

28. The energy of the  $2p$  to  $1s$  Lyman transition is

$$E = (-13.60570 \text{ eV}) \left( \frac{1}{2^2} - \frac{1}{1^2} \right) = 10.20428 \text{ eV}$$

and its wavelength (in the absence of fine structure) is

$$\lambda = \frac{hc}{E} = \frac{1239.842 \text{ eV} \cdot \text{nm}}{10.20428 \text{ eV}} = 121.5022 \text{ nm}$$

With the fine structure energy splitting of  $4.5 \times 10^{-5} \text{ eV}$ , the wavelength splitting is

$$\Delta\lambda = \frac{\lambda^2}{hc} \Delta E = \frac{(121.5 \text{ nm})^2}{1240 \text{ eV} \cdot \text{nm}} (4.5 \times 10^{-5} \text{ eV}) = 0.00054 \text{ nm}$$

The fine structure splits one level up by  $0.5\Delta E$  and the other down by the same amount, so the wavelengths are

$$\lambda + \frac{1}{2}\Delta\lambda = 121.5024 \text{ nm} \quad \text{and} \quad \lambda - \frac{1}{2}\Delta\lambda = 121.5019 \text{ nm}$$

1. (a) For a  $2p$  electron,  $n = 2$ ,  $l = 1$ ,  $m_l = 0, \pm 1$  and  $m_s = \pm 1/2$ , so the possible sets of quantum numbers  $(n, l, m_l, m_s)$  are:  
 $(2, 1, +1, +1/2)$ ,  $(2, 1, +1, -1/2)$ ,  $(2, 1, 0, +1/2)$ ,  $(2, 1, 0, -1/2)$ ,  $(2, 1, -1, +1/2)$ ,  $(2, 1, -1, -1/2)$   
(b) There are 6 possible sets of quantum numbers for each electron, so the total number of possibilities for 2 electrons is  $6 \times 6 = 36$ .  
(c) The Pauli principle prevents the two sets from being identical. There will be 6 combinations in which the two sets are identical; eliminating these combinations leaves 30 allowed combinations.  
(d) Because the  $n$  values are different, the Pauli principle does not restrict the number of combinations, so there will be 36 possible combinations.
  
2. (a) The two electrons in the  $1s$  level have  $m_s$  of  $+1/2$  and  $-1/2$ , so they do not contribute to the total  $m_s$ , and the same is true for the two electrons in the  $2s$  level. In the  $2p$  level, there are three different possible values of  $m_l$ , and for each of those values we can assign a set of quantum numbers with  $m_s = +1/2$ , so the maximum possible value of the total  $m_s$  is  $+3/2$ .  
(b)  $(n, l, m_l, m_s) = (2, 1, +1, +1/2)$ ,  $(2, 1, 0, +1/2)$ ,  $(2, 1, -1, +1/2)$   
(c) There is only one possible value of the total  $m_l$  in the states that maximize  $m_s$ , and from the states listed in (b) that value is  $+1 + 0 + (-1) = 0$ .  
(d) We could maximize the total  $m_l$  by giving the first  $2p$  electron  $m_l = +1$ , and the second electron can also have  $m_l = +1$  if we give these two electrons opposite values of  $m_s$ . The third electron cannot have  $m_l = +1$ , so we must assign it  $m_l = 0$  and the maximum total  $m_l$  is  $+2$ .

4. (a) In beryllium ( $1s^2 2s^2$ ) the smallest energy jump is from  $2s$  to  $2p$ .
- (b) In neon ( $1s^2 2s^2 2p^6$ ) the smallest energy jump is from  $2p$  to  $3s$ .
- (c) From Figure 8.1 we see that the  $2s \rightarrow 2p$  energy difference is smaller than the  $2p \rightarrow 3s$  difference, so the minimum absorption energy would be smaller for beryllium.

11. Singly ionized lithium has two electrons. When one of those is excited to a higher level, it is screened by the one electron remaining in the  $1s$  level so  $Z_{\text{eff}} = 3 - 1 = 2$ . The expected energy when the outer electron is excited to the  $2p$  level is

$$E_n = (-13.6 \text{ eV}) \frac{Z_{\text{eff}}^2}{n^2} = (-13.6 \text{ eV}) \frac{2^2}{2^2} = -13.6 \text{ eV}$$

which agrees very well with the measured value of  $-13.4 \text{ eV}$ . When the outer electron is in the  $3d$  level, its expected energy is

$$E_n = (-13.6 \text{ eV}) \frac{Z_{\text{eff}}^2}{n^2} = (-13.6 \text{ eV}) \frac{2^2}{3^2} = -6.0 \text{ eV}$$

in excellent agreement with the measured value.

8. (a)  $[\text{He}]2s^22p^1$  (b)  $[\text{He}]2s^22p^4$  (c)  $[\text{Ne}]3s^23p^6$  (d)  $[\text{Ar}]4s^23d^{10}$

16. Solving Equation 8.4 for  $Z$  with  $\Delta E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{0.1940 \text{ nm}} = 6392 \text{ eV}$ , we obtain

$$Z = 1 + \sqrt{\frac{\Delta E}{10.2 \text{ eV}}} = 1 + \sqrt{\frac{6392 \text{ eV}}{10.2 \text{ eV}}} = 26$$

so the element is iron.

17. Ca ( $Z = 20$ ):  $\Delta E = (10.2 \text{ eV})(Z - 1)^2 = (10.2 \text{ eV})(19)^2 = 3.68 \text{ keV}$   
Zr ( $Z = 40$ ):  $\Delta E = (10.2 \text{ eV})(Z - 1)^2 = (10.2 \text{ eV})(39)^2 = 15.5 \text{ keV}$   
Hg ( $Z = 80$ ):  $\Delta E = (10.2 \text{ eV})(Z - 1)^2 = (10.2 \text{ eV})(79)^2 = 63.7 \text{ keV}$

The values computed from Moseley's law are smaller than the measured values, and the discrepancy increases as  $Z$  increases.

27. (a) For the 3s outer electron of sodium, inserting  $E_3 = -5.14 \text{ eV}$  into Equation 8.1 gives

$$Z_{\text{eff}} = n \sqrt{\frac{E_n}{-13.6 \text{ eV}}} = 3 \sqrt{\frac{-5.14 \text{ eV}}{-13.6 \text{ eV}}} = 1.84$$

The simple screening model predicts  $Z_{\text{eff}} = 1$ , so clearly the 3s electron is slightly penetrating the inner orbits and so is less screened by the inner electrons.

(b) For the 4f state,

$$Z_{\text{eff}} = n \sqrt{\frac{E_n}{-13.6 \text{ eV}}} = 4 \sqrt{\frac{-0.85 \text{ eV}}{-13.6 \text{ eV}}} = 1.00$$

so the screening is complete, with the 11 positive charges in the nucleus screened by the 10 electrons in the  $n = 1$  and  $n = 2$  shells.

30. The wavelength difference is  $\Delta\lambda = 0.59$  nm. By taking differentials of  $E = hc/\lambda$ , we can find the corresponding energy difference:

$$\Delta E = \frac{hc}{\lambda^2} \Delta\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{(590 \text{ nm})^2} (0.59 \text{ nm}) = 2.1 \times 10^{-3} \text{ eV}$$

This energy difference comes from the interaction of a magnetic field  $B$  with a magnetic moment that we assume is of the order of  $1 \mu_B$ . The energy difference between the cases with the magnetic moment parallel to  $B$  and antiparallel to  $B$  is (see Figure 7.25)

$\Delta E = 2\mu_B B$ , so

$$B = \frac{\Delta E}{2\mu_B} = \frac{2.1 \times 10^{-3} \text{ eV}}{2(5.8 \times 10^{-5} \text{ eV/T})} = 18 \text{ T}$$

This is quite a large magnetic field, of the order of the largest that can be produced in the laboratory with superconducting electromagnets.