

Chem 403—Physical Chemistry Homework Solutions
Chapter 10

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- E10.17(a)** These electrons are not equivalent (different subshells); hence all the terms that arise from the vector model and the Clebsch–Gordan series are allowed (Example 10.6).

$$L = l_1 + l_2, \dots, |l_1 - l_2| \text{ [10.44]} = 2 \text{ only,}$$

$$S = s_1 + s_2, \dots, |s_1 - s_2| = 1, 0.$$

The allowed terms are then 3D and 1D . The possible values of J are given by

$$J = L + S, \dots, |L - S| \text{ [10.46]} = 3, 2, 1 \text{ for } ^3D \text{ and } 2 \text{ for } ^1D.$$

The allowed complete term symbols are then

$$\boxed{^3D_3, ^3D_2, ^3D_1, ^1D_2}.$$

The $\boxed{^3D}$ set of terms are the lower in energy [Hund's rule].

COMMENT. Hund's rule in the form given in the text does not allow the energies of the triplet terms to be distinguished. Experimental evidence indicates that 3D_1 is lowest.

- E10.18(a)** Use the Clebsch–Gordan series in the form

$$J = L + S, L + S - 1, \dots, |L - S|.$$

The number of states (M_J values) is $2J + 1$ in each case.

(a) $L = 0, S = 0$; hence $\boxed{J = 0}$ and there is only $\boxed{1}$ state ($M_J = 0$).

(b) $L = 1, S = \frac{1}{2}$; hence $J = \boxed{\frac{3}{2}, \frac{1}{2}}$ ($^2P_{3/2}, ^2P_{1/2}$) with 4, 2 states respectively.

(c) $L = 1, S = 1$; hence $J = \boxed{2, 1, 0}$ ($^3P_2, ^3P_1, ^3P_0$) with 5, 3, 1 states respectively.

- E10.19(a)** Closed shells and subshells do not contribute to either L or S and thus are ignored in what follows.

(a) $\text{Li}[\text{He}]2s^1: S = \frac{1}{2}, L = 0; J = \frac{1}{2}$, so the only term is $\boxed{^2S_{1/2}}$.

(b) $\text{Na}[\text{He}]3p^1: S = \frac{1}{2}, L = 1; J = \frac{3}{2}, \frac{1}{2}$, so the terms are $\boxed{^2P_{3/2} \text{ and } ^2P_{1/2}}$.

Solutions to problems

Solutions to numerical problems

- P10.2** All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \left[10.1, \text{ with } \bar{\nu} = \frac{1}{\lambda} \right] \quad R_H = 109\,677 \text{ cm}^{-1}$$

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

$$\frac{1}{\lambda_{\max} R_H} = \frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} = \frac{2n_1 + 1}{n_1^2(n_1 + 1)^2}$$

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

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

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

(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.

P10.4 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 10.1 is a description consistent with the data in the problem statement.

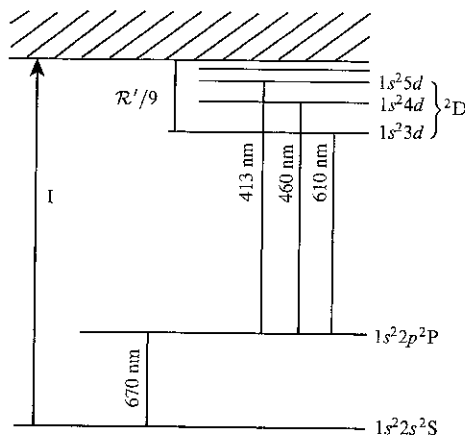


Figure 10.1

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

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

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

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

from which we can write

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

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

The binding energies are therefore

$$E(1s^2 3d^1, {}^2D) = \frac{R'}{9} = -12\,213 \text{ cm}^{-1}$$

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

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

Therefore, the ionization energy is

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

P10.6 The ground term is $[\text{Ar}]4s^1 {}^2S_{1/2}$ and the first excited is $[\text{Ar}]4p^1 {}^2P$. The latter has two levels with $J = 1 + \frac{1}{2} = \frac{3}{2}$ and $J = 1 - \frac{1}{2} = \frac{1}{2}$ which are split by spin-orbit coupling (Section 10.8). Therefore, ascribe the transitions to $\boxed{{}^2P_{3/2} \rightarrow {}^2S_{1/2}}$ and $\boxed{{}^2P_{1/2} \rightarrow {}^2S_{1/2}}$ (since both are allowed). For these values of J , the splitting is equal to $\frac{3}{2}A$ (Example 10.5). Hence, since

$$(766.70 \times 10^{-7} \text{ cm})^{-1} - (770.11 \times 10^{-7} \text{ cm})^{-1} = 57.75 \text{ cm}^{-1}$$

$$\text{we can conclude that } A = \boxed{38.50 \text{ cm}^{-1}}$$

P10.8 The Rydberg constant for positronium (R_{Ps}) is given by

$$\begin{aligned} R_{\text{Ps}} &= \frac{R}{1 + \frac{m_e}{m_e}} = \frac{R}{1 + 1} = \frac{1}{2}R \quad [10.16; \text{also Problem 10.7; } m(\text{positron}) = m_e] \\ &= 54\,869 \text{ cm}^{-1} \quad [R = 109\,737 \text{ cm}^{-1}] \end{aligned}$$

Hence

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} = (54\,869\text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad n = 3, 4, \dots \\ &= \boxed{7621\text{ cm}^{-1}}, \boxed{10\,288\text{ cm}^{-1}}, \boxed{11\,522\text{ cm}^{-1}}, \dots\end{aligned}$$

The binding energy of Ps is

$$E = -hcR_{\text{Ps}}, \text{ corresponding to } (-)54\,869\text{ cm}^{-1}$$

The ionization energy is therefore $54\,869\text{ cm}^{-1}$, or $\boxed{6.80\text{ eV}}$.

P10.10 If we assume that the innermost electron is a hydrogen-like $1s$ orbital we may write

$$r^* = \frac{a_0}{Z} [\text{Example 10.3}] = \frac{52.92\text{ pm}}{126} = \boxed{0.420\text{ pm}}$$

Solutions to theoretical problems

P10.12 In each case we need to show that

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

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

$$\left. \begin{aligned} \psi_{1s} &= R_{1,0} Y_{0,0} \\ \psi_{2s} &= R_{2,0} Y_{0,0} \end{aligned} \right\} Y_{0,0} = \left(\frac{1}{4\pi} \right)^{1/2} \quad [\text{Table 9.3}]$$

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

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

Hence, the functions are orthogonal.

(b) We use the p_x and p_y orbitals in the form given in Section 10.2(f), eqn 10.24

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

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 10.2(f), eqn 10.24)

$$p_x = f(r) \sin \theta \cos \phi \quad p_y = f(r) \sin \theta \sin \phi$$

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

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

P10.14 We use the p_x and p_y orbitals in the form (Section 10.2(f))

$$p_x = r f(r) \sin \theta \cos \phi \quad p_y = r f(r) \sin \theta \sin \phi$$

and use $\cos \phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$ and $\sin \phi = \frac{1}{2i}(e^{i\phi} - e^{-i\phi})$ then

$$p_x = \frac{1}{2} r f(r) \sin \theta (e^{i\phi} + e^{-i\phi}) \quad p_y = \frac{1}{2i} r f(r) \sin \theta (e^{i\phi} - e^{-i\phi})$$

$$\hat{l}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi} \quad [\text{Problem 9.28 and Section 9.6 and eqn 9.46}]$$

$$\hat{l}_z p_x = \frac{\hbar}{2} r f(r) \sin \theta e^{i\phi} - \frac{\hbar}{2} r f(r) \sin \theta e^{-i\phi} = i\hbar p_y \neq \text{constant} \times p_x$$

$$\hat{l}_z p_y = \frac{\hbar}{2i} r f(r) \sin \theta e^{i\phi} + \frac{\hbar}{2i} r f(r) \sin \theta e^{-i\phi} = -i\hbar p_x \neq \text{constant} \times p_y$$

Therefore, neither p_x nor p_y are eigenfunctions of \hat{l}_z . However, $p_x + ip_y$ and $p_x - ip_y$ are eigenfunctions

$$p_x + ip_y = r f(r) \sin \theta e^{i\phi} \quad p_x - ip_y = r f(r) \sin \theta e^{-i\phi}$$

since both $e^{i\phi}$ and $e^{-i\phi}$ are eigenfunctions of \hat{l}_z with eigenvalues $+\hbar$ and $-\hbar$.

P10.16
$$\psi_{1s} = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \quad [10.18]$$

The probability of the electron being within a sphere of radius r' is

$$\int_0^{r'} \int_0^\pi \int_0^{2\pi} \psi_{1s}^2 r^2 \, dr \, \sin \theta \, d\theta \, d\phi$$

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

$$\frac{1}{\lambda_{\max} R_H} = \frac{1}{n_1^2} - \frac{1}{(n_1 + 1)^2} = \frac{2n_1 + 1}{n_1^2(n_1 + 1)^2},$$

$$\lambda_{\max} R_H = \frac{n_1^2(n_1 + 1)^2}{2n_1 + 1} = (12\,368 \times 10^{-9} \text{ m}) \times (109\,677 \times 10^2 \text{ m}^{-1}) = 135.65.$$

Since $n_1 = 1, 2, 3$, and 4 have already been accounted for, try $n_1 = 5, 6, \dots$. With $n_1 = 6$ we get $\frac{n_1^2(n_1 + 1)^2}{2n_1 + 1} = 136$. Hence, the Humphreys series is $n_2 \rightarrow 6$ and the transitions are given by

$$\frac{1}{\lambda} = (109\,677 \text{ cm}^{-1}) \times \left(\frac{1}{36} - \frac{1}{n_2^2} \right), \quad n_2 = 7, 8, \dots$$

and occur at $12\,372 \text{ nm}$, 7503 nm , 5908 nm , 5129 nm , \dots , 3908 nm (at $n_2 = 15$), converging to 3282 nm as $n_2 \rightarrow \infty$, in agreement with the quoted experimental result.

P10.3 A Lyman series corresponds to $n_1 = 1$; hence

$$\tilde{\nu} = R_{\text{Li}^{2+}} \left(1 - \frac{1}{n^2} \right), \quad n = 2, 3, \dots \quad \left[\tilde{\nu} = \frac{1}{\lambda} \right].$$

Therefore, if the formula is appropriate, we expect to find that $\tilde{\nu} \left(1 - \frac{1}{n^2} \right)^{-1}$ is a constant ($R_{\text{Li}^{2+}}$).

We therefore draw up the following table.

n	2	3	4
$\tilde{\nu}/\text{cm}^{-1}$	740747	877924	925933
$\tilde{\nu} \left(1 - \frac{1}{n^2} \right)^{-1} / \text{cm}^{-1}$	987663	987665	987662

Hence, the formula does describe the transitions, and $R_{\text{Li}^{2+}} = 987\,663 \text{ cm}^{-1}$. The Balmer transitions lie at

$$\begin{aligned} \tilde{\nu} &= R_{\text{Li}^{2+}} \left(\frac{1}{4} - \frac{1}{n^2} \right) \quad n = 3, 4, \dots \\ &= (987\,663 \text{ cm}^{-1}) \times \left(\frac{1}{4} - \frac{1}{n^2} \right) = \boxed{137\,175 \text{ cm}^{-1}}, \boxed{185\,187 \text{ cm}^{-1}}, \dots \end{aligned}$$

The ionization energy of the ground-state ion is given by

$$\tilde{\nu} = R_{\text{Li}^{2+}} \left(1 - \frac{1}{n^2} \right), \quad n \rightarrow \infty$$

and hence corresponds to

$$\tilde{\nu} = 987\,663\text{cm}^{-1}, \quad \text{or} \quad \boxed{122.5\text{ eV}}.$$

P10.5 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 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.

P10.7 $R_H = k\mu_H, \quad R_D = k\mu_D, \quad R = k\mu$ [10.16]

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

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

$$R_H = k\mu_H = \frac{km_e}{1 + (m_e/m_p)} = \frac{R}{1 + (m_e/m_p)}.$$

Likewise, $R_D = \frac{R}{(1 + (m_e/m_d))}$ where m_p is the mass of the proton and m_d the mass of the deuteron.

The two lines in question lie at

$$\frac{1}{\lambda_H} = R_H \left(1 - \frac{1}{4}\right) = \frac{3}{4}R_H \quad \frac{1}{\lambda_D} = R_D \left(1 - \frac{1}{4}\right) = \frac{3}{4}R_D$$

and hence

$$\frac{R_H}{R_D} = \frac{\lambda_D}{\lambda_H} = \frac{\tilde{\nu}_H}{\tilde{\nu}_D}.$$

Then, since

$$\frac{R_H}{R_D} = \frac{1 + (m_e/m_d)}{1 + (m_e/m_p)}, \quad m_d = \frac{m_e}{(1 + (m_e/m_p))(R_H/R_D) - 1}$$

and we can calculate m_d from

$$\begin{aligned} m_d &= \frac{m_e}{(1 + (m_e/m_p))(\lambda_D/\lambda_H) - 1} = \frac{m_e}{(1 + (m_e/m_p))(\tilde{\nu}_H/\tilde{\nu}_D) - 1} \\ &= \frac{9.10939 \times 10^{-31} \text{ kg}}{\left(1 + \frac{9.1039 \times 10^{-31} \text{ kg}}{1.67262 \times 10^{-27} \text{ kg}}\right) \times \left(\frac{82259.098 \text{ cm}^{-1}}{82281.476 \text{ cm}^{-1}}\right)^{-1}} \\ &= \boxed{3.3429 \times 10^{-27} \text{ kg}}. \end{aligned}$$

Since $I = Rhc$,

$$\frac{I_D}{I_H} = \frac{R_D}{R_H} = \frac{\tilde{\nu}_D}{\tilde{\nu}_H} = \frac{82281.476 \text{ cm}^{-1}}{82259.098 \text{ cm}^{-1}} = \boxed{1.000272}.$$

- P10.9** (a) The splitting of adjacent energy levels is related to the difference in wavenumber of the spectral lines as follows:

$$\begin{aligned} hc\Delta\tilde{\nu} = \Delta E = \mu_B B, \quad \text{so } \Delta\tilde{\nu} &= \frac{\mu_B B}{hc} = \frac{(9.274 \times 10^{-24} \text{ J T}^{-1})(2 \text{ T})}{(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{10} \text{ cm s}^{-1})} \\ \Delta\tilde{\nu} &= \boxed{0.9 \text{ cm}^{-1}}. \end{aligned}$$

- (b) Transitions induced by absorbing visible light have wavenumbers in the tens of thousands of reciprocal centimeters, so normal Zeeman splitting is **small** compared to the difference in energy of the states involved in the transition. Take a wavenumber from the middle of the visible spectrum as typical:

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{600 \text{ nm}} \left(\frac{10^9 \text{ nm m}^{-1}}{10^2 \text{ cm m}^{-1}} \right) = 1.7 \times 10^4 \text{ cm}^{-1}.$$

Or take the Balmer series as an example, as suggested in the problem; the Balmer wavenumbers are (eqn 10.1):

$$\tilde{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{n^3} \right).$$

The smallest Balmer wavenumber is

$$\tilde{\nu} = (109\,677 \text{ cm}^{-1}) \times (1/4 - 1/9) = 15\,233 \text{ cm}^{-1}$$

and the upper limit is

$$\tilde{\nu} = (109\,677 \text{ cm}^{-1}) \times (1/4 - 0) = 27\,419 \text{ cm}^{-1}.$$

deduce that, if H commutes with \hat{l}_z it must also commute with \hat{l}_x and \hat{l}_y since they are related to each other by a simple transformation of coordinates. This proves useful in establishing the commutation of l^2 and H . We form

$$\hat{l}^2 = \hat{l} \cdot \hat{l} = (\hat{i}l_x + \hat{j}l_y + \hat{k}l_z) \cdot (\hat{i}l_x + \hat{j}l_y + \hat{k}l_z) = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2.$$

If H commutes with each of \hat{l}_x , \hat{l}_y , and \hat{l}_z it must commute with \hat{l}_x^2 , \hat{l}_y^2 , and \hat{l}_z^2 . Therefore it also commutes with \hat{l}^2 . Thus H commutes with both \hat{l}^2 and \hat{l}_z .

COMMENT. As described at the end of Section 8.6, the physical properties associated with non-commuting operators cannot be simultaneously known with precision. However, since H , \hat{l}^2 , and \hat{l}_z commute we may simultaneously have exact knowledge of the energy, the total orbital angular momentum, and the projection of the orbital angular momentum along an arbitrary axis.

P10.17

$$\begin{aligned} \langle r^m \rangle_{nl} &= \int r^m |\psi_{nl}|^2 d\tau = \int_0^\infty \int_0^{2\pi} \int_0^\pi r^{m+2} |R_{nl} Y_{l0}|^2 \sin(\theta) d\theta d\phi dr \\ &= \int_0^\infty r^{m+2} |R_{nl}|^2 dr \int_0^{2\pi} \int_0^\pi |Y_{l0}|^2 \sin(\theta) d\theta d\phi = \int_0^\infty r^{m+2} |R_{nl}|^2 dr. \end{aligned}$$

With $r = (na_0/2Z)\rho$ and $m = -1$, the expectation value is

$$\langle r^{-1} \rangle_{nl} = \left(\frac{na_0}{2Z} \right)^2 \int_0^\infty \rho |R_{nl}|^2 d\rho.$$

$$\begin{aligned} \text{(a)} \quad \langle r^{-1} \rangle_{1s} &= \left(\frac{a_0}{2Z} \right)^2 \left\{ 2 \left(\frac{Z}{a_0} \right)^{3/2} \right\}^2 \int_0^\infty \rho e^{-\rho} d\rho \quad [\text{Table 10.1}] \\ &= \boxed{\frac{Z}{a_0}} \quad \text{because} \quad \int_0^\infty \rho e^{-\rho} d\rho = 1. \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \langle r^{-1} \rangle_{2s} &= \left(\frac{a_0}{Z} \right)^2 \left\{ \frac{1}{8^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \right\}^2 \int_0^\infty \rho (2 - \rho)^2 e^{-\rho} d\rho \quad [\text{Table 10.1}] \\ &= \frac{Z}{8a_0} (2) \quad \text{because} \quad \int_0^\infty \rho (2 - \rho)^2 e^{-\rho} d\rho = 2. \end{aligned}$$

$$\langle r^{-1} \rangle_{2s} = \boxed{\frac{Z}{4a_0}}.$$

$$\begin{aligned} \text{(c)} \quad \langle r^{-1} \rangle_{2p} &= \left(\frac{a_0}{Z} \right)^2 \left\{ \frac{1}{24^{1/2}} \left(\frac{Z}{a_0} \right)^{3/2} \right\}^2 \int_0^\infty \rho^3 e^{-\rho} d\rho \quad [\text{Table 10.1}] \\ &= \frac{Z}{24a_0} (6) \quad \text{because} \quad \int_0^\infty \rho^3 e^{-\rho} d\rho = 6. \end{aligned}$$

$$\langle r^{-1} \rangle_{2p} = \boxed{\frac{Z}{4a_0}}.$$

The general formula for a hydrogenic orbital is $\langle r^{-1} \rangle_{nl} = \frac{Z}{n^2 a_0}$.