

Third Edition

Solutions Manual for
**Principles of
Physical Chemistry**

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WILEY

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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 °C), 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 $\lambda = c_0/\nu$ with c_0 being the speed of light (2.998×10^{10} cm s⁻¹), so

$$\lambda = \frac{2.998 \times 10^{10} \text{ cm s}^{-1}}{2.0 \times 10^9 \text{ s}^{-1}} = 1.5 \times 10^1 \text{ cm} = 15.0 \text{ cm}$$

Hence, the oven is about 2λ 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

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

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 ΔT is the change in temperature (80 – 25) °C. Thus

$$Q = 250 \text{ g} \cdot 4.184 \text{ J g}^{-1} \text{ °C}^{-1} \cdot 55 \text{ °C} = 57.530 \text{ kJ}$$

so that the number of 2.0 GHz photons will be

$$\frac{Q}{E} = \frac{57.530 \text{ kJ}}{1.3 \times 10^{-24} \text{ J}} = 4.4 \times 10^{28}$$

Because we have ignored any extraneous losses (e.g., heat conduction to the container and convective cooling), 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 5.8×10^{-19} 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 (2.998×10^8 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 and 1200 nm photons are $\frac{1}{2} \cdot 6.60 \times 10^{-19} = 3.30 \times 10^{-19} \text{ J}$ and $\frac{1}{4} \cdot 6.60 \times 10^{-19} = 1.65 \times 10^{-19} \text{ J}$, 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** Consider an electron with a kinetic energy of 1.0 eV (i.e., it has been accelerated across a 1 V potential difference). Compute the momentum $p = mv$ of this electron. Compare this momentum to that of a “typical” 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 ($3.00 \times 10^8 \text{ m/s}$) 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 $p = mv$ is related to the kinetic energy by $E_{\text{kin}} = \frac{1}{2}mv^2 = p^2/(2m)$, so we find the momentum by

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

The momentum of a “typical” gas-phase nitrogen molecule (N_2) is

$$\begin{aligned} p_{\text{N}_2 \text{ molecule}} &= mv = 4.650 \times 10^{-26} \text{ kg} \cdot 500 \text{ m s}^{-1} \\ &= 2.32 \times 10^{-23} \text{ kg m s}^{-1} \end{aligned}$$

which is about 43 times greater than the momentum of the electron.

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! While this speed is significant, it is still small enough to neglect relativistic effects.

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

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

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.

- E1.4** A typical value for a particle’s kinetic energy at 25 °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)
 - a 10.0 μ diameter polystyrene bead ($0.300 \text{ g/cm}^3 = 300 \text{ kg/m}^3$)
 - a 50.0 nm radius colloidal particle of Ag ($10.5 \text{ g/cm}^3 = 10,500 \text{ kg/m}^3$)
 - Buckminster fullerene (C_{60}) (0.720 kg/mol)
 - He atom ($4.0 \text{ g/mol} = 4.0 \times 10^{-3} \text{ kg/mol}$).

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

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

Hence we find

a) for the ping pong ball

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

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

$$m = \left(\frac{4}{3}\right) \pi \left(\frac{10 \times 10^{-6}}{2}\right)^3 \text{ m}^3 \left(300 \frac{\text{kg}}{\text{m}^3}\right) = 1.57 \times 10^{-13} \text{ kg}$$

and then find its speed by

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

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

$$m = \left(\frac{4}{3}\right) \pi (50 \times 10^{-9})^3 \text{ m}^3 \left(10500 \frac{\text{kg}}{\text{m}^3}\right) = 5.50 \times 10^{-18} \text{ kg}$$

and then find its speed by

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

d) for the Buckminsterfullerene we first compute its mass by

$$m = \frac{0.720 \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.19 \times 10^{-24} \text{ kg}$$

and then find its speed by

$$v = \sqrt{\frac{2 \cdot 6.21 \times 10^{-21} \text{ J}}{1.19 \times 10^{-24} \text{ kg}}} = 102 \text{ m/s}$$

e) for the He atom we first compute its mass by

$$m = \frac{4.0 \times 10^{-3} \text{ kg mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 6.64 \times 10^{-27} \text{ kg}$$

and then find its speed by

$$v = \sqrt{\frac{2 \cdot 6.21 \times 10^{-21} \text{ J}}{6.64 \times 10^{-27} \text{ kg}}} = 1370 \text{ m/s}$$

To find the de Broglie wavelengths Λ , we use the fundamental relation

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

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

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

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

particle	Λ /m
ping-pong ball	1.16×10^{-22}
polystyrene bead	1.50×10^{-17}
Ag particle	2.08×10^{-15}
fullerene, C ₆₀	5.43×10^{-12}
He atom	7.28×10^{-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.

E1.5 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

- Fig. 1.2a of the textbook gives a schematic of the photoelectric effect apparatus.
- The principal implication is that light can behave as a particle.
- 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.

E1.6 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.

- 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?
- If you direct an electron beam onto the aperture, how large must the speed of the electrons be so that diffraction can be observed?
- 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 goal is to 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,

- 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 $2.998 \times 10^{10} \text{ cm s}^{-1} / 10^{-7} \text{ cm} = 2.998 \times 10^{17} \text{ s}^{-1}$.
- We need to find the electron's wavelength through the de Broglie relationship, $\Lambda = h/(mv)$. For a 1 cm wavelength $v = (6.626 \times 10^{-34} \text{ J s}) / (9.11 \times 10^{-31} \text{ kg} \cdot 0.01 \text{ m}) = 7.273 \times 10^{-2} \text{ cm s}^{-1}$. For a 10^{-7} cm wavelength $v = (6.626 \times 10^{-34} \text{ J s}) / (9.11 \times 10^{-31} \text{ kg}) (10^{-9} \text{ m}) = 7.273 \times 10^5 \text{ cm s}^{-1}$.
- We need to find the neutron's wavelength through the de Broglie relationship, $\Lambda = h/(mv)$. For a 1 cm wavelength $v = (6.626 \times 10^{-34} \text{ J s}) / (1.675 \times 10^{-27} \text{ kg} \cdot 0.01 \text{ m}) = 3.956 \times 10^{-5} \text{ cm s}^{-1}$. For a 10^{-7} cm wavelength $v = (6.626 \times 10^{-34} \text{ J s}) / (1.675 \times 10^{-27} \text{ kg} \cdot 10^{-9} \text{ m}) = 3.956 \times 10^2 \text{ cm s}^{-1}$.

E1.7 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,

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

and find that the momentum of a photon is

$$p = \frac{h}{\lambda}$$

Thus for a wavelength of $\lambda = 590 \text{ nm}$ we obtain

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

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

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

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 *Laser Trapping of Neutral Particles*, by S. Chu, Scientific American, February 1992, p. 71).

E1.8 Imagine you build an experimental apparatus in which you can use a photon to eject an electron from an H-atom; i.e., absorb a photon and generate a proton and a free electron. This is called a photoelectron experiment. Imagine that you perform this 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 4π 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 photons of energy much higher than that which is needed to eject an electron from the hydrogen atom.

- 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?
- 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

- The photoelectrons should be emitted with equal probability into all 4π 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.
- Assuming that photoelectrons and photons are both emitted isotropically (independently of direction) there is no change in the analysis.

E1.9 Using Fig. 1.6, calculate the distance x between the intensity maxima, P_1 and P_2 , in terms of the wavelength of the incident light and the parameters d and a . If your apparatus has $d = 1.7 \mu\text{m}$ and $a = 1 \text{ m}$, and you illuminate the slit with monochromatic light of $\lambda = 640 \text{ nm}$ (red light of a laser pointer), what is the distance x in the figure?

Solutions

Using Fig. E1.9 we can calculate the distance x between the intensity maxima, P_1 and P_2 . The point P_1 is the location where a light ray from each slit traverses the same distance to the screen. For this reason the phases of the light waves arriving at point P_1 are the same, and we obtain an intensity maximum at point P_1 . The point P_2 is the position where the light ray from the lower slit travels an extra distance of one wavelength and constructively interferes with a light ray from the upper slit. Thus, at point P_2 we find the next intensity maximum: the distances r_1 and r_2 differ by λ ; thus, the phases of the two waves arriving at point P_2 are the same.

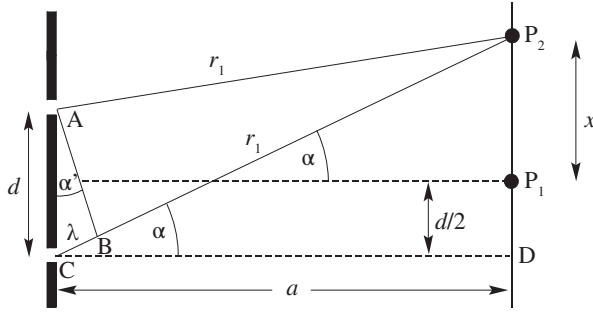


Figure E1.9 Diffraction of light on a double slit.

We restrict our consideration to the case that the distance d between the slits is much smaller than the distance between the points P_1 and P_2 . In this case the angle ABC is approximately 90° , and we can set $\alpha' \approx \alpha$ (the triangle ABC is approximately a right triangle). Then we obtain

$$\frac{x + d/2}{a} = \tan \alpha \text{ (triangle } P_2 CD), \quad \frac{\lambda}{d} = \sin \alpha \text{ (triangle } ABC) \quad (1E9.1)$$

In addition, we can use trigonometry to relate the tangent of the angle to its sine, so that

$$\tan \alpha = \frac{\sin \alpha}{\cos \alpha} = \frac{\sin \alpha}{\sqrt{1 - \sin^2 \alpha}}$$

Now we can combine these results to relate the separation x between the intensity maxima to the wavelength and the parameters d and a

$$\frac{x + d/2}{a} = \frac{\lambda/d}{\sqrt{1 - (\lambda/d)^2}} \quad (1E9.2)$$

We can rearrange this expression to solve for x and obtain

$$x = \frac{a\lambda}{d} \frac{1}{\sqrt{1 - \left(\frac{\lambda}{d}\right)^2}} - \frac{d}{2}$$

Because the distance x is much larger than $d/2$, we can simplify this expression as

$$x = \frac{a\lambda}{d} \frac{1}{\sqrt{1 - \left(\frac{\lambda}{d}\right)^2}}$$

As an example, we illuminate a double slit of width $d = 1.7 \mu\text{m}$ with the light of a red laser pointer ($\lambda = 640 \text{ nm}$). For a screen at a distance of $a = 1 \text{ m}$ we calculate

$$x = \frac{(1 \text{ m} \cdot 640 \text{ nm})}{1.7 \mu\text{m}} \frac{1}{\sqrt{1 - \left(\frac{640 \text{ nm}}{1.7 \mu\text{m}}\right)^2}} = 0.376 \text{ m} \cdot 1.079 = 40.6 \text{ cm}$$

We can solve this equation for the wavelength λ .

$$\lambda = \frac{a}{xd} \frac{1}{\sqrt{1 - \left(\frac{\lambda}{d}\right)^2}}$$

Note that the remaining term with λ/d is a correction term, and we can approximate it by setting $\tan \alpha \approx \sin \alpha$ in Equation (1E9.1) leading to

$$\frac{x}{a} = \frac{\lambda}{d} \quad (1E9.3)$$

and

$$\lambda = \frac{xd}{a} \sqrt{1 - \left(\frac{\lambda}{d}\right)^2} = \frac{xd}{a} \sqrt{1 - \left(\frac{x}{a}\right)^2}$$

With the data $a = 1 \text{ m}$, $d = 1.7 \times 10^{-6} \text{ m}$, and $x = 40.6 \text{ cm}$ from our example for λ we obtain

$$\lambda = \frac{0.406 \text{ m} \cdot 1.7 \times 10^{-6} \text{ m}}{1 \text{ m}} \sqrt{1 - \left(\frac{0.406 \text{ m}}{1 \text{ m}}\right)^2} = 690 \times 10^{-9} \text{ m} \cdot 0.914 = 631 \text{ nm}$$

This is less than the expected 640 nm by 1.4%.

We can improve the calculation by using Equation (1E9.2) instead of Equation (1E9.3)

$$\frac{x}{a} = \frac{\lambda}{d} \frac{1}{\sqrt{1 - \left(\frac{\lambda}{d}\right)^2}} = \frac{\lambda}{d} \frac{1}{\sqrt{1 - \left(\frac{x}{a}\right)^2}}$$

or

$$\frac{\lambda}{d} = \frac{x}{a} \sqrt{1 - \left(\frac{x}{a}\right)^2}$$

leading to the improved equation

$$\lambda = \frac{xd}{a} \sqrt{1 - \left(\frac{\lambda}{d}\right)^2} = \frac{xd}{a} \sqrt{1 - \left[\left(\frac{x}{a}\right)^2 \left(1 - \left(\frac{x}{a}\right)^2\right)\right]}$$

With the data $a = 1 \text{ m}$, $d = 1.7 \times 10^{-6} \text{ m}$, and $x = 40.6 \text{ cm}$ for λ we obtain the correct value:

$$\lambda = \frac{0.406 \text{ m} \cdot 1.7 \times 10^{-6} \text{ m}}{1 \text{ m}} \cdot \sqrt{1 - \left[\left(\frac{0.406 \text{ m}}{1 \text{ m}}\right)^2 \left(1 - \left(\frac{0.406 \text{ m}}{1 \text{ m}}\right)^2\right)\right]} = 690 \times 10^{-9} \text{ m} \cdot 0.928 = 640 \text{ nm}$$

Note that optical measurements are very precise and it is a good choice to use equally precise equations to describe the experiments.

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 λ is the wavelength of the light. Analyze these data using a least squares analysis. Find the workfunction E_{work} of the metal and determine a value for Planck's constant. The workfunction 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}/eV	λ/nm	E_{kin}/eV	λ/nm
0.60	436	0.35	260
1.00	366	0.48	254
1.50	313	0.73	230
2.30	254	1.02	210
3.00	210	1.25	200

Solutions

In analogy to the discussion in Section 1.2.2.5, we plot the kinetic energy versus the photon frequency $\nu = c/\lambda$. We begin by constructing a data table for an electron's maximum kinetic energy and the frequency of the light for each metal (Fig. P1.1). By way of example, we calculate the frequency for light with a wavelength of $43.6 \times 10^{-6} \text{ cm} = 43.6 \times 10^{-8} \text{ m}$, as

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{43.6 \times 10^{-8} \text{ m}} = 6.88 \times 10^{14} \text{ s}^{-1}$$

and for a kinetic energy $E_{\text{kin}} = 0.60 \text{ eV}$ we find

$$E_{\text{kin}} = 0.60 \text{ eV} \cdot \frac{1.602 \times 10^{-19} \text{ J}}{1 \text{ eV}} = 0.96 \times 10^{-19} \text{ J}$$

Proceeding in like manner, for sodium we find the values in the table

$E_{\text{kin}} / \text{eV}$	λ / nm	$E_{\text{kin}} / 10^{-20} \text{ J}$	$\nu / 10^{14} \text{ s}^{-1}$
0.60	436	9.6	6.88
1.00	366	16.0	8.19
1.50	313	24.0	9.58
2.30	254	36.9	11.8
3.00	210	48.1	14.3

and for copper we find the values in the table below.

$E_{\text{kin}} / \text{eV}$	λ / nm	$E_{\text{kin}} / 10^{-20} \text{ J}$	$\nu / 10^{14} \text{ s}^{-1}$
0.35	260	5.6	11.53
0.48	254	7.7	11.80
0.73	230	11.7	13.03
1.02	210	16.3	14.28
1.25	200	20.0	14.99

In Figure P1.1, we plot data as E_{kin} versus ν . The slopes of the lines through the data should both be equal to h , and the x -intercept gives the frequency corresponding to the work function for the metal.

For sodium, the slope is $h = 5.29 \times 10^{-34} \text{ J s}$ and the x -intercept is $\nu = 5.06 \times 10^{14} \text{ s}^{-1}$. Thus the work function is $h\nu = 6.626 \times 10^{-34} \text{ J s} \cdot 5.06 \times 10^{14} \text{ s}^{-1} = 3.35 \times 10^{-19} \text{ J}$ or 2.09 eV. The value reported in the *CRC Handbook of Chemistry and Physics* is 2.75 eV. The value obtained for the slope differs by about 20% from the more modern and precise value of h .

For copper, the slope is $h = 3.88 \times 10^{-34} \text{ J s}$ and the x -intercept is $\nu = 9.97 \times 10^{14} \text{ s}^{-1}$. Thus the work function is $h\nu = 6.626 \times 10^{-34} \text{ J s} \cdot 9.97 \times 10^{14} \text{ s}^{-1} = 6.61 \times 10^{-19} \text{ J}$ or 4.12 eV. The values reported in the *CRC Handbook of Chemistry and Physics* range from 4.48 eV to 4.94 eV. The value obtained for the slope differs substantially, about 40%, from the modern value of h .

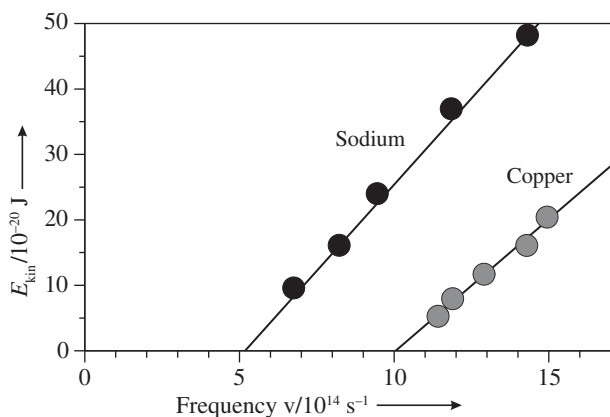


Figure P1.1 Photoelectric effect. Kinetic energy of the ejected electrons versus frequency ν of the photon for sodium (black) and copper (grey). The solid lines are regression curves.

- P1.2** Find a formula for the amplitude distribution on the screen in the double-slit experiment in Fig. 1.6. For arbitrary distances r_1 and r_2 between the slits and the point P_2 , the resulting wave displacement φ on the screen can be written

as a superposition of the waves φ_1 and φ_2 originating from each slit, so that

$$\varphi = \varphi_1 + \varphi_2 = A \sin\left(\frac{2\pi(vt - r_1)}{\lambda}\right) + A \sin\left(\frac{2\pi(vt - r_2)}{\lambda}\right)$$

Show that the resulting waveform can be written as

$$\varphi = 2A \sin\left(\frac{\pi(2vt - r_1 - r_2)}{\lambda}\right) \cos\left(\frac{\pi(r_2 - r_1)}{\lambda}\right) = \psi(x) \sin\left(\frac{\pi(2vt - r_1 - r_2)}{\lambda}\right)$$

where the wave's amplitude is $\psi(x) = 2A \cos(\pi(r_2 - r_1)/\lambda)$. Simplify this expression for $\psi(x)$ further by realizing that $r_2 - r_1 = dx/a$ for $x \ll a$. Identify where the wave amplitude has extrema: minima and maxima.

Solutions

We generalize the treatment in Section 1.1.2 (shown in Fig. 1.6) for arbitrary distances r_1 and r_2 between the slits and the point P_2 . From the wave displacements φ_1 and φ_2 we calculate the resulting displacement φ at point P_2 .

$$\varphi = \varphi_1 + \varphi_2 = A \sin\left(\frac{2\pi(vt - r_1)}{\lambda}\right) + A \sin\left(\frac{2\pi(vt - r_2)}{\lambda}\right)$$

With the relation $\sin \alpha + \sin \beta = 2 \sin\left(\frac{\alpha + \beta}{2}\right) \cos\left(\frac{\alpha - \beta}{2}\right)$, we get

$$\varphi = 2A \sin\left(\frac{\pi(2vt - r_1 - r_2)}{\lambda}\right) \cos\left(\frac{\pi(r_2 - r_1)}{\lambda}\right)$$

This corresponds to a wave with the maximum displacement

$$\psi = 2A \cdot \cos\left(\frac{\pi(r_2 - r_1)}{\lambda}\right)$$

Because $r_2 - r_1 = xd/a$ for $x \ll a$ and $d/2 \ll x$, we then obtain

$$\psi = 2A \cdot \cos\left(\frac{\pi d}{\lambda a} x\right)$$

The maxima of ψ are then at the positions $x = 0, \lambda a/d, 2\lambda a/d$, and so on, while the minima are at $x = \lambda a/(2d), 3\lambda a/(2d)$, and so on.

- P1.3** The essential ideas of the photoelectric effect can be applied to atoms and molecules, as well. Consider a sample of Ne gas that is exposed to high energy electromagnetic radiation; i.e., light. If a 58.5 eV source of UV light shines on a sample of Ne gas one observes two distinct distributions of photoelectron kinetic energies at 17.5 eV and at 44.5 eV. In addition, if X-ray photons of 1.28 keV shine on a sample of Ne three distinct distributions of photoelectron energies can be seen at 417 eV, 1.24 keV, and 1.27 keV. What information about the electronic structure of a neon atom can you obtain from these data? Make a hypothesis about your observations. How might you test your hypothesis? Describe a set of experiments that could be performed.

Solutions

The 58.5 eV source tells us that there are at least two energy levels, and they are located at energies of $(58.5 - 17.5) = 41.0$ eV and $(58.5 - 44.5) = 14.0$ eV below the vacuum level (the zero of energy is a free electron with zero excess kinetic energy). Similarly, the 1.28 keV source tells us that there are at least three energy levels, and these three are located at $(1280 - 417)$ eV = 863 eV, $(1280 - 1240)$ eV = 40 eV, and $(1280 - 1270)$ eV = 10 eV below the vacuum level. Note that we expect the error in these measurements to be of the order of 10 eV, whereas they are significantly less in the earlier experiments.

These two experiments give comparable results for the two more weakly bound electronic energy states (within experimental error/significant digits). One way to support this hypothesis is to look at the UV absorption spectrum for lines in the appropriate region.

P1.4 This problem explores the shape of a diffraction pattern made by a wave passing through a single slit. The intensity profile $I(\theta)$ of a wave passing through a slit of width w is given by

$$I(\theta) = I_{\max} \left(\frac{\sin \left(\frac{\pi w}{\lambda} \sin(\theta) \right)}{\frac{\pi w}{\lambda} \sin(\theta)} \right)^2$$

where I_{\max} is the maximum intensity, λ is the wavelength, and θ is the angular distribution of the intensity pattern. Using a spreadsheet program (e.g., Excel) plot this function over the range of -90° to $+90^\circ$ for five different values of the ratio w/λ . Comment on how the diffraction pattern changes as this parameter is changed. In Exercise E1.4 you calculated de Broglie wavelengths for different particles. Based on those calculations and the results of your diffraction calculations, comment on the likelihood of being able to observe diffraction for the different particles in Exercise E1.4.

Solutions

Figure P1.4a illustrates a wave incident on a slit and defines the angle θ .

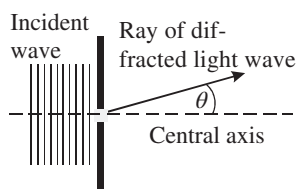


Figure P1.4a Diffraction on a slit.

Figure P1.4b plots the equation for three values of $a = w/\lambda$; namely $a = 0.4$, $a = 2.0$, and $a = 10.0$. As the plots show there is less diffraction when the wavelength of the light is small compared to the width of the aperture; i.e., the dashed black line shows a sharp transmission of the particle at a single well-defined angle. In contrast when the wavelength of the particle becomes similar to or larger than the slit, the wave is strongly diffracted and the amplitude appears at high angles.

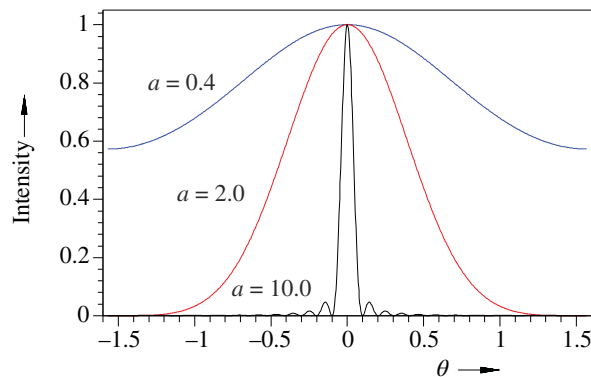


Figure P1.4b Diffraction on a slit: intensity distributions are plotted for three different values of the parameter $a = w/\lambda$.

Based on this analysis we would expect that He atoms could diffract from solid surfaces because their de Broglie wavelength is similar in magnitude to interatomic spacing in solids. In contrast, the other particles in E1.4 have de Broglie wavelengths that are quite small, and it would be much more difficult to observe diffraction with them.

P1.5 The intensity distribution behind a slit of width w is a special case of the distribution behind a grating with N grooves spaced at distance d . For a grating the intensity is

$$I(\theta) = \text{const} \cdot \left(\frac{\sin \left(\frac{\pi N d}{\lambda} \sin(\theta) \right)}{\sin \left[\frac{\pi d}{\lambda} \sin(\theta) \right]} \right)^2 \quad (1P5.1)$$

Calculate the intensity distribution for gratings with different numbers of grooves. Choose $d = 1.7 \mu\text{m}$, $\lambda = 500 \text{ nm}$ and perform calculations for $N = 2, 10, 100$, and 1000 . Based on your results comment on how the groove number affects the resolution of a wavelength determination.

Solutions

The equation is plotted below in two different plots. The $N = 100$ result is shown in both panels so that comparisons can be drawn. In each case the function is normalized to unity height by dividing its value by N^2 . Note that the limiting value of $I(\theta)$ is N^2 at $\theta = 0$. This means that the peak intensity increases substantially with N .

From Fig. P1.5 it is clear that increasing N , decreases the linewidth and thereby increasing the precision for determining λ .

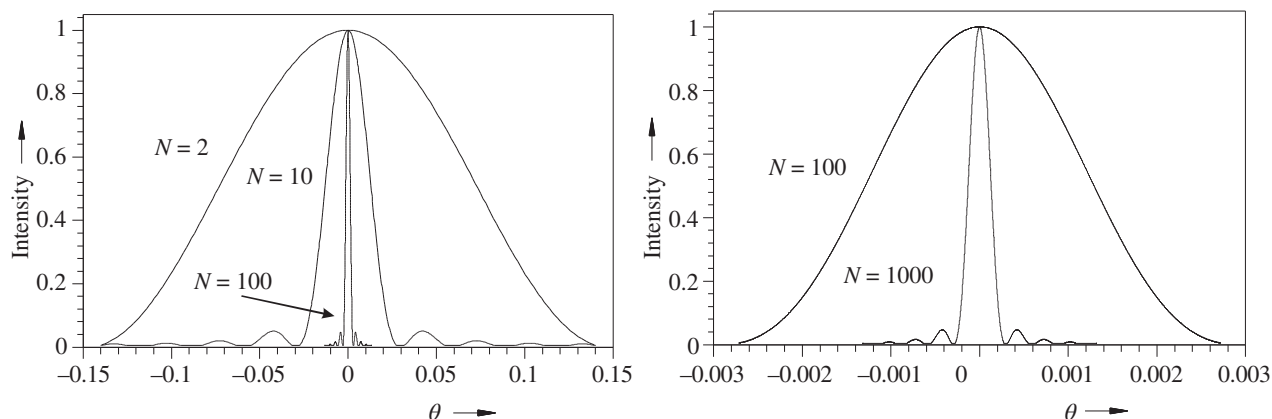


Figure P1.5 Equation (1P5.1) is plotted in two figures. The left panel shows plots for $N = 2, N = 10$, and $N = 100$. The right panel shows the plots for $N = 100$ and $N = 1000$. Note the change in scale for the two different abscissas and that the magnitude of the plots are normalized to 1.

- P1.6** In the early part of the twentieth century, many of the experiments that laid the foundation for quantum mechanics and wave-particle duality were performed. Because of their importance, many of these findings were recognized by awarding the Nobel Prize. Select a Nobel Prize lecture for one of these “classic” studies, explain, and summarize the findings. See <https://www.nobelprize.org>.

Solutions

No answer is given because of the number of possible Nobel prize choices and the diversity of acceptable responses.

- P1.7** In order to gain some elementary experience with probabilities, consider the following thought experiment. Imagine a thin, rectangular, metal film (ca. 100 nm thick). Now place electron detectors on each side (left and right) of the metal film to face each surface of the metal. Imagine shining photons of energy greater than the metal’s work function on the film and collecting the electrons. Assume that we can make the film thick enough so that it behaves like the bulk metal, but thin enough that the light source goes completely through the film. In this case, the electrons could escape out of either face of the metal film with equal probability. Can you predict which face (left or right) emits an electron first? How does the distribution (left versus right) of collected electrons evolve as the experiment proceeds, for the first 100 electrons that are detected?

You can answer these questions by making an analogy to the case of a two-sided coin and denote one side “heads” and the other “tails.”

- If the coin is flipped once, will it give heads? How many times will a coin flip yield heads if it is flipped one-hundred times? Comment on your ability to accurately predict the result of these two sets of experiments?
- Using your coin, perform the experiment by flipping it one-hundred times and recording the results. Before each time you flip the coin make a prediction of the outcome, record the outcome. What percentage of the time was your result correct?
- Using your data from b), calculate the fraction of total times heads was obtained, after successive flipping of the coin. Make a plot of your fraction versus the number of times you flip the coin. How rapidly does your data converge to the limiting value? Compare your results to your predictions in part a).

d) Apply your understanding to the electron experiment.

Solutions

- a) On average the probability is one-half. For 100 coin flips, we expect to see “heads” about 50 times. Because it is probabilistic, the number may not be exactly 50.
- b) A variable answer here, based on the individual experiment.
- c) The plot should show that the observed value for the fraction converges on one-half as the number of trials increases.
- d) You cannot predict which surface will emit an electron first though after counting a large number of electrons, you will find that $\frac{1}{2}$ are emitted from each surface.

P1.8 In Section 1.4 we discussed how the outcome of many events can be predicted with certainty, but that of individual events cannot, since quantum mechanics only predicts probabilities. Let us use this feature of probability to make a certain prediction. You will need to obtain or borrow a globe of the planet earth, hopefully fairly precise and not too fragile. Can you predict the land-to-water ratio of the planet’s surface? Can you measure the land-to-water ratio of the planet’s surface? Rather than use a deterministic method (e.g., a ruler), we will use a probabilistic method to determine the land-to-water ratios. Perform the following experiment a number of different times. Toss the globe into the air (or to a friend) and catch it. Record whether your right index finger landed on water or land. Perform this experiment over (and over) and calculate the fraction of times your right index finger ended up on water. Plot your fraction versus the number of trials and determine the value at which it converges. How does this value relate to the known value? Comment on the agreement between your result and the known value. How can your experiment be improved?

Solutions

In the limit of a large number of observations approximately 70% will result in landing in water. This type of testing is called Monte Carlo testing, a simulation method which is useful in physical chemistry when probabilistic arguments are made.

2

Essential Aspects of Structure and Bonding

2.1 Exercises

- E2.1** The potential energy $V(r)$ of interaction between a proton (charge of $+e$) and an electron (charge of $-e$) is given, according to Coulomb's law, by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

where $e = 1.602 \times 10^{-19}$ C, $\epsilon_0 = 8.854 \times 10^{-12}$ C² m⁻¹ J⁻¹, and r is the distance between the particles. Use V to compute the electrostatic force f_{electric} between these two particles at a distance of 300 pm. Compute the gravitational force f_{gravity} between these two particles at a distance of 300 pm. Note that $m_e = 9.109 \times 10^{-31}$ kg, $m_p = 1.67 \times 10^{-27}$ kg, and the gravitational constant is $G = 6.67 \times 10^{-11}$ N m²/kg². Compare f_{gravity} to f_{electric} . Is it reasonable to ignore gravitational effects when we describe the interaction of an electron and a proton?

Solution

The force is the derivative of the potential energy with respect to the distance, thus

$$f_{\text{electric}} = -\frac{dV}{dr} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2}$$

and the electrostatic force for the situation in the problem is given by

$$f_{\text{electric}} = \frac{(1.602 \times 10^{-19} \text{ C})^2}{4\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}) (300 \times 10^{-12} \text{ m})^2} = 2.56 \times 10^{-9} \text{ N}$$

For comparison the gravitational force is given by

$$f_{\text{gravity}} = G \cdot \frac{m_e m_p}{r^2} = \left(6.67 \times 10^{-11} \frac{\text{N} \cdot \text{m}^2}{\text{kg}^2} \right) = \frac{9.109 \times 10^{-31} \text{ kg} \cdot 1.67 \times 10^{-27} \text{ kg}}{(300 \times 10^{-12} \text{ m})^2} = 1.13 \times 10^{-48} \text{ N}$$

and the force due to gravity is much less (30 orders of magnitude) than that arising from electrostatics.

- E2.2** Consider two charged particles, an electron and a proton. Compute the electrostatic energy between a proton and an electron at 100 pm, 1.0 nm, and 10.0 nm. Express your answer in J and in electron volts (1 eV = 1.602×10^{-19} J). Evaluate the distance at which the potential energy is 13.6 eV below the dissociation limit (i.e., zero). Compare this distance to the average distance \bar{r} that we found in Section 2.4.2 for the H atom.

Extension: Use a spreadsheet program (e.g., Excel) to plot the electrostatic potential energy as a function of the distance.

Solution

The electrostatic potential energy between two charged particles is given by

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

For an electron–proton pair, the magnitude of the charge is 1.602×10^{-19} C. This makes the energy at 100 pm equal to

$$V(r) = \frac{(-1.602 \times 10^{-19} \text{ C}) \cdot (+1.602 \times 10^{-19} \text{ C})}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}) (100. \times 10^{-12} \text{ m})} = -2.307 \times 10^{-18} \text{ J}$$

This energy corresponds to

$$2.307 \times 10^{-18} \text{ J} \cdot \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) = 14.40 \text{ eV}$$

Similarly at 1.0 nm, $V = -2.307 \times 10^{-19}$ J and -1.440 eV, and at 10.0 nm, $V = -2.307 \times 10^{-20}$ J and -0.1440 eV.

The distance corresponding to an energy of -13.6 eV $= -21.79 \times 10^{-19}$ J is

$$r = \frac{q_1 q_2}{4\pi\epsilon_0 V} = \frac{(-1.602 \times 10^{-19} \text{ C}) \cdot (+1.602 \times 10^{-19} \text{ C})}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ m}^{-1} \text{ J}^{-1}) (-21.79 \times 10^{-19} \text{ J})} = 67.6 \times 10^{-12} \text{ m} = 67.6 \text{ pm}$$

This distance is comparable to the 90 pm found for the average distance of the electron from the proton in the box model approximation for the hydrogen atom.

- E2.3** Use the fact that the size of a He atom is about 220 pm in diameter to estimate the kinetic energy of the electrons in this atom. In particular, use the one-dimensional box model to estimate the electron's de Broglie wavelength and then its average kinetic energy. Report your answer in J and in eV. Also estimate the average speed of the electron. At what fraction of the speed of light is the electron traveling?

Solution

If a He atom in its electronic ground state is about 220 pm in diameter the wavelength describing the electronic state is about twice this size, or about 440 pm. Given this wavelength, the de Broglie relationship gives the momentum p as

$$p = mv = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{440 \times 10^{-12} \text{ m}} = 1.506 \times 10^{-24} \text{ kg m s}^{-1}$$

This momentum corresponds to an average kinetic energy \bar{T} that is given by

$$\bar{T} = \frac{1}{2}mv^2 = \frac{1}{2}m \frac{p^2}{m^2} = \frac{1}{2} \frac{p^2}{m} = \frac{(1.506 \times 10^{-24} \text{ kg m s}^{-1})^2}{2 \cdot 9.11 \times 10^{-31} \text{ kg}} = 1.245 \times 10^{-18} \text{ J} = 7.715 \text{ eV}$$

The average speed can be obtained in a number of ways. One is from the momentum, i.e.,

$$v = \frac{p}{m} = \frac{1.506 \times 10^{-24} \text{ kg m s}^{-1}}{9.11 \times 10^{-31} \text{ kg}} = 1.653 \times 10^6 \text{ m s}^{-1} = 0.0055 c_0$$

where c_0 is the speed of light.

- E2.4** Approximate an H_2 molecule as a one-dimensional box of length 216 pm (found from the bond length plus twice the atomic radius) which confines its valence electrons. Determine the kinetic energy of an electron that has a wavelength of twice the box length. Use this kinetic energy with the known ionization potential (or electron binding energy) of H_2 , which is 15.43 eV, to estimate the potential energy of the electron.

Solution

Modeling the H_2 molecule as a one-dimensional box of length 216 pm gives the kinetic energy in the $n = 1$ level to be

$$E_{\text{kin}} = \frac{h^2}{8mL^2} n^2 = \frac{h^2}{8mL^2}$$

Because the H_2 molecule has two electrons, both in the $n = 1$ level, the energy is

$$E_{\text{kin}} = 2 \cdot \frac{h^2}{8mL^2} = \frac{2 \cdot (6.626 \times 10^{-34} \text{ J s})^2}{8 \cdot 9.11 \times 10^{-31} \text{ kg} \cdot (216 \times 10^{-12} \text{ m})^2} = 25.82 \times 10^{-19} \text{ J} = 16.12 \text{ eV}$$

This kinetic energy, when combined with the known ionization energy E_{ion} (or electron binding energy), gives an estimate of the average potential energy \bar{V} of the energy, namely

$$E_{\text{total}} = E_{\text{kin}} + \bar{V} = -E_{\text{ion}}$$

Solving for \bar{V} we find

$$\bar{V} = -E_{\text{ion}} - E_{\text{kin}} = -15.43 \text{ eV} - 16.12 \text{ eV} = -31.55 \text{ eV}$$

Note: This value is near to what one expects from the Virial Theorem, which states that $\bar{T} = -\frac{1}{2}\bar{V}$.

- E2.5** Consider the three one-dimensional wavefunctions sketched in Figure E2.5. Each wavefunction (A, B, and C) is plotted versus the x coordinate whose scale is set by tic marks at zero and one. Order these wavefunctions by their kinetic energy.

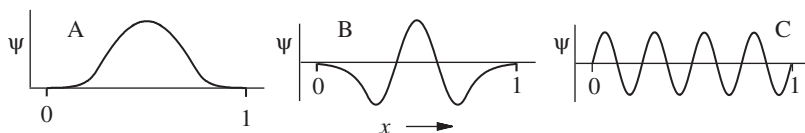


Figure E2.5 Each panel shows a sketch of a plausible wavefunction ψ versus a normalized coordinate x .

Solution

The energy of a wavefunction for a constant length box increases as the wavelength decreases, or as the number of nodes in the wavefunction increases. Thus the energy of wavefunction A is less than that for wavefunction B, which is less than that for wavefunction C.

- E2.6** In Fig. 2.6 the wavefunction for an electron trapped in a one-dimensional box is plotted for various values of the total energy, which happens to be the kinetic energy. What observations can you make about the shape of the electron wave as the kinetic energy increases? Realizing that the “node” of a mathematical function occurs at a point where the function changes sign (from plus to minus, or minus to plus) make a quantitative hypothesis about the number of nodes and the kinetic energy of an electron wave.

Solution

The wavefunction has more nodes as the energy increases; hence, it has a smaller de Broglie wavelength. The decrease in de Broglie wavelength corresponds to a higher momentum and kinetic energy. For the simple particle-in-a-box wavefunction, the number of nodes k_{nodes} in the wavefunction is equal to $n - 1$ where n is the quantum number; hence, the kinetic energy is proportional to $(k_{\text{nodes}} + 1)^2$, it is strongly increasing with the number of nodes.

- E2.7** Equation (2.13) gives a standing wave for a particle in a one-dimensional box with n as an integer. Plot this function for a box of length 100 pm and n values of 1, 2, 5, and 10. Also plot the function for five non-integer n values between 1 and 2. Describe the differences you observe for the functions. Describe the necessary characteristics for a standing wave of the box.

Solutions

The wavefunctions for integer values are plotted in the three panels of Fig. E2.7a. In each panel the $n = 1$ function is shown as a solid black curve. The grey curves show the wavefunction plots for each of the n values: $n = 2$ in the left panel, $n = 5$ in the center panel, and $n = 10$ in the right panel. For each of the wavefunctions we see that it has a zero at the edges of the box. We also see that the number of nodes for the wavefunctions is given by $n - 1$. In these plots the wavefunctions have been normalized by the factor $\sqrt{2/L}$.

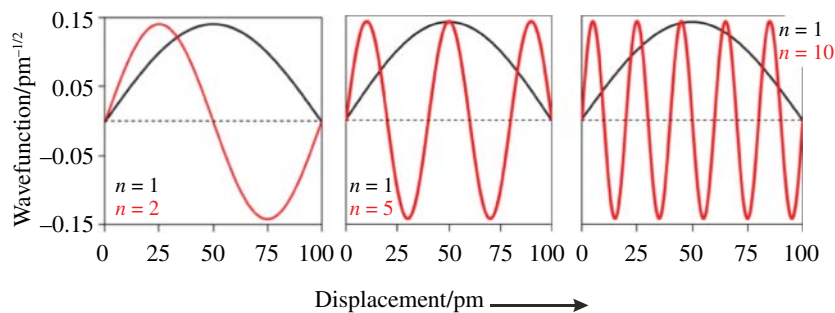


Figure E2.7a Wavefunctions for a particle in a one-dimensional box for $n = 2$, $n = 5$, and $n = 10$ and compared to that for $n = 1$, in each case.

Figure E2.7b shows the wavefunction plotted for five non-integer values of n . The black curve in each panel shows the case of $n = 1$, as a reference. In the left-most panel, the solid grey line is the case of $n = 1.1$ and the dashed grey line is the case of $n = 1.3$. In the center panel the solid grey line is the case of $n = 1.5$ and the dashed grey curve is the case of $n = 1.7$. The rightmost panel shows the case of $n = 1.9$ for the solid grey line. Note that in the cases of noninteger values of n the wavefunctions are not zero at the right border of the box, in contrast to the fact that the solutions of the Schrödinger equation must vanish at this point.

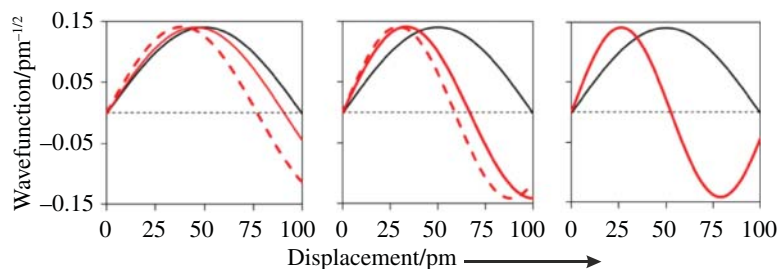


Figure E2.7b Wavefunctions for a particle in a one-dimensional box for $n = 1$, $n = 1.1$ and 1.3 (left), $n = 1$, $n = 1.5$, and $n = 1.7$ (center) and $n = 1$, $n = 1.9$ (right).

E2.8 Use the resonance condition of Equation (2.12) to derive the kinetic energy expression of Equation (2.14).

Solution

We begin by writing the expression for the kinetic energy classically, and then substitute for the speed using the de Broglie relationship

$$T_n = \frac{1}{2}m_e v^2 = \frac{1}{2}m_e \left(\frac{h}{m_e \Lambda} \right)^2$$

which gives on substitution of the resonance condition ($\Lambda = 2L/n$)

$$T_n = \frac{1}{2}m_e \left(\frac{h}{m_e (2L/n)} \right)^2 = \frac{1}{2}m_e \left(\frac{n^2 h^2}{m_e^2 4L^2} \right)$$

or

$$T_n = \frac{1}{2}m_e \left(\frac{n^2 h^2}{m_e^2 4L^2} \right) = \frac{h^2}{8m_e L^2} n^2$$

E2.9 In our box model of the hydrogen atom, we found that the ground-state electron wave corresponded to a box length of 376 pm. However, the proton is also contained in this volume of space. Are the wave characteristics of the proton important to consider in this case? Explain.

Solutions

The wavelength of the proton will be 1837 times smaller than that of the electron or $(376 \text{ pm})/1837 = 0.205 \text{ pm}$ because the mass of the proton is 1837 times larger. This value is small enough (i.e., much smaller than the “box size” of 376 pm) that the wave nature of the proton does not need to be considered.

- E2.10** Reproduce Fig. 2.10 using a spreadsheet program, such as Excel, and find the value of L that minimizes the energy. Also determine the minimum value of L analytically, i.e., set the first derivative of the energy with respect to L equal to zero and solve for L . Compare your numerical and analytical results.

Solution

The energy is given by Equation (2.27) of the text and it is plotted in Fig. E2.10. The energy minimum is found to fall between 374 pm and 375 pm. See the Excel sheet “ch2_e10.xls.”

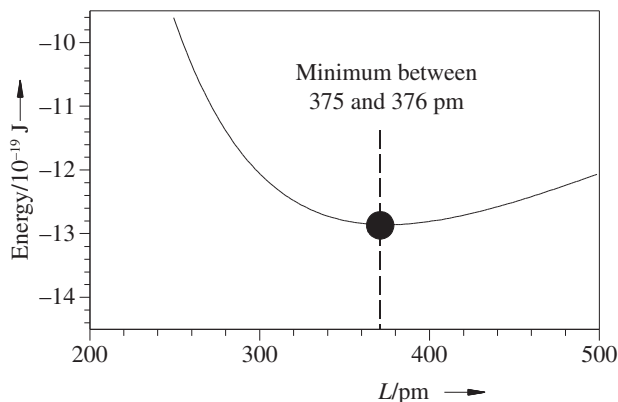


Figure E2.10 A plot of the variational energy for the H-atom, in which the electron wavefunction is approximated by a one-dimensional particle in box wavefunction, as a function of the box length L .

The analytical derivation of the box side length L that minimizes the energy is provided in Box 2.1 and is given here also. We begin with Equation (2.27), namely

$$\epsilon = \frac{3h^2}{8m_e L^2} - \frac{1}{4\pi\epsilon_0} \frac{4.18 \cdot e^2}{L}$$

To find the value of the parameter L that lies at the minimum of the energy function we take the derivative and set it equal to zero, and find

$$\left(\frac{d\epsilon}{dL}\right)_{L=L_{\min}} = -\frac{6h^2}{8m_e L_{\min}^3} + \frac{1}{4\pi\epsilon_0} \frac{4.18 \cdot e^2}{L_{\min}^2} = 0$$

If we solve this equation for L_{\min} , we find

$$L_{\min} = 4\pi\epsilon_0 \frac{h^2}{m_e e^2} \frac{3}{4 \times 4.18} = 375 \text{ pm}$$

Formally we would need to take a second derivative and analyze it also, in order to prove that this value of L is a minimum. From the plot of the function above it is clear that the extremum must be a minimum.

- E2.11** Use Equation (2.20) to determine the average potential energy of an electron in the H atom, \bar{V} . Use this average potential energy to determine the average value of $1/r$. Compare your value for $1/r$ to the value of $1/a_0$. Comment on your result.

Solutions

Equation (2.20) writes the energy of the ground state of the hydrogen atom as

$$E = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_0} = -21.8 \times 10^{-19} \text{ J}$$

and using the Virial theorem we can write that

$$\bar{V} = 2E = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0} = -43.6 \times 10^{-19} \text{ J}$$

Using Coulomb's law, the potential energy is given by

$$V = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

so that

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \cdot \overline{1/r} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{a_0}$$

and we see that

$$\overline{1/r} = \frac{1}{a_0}$$

E2.12 To explore the properties of the particle in the box wavefunctions further, perform the MathCAD exercise, titled PinBwaves.mcd, and answer the questions:

- For each of the above wavefunctions ($n = 1$ and $n = 2$), find the number of nodes.
- Plot out the eigenfunctions corresponding to quantum numbers 2 and 3.
- From the graph, read off the position at which the nodes can be found for the cases of $n = 1, 2, 3$, and 4.
- Plot the probability density, or the square of the wavefunctions for $n = 3$ and $n = 4$.

Solution

The solutions to the questions and activities requested in the MathCAD exercise are given in Figs. E2.12a and E2.12b. It is also available as PinBwaves_solutions.mcd.

- The $n = 1$ wavefunction has no nodes and the $n = 2$ wavefunction has one node.
- The MathCAD plots for $n = 2$ and $n = 3$ are

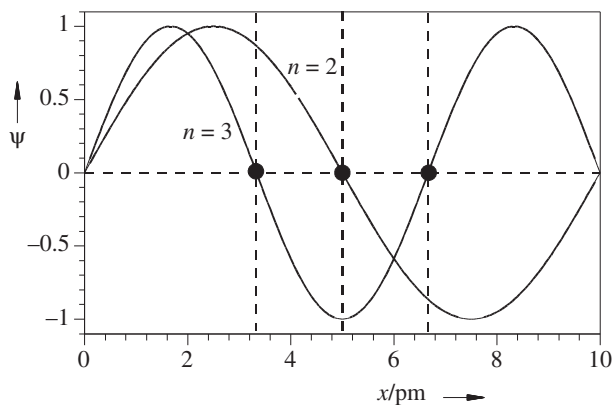


Figure E2.12a Plots of the wavefunction of a particle in a one-dimensional box for $n = 2$ and $n = 3$.

- For $n = 1$ we have no node, for $n = 2$ a node occurs at $x = 5$ pm; for $n = 3$ nodes occur at $x = 3.333$ pm and $x = 6.666$ pm; and for $n = 4$ nodes occur at $x = 2.5$ pm, $x = 5.0$ pm, and $x = 7.5$ pm.
- The probability density plots for $n = 3$ and $n = 4$ are

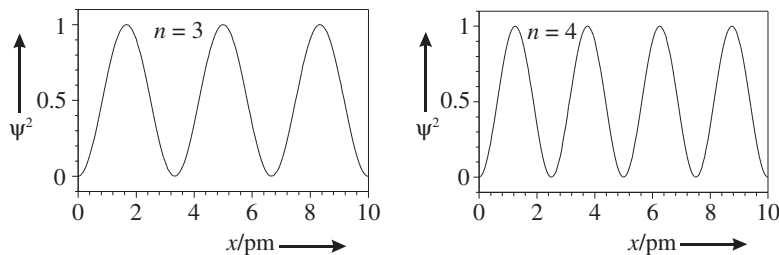


Figure E2.12b Plots of the probability density of a particle in a one-dimensional box for $n = 3$ and $n = 4$.

- E2.13** Using Equation (2.1) find the energy that corresponds to the 589 nm Na emission line (see Fig. 2.1). Compare your result to the energy spacing shown in the electron energy loss spectrum of Fig. 2.2.

Solution

The energy of a 589 nm photon is

$$E = \frac{hc_0}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{589 \times 10^{-9} \text{ m}} = 3.373 \times 10^{-19} \text{ J} \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \right) = 2.105 \text{ eV}$$

This value is exactly the spacing between lines in the energy loss spectrum, suggesting that similar energy levels are involved.

- E2.14** When an electron is bound to a proton it makes a hydrogen atom, for which the accepted atomic diameter is 128 pm.
- Estimate the largest wavelength that an electron could have if it were trapped inside of a box of this size; assume that the wave has to go to zero at the boundaries of the box. From this wavelength calculate the average kinetic energy for the electron.
 - Perform an estimation similar to that of part a) for an electron that is confined in i) a benzene ring, ii) a C₆₀ molecule, or iii) a 10 nm diameter Au colloid. Estimate the diameters of benzene and C₆₀ by using their density and the molecular weights.
 - Based on your calculations, discuss how you expect the kinetic energy of an electron to change as you change its ability to delocalize throughout a molecule or a nanometer-sized particle.

Solution

- a) The appropriate box size would be approximately the diameter d of the atom or 128 pm; this distance corresponds to one-half of the de Broglie wavelength, which is then 256 pm. The average kinetic energy is given by

$$E = \frac{p^2}{2m} = \frac{(h/\Lambda)^2}{2m} = \frac{h^2}{8mL^2}$$

For $\Lambda = 2L = 256$ pm we find $L = 128$ pm; thus, the kinetic energy is 3.68×10^{-18} J.

- b) The volume of one molecule of the substance is found from the density ρ and the molar mass \mathbf{M} of the substance as

$$V_{\text{molecule}} = \frac{m}{\rho} = \frac{\mathbf{M}/N_A}{\rho} = \frac{\mathbf{M}}{\rho N_A}$$

The volume of the molecule is related to its diameter d (assuming the molecule is spherical) by

$$V_{\text{molecule}} = \frac{4}{3} \pi \left(\frac{d}{2} \right)^3$$

For the three species of interest here at 293 K

Species	$\mathbf{M}/(\text{g mol}^{-1})$	$\rho/(\text{g mL}^{-1})$	$V_{\text{molecule}}/(\text{nm}^3)$	$d/(\text{pm})$	$\Lambda/(\text{nm})$	$E/(\text{J})$
Benzene	78.11	0.8765	0.1480	656.2	1.312	3.500×10^{-20}
C60	720.6	1.197	0.9997	999.9	1.999	1.508×10^{-20}
10 nm Au	6.050×10^6	19.32	520	10,000	20.0	1.5×10^{-22}

- c) As the size of the particle increases, the electron delocalizes more and its kinetic energy decreases. The lowest kinetic energy of the electron will correspond to a de Broglie wavelength of $2d$; $\Lambda = 2d$.

2.2 Problems

- P2.1** Figure P2.1a shows an atomic emission spectrum from excited electronic states of the hydrogen atom to its lower energy electronic state with principal quantum number $n = 2$, the Balmer series. The first few lines correspond to: $H_\alpha = 656.28$ nm, $H_\beta = 486.13$ nm, $H_\gamma = 434.05$ nm, $H_\delta = 410.17$ nm. Use these wavelengths to determine the energy level spacing between the ground state and each of these excited states. Make an energy level diagram which shows the ground electronic state and these first few excited states. In your diagram, set the zero of energy to correspond to the separated electron and proton and use the fact that the ground electronic state lies 13.6 eV below this value. What do you think the H_∞ label indicates?

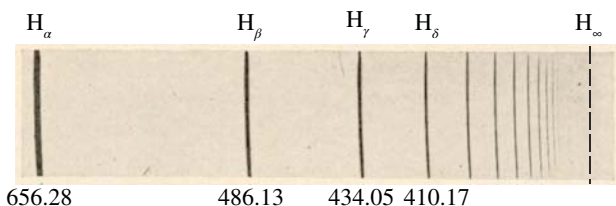


Figure P2.1a Emission lines of the Balmer series. The image is taken from G. Herzberg, *Atomic Spectra and Atomic Structure* (Prentice Hall, New York 1937). The numbers denote the wavelengths measured in units of nm.

Compare and contrast the energy level structure you found here for the H-atom to that calculated for an electron confined in a one-dimensional energy well whose potential energy does not change with displacement, see Fig. 2.6. Do you think that we will need to develop a more detailed model for the structure of the hydrogen atom, than the box potential? Please explain your answer in detail.

Solution

Begin by recognizing the quantum numbers and calculating the energies associated with each transition. For example, from the 656.28 nm wavelength, we find that

$$\begin{aligned}\Delta E &= \frac{hc_0}{\lambda} = \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s}) (2.9979 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{656.28 \times 10^{-9} \text{ m}} \\ &= 3.0268 \times 10^{-19} \text{ J}\end{aligned}$$

Proceeding in a like manner for the other wavelengths we find the values in the table below. The H_∞ label in the figure indicates a transition from $n_{\text{upper}} = \infty$ to $n_{\text{lower}} = 2$.

	n_{lower}	n_{upper}	λ/nm	$\Delta E/10^{-19} \text{ J}$
H_α	2	3	656.28	3.0268
H_β	2	4	486.13	4.0862
H_γ	2	5	434.05	4.5765
H_δ	2	6	410.17	4.8429

The energy level spacings, which can be deduced from these calculations, are shown in Fig. P2.1b; and they disagree strongly with those represented by Fig. 2.6 in the text. Namely, the energy levels get closer together as n increases for an H-atom, whereas a one-dimensional box model results in energy levels that get farther apart as the quantum number increases—a clear disagreement. Equation (2.14) and Fig. 2.6 describe the kinetic energy for a particle in a one-dimensional box and is not a model for the H-atom. A model for the H-atom must be three-dimensional and has to include a Coulomb potential energy contribution, as described in Section 2.42.

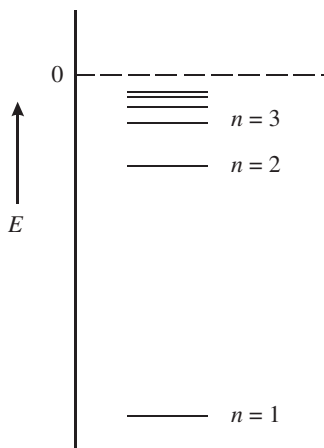


Figure P2.1b Plot of the H-atom energy levels. Note that the levels converge on the $E = 0$ limit as the principal quantum number becomes large.

- P2.2** Figure P2.2 shows data that were measured using a Franck–Hertz apparatus with Ne gas rather than Na gas. It is reproduced from M.M. Kash and G.C. Shields, *J. Chem. Ed.* 1994, **71**, 466. Use these data to determine the resonance energy for excitation of Ne atoms. The data are collected for two values of the opposing voltage. You may use either data set.

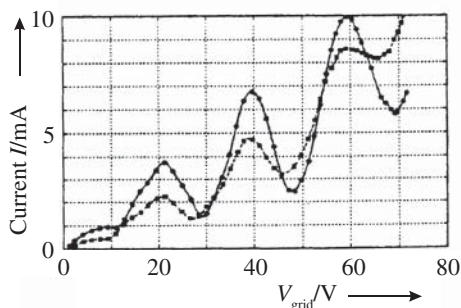


Figure P2.2 Plots of the current–voltage profiles observed in a Franck–Hertz experiment for Ne gas.

The authors describe how the gas emits a red glow when the atoms get excited. Using the energy difference that you found from the current–voltage curve, calculate the wavelength of a photon that an excited Ne atom can emit. Could such photons explain the red glow?

Solution

The three apparent maxima in the largest amplitude curve (shown in smoothed form) occur at 59.28, 39.39, and 20.93 V. The average voltage difference between successive peaks is thus 19.18 V. This value of the electric potential corresponds to an energy difference of 3.072×10^{-18} J. This energy difference then corresponds to photons of wavelength 64.6 nm, which would be in the far UV. The observed red glow in a tube of excited neon probably arises from transitions involving two excited states.

- P2.3** Show that a standing wave with nodes at the positions $x = 0$ and $x = L$ is formed from the overlap of two traveling waves of the same wavelength moving in opposite directions. Note that a wave traveling from left to right with speed v can be described by

$$\varphi_+ = A \sin \left(\frac{2\pi(vt - x)}{\Lambda} \right)$$

and when this wave is reflected at the right boundary the back traveling wave is described by

$$\varphi_- = -A \sin \left(\frac{2\pi(vt + x)}{\Lambda} \right)$$

Solution

The waves interfere. Using superposition, the displacement φ at a point x is given by

$$\varphi = \varphi_+ + \varphi_- = A \left[\sin \left(\frac{2\pi(vt - x)}{\Lambda} \right) - \sin \left(\frac{2\pi(vt + x)}{\Lambda} \right) \right]$$

Using the trigonometric relation, $\sin \alpha - \sin \beta = 2 \cos \left(\frac{\alpha + \beta}{2} \right) \sin \left(\frac{\alpha - \beta}{2} \right)$, we find that

$$\varphi = 2A \cos \left(\frac{2\pi vt}{\Lambda} \right) \cdot \sin \left(\frac{2\pi x}{\Lambda} \right) = \cos \left(\frac{2\pi vt}{\Lambda} \right) \cdot \psi$$

with $\psi = 2A \cdot \sin(2\pi x/\Lambda)$ where ψ is the equation for a standing wave. With $\Lambda = 2L/n$ we obtain

$$\psi = 2A \cdot \sin \left(\frac{\pi x n}{L} \right), \quad n = 1, 2, \dots$$

Note that φ changes in time; however, it is always zero at $x = 0$ and $x = L$.

- P2.4** Since ψ^2 is a probability function, i.e., the probability of finding an electron in a region of space, we can use it to compute the statistical outcome of measurements. Explore this application, for a simple situation in which you know the answer, by computing the average value of an electron's position in the ground electronic state of a box. Use a spreadsheet program, to numerically determine the average position of an electron for the ground-state wavefunction of the particle in a box of length 100 pm. Take the wavefunction to be

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \left(\frac{\pi x}{L} \right)$$

Remember that the average position \bar{x} for a discrete set of values is given by

$$\bar{x} = \sum_{i=1}^N x_i P_i, \quad P_i = \rho \cdot \Delta x_i$$

where x_i is the value of the displacement in the i th element and P_i is the probability in the i th element. In our case P_i is the electron probability density ρ times Δx_i .

Perform the same calculation analytically, for which the average value is given by

$$\bar{x} = \int_0^L x \psi^2 dx$$

and compare your findings in the two cases.

Solution

The Excel sheet titled "ch2_p5.xls" performs the numerical sum and finds an average value of 50 pm. This sheet is provided on Wiley's website. Hence the average displacement of the particle is at the center of the box, $L/2$.

To perform the result analytically, we first verify that $\psi(x)$ is normalized; hence, we must evaluate

$$\int_0^L \psi^2 dx = \frac{2}{L} \int_0^L \sin^2 \left(\frac{\pi x}{L} \right) dx$$

From Appendix B.1 we know that

$$\int \sin^2(z) dz = \frac{z}{2} - \frac{1}{4} \sin 2z$$

Making the substitution that $z = \pi x/L$, we find

$$\int_0^L \psi^2 dx = \frac{2}{\pi} \int_0^\pi \sin^2(z) dz = \frac{2}{\pi} \left(\frac{z}{2} - \frac{1}{4} \sin 2z \right)_0^\pi = \frac{2}{\pi} \left(\frac{\pi}{2} - \frac{1}{4} \sin 2\pi \right) - \frac{2}{\pi} \left(\frac{0}{2} - \frac{1}{4} \sin 0 \right) = 1$$

Having verified that the wavefunctions are normalized, we can evaluate \bar{x} by

$$\bar{x} = \int_0^L x \psi^2 dx = \frac{2}{L} \int_0^L x \sin^2 \left(\frac{\pi x}{L} \right) dx$$

From Appendix B.1 we know that

$$\int z \sin^2(z) = \frac{z^2}{4} - \frac{z}{4} \sin 2z - \frac{\cos 2z}{8}$$

Making the substitution that $z = \pi x/L$, we find

$$\begin{aligned} \bar{x} &= \int_0^L x \psi^2 dx = \frac{2L}{\pi^2} \int_0^\pi \sin^2(z) dz = \frac{2L}{\pi^2} \left(\frac{z^2}{4} - \frac{z}{4} \sin 2z - \frac{\cos 2z}{8} \right) \Big|_0^\pi \\ &= \frac{2L}{\pi^2} \left(\frac{\pi^2}{4} - 0 - \frac{1}{8} \right) - \frac{2L}{\pi^2} \left(0 - 0 - \frac{1}{8} \right) = \frac{L}{2} \end{aligned}$$

The analytical and numerical results are in excellent agreement.

- P2.5** Use Equation (2.25) in Section 2.4.1 to show that the mean potential energy \bar{V} for an electron in the ground state of the H-atom (ρ is given by Equation (2.22)) is $\bar{V} = -e^2/(4\pi\epsilon_0 a_0)$. Hint: Proceed by converting the integral over all space into spherical coordinates: i.e.,

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \int_{\text{all space}} \frac{1}{r} \rho d\tau = -\frac{e^2}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty \frac{1}{r} \rho r^2 dr$$

Solution

Because the Coulomb potential of the proton is isotropic in space, we proceed by using spherical coordinates to perform the integral. Thus we can write

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \int_{\text{all space}} \frac{1}{r} \rho d\tau = -\frac{e^2}{4\pi\epsilon_0} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty \frac{1}{r} \rho r^2 dr$$

Because the probability density ρ depends only on r , the integration of the angles θ and ϕ is straightforward and gives the solid angle 4π . Using Equation (2.22) we can write

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \int_0^\infty \frac{1}{r} \frac{1}{\pi a_0^3} \exp(-2r/a_0) 4\pi r^2 dr = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{\pi a_0^3} \int_0^\infty r \exp(-2r/a_0) dr$$

With the substitutions $x = 2r/a_0$ and $dx = 2dr/a_0$, this expression can be converted into

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{\pi a_0^3} \frac{a_0}{2} \frac{a_0}{2} \int_0^\infty x \cdot \exp(-x) \cdot dx$$

According to Appendix B the integral is

$$\int_0^\infty x \cdot \exp(-x) \cdot dx = 1! = 1$$

and for the mean potential energy we obtain

$$\bar{V} = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{\pi a_0^3} \frac{a_0}{2} \frac{a_0}{2} \cdot 1 = -\frac{e^2}{4\pi\epsilon_0 a_0}$$

- P2.6** As we have discussed, the ionization energy of a hydrogen atom is the energy required to remove its electron. The table below provides the measured ionization energies for the hydrogen atom and six atomic ions, each of which contains only one electron. From Coulomb's law, we expect the potential energy of the electron to depend on the nuclear charge, or atomic number. Analyze the data and empirically determine this dependence. Given these ionization energies, estimate the kinetic energy of the electron and the electron's average speed. Do we need to account for relativistic effects?

Atomic Number (Z)	Atom/Ion	Ionization Energy (IE)
1	H	13.60 eV
2	He ⁺	54.40 eV
3	Li ²⁺	122.43 eV
4	Be ³⁺	217.67 eV
5	B ⁴⁺	340.11 eV
6	C ⁵⁺	489.81 eV

Solution

We begin by constructing a table which converts the ionization energy from eV into Joule, determines the electron speed, and compares that speed to the speed of light (c_0)

Z	Species	IE/(10 ⁻¹⁸ J)	\bar{T} (10 ⁻¹⁸ J)	v /(m s ⁻¹)	v/c_0
1	H	2.179	2.179	2.187×10^6	0.00732
2	He ⁺	8.715	8.715	4.374×10^6	0.01463
3	Li ²⁺	19.61	19.61	6.562×10^6	0.02195
4	Be ³⁺	34.87	34.87	8.750×10^6	0.02927
5	B ⁴⁺	54.49	54.49	1.094×10^7	0.03658
6	C ⁵⁺	78.47	78.47	1.313×10^7	0.04390

By way of example, consider the calculations for He⁺. In this case the energy conversion proceeds by

$$IE = 54.4 \text{ eV} \cdot \frac{1.602177 \times 10^{-19} \text{ J}}{\text{eV}} = 8.715 \times 10^{-18} \text{ J}$$

From Equation (2.30) of the text, we see that the average kinetic energy \bar{T} is the same as this ionization energy. To find the average speed we use the basic formula $T = mv^2/2$ so that for He⁺

$$v = \sqrt{\frac{2 \cdot 8.715 \times 10^{-18}}{9.1094 \times 10^{-31}}} \text{ m/s} = 4.374 \times 10^6 \text{ m/s}$$

Because each of the atomic ions is a one-electron system, the origin of the ionization energy difference must come from the nuclear charge differences; hence, we assume that

$$\text{Ionization Energy} = \text{constant} \cdot Z^m$$

To determine m , we plot $\ln(IE/10^{-18} \text{ J})$ versus $\ln(Z)$ and find that $m = 2.00$ provides the best fit to the data. The data for the ionization energy versus the atomic number are plotted in Figure P2.6 and clearly show that the ionization energy increases as the square of the atomic number.

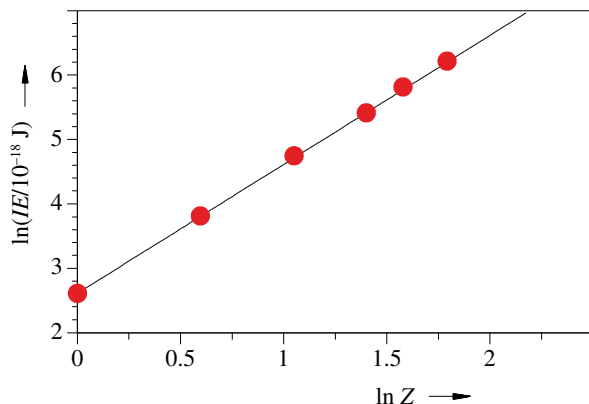


Figure P2.6 The natural logarithm of the ionization energy (IE) is plotted versus the natural logarithm of the atomic number Z .

The second question asks if relativity needs to be considered. From the data we see that the maximum speed for these ions is less than 5% of the speed of light; thus, relativistic effects do not need to be considered.

- P2.7** Given the expression for the energy of an electron trapped in a one-dimensional box, $E_{kin} = \left[\hbar^2 / 8m_e L^2 \right] \cdot n^2$, see Equation (2.14), describe how the energy changes with the size of the box. Make a plot/graph which shows this dependence for $n = 1$, $n = 2$, and $n = 3$. Based on your findings describe how you would expect the electronic energy levels of a chain of hydrogen atoms to change as the number of atoms in the chain is increased. Remember that as you increase the number of atoms in the chain, you are increasing the box length and the number of electrons.

Solution

The kinetic energy E_{kin} of the electron decreases as the box length becomes larger because it can delocalize more. In each case the dependence is a decrease that falls off as $1/L^2$. Figure P2.7 shows plots of the kinetic energy versus the length L for each of the cases: $n = 1$, $n = 2$, and $n = 3$.

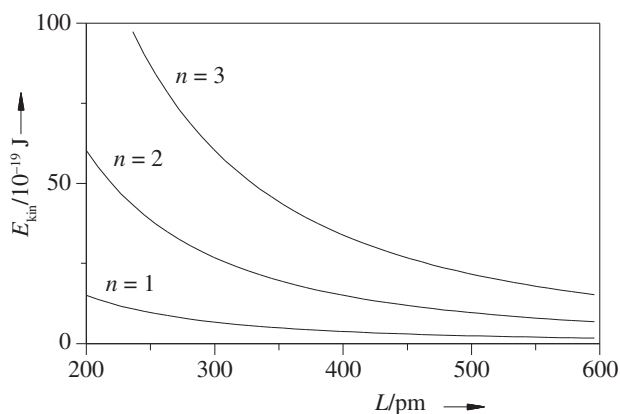


Figure P2.7 Kinetic energy versus the box length L for each of the cases: $n = 1$, $n = 2$, and $n = 3$.

While a chain of real H-atoms would spontaneously segregate into H_2 diatoms, we consider here the artificial condition in which the distance between the H-atoms in the chain is restricted to be fixed at the value $2a_0$. For a chain of N hydrogen atoms we can write the box length as $L = N \cdot 2a_0$. If we model the H-atom chain as a box, the electrons delocalize and the kinetic energy of each energy level n decreases as $1/L^2$; i.e., $1/N^2$. The number of electrons grows as N and the value of the quantum number for the most weakly bound electron is $n = N/2$ for N even and $n = (N + 1)/2$ for N odd. Consequently we expect that the kinetic energy of the most weakly bound electron will decrease as $1/N$.

- P2.8** Using the probability density given by Equation (2.22), compute the average distance of the electron from the proton in a hydrogen atom.

Solutions

The average distance is given by

$$\bar{r} = \int r \cdot \rho(r) \cdot d\tau \text{ where the integral is taken over all space}$$

From Equation (2.22) we see that the probability density depends only on the distance r , not the angles so that

$$\bar{r} = 4\pi \int_0^\infty r \cdot \rho(r) \cdot r^2 dr = \frac{4}{a_0^3} \int_0^\infty r^3 \cdot \exp(-2r/a_0) \cdot dr$$

where we have substituted the expression for $\rho(r)$. If we substitute $x = 2r/a_0$, we find

$$\bar{r} = \frac{1}{a_0} \int_0^\infty x^3 \cdot \exp(-x) \cdot dx$$

Using the integral from Appendix B.1, namely $\int_0^\infty x^n \cdot \exp(-x) \cdot dx = n!$, we find that

$$\bar{r} = \frac{a_0}{4} \int_0^\infty x^3 \cdot \exp(-x) \cdot dx = \frac{a_0}{4} \cdot 6 = \frac{3}{2}a_0$$

- P2.9** The table shows the variational energy $\epsilon/(10^{-19} \text{ J})$ as a function of the parameters L and b for the box model wavefunctions of H_2^+ . The internuclear distance is set at the experimental value of 106 pm. Plot these data and show that they generate a well-defined minimum. Determine the optimized values for L and b . Comment on the results.

L/pm	$b = 1.20$	$b = 1.25$	$b = 1.30$	$b = 1.35$	$b = 1.40$	$b = 1.45$	$b = 1.50$
200	-11.197	-11.779	-12.223	-12.544	-12.753	-12.885	-12.937
220	-13.910	-14.236	-14.451	-14.5637	-14.601	-14.5742	-14.475
240	-15.218	-15.358	-15.405	-15.387	-15.297	-15.157	-14.973
260	-15.644	-15.656	-15.593	-15.466	-15.300	-15.079	-14.839
280	-15.530	-15.441	-15.300	-15.103	-14.878	-14.606	-14.323
300	-15.073	-14.914	-14.715	-14.468	-14.200	-13.898	-13.581
320	-14.403	-14.196	-13.950	-13.674	-13.372	-13.056	-12.714
340	-13.608	-13.368	-13.087	-12.793	-12.468	-12.136	-11.792

Solutions

Figure P2.9a shows plots of ϵ versus L for four different values of b .

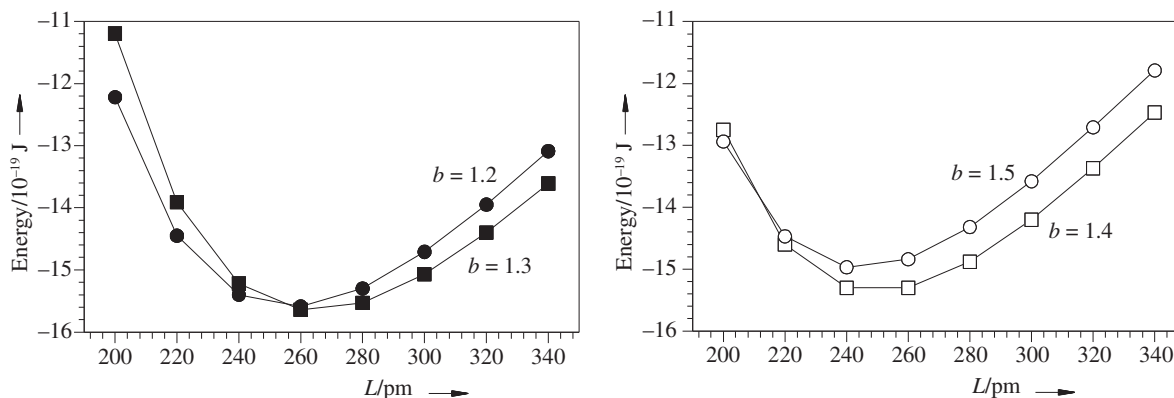


Figure P2.9a Variational energy ϵ of a particle in a three-dimensional box versus the box length L for four different values of the parameter b .

Using plots of this sort we find the value of L that minimizes the energy for each of the values of b ; L_{\min} . The values reported in the table below were obtained by fitting the curve to a cubic equation and then finding the minimum energy from the fit parameters (Fig. P2.9b).

b	1.20	1.25	1.30	1.35	1.40	1.45	1.50
L_{\min}/pm	264	260	257	254	252	249	247
$\epsilon/10^{-19} \text{ J}$	-15.241	-15.656	-15.611	-15.442	-15.299	-15.122	-14.926

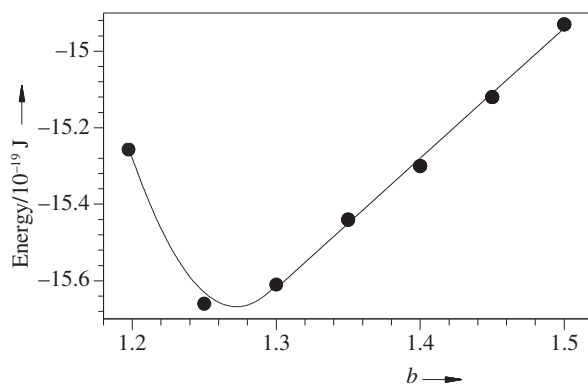


Figure P2.9b Variational energy of an electron in the field of two protons (H_2^+ model), with a three-dimensional box trial function, is plotted versus the box parameter b .

Figure P2.9b plots the minimum energy versus b and indicates that the optimized value of b lies between 1.2 and 1.3. The fact that b is greater than one indicates that the wavefunctions are more delocalized along the x -direction than along y or z .

3

Schrödinger Equation

3.1 Exercises

E3.1 Verify that Equation (3.38) is a solution of the Schrödinger Equation (3.31) for a particle in a three-dimensional box.

Solution

To verify this result we need to find the second partial derivatives of the wavefunction with respect to the variables x , y , and z , and then substitute into the Schrödinger Equation (3.31). To find the second partial derivative with respect to y , we first take the partial derivative with respect to y

$$\frac{\partial \psi}{\partial y} = A \left(\frac{n_y \pi}{L_y} \right) \sin \left(\frac{n_x \pi x}{L_x} \right) \cos \left(\frac{n_y \pi y}{L_y} \right) \sin \left(\frac{n_z \pi z}{L_z} \right)$$

and then take the partial derivative of this result, to find the second partial derivative with respect to y , namely

$$\frac{\partial^2 \psi}{\partial y^2} = -A \left(\frac{n_y \pi}{L_y} \right)^2 \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \left(\frac{n_y \pi y}{L_y} \right) \sin \left(\frac{n_z \pi z}{L_z} \right) = - \left(\frac{n_y \pi}{L_y} \right)^2 \psi.$$

We proceed in like fashion for the second partial derivative with respect to z . First we find the partial derivative with respect to z

$$\frac{\partial \psi}{\partial z} = A \left(\frac{n_z \pi}{L_z} \right) \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \left(\frac{n_y \pi y}{L_y} \right) \cos \left(\frac{n_z \pi z}{L_z} \right)$$

and then the second partial derivative with respect to z

$$\frac{\partial^2 \psi}{\partial z^2} = -A \left(\frac{n_z \pi}{L_z} \right)^2 \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \left(\frac{n_y \pi y}{L_y} \right) \sin \left(\frac{n_z \pi z}{L_z} \right) = - \left(\frac{n_z \pi}{L_z} \right)^2 \psi.$$

Proceeding in a like fashion for the x variable, we find that

$$\frac{\partial^2 \psi}{\partial x^2} = -A \left(\frac{n_x \pi}{L_x} \right)^2 \sin \left(\frac{n_x \pi x}{L_x} \right) \sin \left(\frac{n_y \pi y}{L_y} \right) \sin \left(\frac{n_z \pi z}{L_z} \right) = - \left(\frac{n_x \pi}{L_x} \right)^2 \psi.$$

Substituting these expressions for the second partial derivative into Equation (3.38) gives

$$-\frac{\hbar^2}{2m_e} \left[- \left(\frac{n_x \pi}{L_x} \right)^2 \psi - \left(\frac{n_y \pi}{L_y} \right)^2 \psi - \left(\frac{n_z \pi}{L_z} \right)^2 \psi \right] = E \psi$$

or

$$E = \frac{\hbar^2}{2m_e} \left[\left(\frac{n_x \pi}{L_x} \right)^2 + \left(\frac{n_y \pi}{L_y} \right)^2 + \left(\frac{n_z \pi}{L_z} \right)^2 \right] = \frac{\hbar^2}{2m_e} \left[\left(\frac{n_x}{L_x} \right)^2 + \left(\frac{n_y}{L_y} \right)^2 + \left(\frac{n_z}{L_z} \right)^2 \right]$$

which is Equation (3.39) of the text.

E3.2 In the spirit of the discussion in Section 3.2.3 consider an electron that is confined to a potential energy well with $V = 0$ in two dimensions and infinitely high walls $V = \infty$ outside of the box. Write the Schrödinger equation for