

13 Atomic structure and atomic spectra

Solutions to exercises

Discussion questions

- E13.1(b)**
- (1) The principal quantum number, n , determines the energy of a hydrogenic atomic orbital through eqn 13.13.
 - (2) The azimuthal quantum number, l , determines the magnitude of the angular momentum of a hydrogenic atomic orbital through the relation $\{l(l + 1)\}^{1/2}\hbar$.
 - (3) The magnetic quantum number, m_l , determines the z -component of the angular momentum of a hydrogenic orbital through the relation $m_l\hbar$.
 - (4) The spin quantum number, s , determines the magnitude of the spin angular momentum through the relation $\{s(s + 1)\}^{1/2}\hbar$. For a hydrogenic atomic orbitals, s can only be $1/2$.
 - (5) The spin quantum number, m_s , determines the z -component of the spin angular momentum through the relation $m_s\hbar$. For hydrogenic atomic orbitals, m_s can only be $\pm 1/2$.
- E13.2(b)**
- (a) A boundary surface for a hydrogenic orbital is drawn so as to contain most (say 90%) of the probability density of an electron in that orbital. Its shape varies from orbital to orbital because the electron density distribution is different for different orbitals.
 - (b) The radial distribution function gives the probability that the electron will be found anywhere within a shell of radius r around the nucleus. It gives a better picture of where the electron is likely to be found with respect to the nucleus than the probability density which is the square of the wavefunction.
- E13.3(b)** The first ionization energies increase markedly from Li to Be, decrease slightly from Be to B, again increase markedly from B to N, again decrease slightly from N to O, and finally increase markedly from N to Ne. The general trend is an overall increase of I_1 with atomic number across the period. That is to be expected since the principal quantum number (electron shell) of the outer electron remains the same, while its attraction to the nucleus increases. The slight decrease from Be to B is a reflection of the outer electron being in a higher energy subshell (larger l value) in B than in Be. The slight decrease from N to O is due to the half-filled subshell effect; half-filled sub-shells have increased stability. O has one electron outside of the half-filled p subshell and that electron must pair with another resulting in strong electron–electron repulsions between them.
- E13.4(b)** An electron has a magnetic moment and magnetic field due to its orbital angular momentum. It also has a magnetic moment and magnetic field due to its spin angular momentum. There is an interaction energy between magnetic moments and magnetic fields. That between the spin magnetic moment and the magnetic field generated by the orbital motion is called spin–orbit coupling. The energy of interaction is proportional to the scalar product of the two vectors representing the spin and orbital angular momenta and hence depends upon the orientation of the two vectors. See Fig. 13.29. The total angular momentum of an electron in an atom is the vector sum of the orbital and spin angular momenta as illustrated in Fig. 13.30 and expressed in eqn 13.46. The spin–orbit coupling results in a splitting of the energy levels associated with atomic terms as shown in Figs 13.31 and 13.32. This splitting shows up in atomic spectra as a fine structure as illustrated in Fig. 13.32.

Numerical exercises

- E13.5(b)** The energy of the photon that struck the Xe atom goes into liberating the bound electron and giving it any kinetic energy it now possesses

$$E_{\text{photon}} = I + E_{\text{kinetic}} \quad I = \text{ionization energy}$$

The energy of a photon is related to its frequency and wavelength

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

and the kinetic energy of an electron is related to its mass and speed

$$E_{\text{kinetic}} = \frac{1}{2}m_e v^2$$

$$\text{So } \frac{hc}{\lambda} = I + \frac{1}{2}m_e v^2 \Rightarrow I = \frac{hc}{\lambda} - \frac{1}{2}m_e v^2$$

$$\begin{aligned} I &= \frac{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1})}{58.4 \times 10^{-9} \text{ m}} \\ &\quad - \frac{1}{2}(9.11 \times 10^{-31} \text{ kg}) \times (1.79 \times 10^6 \text{ m s}^{-1})^2 \\ &= \boxed{1.94 \times 10^{-18} \text{ J}} = 12.1 \text{ eV} \end{aligned}$$

- E13.6(b)** The radial wavefunction is [Table 13.1]

$R_{3,0} = A \left(6 - 2\rho + \frac{1}{9}\rho^2\right) e^{-\rho/6}$ where $\rho \equiv \frac{2Zr}{a_0}$, and A is a collection of constants. Differentiating with respect to ρ yields

$$\begin{aligned} \frac{dR_{3,0}}{d\rho} = 0 &= A \left(6 - 2\rho + \frac{1}{9}\rho^2\right) \times \left(-\frac{1}{6}\right) e^{-\rho/6} + \left(-2 + \frac{2}{9}\rho\right) A e^{-\rho/6} \\ &= A e^{-\rho/6} \left(-\frac{\rho^2}{54} + \frac{5}{9}\rho - 3\right) \end{aligned}$$

This is a quadratic equation

$$0 = a\rho^2 + b\rho + c \quad \text{where } a = -\frac{1}{54}, \quad b = \frac{5}{9}, \quad \text{and } c = -3.$$

The solution is

$$\rho = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = 15 \pm 3\sqrt{7}$$

$$\text{so } r = \boxed{\left(\frac{15}{2} \pm \frac{3(7^{1/2})}{2}\right) \frac{a_0}{Z}}$$

Numerically, this works out to $\rho = 7.65$ and 2.35 , so $r = \boxed{11.5a_0/Z}$ and $\boxed{3.53a_0/Z}$. Substituting $Z = 1$ and $a_0 = 5.292 \times 10^{-11} \text{ m}$, $r = 607 \text{ pm}$ and 187 pm .

The other maximum in the wavefunction is at $\boxed{r = 0}$. It is a physical maximum, but not a calculus maximum: the first derivative of the wavefunction does not vanish there, so it cannot be found by differentiation.

E13.7(b) The radial wavefunction is [Table 13.1]

$$R_{3,1} = A \left(4 - \frac{1}{3}\rho\right) \rho e^{-\rho/6} \quad \text{where} \quad \rho = \frac{2Zr}{a_0}$$

The radial nodes occur where the radial wavefunction vanishes. This occurs at

$$\rho = 0, \quad \boxed{r = 0}$$

and when

$$\left(4 - \frac{1}{3}\rho\right) = 0, \quad \text{or} \quad \frac{\rho}{3} = 4, \quad \text{or} \quad \rho = 12$$

$$\text{then } r = \frac{\rho a_0}{2Z} = \frac{\rho a_0}{2} = \frac{12a_0}{2} = \boxed{6a_0} = 3.18 \times 10^{-10} \text{ m}$$

E13.8(b) Normalization requires

$$\int |\psi|^2 d\tau = 1 = \int_0^\infty \int_0^\pi \int_0^{2\pi} [N(2 - r/a_0)e^{-r/2a_0}]^2 d\phi \sin\theta d\theta r^2 dr$$

$$1 = N^2 \int_0^\infty e^{-r/a_0} (2 - r/a_0)^2 r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

Integrating over angles yields

$$1 = 4\pi N^2 \int_0^\infty e^{-r/a_0} (2 - r/a_0)^2 r^2 dr$$

$$= 4\pi N^2 \int_0^\infty e^{-r/a_0} (4 - 4r/a_0 + r^2/a_0^2) r^2 dr = 4\pi N^2 (8a_0^3)$$

$$\text{In the last step, we used } \int_0^\infty e^{-r/k} r^2 dr = 2k^3, \int_0^\infty e^{-r/k} r^3 dr = 6k^4, \text{ and } \int_0^\infty e^{-r/k} r^4 dr = 24k^5$$

$$\text{So } \boxed{N = \frac{1}{4\sqrt{2\pi a_0^3}}}$$

E13.9(b) The average kinetic energy is

$$\langle \hat{E}_K \rangle = \int \psi^* \hat{E}_K \psi d\tau$$

$$\text{where } \psi = N(2 - \rho)e^{-\rho/2} \text{ with } N = \frac{1}{4} \left(\frac{Z^3}{2\pi a_0^3} \right)^{1/2} \text{ and } \rho \equiv \frac{Zr}{a_0} \text{ here}$$

$$\hat{E}_K = -\frac{\hbar^2}{2m} \nabla^2 \quad d\tau = r^2 \sin\theta dr d\theta d\phi = \frac{a_0^3 \rho^2 \sin\theta d\rho d\theta d\phi}{Z^3}$$

In spherical polar coordinates, three of the derivatives in ∇^2 are derivatives with respect to angles, so those parts of $\nabla^2 \psi$ vanish. Thus

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{\partial^2 \psi}{\partial \rho^2} \left(\frac{\partial \rho}{\partial r} \right)^2 + \frac{2Z}{\rho a_0} \left(\frac{\partial \psi}{\partial \rho} \right) \frac{\partial \rho}{\partial r} = \left(\frac{Z}{a_0} \right)^2 \times \left(\frac{\partial^2 \psi}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \psi}{\partial \rho} \right)$$

$$\begin{aligned}\frac{\partial \rho}{\partial r} &= N(2 - \rho) \times \left(-\frac{1}{2}\right) e^{-\rho/2} - N e^{-\rho/2} = N \left(\frac{1}{2}\rho - 2\right) e^{-\rho/2} \\ \frac{\partial^2 \psi}{\partial \rho^2} &= N \left(\frac{1}{2}\rho - 2\right) \times \left(-\frac{1}{2}\right) e^{-\rho/2} + \frac{1}{2} N e^{-\rho/2} = N \left(\frac{3}{2} - \frac{1}{4}\rho\right) e^{-\rho/2} \\ \nabla^2 \psi &= \left(\frac{Z}{a_0}\right)^2 N e^{-\rho/2} (-4/\rho + 5/2 - \rho/4)\end{aligned}$$

and

$$\begin{aligned}\langle \hat{E}_K \rangle &= \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2 - \rho) e^{-\rho/2} \left(\frac{Z}{a_0}\right)^2 \times \left(\frac{-\hbar^2}{2m}\right) \\ &\quad \times N e^{-\rho/2} (-4/\rho + 5/2 - \rho/4) \frac{a_0^3 d\phi \sin \theta d\theta \rho^2 d\rho}{Z^3}\end{aligned}$$

The integrals over angles give a factor of 4π , so

$$\langle \hat{E}_K \rangle = 4\pi N^2 \left(\frac{a_0}{Z}\right) \times \left(\frac{-\hbar^2}{2m}\right) \int_0^\infty (2 - \rho) \times \left(-4 + \frac{5}{2}\rho - \frac{1}{4}\rho^2\right) \rho e^{-\rho} d\rho$$

The integral in this last expression works out to -2 , using $\int_0^\infty e^{-\rho} \rho^n d\rho = n!$ for $n = 1, 2$, and 3 . So

$$\langle \hat{E}_K \rangle = 4\pi \left(\frac{Z^3}{32\pi a_0^3}\right) \times \left(\frac{a_0}{Z}\right) \times \left(\frac{\hbar^2}{m}\right) = \boxed{\frac{\hbar^2 Z^2}{8ma_0^2}}$$

The average potential energy is

$$\langle V \rangle = \int \psi^* V \psi d\tau \quad \text{where} \quad V = -\frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{Z^2 e^2}{4\pi\epsilon_0 a_0 \rho}$$

$$\text{and } \langle V \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} N(2 - \rho) e^{-\rho/2} \left(-\frac{Z^2 e^2}{4\pi\epsilon_0 a_0 \rho}\right) N(2 - \rho) e^{-\rho/2} \frac{a_0^3 \rho^2 \sin \theta d\rho d\theta d\phi}{Z^3}$$

The integrals over angles give a factor of 4π , so

$$\langle V \rangle = 4\pi N^2 \left(-\frac{Z^2 e^2}{4\pi\epsilon_0 a_0}\right) \times \left(\frac{a_0^3}{Z^3}\right) \int_0^\infty (2 - \rho)^2 \rho e^{-\rho} d\rho$$

The integral in this last expression works out to 2 , using $\int_0^\infty e^{-\rho} \rho^n d\rho = n!$ for $n = 1, 2, 3$, and 4 . So

$$\langle V \rangle = 4\pi \left(\frac{Z^3}{32\pi a_0^3}\right) \times \left(-\frac{Z^2 e^2}{4\pi\epsilon_0 a_0}\right) \times \left(\frac{a_0^3}{Z^3}\right) \times (2) = \boxed{-\frac{Z^2 e^2}{16\pi\epsilon_0 a_0}}$$

E13.10(b) The radial distribution function is defined as

$$P = 4\pi r^2 \psi^2 \quad \text{so} \quad P_{3s} = 4\pi r^2 (Y_{0,0} R_{3,0})^2,$$

$$\boxed{P_{3s} = 4\pi r^2 \left(\frac{1}{4\pi}\right) \times \left(\frac{1}{243}\right) \times \left(\frac{Z}{a_0}\right)^3 \times (6 - 6\rho + \rho^2)^2 e^{-\rho}}$$

$$\text{where } \rho \equiv \frac{2Zr}{na_0} = \frac{2Zr}{3a_0} \quad \text{here.}$$

But we want to find the most likely radius, so it would help to simplify the function by expressing it in terms either of r or ρ , but not both. To find the most likely radius, we could set the derivative of P_{3s} equal to zero; therefore, we can collect all multiplicative constants together (including the factors of a_0/Z needed to turn the initial r^2 into ρ^2) since they will eventually be divided into zero

$$P_{3s} = C^2 \rho^2 (6 - 6\rho + \rho^2)^2 e^{-\rho}$$

Note that not all the extrema of P are maxima; some are minima. But all the extrema of $(P_{3s})^{1/2}$ correspond to maxima of P_{3s} . So let us find the extrema of $(P_{3s})^{1/2}$

$$\begin{aligned} \frac{d(P_{3s})^{1/2}}{d\rho} = 0 &= \frac{d}{d\rho} C\rho(6 - 6\rho + \rho^2)e^{-\rho/2} \\ &= C[\rho(6 - 6\rho + \rho^2) \times (-\frac{1}{2}) + (6 - 12\rho + 3\rho^2)]e^{-\rho/2} \end{aligned}$$

$$0 = C(6 - 15\rho + 6\rho^2 - \frac{1}{2}\rho^3)e^{-\rho/2} \quad \text{so} \quad 12 - 30\rho + 12\rho^2 - \rho^3 = 0$$

Numerical solution of this cubic equation yields

$$\rho = 0.49, \quad 2.79, \quad \text{and} \quad 8.72$$

corresponding to

$$r = \boxed{0.74a_0/Z, 4.19a_0/Z, \text{ and } 13.08a_0/Z}$$

Comment. If numerical methods are to be used to locate the roots of the equation which locates the extrema, then graphical/numerical methods might as well be used to locate the maxima directly. That is, the student may simply have a spreadsheet compute P_{3s} and examine or manipulate the spreadsheet to locate the maxima.

E13.11(b) Orbital angular momentum is

$$\langle \hat{L}^2 \rangle^{1/2} = \hbar(l(l+1))^{1/2}$$

There are l angular nodes and $n - l - 1$ radial nodes

(a) $n = 4, l = 2$, so $\langle \hat{L}^2 \rangle^{1/2} = 6^{1/2}\hbar = \boxed{2.45 \times 10^{-34} \text{ J s}}$ angular nodes radial node

(b) $n = 2, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34} \text{ J s}}$ angular node radial nodes

(c) $n = 3, l = 1$, so $\langle \hat{L}^2 \rangle^{1/2} = 2^{1/2}\hbar = \boxed{1.49 \times 10^{-34} \text{ J s}}$ angular node radial node

E13.12(b) For $l > 0, j = l \pm 1/2$, so

(a) $l = 1$, so $j = \boxed{1/2 \text{ or } 3/2}$

(b) $l = 5$, so $j = \boxed{9/2 \text{ or } 11/2}$

E13.13(b) Use the Clebsch–Gordan series in the form

$$J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$$

Then, with $j_1 = 5$ and $j_2 = 3$

$$J = \boxed{8, 7, 6, 5, 4, 3, 2}$$

E13.14(b) The degeneracy g of a hydrogenic atom with principal quantum number n is $g = n^2$. The energy E of hydrogenic atoms is

$$E = -\frac{hcZ^2\mathcal{R}_H}{n^2} = -\frac{hcZ^2\mathcal{R}_H}{g}$$

so the degeneracy is

$$g = -\frac{hcZ^2\mathcal{R}_H}{E}$$

$$(a) \quad g = -\frac{hc(2)^2\mathcal{R}_H}{-4hc\mathcal{R}_H} = \boxed{1}$$

$$(b) \quad g = -\frac{hc(4)^2\mathcal{R}_H}{-\frac{1}{4}hc\mathcal{R}_H} = \boxed{64}$$

$$(c) \quad g = -\frac{hc(5)^2\mathcal{R}_H}{-hc\mathcal{R}_H} = \boxed{25}$$

E13.15(b) The letter F indicates that the total orbital angular momentum quantum number L is 3; the superscript 3 is the multiplicity of the term, $2S + 1$, related to the spin quantum number $S = 1$; and the subscript 4 indicates the total angular momentum quantum number J .

E13.16(b) The radial distribution function varies as

$$P = 4\pi r^2 \psi^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

The maximum value of P occurs at $r = a_0$ since

$$\frac{dP}{dr} \propto \left(2r - \frac{2r^2}{a_0}\right) e^{-2r/a_0} = 0 \quad \text{at } r = a_0 \quad \text{and } P_{\max} = \frac{4}{a_0} e^{-2}$$

P falls to a fraction f of its maximum given by

$$f = \frac{\frac{4r^2}{a_0^3} e^{-2r/a_0}}{\frac{4}{a_0} e^{-2}} = \frac{r^2}{a_0^2} e^{-2r/a_0}$$

and hence we must solve for r in

$$\frac{f^{1/2}}{e} = \frac{r}{a_0} e^{-r/a_0}$$

$$(a) \quad f = 0.50$$

$$0.260 = \frac{r}{a_0} e^{-r/a_0} \quad \text{solves to } r = 2.08a_0 = \boxed{110 \text{ pm}} \quad \text{and to } r = 0.380a_0 = \boxed{20.1 \text{ pm}}$$

$$(b) \quad f = 0.75$$

$$0.319 = \frac{r}{a_0} e^{-r/a_0} \quad \text{solves to } r = 1.63a_0 = \boxed{86 \text{ pm}} \quad \text{and to } r = 0.555a_0 = \boxed{29.4 \text{ pm}}$$

In each case the equation is solved numerically (or graphically) with readily available personal computer software. The solutions above are easily checked by substitution into the equation for f . The radial distribution function is readily plotted and is shown in Fig. 13.1.

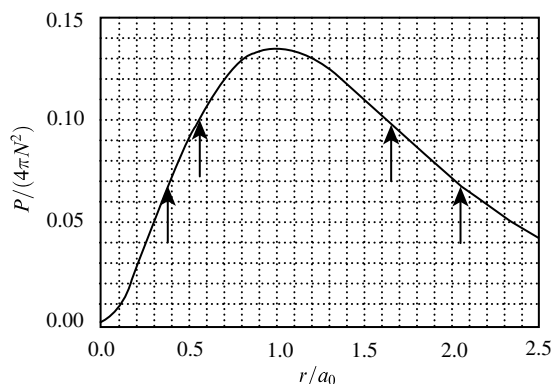


Figure 13.1

E13.17(b) (a) $5d \rightarrow 2s$ is **not** an allowed transition, for $\Delta l = -2$ (Δl must equal ± 1).

(b) $5p \rightarrow 3s$ is **allowed**, since $\Delta l = -1$.

(c) $5p \rightarrow 3f$ is **not** allowed, for $\Delta l = +2$ (Δl must equal ± 1).

E13.18(b) For each l , there are $2l + 1$ values of m_l and hence $2l + 1$ orbitals—each of which can be occupied by two electrons, so maximum occupancy is $2(2l + 1)$

(a) $2s: l = 0$; maximum occupancy = **2**

(b) $4d: l = 2$; maximum occupancy = **10**

(c) $6f: l = 3$; maximum occupancy = **14**

(d) $6h: l = 5$; maximum occupancy = **22**

E13.19(b) $V^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 = [\text{Ar}]3d^3$

The only unpaired electrons are those in the $3d$ subshell. There are three. $S = \frac{3}{2}$ and $\frac{3}{2} - 1 = \frac{1}{2}$.

For $S = \frac{3}{2}$, $M_S = \pm \frac{1}{2}$ and $\pm \frac{3}{2}$

for $S = \frac{1}{2}$, $M_S = \pm \frac{1}{2}$

E13.20(b) (a) Possible values of S for four electrons in different orbitals are **2, 1, and 0**; the multiplicity is $2S + 1$, so multiplicities are **5, 3, and 1** respectively.

(b) Possible values of S for five electrons in different orbitals are **$5/2, 3/2$, and $1/2$** ; the multiplicity is $2S + 1$, so multiplicities are **6, 4, and 2** respectively.

E13.21(b) The coupling of a p electron ($l = 1$) and a d electron ($l = 2$) gives rise to $L = 3$ (F), 2 (D), and 1 (P) terms. Possible values of S include 0 and 1. Possible values of J (using Russell–Saunders coupling) are 3, 2, and 1 ($S = 0$) and 4, 3, 2, 1, and 0 ($S = 1$). The term symbols are

$${}^1F_3; {}^3F_4, {}^3F_3, {}^3F_2; {}^1D_2; {}^3D_3, {}^3D_2, {}^3D_1; {}^1P_1; {}^3P_2, {}^3P_1, {}^3P_0.$$

Hund's rules state that the lowest energy level has maximum multiplicity. Consideration of spin–orbit coupling says the lowest energy level has the lowest value of $J(J + 1) - L(L + 1) - S(S + 1)$. So the lowest energy level is **3F_2**

- E13.22(b)** (a) ${}^3\text{D}$ has $S = 1$ and $L = 2$, so $J = \boxed{3, 2, \text{ and } 1}$ are present. $J = 3$ has $\boxed{7}$ states, with $M_J = 0, \pm 1, \pm 2, \text{ or } \pm 3$; $J = 2$ has $\boxed{5}$ states, with $M_J = 0, \pm 1, \text{ or } \pm 2$; $J = 1$ has $\boxed{3}$ states, with $M_J = 0, \text{ or } \pm 1$.
- (b) ${}^4\text{D}$ has $S = 3/2$ and $L = 2$, so $J = \boxed{7/2, 5/2, 3/2, \text{ and } 1/2}$ are present. $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm 7/2, \pm 5/2, \pm 3/2 \text{ or } \pm 1/2$; $J = 5/2$ has $\boxed{6}$ possible states, with $M_J = \pm 5/2, \pm 3/2 \text{ or } \pm 1/2$; $J = 3/2$ has $\boxed{4}$ possible states, with $M_J = \pm 3/2 \text{ or } \pm 1/2$; $J = 1/2$ has $\boxed{2}$ possible states, with $M_J = \pm 1/2$.
- (c) ${}^2\text{G}$ has $S = 1/2$ and $L = 4$, so $J = \boxed{9/2 \text{ and } 7/2}$ are present. $J = 9/2$ has $\boxed{10}$ possible states, with $M_J = \pm 9/2, \pm 7/2, \pm 5/2, \pm 3/2 \text{ or } \pm 1/2$; $J = 7/2$ has $\boxed{8}$ possible states, with $M_J = \pm 7/2, \pm 5/2, \pm 3/2 \text{ or } \pm 1/2$.

E13.23(b) Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

- (a) $\text{Sc}[\text{Ar}]3d^14s^2$: $S = \frac{1}{2}$, $L = 2$; $J = \frac{5}{2}, \frac{3}{2}$, so the terms are $\boxed{{}^2\text{D}_{5/2} \text{ and } {}^2\text{D}_{3/2}}$
- (b) $\text{Br}[\text{Ar}]3d^{10}4s^24p^5$. We treat the missing electron in the $4p$ subshell as equivalent to a single "electron" with $l = 1$, $s = \frac{1}{2}$. Hence $L = 1$, $S = \frac{1}{2}$, and $J = \frac{3}{2}, \frac{1}{2}$, so the terms are $\boxed{{}^2\text{P}_{3/2} \text{ and } {}^2\text{P}_{1/2}}$

Solutions to problems

Solutions to numerical problems

P13.2

All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = \mathcal{R}_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \left[13.1, \text{ with } \tilde{\nu} = \frac{1}{\lambda} \right] \quad \mathcal{R}_H = 109\,677 \text{ cm}^{-1}$$

Find n_1 from the value of λ_{max} , which arises from the transition $n_1 + 1 \rightarrow n_1$

$$\frac{1}{\lambda_{\text{max}} \mathcal{R}_H} = \frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} = \frac{2n_1 + 1}{n_1^2(n_1 + 1)^2}$$

$$\lambda_{\text{max}} \mathcal{R}_H = \frac{n_1^2(n_1 + 1)^2}{2n_1 + 1} = (656.46 \times 10^{-9} \text{ m}) \times (109\,677 \times 10^2 \text{ m}^{-1}) = 7.20$$

and hence $n_1 = 2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n_2^2} \right), \quad n_2 = 3, 4, 5, 6$$

The next line has $n_2 = 7$, and occurs at

$$\tilde{\nu} = \frac{1}{\lambda} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{49} \right) = \boxed{397.13 \text{ nm}}$$

The energy required to ionize the atom is obtained by letting $n_2 \rightarrow \infty$. Then

$$\tilde{\nu}_{\infty} = \frac{1}{\lambda_{\infty}} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{4} - 0 \right) = 27\,419 \text{ cm}^{-1}, \quad \text{or } \boxed{3.40 \text{ eV}}$$

(The answer, 3.40 eV, is the ionization energy of an H atom that is already in an excited state, with $n = 2$.)

Comment. The series with $n_1 = 2$ is the Balmer series.

P13.4 The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of 2D terms correspond to $1s^23d$, $1s^24d$, etc. Figure 13.2 is a description consistent with the data in the problem statement.

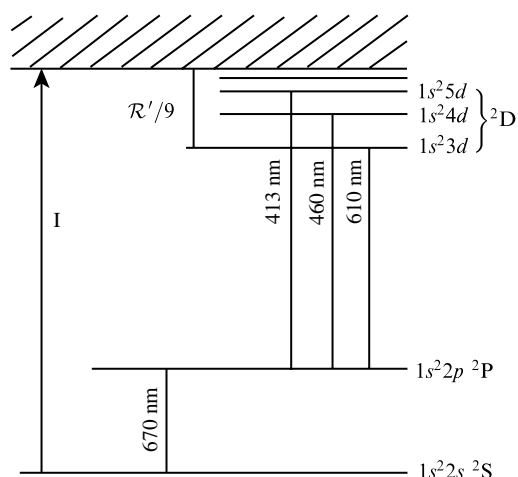


Figure 13.2

If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2D) = -\frac{hc\mathcal{R}'}{n^2} \quad [n = 3, 4, 5, \dots]$$

Then for the ${}^2D \rightarrow {}^2P$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^22p^1, {}^2P)|}{hc} - \frac{\mathcal{R}'}{n^2} \quad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}, \tilde{\nu} = \frac{\Delta E}{hc} \right]$$

from which we can write

$$\frac{|E(1s^22p^1, {}^2P)|}{hc} = \frac{1}{\lambda} + \frac{\mathcal{R}'}{n^2} = \begin{cases} \frac{1}{610.36 \times 10^{-7} \text{ cm}} + \frac{\mathcal{R}'}{9} & \text{(a)} \\ \frac{1}{460.29 \times 10^{-7} \text{ cm}} + \frac{\mathcal{R}'}{16} & \text{(b)} \\ \frac{1}{413.23 \times 10^{-7} \text{ cm}} + \frac{\mathcal{R}'}{25} & \text{(c)} \end{cases}$$

$$\text{Then } \left. \begin{array}{l} \text{(b) - (a) solves to } \mathcal{R}' = 109\,886 \text{ cm}^{-1} \\ \text{(a) - (c) solves to } \mathcal{R}' = 109\,910 \text{ cm}^{-1} \\ \text{(b) - (c) solves to } \mathcal{R}' = 109\,963 \text{ cm}^{-1} \end{array} \right\} \text{Mean} = 109\,920 \text{ cm}^{-1}$$

The binding energies are therefore

$$E(1s^23d^1, {}^2D) = \frac{\mathcal{R}'}{9} = -12\,213 \text{ cm}^{-1}$$

$$E(1s^22p^1, {}^2P) = -\frac{1}{610.36 \times 10^{-7} \text{ cm}} - 12\,213 \text{ cm}^{-1} = -28\,597 \text{ cm}^{-1}$$

$$E(1s^22s^1, {}^2S) = -\frac{1}{670.78 \times 10^{-7} \text{ cm}} - 28\,597 \text{ cm}^{-1} = -43\,505 \text{ cm}^{-1}$$

Therefore, the ionization energy is

$$I(1s^2 2s^1, ^2S) = 43\,505 \text{ cm}^{-1}, \quad \text{or} \quad \boxed{5.39 \text{ eV}}$$

P13.5

The $7p$ configuration has just one electron outside a closed subshell. That electron has $l = 1$, $s = 1/2$, and $j = 1/2$ or $3/2$, so the atom has $L = 1$, $S = 1/2$, and $J = 1/2$ or $3/2$. The term symbols are $\boxed{^2P_{1/2}}$ and $\boxed{^2P_{3/2}}$, of which the former has the lower energy. The $6d$ configuration also has just one electron outside a closed subshell; that electron has $l = 2$, $s = 1/2$, and $j = 3/2$ or $5/2$, so the atom has $L = 2$, $S = 1/2$, and $J = 3/2$ or $5/2$. The term symbols are $\boxed{^2D_{3/2}}$ and $\boxed{^2D_{5/2}}$, of which the former has the lower energy. According to the simple treatment of spin-orbit coupling, the energy is given by

$$E_{l,s,j} = \frac{1}{2}hcA[j(j+1) - l(l+1) - s(s+1)]$$

where A is the spin-orbit coupling constant. So

$$E(^2P_{1/2}) = \frac{1}{2}hcA[\frac{1}{2}(1/2+1) - 1(1+1) - \frac{1}{2}(1/2+1)] = -hcA$$

$$\text{and } E(^2D_{3/2}) = \frac{1}{2}hcA[\frac{3}{2}(3/2+1) - 2(2+1) - \frac{1}{2}(1/2+1)] = -\frac{3}{2}hcA$$

This approach would predict the ground state to be $\boxed{^2D_{3/2}}$

Comment. The computational study cited above finds the $^2P_{1/2}$ level to be lowest, but the authors caution that the error of similar calculations on Y and Lu is comparable to the computed difference between levels.

P13.7

$$\mathcal{R}_H = k\mu_H, \quad \mathcal{R}_D = k\mu_D, \quad \mathcal{R} = k\mu \quad [18]$$

where \mathcal{R} corresponds to an infinitely heavy nucleus, with $\mu = m_e$.

$$\text{Since } \mu = \frac{m_e m_N}{m_e + m_N} \quad [N = \text{p or d}]$$

$$\mathcal{R}_H = k\mu_H = \frac{km_e}{1 + \frac{m_e}{m_p}} = \frac{\mathcal{R}}{1 + \frac{m_e}{m_p}}$$

Likewise, $\mathcal{R}_D = \frac{\mathcal{R}}{1 + \frac{m_e}{m_d}}$ where m_p is the mass of the proton and m_d the mass of the deuteron. The two lines in question lie at

$$\frac{1}{\lambda_H} = \mathcal{R}_H \left(1 - \frac{1}{4}\right) = \frac{3}{4}\mathcal{R}_H \quad \frac{1}{\lambda_D} = \mathcal{R}_D \left(1 - \frac{1}{4}\right) = \frac{3}{4}\mathcal{R}_D$$

and hence

$$\frac{\mathcal{R}_H}{\mathcal{R}_D} = \frac{\lambda_D}{\lambda_H} = \frac{\tilde{\nu}_H}{\tilde{\nu}_D}$$

Then, since

$$\frac{\mathcal{R}_H}{\mathcal{R}_D} = \frac{1 + \frac{m_e}{m_d}}{1 + \frac{m_e}{m_p}}, \quad m_d = \frac{m_e}{\left(1 + \frac{m_e}{m_p}\right) \frac{\mathcal{R}_H}{\mathcal{R}_D} - 1}$$

and we can calculate m_d from

$$\begin{aligned}
 m_d &= \frac{m_e}{\left(1 + \frac{m_e}{m_p}\right) \frac{\lambda_D}{\lambda_H} - 1} = \frac{m_e}{\left(1 + \frac{m_e}{m_p}\right) \frac{\tilde{\nu}_H}{\tilde{\nu}_D} - 1} \\
 &= \frac{9.10939 \times 10^{-31} \text{ kg}}{\left(1 + \frac{9.10939 \times 10^{-31} \text{ kg}}{1.67262 \times 10^{-27} \text{ kg}}\right) \times \left(\frac{82\,259.098 \text{ cm}^{-1}}{82\,281.476 \text{ cm}^{-1}}\right) - 1} = \boxed{3.3429 \times 10^{-27} \text{ kg}}
 \end{aligned}$$

Since $I = Rhc$,

$$\frac{I_D}{I_H} = \frac{\mathcal{R}_D}{\mathcal{R}_H} = \frac{\tilde{\nu}_D}{\tilde{\nu}_H} = \frac{82\,281.476 \text{ cm}^{-1}}{82\,259.098 \text{ cm}^{-1}} = \boxed{1.000\,272}$$

P13.10 If we assume that the innermost electron is a hydrogen-like $1s$ orbital we may write

$$r^* = \frac{a_0}{Z} [\text{Example 13.3}] = \frac{52.92 \text{ pm}}{126} = \boxed{0.420 \text{ pm}}$$

Solutions to theoretical problems

P13.12 Consider $\psi_{2p_z} = \psi_{2,1,0}$ which extends along the z -axis. The most probable point along the z -axis is where the radial function has its maximum value (for ψ^2 is also a maximum at that point). From Table 13.1 we know that

$$R_{21} \propto \rho e^{-\rho/4}$$

and so $\frac{dR}{d\rho} = \left(1 - \frac{1}{4}\rho\right) e^{-\rho/4} = 0$ when $\rho = 4$.

Therefore, $r^* = \frac{2a_0}{Z}$, and the point of maximum probability lies at $z = \pm \frac{2a_0}{Z} = \boxed{\pm 106 \text{ pm}}$

Comment. Since the radial portion of a $2p$ function is the same, the same result would have been obtained for all of them. The direction of the most probable point would, however, be different.

P13.13 In each case we need to show that

$$\int_{\text{all space}} \psi_1^* \psi_2 \, d\tau = 0$$

$$\text{(a)} \quad \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{1s} \psi_{2s} r^2 \, dr \sin \theta \, d\theta \, d\phi \stackrel{?}{=} 0$$

$$\left. \begin{aligned} \psi_{1s} &= R_{1,0} Y_{0,0} \\ \psi_{2s} &= R_{2,0} Y_{0,0} \end{aligned} \right\} Y_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2} \quad [\text{Table 12.3}]$$

Since $Y_{0,0}$ is a constant, the integral over the radial functions determines the orthogonality of the functions.

$$\int_0^\infty R_{1,0} R_{2,0} r^2 \, dr$$

$$R_{1,0} \propto e^{-\rho/2} = e^{-Zr/a_0} \quad \left[\rho = \frac{2Zr}{a_0} \right]$$

$$R_{2,0} \propto (2 - \rho/2) e^{-\rho/4} = \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} \quad \left[\rho = \frac{2Zr}{a_0} \right]$$

$$\begin{aligned} \int_0^\infty R_{1,0} R_{2,0} r^2 dr &\propto \int_0^\infty e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} r^2 dr \\ &= \int_0^\infty 2e^{-(3/2)Zr/a_0} r^2 dr - \int_0^\infty \frac{Z}{a_0} e^{-(3/2)Zr/a_0} r^3 dr \\ &= \frac{2 \times 2!}{\left(\frac{3}{2} \frac{Z}{a_0}\right)^3} - \left(\frac{Z}{a_0}\right) \times \frac{3!}{\left(\frac{3}{2} \frac{Z}{a_0}\right)^4} = \boxed{0} \end{aligned}$$

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 13.2(f), eqn 25

$$p_x \propto x, \quad p_y \propto y$$

Thus

$$\int_{\text{all space}} p_x p_y dx dy dz \propto \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} xy dx dy dz$$

This is an integral of an odd function of x and y over the entire range of variable from $-\infty$ to $+\infty$, therefore, the integral is zero. More explicitly we may perform the integration using the orbitals in the form (Section 13.2(f), eqn 13.25)

$$\begin{aligned} p_x &= f(r) \sin \theta \cos \phi & p_y &= f(r) \sin \theta \sin \phi \\ \int_{\text{all space}} p_x p_y r^2 dr \sin \theta d\theta d\phi &= \int_0^\infty f(r)^2 r^2 dr \int_0^\pi \sin^2 \theta d\theta \int_0^{2\pi} \cos \phi \sin \phi d\phi \end{aligned}$$

The first factor is nonzero since the radial functions are normalized. The second factor is $\frac{\pi}{2}$. The third factor is zero. Therefore, the product of the integrals is zero and the functions are orthogonal.

P13.14
$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + V_{\text{eff}} \right] R = ER \quad [13.11] \quad (1)$$

$$\text{where } V_{\text{eff}} = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} = -\frac{Z\hbar^2}{\mu a_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Using $\rho = Zr/a_0$, the derivative term of the Hamiltonian can be written in the form

$$\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} = \left(\frac{Z}{a_0} \right)^2 \times \left[\frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} \right] \equiv D_{\text{op}} \quad (2)$$

To determine E_{2s} and E_{2p} , we will evaluate the left side of (1) and compare the result to the right side.

$$\begin{aligned} 2s \text{ orbital. } R_{2s} &= N_{2s} (2 - \rho) e^{-\rho/2} \quad \text{where } \rho \equiv Zr/a_0 \text{ here} \\ \frac{dR_{2s}}{d\rho} &= N_{2s} \left\{ -1 - \frac{1}{2}(2 - \rho) \right\} e^{-\rho/2} = N_{2s} \left\{ \frac{\rho - 4}{2} \right\} e^{-\rho/2} = \frac{\rho - 4}{2(2 - \rho)} R_{2s} \\ \frac{d^2 R_{2s}}{d\rho^2} &= N_{2s} \left\{ \frac{1}{2} - \frac{1}{4}(\rho - 4) \right\} e^{-\rho/2} = N_{2s} \left\{ \frac{3}{2} - \frac{\rho}{4} \right\} e^{-\rho/2} = \frac{6 - \rho}{4(2 - \rho)} R_{2s} \end{aligned}$$

$$\begin{aligned}
 -\frac{\hbar^2}{2\mu} D_{\text{op}} R_{2s} &= -\frac{\hbar^2}{2\mu} \left\{ \frac{6-\rho}{4(2-\rho)} + \frac{\rho-4}{\rho(2-\rho)} \right\} \times \left(\frac{Z}{a_0} \right)^2 R_{2s} \\
 &= \left(-\frac{\hbar^2}{2\mu} \right) \times \left(\frac{\rho-8}{4\rho} \right) \times \left(\frac{Z}{a_0} \right)^2 R_{2s} \\
 V_{\text{eff}} R_{2s} &= -\frac{Z\hbar^2}{\mu a_0 r} R_{2s} = -\left(\frac{Z}{a_0} \right)^2 \times \left(\frac{\hbar^2}{\mu} \right) \frac{1}{\rho} R_{2s} \\
 \left[-\frac{\hbar^2}{2\mu} D_{\text{op}} + V_{\text{eff}} \right] R_{2s} &= \left(\frac{Z}{a_0} \right)^2 \times \left(-\frac{\hbar^2}{2\mu} \right) \times \left\{ \frac{\rho-8}{4\rho} + \frac{2}{\rho} \right\} R_{2s} \\
 &= -\frac{Z^2 \hbar^2}{2\mu a_0^2} \left(\frac{1}{4} \right) R_{2s}
 \end{aligned}$$

Therefore
$$E_{2s} = -\frac{1}{4} \left(\frac{Z^2 \hbar^2}{2\mu a_0^2} \right) \quad (3)$$

2p orbital. $R_{2p} = N_{2p} \rho e^{-\rho/2}$ where $\rho \equiv Zr/a_0$ here

$$\begin{aligned}
 \frac{dR_{2p}}{d\rho} &= N_{2p} \left\{ 1 - \frac{\rho}{2} \right\} e^{-\rho/2} = \frac{2-\rho}{2\rho} R_{2p} \\
 \frac{d^2 R_{2p}}{d\rho^2} &= N_{2p} \left\{ -\frac{1}{2} - \frac{1}{2} \left(1 - \frac{\rho}{2} \right) \right\} e^{-\rho/2} = \frac{\rho-4}{4\rho} R_{2p} \\
 -\frac{\hbar^2}{2\mu} D_{\text{op}} R_{2p} &= -\frac{\hbar^2}{2\mu} \left\{ \frac{\rho-4}{4\rho} + \frac{4-2\rho}{2\rho^2} \right\} \times \left(\frac{Z}{a_0} \right)^2 R_{2p} \\
 &= -\frac{\hbar^2}{2\mu} \left\{ \frac{\rho^2 - 8\rho + 8}{4\rho^2} \right\} \times \left(\frac{Z}{a_0} \right)^2 R_{2p} \\
 V_{\text{eff}} R_{2p} &= \left[-\frac{Z\hbar^2}{\mu a_0 r} + \frac{\hbar^2}{\mu r^2} \right] R_{2p} = \left[-\left(\frac{Z}{a_0} \right)^2 \times \left(\frac{\hbar^2}{\mu} \right) \frac{1}{\rho} + \left(\frac{Z}{a_0} \right)^2 \times \left(\frac{\hbar^2}{\mu} \right) \frac{1}{\rho^2} \right] R_{2p} \\
 &= \left(\frac{Z}{a_0} \right)^2 \times \left(-\frac{\hbar^2}{2\mu} \right) \times \left[\frac{2(\rho-1)}{\rho^2} \right] R_{2p} \\
 \left[-\frac{\hbar^2}{2\mu} D_{\text{op}} + V_{\text{eff}} \right] R_{2p} &= \left(\frac{Z}{a_0} \right)^2 \times \left(-\frac{\hbar^2}{2\mu} \right) \times \left\{ \frac{\rho^2 - 8\rho + 8}{4\rho^2} + \frac{2(\rho-1)}{\rho^2} \right\} R_{2p} \\
 &= -\frac{Z^2 \hbar^2}{2\mu a_0^2} \left(\frac{\rho^2}{4\rho^2} \right) R_{2p} = -\frac{Z^2 \hbar^2}{2\mu a_0^2} \left(\frac{1}{4} \right) R_{2p}
 \end{aligned}$$

Therefore
$$E_{2p} = -\frac{1}{4} \left(\frac{Z^2 \hbar^2}{2\mu a_0^2} \right) \quad (4)$$

Comparison of eqns (3) and (4) reveals that $E_{2s} = E_{2p}$.

- P13.15** (a) We must show that $\int |\psi_{3p_x}|^2 d\tau = 1$. The integrations are most easily performed in spherical coordinate (Fig. 11).

$$\begin{aligned} \int |\psi_{3p_x}|^2 d\tau &= \int_0^{2\pi} \int_0^\pi \int_0^\infty |\psi_{3p_x}|^2 r^2 \sin(\theta) dr d\theta d\phi \\ &= \int_0^{2\pi} \int_0^\pi \int_0^\infty \left| R_{31}(\rho) \left\{ \frac{Y_{1-1} - Y_{11}}{\sqrt{2}} \right\} \right|^2 r^2 \sin(\theta) dr d\theta d\phi \quad (\text{Table 13.1, eqn 13.25}) \\ &\quad \text{where } \rho = 2r/a_0, r = \rho a_0/2, dr = (a_0/2) d\rho. \\ &= \frac{1}{2} \int_0^{2\pi} \int_0^\pi \int_0^\infty \left(\frac{a_0}{2} \right)^3 \left[\left(\frac{1}{27(6)^{1/2}} \right) \left(\frac{1}{a_0} \right)^{3/2} \left(4 - \frac{1}{3}\rho \right) \rho e^{-\rho/6} \right]^2 \\ &\quad \times \left[\left(\frac{3}{8\pi} \right)^{1/2} 2 \sin(\theta) \cos(\phi) \right]^2 \rho^2 \sin(\theta) d\rho d\theta d\phi \\ &= \frac{1}{46\,656\pi} \int_0^{2\pi} \int_0^\pi \int_0^\infty \left| \left(4 - \frac{1}{3}\rho \right) \rho e^{-\rho/6} \sin(\theta) \cos(\phi) \right|^2 \rho^2 \sin(\theta) d\rho d\theta d\phi \\ &= \frac{1}{46\,656\pi} \underbrace{\int_0^{2\pi} \cos^2(\phi) d\phi}_\pi \underbrace{\int_0^\pi \sin^3(\theta) d\theta}_{4/3} \underbrace{\int_0^\infty \left(4 - \frac{1}{3}\rho \right)^2 \rho^4 e^{-\rho/3} d\rho}_{34992} \\ &= 1 \quad \text{Thus, } \psi_{3p_x} \text{ is normalized to 1.} \end{aligned}$$

We must also show that $\int \psi_{3p_x} \psi_{3d_{xy}} d\tau = 0$

Using Tables 12.3 and 13.1, we find that

$$\begin{aligned} \psi_{3p_x} &= \frac{1}{54(2\pi)^{1/2}} \left(\frac{1}{a_0} \right)^{3/2} \left(4 - \frac{1}{3}\rho \right) \rho e^{-\rho/6} \sin(\theta) \cos(\phi) \\ \psi_{3d_{xy}} &= R_{32} \left\{ \frac{Y_{22} - Y_{2-2}}{\sqrt{2}i} \right\} \\ &= \frac{1}{32(2\pi)^{1/2}} \left(\frac{1}{a_0} \right)^{3/2} \rho^2 e^{-\rho/6} \sin^2(\theta) \sin(2\phi) \end{aligned}$$

where $\rho = 2r/a_0, r = \rho a_0/2, dr = (a_0/2)d\rho$.

$$\int \psi_{3p_x} \psi_{3d_{xy}} d\tau = \text{constant} \times \int_0^\infty \rho^5 e^{-\rho/3} d\rho \underbrace{\int_0^{2\pi} \cos(\phi) \sin(2\phi) d\phi}_0 \int_0^\pi \sin^4(\theta) d\theta$$

Since the integral equals zero, ψ_{3p_x} and $\psi_{3d_{xy}}$ are orthogonal.

(b) Radial nodes are determined by finding the ρ values ($\rho = 2r/a_0$) for which the radial wavefunction equals zero. These values are the roots of the polynomial portion of the wavefunction.

For the $3s$ orbital $6 - 6\rho + \rho^2 = 0$ when $\rho_{\text{node}} = 3 + \sqrt{3}$ and $\rho_{\text{node}} = 3 - \sqrt{3}$.

The $3s$ orbital has these two spherically symmetrical nodes. There is no node at $\rho = 0$ so we conclude that there is a finite probability of finding a $3s$ electron at the nucleus.

For the $3p_x$ orbital $(4 - \rho)(\rho) = 0$ when $\rho_{\text{node}} = 0$ and $\rho_{\text{node}} = 4$.

There is a zero probability of finding a $3p_x$ electron at the nucleus.

For the $3d_{xy}$ orbital $\rho_{\text{node}} = 0$ is the only radial node.

$$\begin{aligned} \langle r \rangle_{3s} &= \int |R_{10}Y_{00}|^2 r \, d\tau = \int |R_{10}Y_{00}|^2 r^3 \sin(\theta) \, dr \, d\theta \, d\phi \\ &= \int_0^\infty R_{10}^2 r^3 \, dr \underbrace{\int_0^{2\pi} \int_0^\pi |Y_{00}|^2 \sin(\theta) \, d\theta \, d\phi}_1 \\ &= \frac{a_0}{3888} \underbrace{\int_0^\infty (6 - 2\rho + \rho^2/9)^2 \rho^3 e^{-\rho/3} \, d\rho}_{52488} \end{aligned}$$

$$\langle r \rangle_{3s} = \frac{27a_0}{2}$$

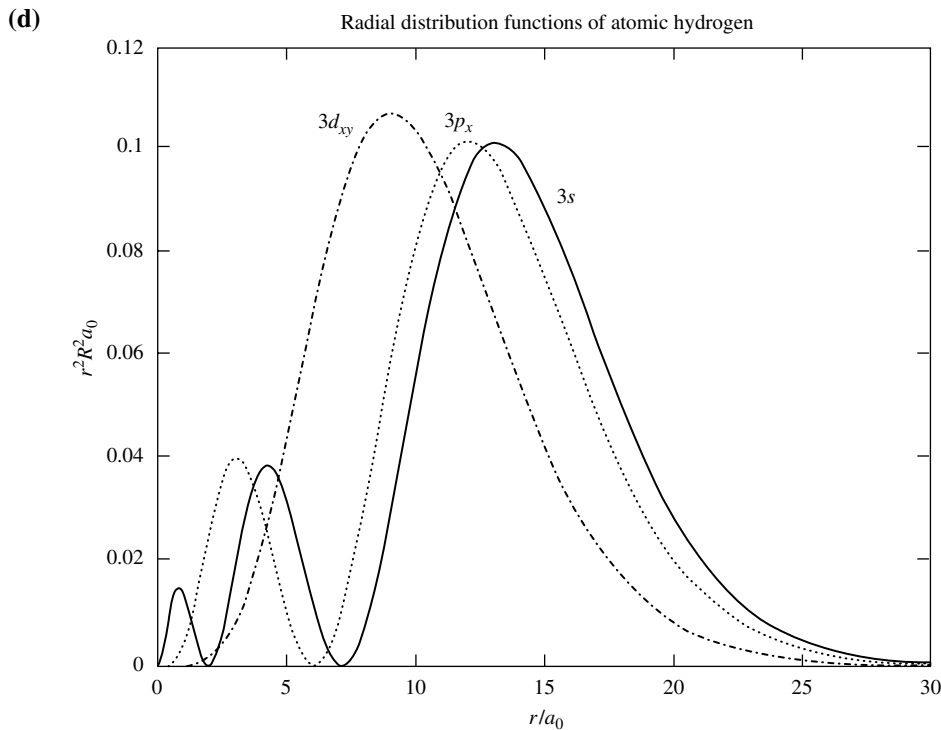


Figure 13.3(a)

The plot shows that the $3s$ orbital has larger values of the radial distribution function for $r < a_0$. This penetration of inner core electrons of multi-electron atoms means that a $3s$ electron

experiences a larger effective nuclear charge and, consequently, has a lower energy than either a $3p_x$ or $3d_{xy}$ electron. This reasoning also lead us to conclude that a $3p_x$ electron has less energy than a $3d_{xy}$ electron.

$$E_{3s} < E_{3p_x} < E_{3d_{xy}}.$$

(e) Polar plots with $\theta = 90^\circ$

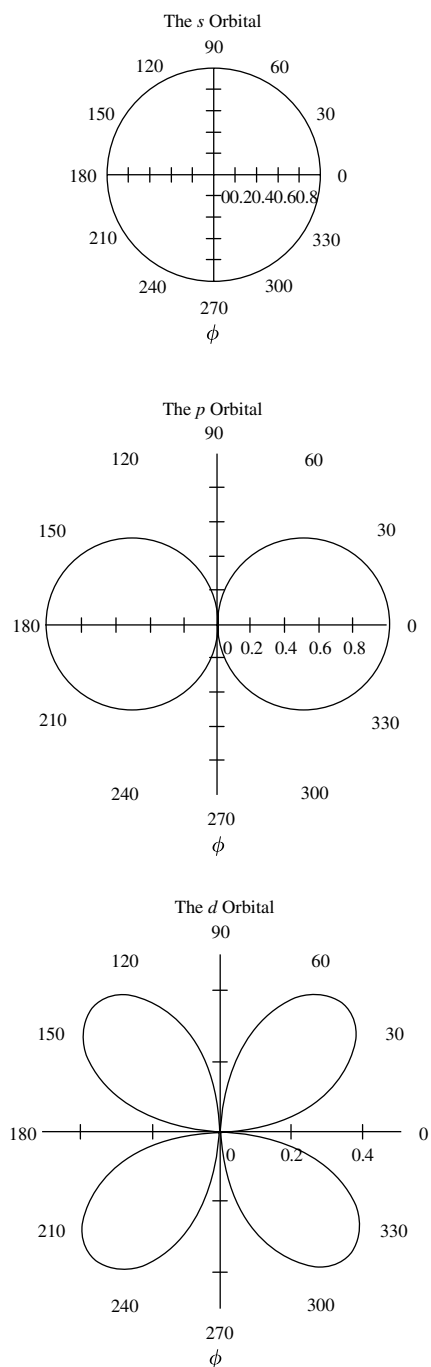


Figure 13.3(b)

Boundary surface plots

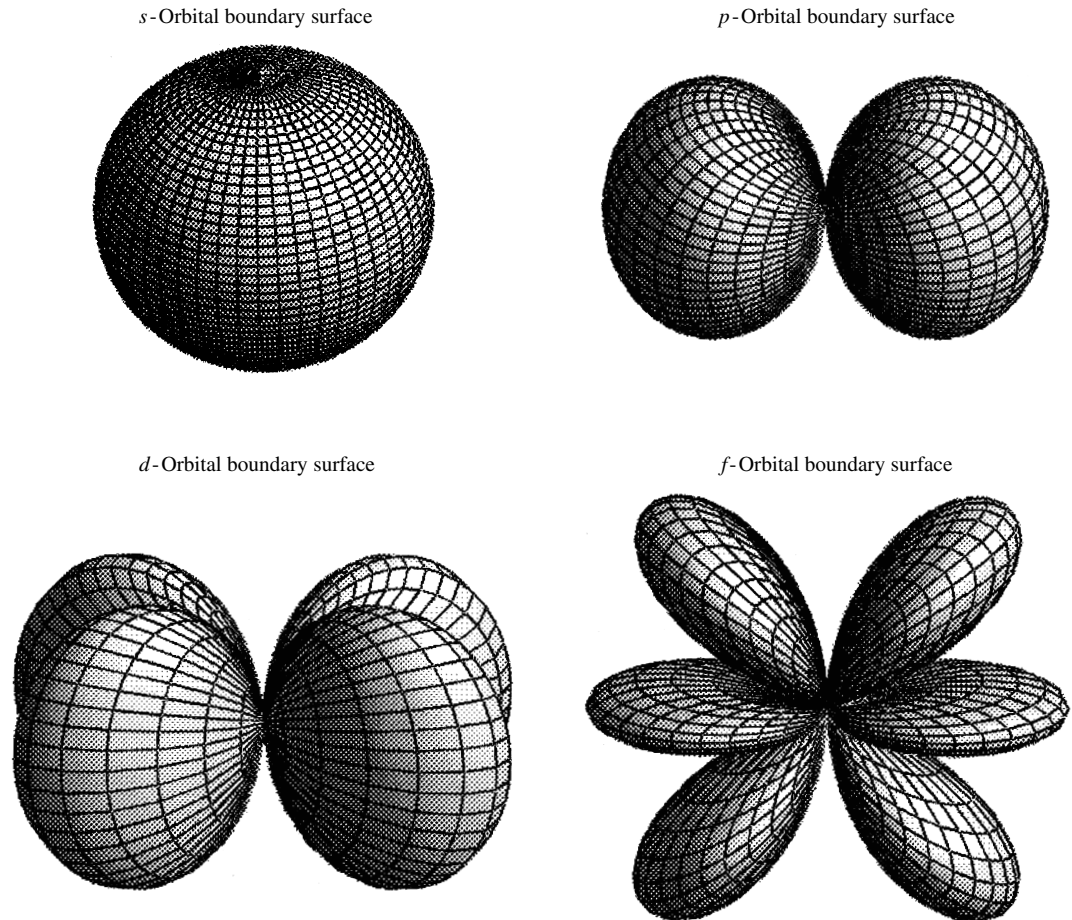


Figure 13.3(c)

P13.20 The attractive Coulomb force = $\frac{Ze^2}{4\pi\epsilon_0} \cdot \frac{1}{r^2}$

The repulsive centrifugal force = $\frac{(\text{angular momentum})^2}{m_e r^3} = \frac{(n\hbar)^2}{m_e r^3}$ [postulated]

The two forces balance when

$$\frac{Ze^2}{4\pi\epsilon_0} \times \frac{1}{r^2} = \frac{n^2\hbar^2}{m_e r^3}, \quad \text{implying that} \quad r = \frac{4\pi n^2 \hbar^2 \epsilon_0}{Ze^2 m_e}$$

The total energy is

$$\begin{aligned}
 E = E_K + V &= \frac{(\text{angular momentum})^2}{2I} - \frac{Ze^2}{4\pi\epsilon_0} \times \frac{1}{r} = \frac{n^2\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \text{[postulated]} \\
 &= \left(\frac{n^2\hbar^2}{2m_e} \right) \times \left(\frac{Ze^2 m_e}{4\pi n^2 \hbar^2 \epsilon_0} \right)^2 - \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \times \left(\frac{Ze^2 m_e}{4\pi n^2 \hbar^2 \epsilon_0} \right) = \boxed{-\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2} \times \frac{1}{n^2}}
 \end{aligned}$$

- P13.21** (a) The trajectory is defined, which is not allowed according to quantum mechanics.
 (b) The angular momentum of a three-dimensional system is given by $\{l(l+1)\}^{1/2}\hbar$, not by $n\hbar$. In the Bohr model, the ground state possesses orbital angular momentum ($n\hbar$, with $n = 1$), but the actual ground state has no angular momentum ($l = 0$). Moreover, the distribution of the electron is quite different in the two cases. The two models can be distinguished experimentally by (a) showing that there is zero orbital angular momentum in the ground state (by examining its magnetic properties) and (b) examining the electron distribution (such as by showing that the electron and the nucleus do come into contact, Chapter 18).

P13.25 *Justification 13.5* noted that the transition dipole moment, μ_{fi} had to be non-zero for a transition to be allowed. The *Justification* examined conditions that allowed the z component of this quantity to be non-zero; now examine the x and y components.

$$\mu_{x,fi} = -e \int \Psi_f^* x \Psi_i d\tau \quad \text{and} \quad \mu_{y,fi} = -e \int \Psi_f^* y \Psi_i d\tau$$

As in the *Justification*, express the relevant Cartesian variables in terms of the spherical harmonics, $Y_{l,m}$. Start by expressing them in spherical polar coordinates:

$$x = r \sin \theta \cos \phi \quad \text{and} \quad y = r \sin \theta \sin \phi.$$

Note that $Y_{1,1}$ and $Y_{1,-1}$ have factors of $\sin \theta$. They also contain complex exponentials that can be related to the sine and cosine of ϕ through the identities (eqns FI1.20 and FI1.21)

$$\cos \phi = 1/2(e^{i\phi} + e^{-i\phi}) \quad \text{and} \quad \sin \phi = 1/2i(e^{i\phi} - e^{-i\phi}).$$

These relations motivate us to try linear combinations $Y_{1,1} + Y_{1,-1}$ and $Y_{1,1} - Y_{1,-1}$ (form Table 12.3; note c here corresponds to the normalization constant in the table):

$$Y_{1,1} + Y_{1,-1} = -c \sin \theta (e^{i\phi} + e^{-i\phi}) = -2c \sin \theta \cos \phi = -2cx/r,$$

$$\text{so } x = -(Y_{1,1} + Y_{1,-1})r/2c;$$

$$Y_{1,1} - Y_{1,-1} = c \sin \theta (e^{i\phi} - e^{-i\phi}) = 2ic \sin \theta \sin \phi = 2icy/r,$$

$$\text{so } y = (Y_{1,1} - Y_{1,-1})r/2ic.$$

Now we can express the integrals in terms of radial wavefunctions $R_{n,l}$ and spherical harmonics Y_{l,m_i}

$$\mu_{x,fi} = \frac{e}{2c} \int_0^\infty R_{n_f, l_f} r R_{n_i, l_i} r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* (Y_{1,1} + Y_{1,-1}) Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi.$$

The angular integral can be broken into two, one of which contains $Y_{1,1}$ and the other $Y_{1,-1}$. According to the “triple integral” relation below Table 12.3, the integral

$$\int_0^\pi \int_0^{2\pi} Y_{l_f, m_{l_f}}^* Y_{1,1} Y_{l_i, m_{l_i}} \sin \theta d\theta d\phi$$

vanishes unless $l_f = l_i \pm 1$ and $m_f = m_i \pm 1$. The integral that contains $Y_{1,-1}$ introduces no further constraints; it vanishes unless $l_f = l_i \pm 1$ and $m_{l_f} = m_{l_i} \pm 1$. Similarly, the y component introduces no further constraints, for it involves the same spherical harmonics as the x component. The whole set of selection rules, then, is that transitions are allowed only if

$$\boxed{\Delta l = \pm 1 \text{ and } \Delta m_l = 0 \text{ or } \pm 1}.$$

- P13.26** (a) The speed distribution in the molecular beam is related to the speed distribution within the chamber by a factor of $v \cos \theta$ as shown in Fig. 13.4. Since an integration over all possible θ must be performed, the $\cos \theta$ factor may be absorbed into the constant of proportionality.

$$f_{\text{beam}}(v) = C v f_{\text{chamber}}(v) \quad \text{where } C \text{ is to be determined}$$

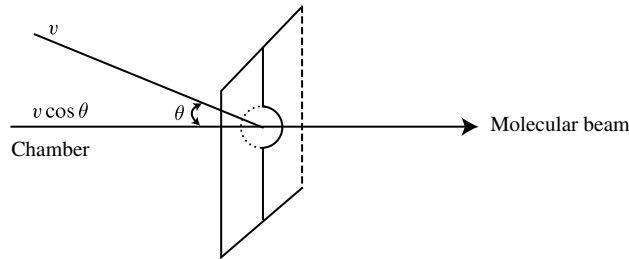


Figure 13.4

By normalization over the possible beam speeds ($0 < v_{\text{beam}} < \infty$)

$$\begin{aligned} f_{\text{beam}} &= C v \left(v^2 e^{-(mv^2/2kT)} \right) \\ &= C v^3 e^{-(mv^2/2kT)} \\ \int_{v=0}^{\infty} f_{\text{beam}} dv &= 1 = C \int_{v=0}^{\infty} v^3 e^{-(mv^2/2kT)} dv = C \left\{ \frac{1}{2(m/2kT)^2} \right\} \\ C &= 2(m/2kT)^2 \\ \langle v^2 \rangle &= \int_{v=0}^{\infty} v^2 f_{\text{beam}}(v) dv = C \int_{v=0}^{\infty} v^5 e^{-(mv^2/2kT)} dv \\ &= C \left\{ \frac{1}{(m/2kT)^3} \right\} = 2 \frac{(m/2kT)^2}{(m/2kT)^3} \\ &= \frac{4kT}{m} \\ \langle E_K \rangle &= \frac{m}{2} \langle v^2 \rangle = \frac{m}{2} \left(\frac{4kT}{m} \right) = \boxed{2kT} \end{aligned}$$

(b)
$$\Delta x = \left(\frac{2\mu_B L^2}{4E_K} \right) \frac{dB}{dz}$$

or
$$\frac{dB}{dz} = \frac{4E_K \Delta x}{2\mu_B L^2} = \frac{4(2kT) \Delta x}{2\mu_B L^2}$$

$$= \frac{4kT \Delta x}{\mu_B L^2}$$

$$= \frac{4(1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (1000 \text{ K}) \times (1.00 \times 10^{-3} \text{ m})}{(9.27402 \times 10^{-24} \text{ J T}^{-1}) \times (50 \times 10^{-2} \text{ m})^2}$$

$$\frac{dB}{dz} = \boxed{23.8 \text{ T m}^{-1}}$$