find the momentum by

$$\begin{aligned} p &= \sqrt{2mE_{kin}} = \sqrt{2(9.11 \times 10^{-31} \text{ kg})(1.0 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})} \\ &= 5.4 \times 10^{-25} \text{ kg m s}^{-1} \end{aligned}$$

The momentum of a "typical" gas phase nitrogen molecule ( $\text{N}_2$ ) is

$$\begin{aligned} p &= mv = (4.650 \times 10^{-26} \text{ kg})(500 \text{ m s}^{-1}) \\ &= 2.32 \times 10^{-23} \text{ kg m s}^{-1} \end{aligned}$$

which is about 43 times greater than the momentum of the electron. While this speed is significant, it is still small enough to neglect relativistic effects.

The electron's speed is

$$v = \frac{p}{m} = \frac{5.403 \times 10^{-25} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 5.931 \times 10^5 \text{ m/s}$$

This value is 0.002, or 0.2%, of the speed of light!

The electron's wavelength can be calculated using the de Broglie relationship, so that

$$\Lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_{kin}}} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{5.40 \times 10^{-25} \text{ kg m s}^{-1}} = 1.23 \text{ nm}$$

where we have used  $5.40 \times 10^{-25} \text{ kg m s}^{-1}$  for the momentum of the electron. This wavelength is 9 to 10 times larger than the characteristic size of an H atom.

For 10 eV electrons  $\Lambda = 0.388 \text{ nm}$ , and for 100 eV electrons  $\Lambda = 123 \text{ pm}$ . The electron wavelength decreases as the square root of its kinetic energy and a 100 eV electron has a wavelength that is similar to the diameter of an H-atom.

**E1.6)** A typical value for a particle's kinetic energy at  $25^\circ\text{C}$  is  $6.21 \times 10^{-21} \text{ J}$ . Use this value of the kinetic energy to estimate the speed of spheres with different masses; i.e.

- a) ping pong ball (2.60 g)
- b) a  $10.0 \mu$  diameter polystyrene bead ( $0.300 \text{ g/cm}^3$ )
- c) a  $50.0 \text{ nm}$  radius colloidal particle of Ag ( $10.5 \text{ g/cm}^3$ )
- d) Buckminster fullerene ( $\text{C}_{60}$ ) ( $0.720 \text{ kg/mol}$ )
- e) He (4.0 amu)

Use these speeds and masses to estimate the de Broglie wavelength of these spheres. Comment on the trend in your wavelengths. For which, if any, of these particles would you expect their wave properties to be important. If the kinetic energy was decreased by 100 times, how would your wavelengths change? Do you think that wave properties would be important under these circumstances?

**Solution:** The speed and kinetic energy are related by

$$E_{kin} = \frac{1}{2}mv^2 \quad \text{so that} \quad v = \sqrt{2E_{kin}/m}$$

Hence we find

- a) for the ping pong ball that

$$v = \sqrt{2(6.21 \times 10^{-21} \text{ J}) / (2.6 \times 10^{-3} \text{ kg})} = 2.19 \times 10^{-9} \text{ m/s}$$

- b) for the polystyrene bead we first compute its mass by

$$m = \left(\frac{4}{3}\right) \pi \left(\frac{10 \times 10^{-6}}{2}\right)^3 \text{ m}^3 \left(0.3 \times 10^3 \frac{\text{kg}}{\text{m}^3}\right) = 1.57 \times 10^{-13} \text{ kg}$$

and then find its speed by

$$v = \sqrt{2(6.21 \times 10^{-21} \text{ J}) / (1.57 \times 10^{-13} \text{ kg})} = 2.81 \times 10^{-4} \text{ m/s}$$

c) for the silver colloid particle we first compute its mass by

$$m = \left(\frac{4}{3}\right) \pi (50 \times 10^{-9})^3 \text{ m}^3 \left(10.5 \times 10^3 \frac{\text{kg}}{\text{m}^3}\right) = 5.50 \times 10^{-18} \text{ kg}$$

and then find its speed by

$$v = \sqrt{2(6.21 \times 10^{-21} \text{ J}) / (5.50 \times 10^{-18} \text{ kg})} = 5.79 \times 10^{-2} \text{ m/s}$$

d) for the Buckminster fullerene that

$$v = \sqrt{2 \left( \frac{6.022 \times 10^{23}}{0.720 \text{ kg}} \right) (6.21 \times 10^{-21} \text{ J})} = 102 \text{ m/s}$$

e) for the He atom that

$$v = \sqrt{2 \left( \frac{6.21 \times 10^{-21} \text{ J}}{4 \text{ amu}} \right) \left( \frac{1 \text{ amu}}{1.660 \times 10^{-27} \text{ kg}} \right)} = 1370 \text{ m/s}$$

To find the de Broglie wavelengths  $\Lambda$ , we use the fundamental relation

$$\Lambda = \frac{h}{mv}$$

By way of example, we consider the Ag colloid particle and calculate

$$\Lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{(5.50 \times 10^{-18} \text{ kg})(5.79 \times 10^{-2} \text{ m/s})} = 2.08 \times 10^{-15} \text{ m}$$

Proceeding in a like manner for each of the cases above we find

particle	$\Lambda / \text{m}$
ping-pong ball	$1.16 \times 10^{-22}$
polystyrene bead	$1.50 \times 10^{-17}$
Ag particle	$2.08 \times 10^{-15}$
fullerene, $\text{C}_{60}$	$5.43 \times 10^{-12}$
He atom	$7.28 \times 10^{-11}$

These numbers suggest that it is not necessary to consider the wave nature of these particles under these conditions; i.e., the wavelength is small compared to the size of structures from which it might collide so that diffraction is not important.

**E1.7)** Describe the photoelectric effect experiment.

- Provide a sketch of the apparatus.
- State the implications of the experiment.
- Describe what is observed in the experiment and how it relates to the experiment's implications.

**Solution:** a) Figure 1.2 (a) of the textbook gives a schematic of the photoelectric effect apparatus.

b) The principal implication is that light can behave as a particle.

c) The two observations are that the stopping potential depends on the light frequency and not on intensity, while the number of photoelectrons depends on light intensity and not frequency. These results are exactly the opposite of the behavior that one expects for a classical wave, and are exactly what would be expected if the light behaved as a particle.

**E1.8)** Describe an experiment, other than the photoelectric effect experiment, that demonstrates the particle nature of light. Provide a sketch of the apparatus you would use, a clear description of what you expect to observe and how it demonstrates the particle nature of light.

**Solution:** The Compton effect demonstrates the particle nature of light. In a Compton effect measurement, light interacts with an atom which is initially at rest. After the interaction, the light is moving away from the atom at an angle, and the atom is also in motion. The experimentally observed angles are described mathematically using the conservation of linear momentum and the conservation of energy principles applicable for particles rather than waves. If light behaved as a wave, the atomic motion would be a simple oscillation about the initial point. The inelastic scattering of the light from the material, causing a frequency shift (wavelength shift).

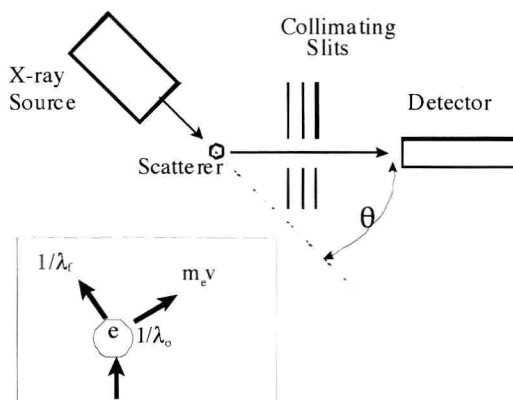


Figure E1.8a This diagram illustrates the concepts of a Compton scattering experiment.

The apparatus sketch indicates a beam of X-rays that are incident on a material such as graphite. The X-rays collide with the electrons and experience a shift in energy and angle of trajectory. The scattered X-rays are detected at a well-defined angle using a set of lead collimating slits. The diagram on the right has an inset that shows a schematic diagram for the scattering process. Assuming that the particles have only kinetic energy and by requiring both the total energy and momentum to be conserved in the scattering process, one can

deduce at what angle the X-ray must be scattered if it loses a certain amount of energy. The equation for this angle is given below, in terms of the shift in the X-ray photon's wavelength

$$\Delta\lambda=\left(\frac{h}{m_e c}\right)(1-\cos\theta)$$

Note that backscattering (at the angle  $\theta = \pi$ ) gives the largest effect. The figures shown below give the spectrum of an X-ray source whose radiation is scattered from a graphite crystal. The data on the left shows photographic images of the scattered X-ray source at three different angles. Densitometer tracings of the spectral intensities are shown on the right side. The data show a clear red shift of some of the spectral lines with increasing scattering angle. Not all of the X-ray lines scatter inelastically. The elastically scattered lines do not shift their energy.

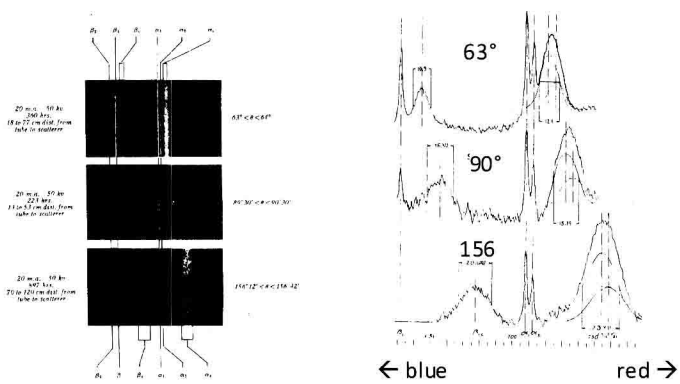


Figure E8.1b These data for the scattering of X-rays from graphite are taken from Dumond, Rev. Mod. Phys. 5 (1933) 1.

See *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles* by R. Eisberg and R. Resnick (Wiley, Ny, 1974) for more discussion of the Compton Effect.

NOTE: Other answers to this question are possible.

**E1.9)** Consider the diffraction of photons, electrons, and neutrons from an aperture with diameter  $d$ . Consider the case where  $d$  is 1 cm and the case where it is  $10^{-7}$  cm.

(a) If you direct a light beam onto the aperture, how large must the wavelength be so that diffraction can be observed? What is the frequency of the light you found?

(b) If you direct an electron beam onto the aperture, how large must the speed of the electrons be so that diffraction can be observed?

(c) We assume that the de Broglie relationship holds not only for electrons, but also for any particle. How large must the speed of the neutrons be for the aperture to diffract a neutron beam?

Do not be disturbed if the answers to these exercises are not experimentally feasible. The problems should help clarify the content of Equations (1.7) and (1.9).

**Solution:** Diffraction occurs when the wavelength of the wave is approximately the same as the size of the aperture. Considering the size of the aperture as 1 cm and  $10^{-7}$  cm,

a) For an aperture of 1 cm, the wavelength is 1 cm, and the corresponding frequency is  $2.998 \times 10^{10} \text{ cm s}^{-1} / 1 \text{ cm} = 2.998 \times 10^{10} \text{ s}^{-1}$ . For a  $10^{-7}$  cm aperture, the wavelength is  $10^{-7}$  cm, and the corresponding frequency is  $2.998 \times 10^{10} \text{ cm s}^{-1} / 10^{-7} \text{ cm} = 2.998 \times 10^{17} \text{ s}^{-1}$ .

b) We need to find the electron's wavelength through the de Broglie relationship,  $\Lambda = h/(mv)$ . For a 1 cm wavelength  $v = (6.626 \times 10^{-34} \text{ J s}) / (9.11 \times 10^{-31} \text{ kg}) (0.01 \text{ m}) = 7.273 \times 10^{-2} \text{ cm s}^{-1}$ . For a  $10^{-7}$  cm wavelength  $v = (6.626 \times 10^{-34} \text{ J s}) / (9.11 \times 10^{-31} \text{ kg}) (10^{-9} \text{ m}) = 7.273 \times 10^5 \text{ cm s}^{-1}$ .

c) We need to find the neutrons's wavelength through the de Broglie relationship,  $\Lambda = h/(mv)$ . For a 1 cm wavelength  $v = (6.626 \times 10^{-34} \text{ J s}) / (1.675 \times 10^{-27} \text{ kg}) (0.01 \text{ m}) = 3.956 \times 10^{-5} \text{ cm s}^{-1}$ . For a  $10^{-7}$  cm wavelength  $v = (6.626 \times 10^{-34} \text{ J s}) / (1.675 \times 10^{-27} \text{ kg}) (10^{-9} \text{ m}) = 3.956 \times 10^2 \text{ cm s}^{-1}$ .

**E1.10)** Describe an experiment that demonstrates the wave nature of matter. Make a sketch that illustrates your observations; *i.e.*, measured data. Draw a sketch of an experimental apparatus that shows the essential components needed in making such a measurement. Explain in words how this experiment demonstrates the wave nature of matter.

**Solution:** Low energy electron and/or neutron diffraction experiments both are examples of the wave nature of particles. In both cases a beam of the particles is focused onto a target, which diffracts the particles towards an angle scannable detector. The reflected particle intensity depends on angle because the wavelength of the particle is of the same magnitude as the spacing between atoms. The schematic diagram shows an electron beam impinging on a Ni crystal and diffracting. By scanning the detector over different angles the electron current (called the collector current below) can be measured.

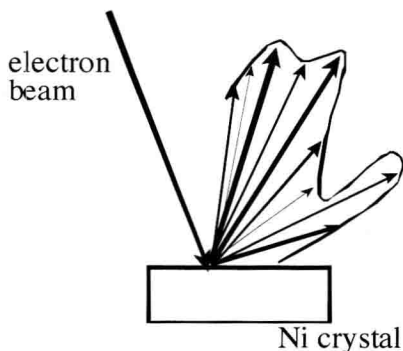


Figure E1.10a- The diagram aims to illustrate that a beam of electrons impinges on a nickel crystal. Rather than simple specular reflection, the electron beam diffracts from the surface.

Davisson and Germer reflected a beam of electrons off of a crystalline Ni target and observed that the electrons diffracted; i.e., produced an intensity pattern that varied in space instead of falling off monotonically from the specular angle. The figure shows data that they collected as a function of bias potential at different scattering angles. For the different detector angles, the peak intensity occurs at different incident electron wavelengths (hence the bombarding potential). Classical particles would not show such a dependence. Diffraction is a wave characteristic and this observation demonstrates that particles, namely electrons, can exhibit wave properties.

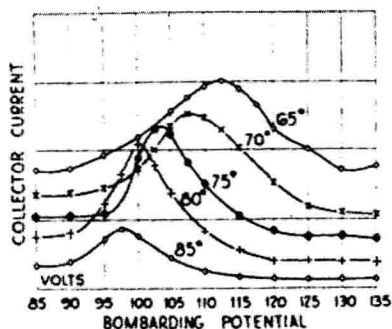


Figure E1.10b. Collector current (detector current) vs. bombarding potential (which determines the incident electron's wavelength) showing plane grating beams near grazing in  $\{110\}$ -azimuth. Taken from Davisson and Germer, *Phys. Rev.* 30 (1927) 705.

The experiment reported by C. Davisson and L. H. Germer (*Phys. Rev.* 30 (1927) 705) also provides an interesting example in serendipity. These initial

investigations did not reveal much structure in the diffraction, however, they inadvertently heated the sample, which caused the Ni to recrystallize into larger crystallites upon cooling. They were observant enough to recognize what had occurred. The Figure shows the data that they obtained before and after the "accident"; i.e., before and after crystal growth has occurred.

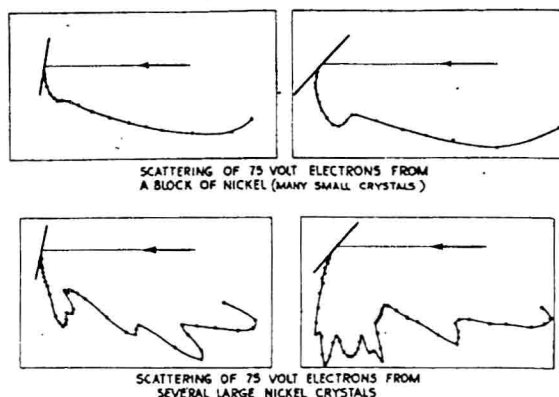


Figure E1.10c –The scattered intensity pattern after annealing (lower panel) reveals substructure associated with diffraction.

**E1.11)** If photons are particles they have momentum. Compute the momentum of a 590 nm photon. Compare this momentum to that of a Na atom moving at a speed of 900 m/s, which is a typical value at 1200 °C. Assume that 590 nm photons collide head on with the sodium atom so that the momentum exchange is twice the photon momentum, how many photons are needed to 'stop' the sodium atom?

**Solution:** Again we employ the de Broglie relationship,  $p = h/\lambda$ , and find that the momentum of a 590 nm photon is

$$p_{590} = \frac{6.626 \times 10^{-34} \text{ J s}}{590 \times 10^{-9} \text{ m}} = 1.123 \times 10^{-27} \text{ kg m s}^{-1}$$

This photon momentum should be compared with the sodium atom's momentum, which is

$$p_{Na} = \left( \frac{22.989 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg} \right) (900 \text{ m/s}) = 3.436 \times 10^{-23} \text{ kg m s}^{-1}$$

Thus interactions with about 30,600 photons would be required to slow a sodium atom to a stop. Processes of this sort are used in the cooling and trapping of atoms (see Nobel Prize of Physics, 1997).



**E1.12)** Imagine performing a photoelectron experiment on single hydrogen atoms, in a chamber where the atoms are surrounded by a thousand electron detectors (numbered *ed1* through *ed1000*), so that all sides (all  $4\pi$  steradians) are sensed and the detected electron's position can be reported. In more technical language, imagine measuring the full angular distribution of photoejected electrons. In addition, assume that the hydrogen atoms are in their ground electronic state, and that the photons irradiate the sample isotropically with an energy much higher than the ionization energy of the hydrogen atom.

(a) If the experiment is performed on a single hydrogen atom, what is the probability that *ed375* detects the photoejected electron? If the experiment is performed on one-hundred hydrogen atoms in succession, what is the probability that *ed375* detects the first photoejected electron? What is the probability that *ed375* detects any photoelectron?

(b) Imagine a related experiment in which hydrogen atoms that are initially excited are injected into a chamber and they emit light. Perform experiments of the same type as in part (a) but detecting photons instead of electrons. Does your analysis change? Explain!

**Solution:** a) The photoelectrons should be emitted with equal probability into all  $4\pi$  steradians. The probability of *ed375* detecting the photoejected electron or the first electron is thus  $1/1000$ . If done 100 times in succession, the probability is now  $100 (1/1000) = 0.10$  for *ed375* to detect any electron.

b) Assuming that photoelectrons and photons are both emitted isotropically (independently of direction) there is no change in the analysis.

## 1.2 Problems

**P1.1)** Consider the following data, taken from O. W. Richardson and K. T. Compton, *Phil. Mag.* 24 (1913) 575, for the photoemission of electrons from a metal substrate.  $E_{kin}$  is the kinetic energy of the photoelectrons and  $\lambda$  is the wavelength of the light. Analyze these data using a least squares analysis. Find the work function  $E_{work}$  of the metal and determine a value for Planck's constant. The work function is the minimum energy that is needed to remove an electron from the metal and place it at the detector some macroscopic distance away.

Sodium		Copper	
$E_{kin}/\text{eV}$	$\lambda/\text{cm}$	$E_{kin}/\text{eV}$	$\lambda/\text{cm}$
0.60	$43.6 \times 10^{-6}$	0.35	$26.0 \times 10^{-6}$
1.00	$36.6 \times 10^{-6}$	0.48	$25.4 \times 10^{-6}$
1.50	$31.3 \times 10^{-6}$	0.73	$23.0 \times 10^{-6}$
2.30	$25.4 \times 10^{-6}$	1.02	$21.0 \times 10^{-6}$
3.00	$21.0 \times 10^{-6}$	1.25	$20.0 \times 10^{-6}$

**Solutions:** In analogy to the discussion in 1.2.2.5, we plot the kinetic energy versus the photon frequency  $\nu = c/\lambda$ . We begin by constructing a data table