CHEM. 327

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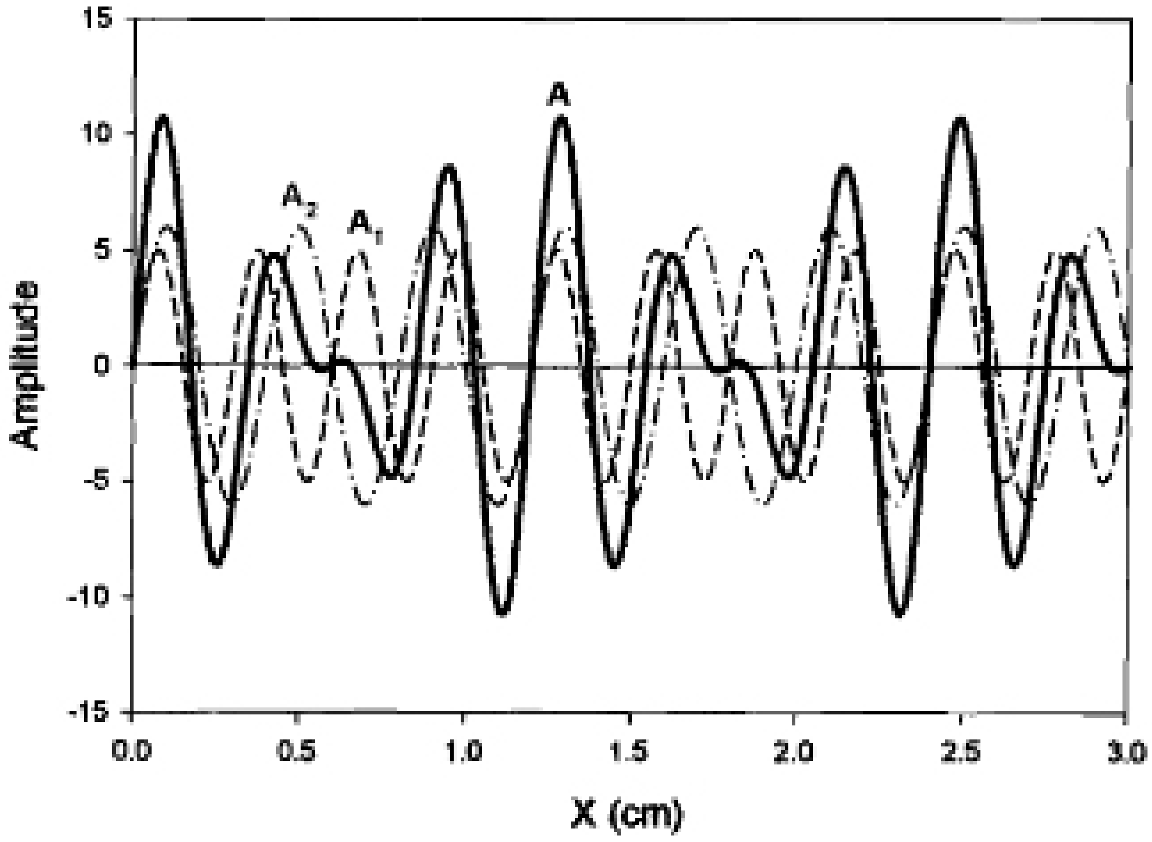
PROBLEM SET 1

1. $A_1 = 5 \sin(20.9439\, x)$

$A_2 = 6 \sin(15.7080\, x)$

$A = A_1 + A_2$



2. $$u = \int_0^\infty u(\nu)\,d\nu = \int_0^\infty \frac{8\pi h\nu^3}{c^3}\frac{d\nu}{(e^{h\nu/kT}-1)}$$

Let $x = \frac{h\nu}{kT}$, $dx = \frac{h}{kT}d\nu$ so $d\nu = \frac{kT}{h}dx$

Then $$u = \frac{8\pi\nu^3 kT}{c^3}\int_0^\infty \frac{dx}{e^x-1}\cdot\frac{(h\nu/kT)^3}{(h\nu/kT)^3}$$

$$= \frac{8\pi(kT)^4}{(hc)^3}\int_0^\infty \frac{x^3}{e^x-1}\,dx = \frac{8\pi(kT)^4}{(hc)^3}\left(\frac{\pi^4}{15}\right)$$

$$u = \frac{8\pi^5(kT)^4}{15(hc)^3} = aT^4$$ (Stephan-Boltzmann law)

3. $$E/s = u\cdot\frac{c}{4}\cdot A = \frac{2\pi^5(kT)^4}{15\,h^3c^2}A$$

$$= \frac{2(3.1416)^5(1.380\times10^{-23}\,J/K)^4(1000\,K)^4(1.00\times10^{-6}\,m^2)}{15(6.626\times10^{-34}\,J\text{-}s)^3(2.998\times10^{8}\,m/s)^2}$$

$$= 5.67\times10^{-2}\,J/s$$

4. $E_e = \frac{hc}{\lambda} - B = \frac{12398\ \text{eV-Å}}{1.937\ \text{Å}} - 3203\ \text{eV} = 3198\ \text{eV}$

$E_e = \frac{1}{2} m v^2 = \frac{1}{2} mc^2 \left(\frac{v}{c}\right)^2$

$v = \left(\frac{2E_e}{mc^2}\right)^{1/2} c = \left[\frac{2(3198\ \text{eV})}{511 \times 10^3\ \text{eV}}\right]^{1/2} (2.998 \times 10^8\ \text{m/s}) = 3.354 \times 10^7\ \text{m/s}$

5. $\lambda' - \lambda = \frac{h}{mc}(1 - \cos\theta) = \frac{hc}{mc^2}(1 - \cos\theta)$; $\theta = 180°$

$= \frac{12398\ \text{eV-Å}}{511 \times 10^3\ \text{eV}}(1 + 1) = 0.04852\ \text{Å}$

$\lambda' = 1.937\ \text{Å} + 0.049\ \text{Å} = 1.986\ \text{Å}$

$E = \frac{hc}{\lambda} = \frac{12398\ \text{eV-Å}}{1.986\ \text{Å}} = 6243\ \text{eV}$

6. photon $\rightsquigarrow$ $\bigcirc \rightarrow$ H_2 molecule

$p_{initial} = p_{final}$ so $p_{H_2} = p_{photon} = E/c = mv$

So $E_{H_2} = \frac{p^2}{2m} = \frac{E_p^2/c^2}{2m_{H_2}}$ but $E_p = \frac{hc}{\lambda}$

Then $E_{H_2} = \frac{(hc)^2}{2m_{H_2}c^2\lambda^2} = \frac{(12398)^2}{2(2.016\ \text{amu})(931.5 \times 10^6\ \text{eV/amu})(589\ \text{Å})^2}$

$E_{H_2} = 1.20 \times 10^{-7}\ \text{eV}$

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

$p = mv = 1.0\ \text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times 300\ \text{m/s} = 0.300\ \text{J-s/m}$

$\lambda = \frac{6.626 \times 10^{-34}\ \text{J-s}}{0.300\ \text{J-s/m}} = 2.21 \times 10^{-33}\ \text{m}$

The trajectory would not be affected by wave properties since the wavelength is infinitesimal compared to the size of the bullet.

8. a). A He atom:

$F_{cent} = F_{coul}$ for each electron:

$$-\frac{mv^2}{r} = -\frac{Ze^2}{r_1^2} + \frac{e^2}{(r_1+r_2)^2}$$

$\uparrow$ attraction of electron 1 to the nucleus

$\uparrow$ repulsion between electron 1 and electron 2

but $r_1 = r_2 = r$ and $r_1 + r_2 = 2r$

so $$\frac{mv^2}{r} = \frac{Ze^2}{r^2} - \frac{e^2}{4r^2} = (Z-\tfrac{1}{4})\frac{e^2}{r^2} \longrightarrow mv^2 = (Z-\tfrac{1}{4})\frac{e^2}{r} \quad (1)$$

The total energy is $$E = \tfrac{1}{2}mv_1^2 + \tfrac{1}{2}mv_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_1+r_2}$$

$$= mv^2 - \frac{2Ze^2}{r} + \frac{e^2}{2r}$$

$$= (Z-\tfrac{1}{4})\frac{e^2}{r} - (2Z-\tfrac{1}{2})\frac{e^2}{r}$$

$$E = -(Z-\tfrac{1}{4})\frac{e^2}{r}$$

Each electron has angular momentum $L = mvr$

so $$r = \frac{L}{mv} \longrightarrow r^2 = \frac{L^2}{m^2v^2} = \frac{L^2}{\frac{m(Z-\frac{1}{4})e^2}{r}}$$ ← from eq. (1) above

Thus $$r = \frac{L^2}{m(Z-\frac{1}{4})e^2}$$

and $$E = \frac{-(Z-\frac{1}{4})e^2}{\frac{L^2}{m(Z-\frac{1}{4})e^2}} = -\frac{m(Z-\frac{1}{4})^2e^4}{L^2}$$

Now let $L = \frac{nh}{2\pi}$

$$E = \frac{-4\pi^2 m(Z-\frac{1}{4})^2 e^4}{n^2h^2}, \text{ but } E_0 = \frac{2\pi^2 m e^4}{h^2}$$ (see eqn for H-atom in notes)

Therefore $$\boxed{E = -2E_0\frac{(Z-\frac{1}{4})^2}{n^2}}$$

b). $E_{He} = -2(13.6)(2-\tfrac{1}{4})^2/1^2 = -83.3\,\text{eV}$

$E_{He^+} = -13.6\,(2)^2/1^2 = -54.4\,\text{eV}$

$E_{ion} = -54.4 - (-83.3) = 28.9\,\text{eV}$ (the experimental ionization energy of He is 24.6 eV)