Errata, *Quantum Chemistry & Spectroscopy* by Thomas Engel

Inside front cover:

In the SI prefixes section, the symbol for centi should be: c

Chapter 2

p 31 Equation 2.33 should read as follows:

$$f(x)=\left(50\left(\frac{x}{b}\right)^2-1\right)e^{-25\frac{x^2}{2b^2}} \qquad -1\le\frac{x}{b}<1$$

$$f(x)=f(x-2b); \quad -1\ge\frac{x}{b}\ge 1$$

p 35 P2.19 should begin:

Find the result of operating with $(1/r^2)(d/dr)(r^2\,d/dr)+2/r$ on the function …

Chapter 5

p 79 The text in problem P5.6 after the second set of equations should read

We assume that the wave approaches the barrier from the negative x direction. The coefficient B cannot be set equal to zero because $B\exp\left[-i\sqrt{(2mE/\hbar^2)}x\right]$ represents reflection from the barrier.

The equations in P5.6a should read

$$A+B=C+D \qquad C\,e^{-\kappa a}+D\,e^{+\kappa a}=F\,e^{+ika}$$

$$A-B=-\frac{i\kappa}{k}(-C+D) \qquad -C\,e^{-\kappa a}+D\,e^{+\kappa a}=\frac{i\kappa}{k}F\,e^{+ika}$$

In, P5.6d, the second text line (between the equation groups) should read:

and the relationship $\cosh^2 x-\sinh^2 x=1$, show that

Chapter 6

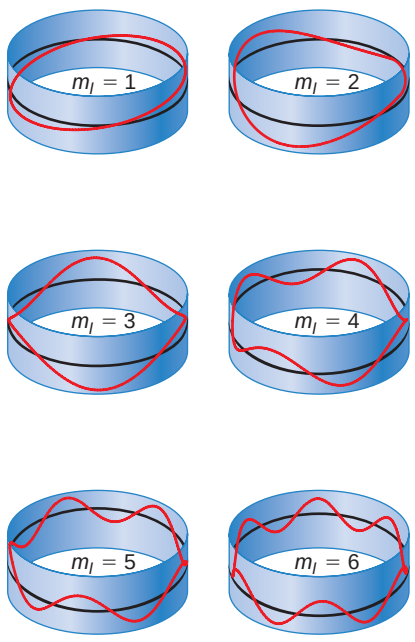
p 84 Equations 6.2 and 6.3 should read:

$$\psi=c_1\alpha+c_2\beta \text{ with } |c_1|^2+|c_2|^2=1 \qquad (6.2)$$

$$\psi=c_3\delta+c_4\gamma \text{ with } |c_3|^2+|c_4|^2=1 \qquad (6.3)$$

Chapter 7

p 111 Figure 7.6 should look like the revised figure below:



p 127 Q7.10 should read as follows:

> What makes the *z* direction special so that we say that $\hat{l}^2$, $\hat{H}$, and $\hat{l}_z$ commute, whereas the individual angular momentum operators $\hat{l}_x, \hat{l}_y,$ and $\hat{l}_z$ don't commute?

p 128 The second exponent of P7.22's display equation should be positive, not negative, so it should read:

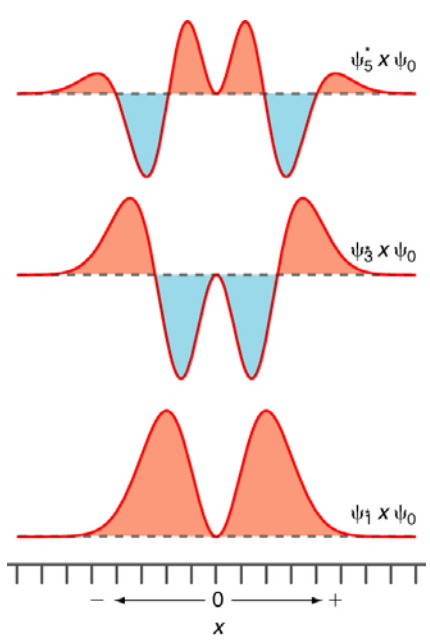
$$\frac{1}{\sqrt{2\pi}} e^{im_l\phi} \text{ and } \frac{1}{\sqrt{2\pi}} e^{in_l\phi},\ m_l \neq n_l$$

Chapter 8

p 136 The third sentence in the paragraph below Example Problem 8.3 should be:

> These parameters, along with the bond energy D_0, are listed in Table 8.3 for selected molecules.

p 138 Replace Figure 8.7 with revised figure below.



p 139 The last equation in Example Problem 8.4 should read

$$l = -\frac{1}{M\varepsilon(\lambda)} \ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\frac{1}{40\ (\text{cm bar})^{-1}\left(2.0\times10^{-6}\ \text{bar}\right)} \ln 0.90 = 1.3\times10^3\ \text{cm}$$

p 153 Equation 8.39 should read:

$$a_2(t) = \mu_x^{21}\frac{E_0}{2}\left(\frac{-1+e^{\frac{i}{\hbar}(E_2-E_1+h\nu)t}}{E_2-E_1+h\nu} + \frac{-1+e^{-\frac{i}{\hbar}(E_2-E_1-h\nu)t}}{E_2-E_1-h\nu}\right)$$

p 154 Equation 8.41 should read

$$\lim\left[\frac{-1+\exp\left[-\frac{i}{\hbar}(E_2-E_1-h\nu)t\right]}{E_2-E_1-h\nu}\right]_{E_2-E_1-h\nu\to 0}$$

$$=\lim\left[\frac{d\left(-1+\exp\left[-\frac{i}{\hbar}(E_2-E_1-h\nu)t\right]\right)\Big/d(E_2-E_1-h\nu)}{d(E_2-E_1-h\nu)\big/d(E_2-E_1-h\nu)}\right]_{E_2-E_1-h\nu\to 0}$$

$$=-\frac{it}{\hbar}\left[\exp\left[-\frac{i}{\hbar}(E_2-E_1-h\nu)t\right]\right]_{E_2-E_1-h\nu\to 0}=-\frac{it}{\hbar}$$

The sentence after Equation 8.41 should read

The important result that emerges from this calculation is that at the resonance condition E_1 - E_2 = $h\nu$, the magnitude of $a_2(t)$ increases linearly with t.

Chapter 9

p 162 Equation 9.2 should read

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right]$$

$$-\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

p 164 The fifth equation in the group in the middle of the page should read

$$n=3,\ l=1\qquad R_{31}(r)=\frac{4}{81\sqrt{6}}\left(\frac{1}{a_0}\right)^{3/2}\left(6\frac{r}{a_0}-\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$$

p 164 The caption for Figure 9.2 should read: …forbidden region in the Coulomb…

p 167 The last sentence of the paragraph below Equation 9.11 should read:

The reduced mass for H is 0.05% less than m_e.

p 174 The solution the Example Problem 9.6 should begin:

The radial probability distribution is

$$P(r)=r^2R^2(r)=\frac{1}{8}\left(\frac{1}{a_0}\right)^3 r^2\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0}.$$

To find the maxima, we plot $P(r)$ and $\frac{dP(r)}{dr}=\frac{r}{8a_0^6}\left(8a_0^3-16a_0^2r+8a_0r^2-r^3\right)e^{-r/a_0}$

versus $\frac{r}{a_0}$ and look for the nodes in this function. These functions are plotted as a function of $\frac{r}{a_0}$ below.

p 177 Q9.10 should read:

What effect does the centripetal potential have in determining the maximum in the radial function for the 3*s*, 3*p*, and 3*d* orbitals?

p 178 The equation in P9.9 should read

$$\psi_{3d_{yz}}(r,\theta,\phi)=\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\sin\phi$$

p 178 In P9.10, $R(r)$ should not appear at the beginning of the equation—so it reads:

$$-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right]+\left[\frac{\hbar^2 l(l+1)}{2\mu r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right]R(r)$$

$$=E\,R(r)\text{ for }l=1$$

Chapter 10

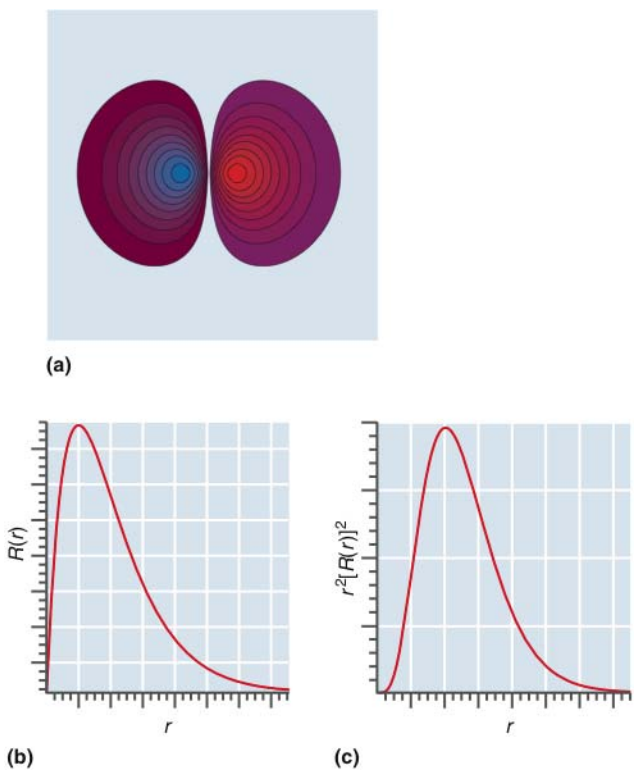
p 190 The fourth sentence of the text below Example Problem 10.3 should be:

To a reasonable approximation, $-\varepsilon_i$ for the highest occupied orbital is the first **ionization energy**.

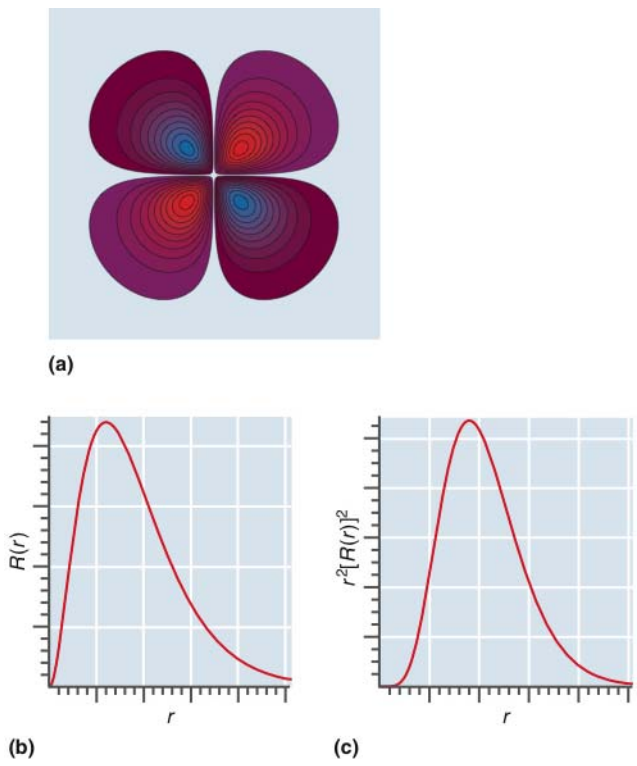
p 199 The third to last sentence on the page should begin:

The degeneracy of these terms is….

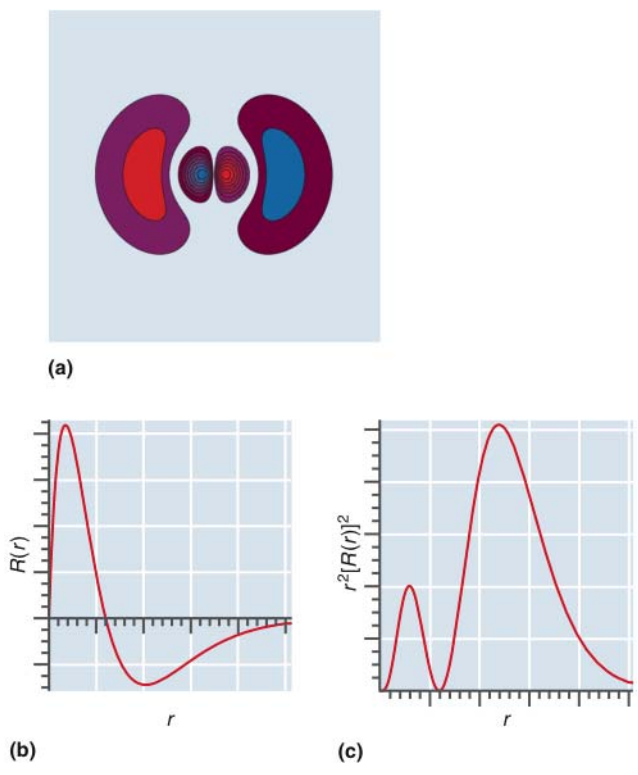
p 208 The figure in Q10.11 should be:



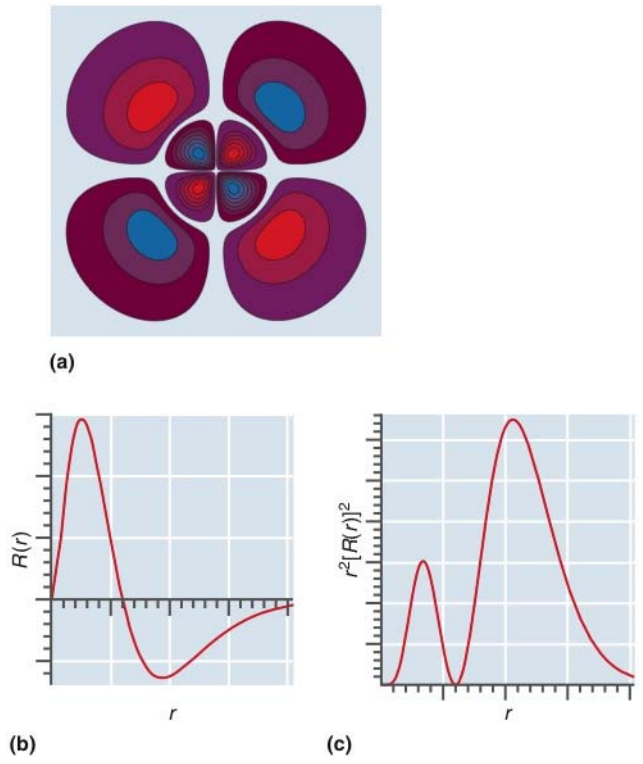
The figure in Q10.12 should be:



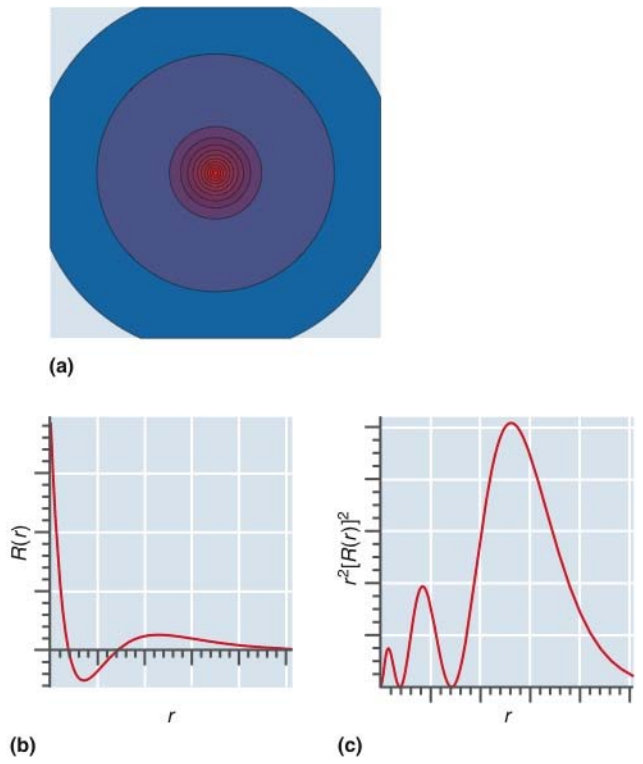
p 209 The figure for Q10.13 should be:



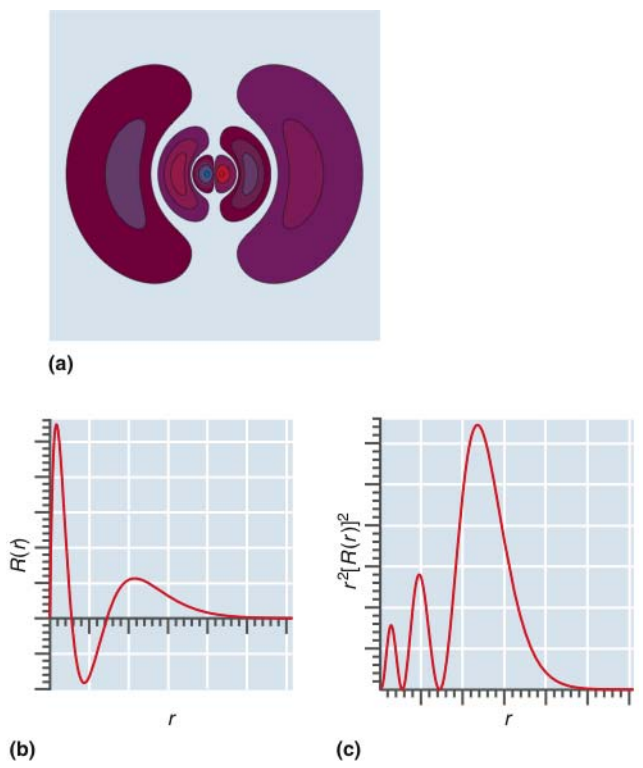
The figure in Q10.14 should be:



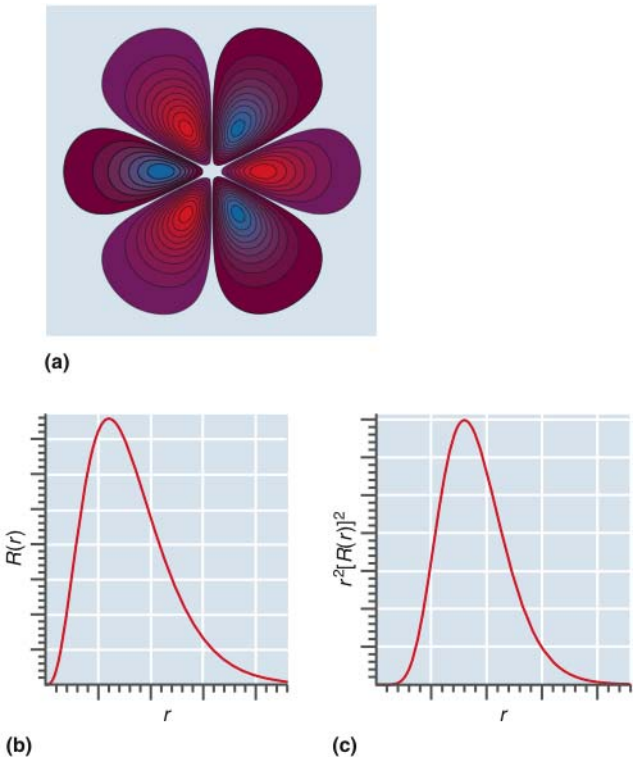
The figure in Q10.15 should be:



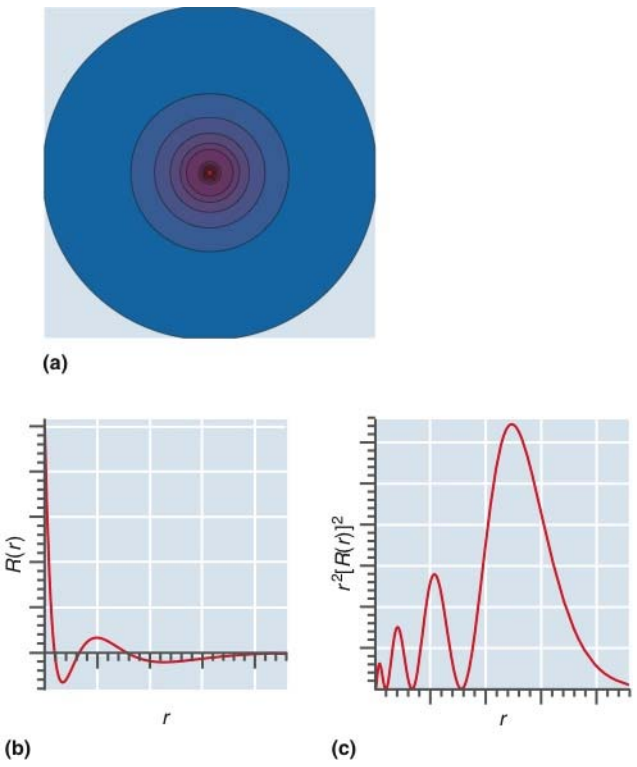
The figure in Q10.16 should be:



p 210 The figure in Q10.17 should be:



The figure in Q10.18 should be:



Chapter 11

p 225 Delete the last sentence in the figure caption of Figure 11.11. The last line of the caption should now be: “particular element.”

p 230 The last sentence in P11.14 should read

> The energy spacing between the D levels is less than for the P levels.]

The second sentence in P11.15 begins:

> For the sodium $3p\ ^2P_{3/2} \rightarrow 3s\ ^2S_{1/2}$ transition, …

Chapter 12

p 235 Make the following change in the first text line below Equation 12.10:

> Assume initially that $\zeta = 1$, in which case ϕ_{H1s_a} is an eigenfunction of the operator

p 245 Q12.8 should read:

> Explain, using Figures 12.8 and 12.9, why $\Delta\psi_g^2 < 0$ and $\Delta\psi_u^2 > 0$ outside of the bonding region of H_2^+.

P 245 The second line of P12.2 should begin: Equation 12.7 gives …

Chapter 13

p 269 The column heads for the table in P13.19 should read:

MO	ε (eV)	c_{N1s}	c_{N2s}	c_{N2pz}	c_{N2px}	c_{N2py}	c_{O1s}	c_{O2s}	c_{O2pz}	c_{O2px}	c_{O2py}

Chapter 14

p 278 The sixth line of the text paragraph after the bullets starts:

Bent's rule says that the H—O—H bond angle will be 109.5°.

The last line of section b of Example Problem 14.4 should read:

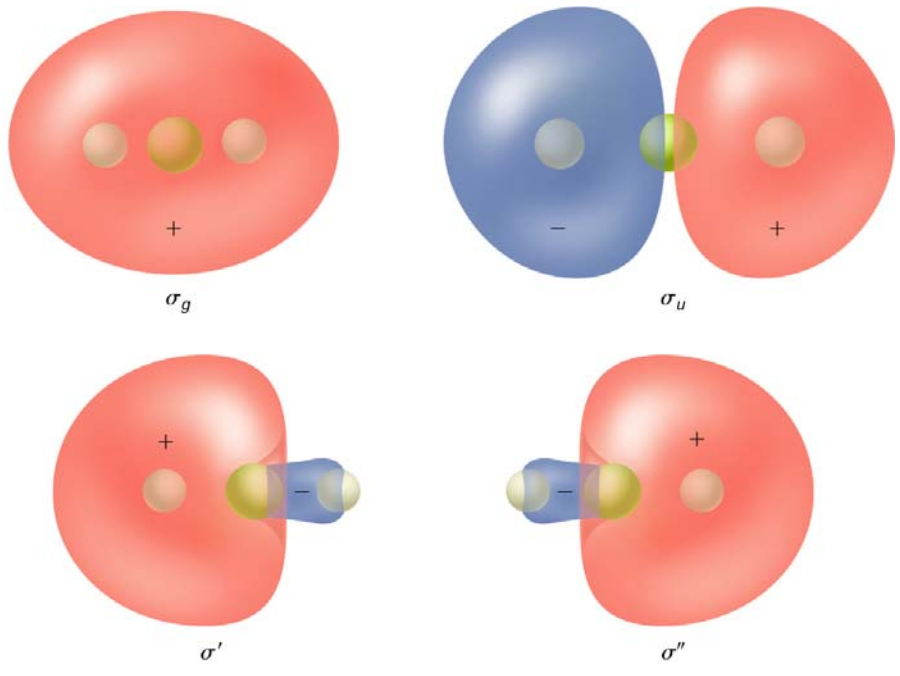
FCH_3 and $ClCH_3$ from 109.5°.

The solution to Example Problem 14.4 should read:

a. To first order, the carbon atom exhibits sp^2 hybridization. Because F is more electronegative than H, the hybridization of the C—F ligand will contain more *p* character than the C—H ligand. Therefore, the F—C—F bond angle will be smaller than the H—C—H bond angle.

b. For both FCH_3 and $ClCH_3$, H is more electropositive than the halogen atom so that the C—H bonds have greater *s* character than the C-halogen bond. This makes the H—C—H bond angle greater than 109.5° in both molecules.

p 288 Figure 14.13 should appear as:



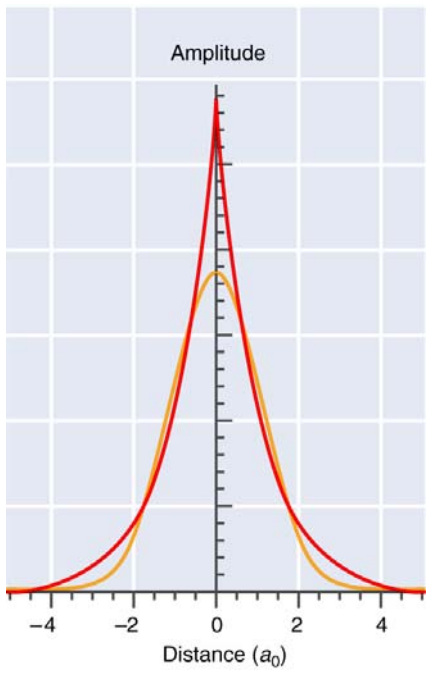
Chapter 15

p 305 Rows five through seven of Table 15.1 should read:

B_2	$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^1(1\pi_u)^1$	$^3\Sigma_g^-$
C_2	$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^2(1\pi_u)^2$	$^1\Sigma_g^+$
N_2^+	$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^2(1\pi_u)^2(3\sigma_g)^1$	$^2\Sigma_g^+$

Chapter 16

p 342 Figure 16.12 should appear as:



p 355 Equation 16.59 should read:

$$q_\mu = P_{\mu\mu} + \sum_{\nu}^{\substack{basis\\functions}} P_{\mu\nu}S_{\mu\nu}$$

Equation 16.61 should read:

$$Q_A = Z_A - q_A$$

p 361 The caption for Figure 16.29 should read

The LUMO (left) and HOMO (right) for acetone identify regions where electrophilic and nucleophilic attack, respectively, are likely to occur.

Chapter 17

p 384 The fourth sentence in the third bulleted item should read

One contains H1 and H2, and the other contains H3 and H4.

p 387 The seventh line in Table 17.2 should read

D_{2h}	E, C_2, C_2', C_2'' , $\sigma, \sigma', \sigma''$, i	C_2F_4

p 396 The sentence immediately following Equation 17.6 should read:

The sum is over the irreducible representations of the group.

p 404 Equation 17.22 should be:

$$n_i = \frac{1}{h}\Gamma_i\Gamma_{reducible} = \frac{1}{h}\chi_i\left(\hat{R}_j\right)g\chi_{reducible}\left(\hat{R}_j\right) = \frac{1}{h}\sum_{j=1}^{h}\chi_i\left(\hat{R}_j\right)\chi_{reducible}\left(\hat{R}_j\right) \quad i = 1, 2, \ldots, N$$

p 410 The caption for Figure 17.11 should read:

The ethene MO that is a basis of the B_{1u} representation.

p 412 The second sentence in P17.17 should end with: $\Gamma_{reducible} = A_1 + E + 2T_2$.

Appendix A

p 453 Equation A.34 should read:

$$f(x) = x - \frac{x^2}{2!} + \frac{2x^3}{3!} - \frac{6x^4}{4!} + \mathrm{K} = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \mathrm{K}$$

p 453 The second sentence following this equation should begin:
For $-1 << x << 1$, the series converges…

p 454 The second line on this page should end … and $\ln(1 \pm x) \approx \pm x$ if $-1 << x << 1$.

Appendix C

p 479 The answer to P6.11 should be $p = 5.275 \times 10^{-24}$ kg m s^{-1} $\frac{\lambda}{b} = 0.0126$

The answer to P6.13 should be $\Delta x = 1.9 \times 10^{-33}$ m

The first answer to P8.7 should be 1.738×10^{-18} J

The answer to P8.18 should be 1.424×10^{-10} m; 1.485×10^{-10} m

p 480 The answer to P11.9 should be

$$-\frac{128\sqrt{2}\,e}{243}a_0$$