## The Hydrogen Atom - Solutions

1. The radial wave function, $P_{n l}(r)$ are given in Table 4.2. For the $1 s$ state of hydrogen:

$$
P_{10}(r)=\frac{2}{\sqrt{a_{0}}}\left(\frac{r}{a_{0}}\right) e^{-r / a_{0}}
$$

where $n=1$ and $l=0$. The radial probability density for this state is:

$$
P_{10}(r)^{2}=\frac{4 r^{2}}{a_{0}^{3}} e^{-2 r / a_{0}}
$$



A plot of this function is easily made using standard plotting software. For example, using MATLAB:
$r=0.0: 0.1$ : 5.0;
$\mathrm{P}=4 * r . * r . * \exp (-2 * r)$; plot(r, $P$ )

This will plot the probability density in units of the Bohr radius, $a_{0}$.
2. Using the radial probability density for the $1 s$ state in the above problem:

$$
P_{10}(r)^{2}=\frac{4 r^{2}}{a_{0}^{3}} e^{-2 r / a_{0}}
$$

The maximum is found by taking the first derivative and equating to zero:

$$
\frac{d}{d r}\left|P_{10}(r)\right|^{2}=\frac{4 r}{a_{0}^{3}} e^{-2 r / a_{0}}-\frac{4 r^{2}}{a_{0}^{4}} e^{-2 r / a_{0}}=0
$$

Divide both sides by $e^{-2 r / a_{0}}$ :

$$
\frac{4 r}{a_{0}^{3}}-\frac{4 r^{2}}{a_{0}^{4}}=0
$$

One solution is $r=0$ but we see that $P_{10}(0)^{2}=0$ and so this cannot be the maximum. The other solution is $r=a_{0}$. This solution is consistent with Bohr model of the hydrogen ground state.
3. The solution to this problem is given exactly in Example 4.4:

$$
\langle r\rangle=\int_{0}^{\infty} r P_{10}(r)^{2} d r
$$

The intermediate steps are given in Example 4.4. The answer is:

$$
\langle r\rangle=\frac{3 a_{0}}{2}
$$

Based on the long tail at large $r$ in the plot of $P_{1 s}$ in Figure 4.7(a), it is easy to conclude that the average value of $r$ should be larger than the maximum of $P_{1 s}$. From the previous problem, we know the maximum of $P_{1 s}$ occurs at $r=a_{0}$ and indeed $\langle r\rangle$ is a factor of 1.5 times larger.
4. Starting with Eqs. (4.7) and (4.8):

$$
d P=|\psi(\mathbf{r})|^{2} r^{2} \sin (\theta) d r d \theta d \psi
$$

and using Eq. (4.4):

$$
\psi(r, \theta, \phi)=\frac{P_{n l}(r)}{r} \Theta_{l m}(\theta) \Phi_{m}(\theta, \phi)
$$

where $P_{n l}(r), \Theta_{l m}(\theta)$, and $\Phi_{m}(\theta, \phi)$ for the 1s state may be found in Tables 4.1 and 4.2. Plugging these in for the $1 s$ state with $Z=1$ :

$$
\psi(r, \theta, \phi)=\frac{1}{\sqrt{\pi}} \frac{1}{a_{0}^{3 / 2}} e^{-r / a_{0}}
$$

Integrating to find the probability:

$$
\begin{aligned}
P & =\int|\psi(r, \theta, \phi)|^{2} r^{2} \sin (\theta) d r d \theta d \phi \\
& =\frac{1}{\pi} \frac{1}{a_{0}^{3}} \int_{0}^{a_{0}} r^{2} e^{-2 r / a_{0}} d r \int_{0}^{\pi} \sin (\theta) d \theta \int_{0}^{2 \pi} d \phi \\
& =\int_{0}^{a_{0}} \frac{4 r^{2}}{a_{0}^{3}} e^{-2 r / a_{0}} d r
\end{aligned}
$$

Substituting $\rho=\frac{r}{a_{0}}$ :

$$
P=2 \int_{0}^{1} \rho^{2} e^{-2 \rho} d \rho
$$

This integral may be solved analytically using integration by parts:

$$
\begin{aligned}
\int_{0}^{1} \rho^{2} e^{-2 \rho} d \rho & =-\left.\frac{1}{2} e^{-2 \rho} \rho^{2}\right|_{0} ^{1}-\int_{0}^{1} 2 \rho\left(-\frac{1}{2} e^{-2 \rho}\right) d \rho \\
& =-\frac{1}{2} e^{-2}+\left.\left(-\frac{1}{2}\right) e^{-2 \rho} \rho\right|_{0} ^{1}-\int_{0}^{1}\left(-\frac{1}{2}\right) e^{-2 \rho} d \rho \\
& =\frac{1}{4}\left(1-5 e^{-2}\right)
\end{aligned}
$$

Numerically, $P=0.081$, so the electron spends $8.1 \%$ of its time inside the Bohr radius.
5. Using a similar approach to that of Problem 2 above, but for the $2 s$ state with $Z=1$,

$$
P_{20}(r)=\sqrt{\frac{1}{2 a_{0}}} \frac{r}{a_{0}}\left(1-\frac{r}{2 a_{0}}\right) e^{-r / 2 a_{0}}
$$

The maximum is found by taking the first derivative and equating to zero:

$$
\sqrt{\frac{1}{2 a_{0}}}\left[\frac{1}{a_{0}}\left(1-\frac{r}{2 a_{0}}\right)+\frac{r}{a_{0}}\left(\frac{-1}{2 a_{0}}\right)+\frac{r}{a_{0}}\left(1-\frac{r}{2 a_{0}}\right)\left(\frac{-1}{2 a_{0}}\right)\right] e^{-r / 2 a_{0}}=0
$$

Divide both sides by $e^{-2 r / a_{0}}$ and multiply through by overall constants:

$$
\left(1-\frac{r}{2 a_{0}}\right)-\frac{r}{2 a_{0}}-\frac{r}{2 a_{0}}\left(1-\frac{r}{2 a_{0}}\right)=0
$$

Setting $x=r / 2 a_{0}$ and collecting terms:

$$
1-3 x+x^{2}=0
$$

Solving the quadratic equation gives:

$$
x=\frac{3 \pm \sqrt{5}}{2}
$$

and substituting back for $x$ gives $r=a_{0}(3 \pm \sqrt{5})$. It is a simple matter to plot $P_{20}(r)$, which shows that the maximum is at $r=a_{0}(3-\sqrt{5})$.
6. The $3 d$ radial function, given by Table 4.2 , is:

$$
\sqrt{\frac{2 Z}{15 a_{0}}} \frac{2}{81}\left(\frac{Z r}{a_{0}}\right)^{3} e^{-Z r / 3 a_{0}}
$$

In units of the Bohr radius $a_{0}$, plotting with MATLAB:

$$
\mathrm{Z}=1 ;
$$



```
r = 0.0 : 0.5 : 70.0;
P3d = 0.0090*sqrt (Z)*Z*Z*Z*r.*r.*r.*exp (-Z*r/3);
plot(r,P3d)
```

This gives the same plot as shown in Figure 4.8. To plot the case with $Z=8$, it is only necessary to change the first line and the range in the second line.

7. The $3 d$ radial function is shown in the previous problem. Taking the derivative and setting it equal to zero:

$$
\left(\frac{Z}{a_{0}}\right)^{3}\left[3 r^{2}+r^{3}\left(\frac{-Z}{3 a_{0}}\right)\right] e^{-Z r / 3 a_{0}}=0
$$

Dividing through by $e^{-Z r / 3 a_{0}}$ and overall constants:

$$
3\left(\frac{r}{a_{0}}\right)^{2}-\frac{Z}{3}\left(\frac{r}{a_{0}}\right)^{3}=0
$$

Since the wave function is zero at $r=0$, this cannot be the maximum. Solving for $r$,

$$
r=\frac{9 a_{0}}{Z}
$$

For $Z=1$, the maximum is at $9 a_{0}$, but for $Z=8$, the maximum is much smaller, at $1.125 a_{0}$. An electron in a $3 d$ orbit is much closer to the $Z=8$ nucleus than for hydrogen with $Z=1$.
8. From Example 4.3 (or Table 4.2 ), the $2 p$ radial probability is

$$
\left|P_{21}(r)\right|^{2} d r=\frac{1}{24 a_{0}}\left(\frac{r}{a_{0}}\right)^{4} e^{-r / a_{0}} d r
$$

Following Example 4.4, but for the average value given here:

$$
\begin{aligned}
& \left\langle\frac{1}{r^{3}}\right\rangle=\int_{0}^{\infty}\left|P_{21}(r)\right|^{2} \frac{1}{r^{3}} d r \\
= & \frac{1}{24 a_{0}} \int_{0}^{\infty}\left(\frac{r}{a_{0}}\right)^{4} e^{-r / a_{0}} \frac{1}{r^{3}} d r
\end{aligned}
$$

Substituting $\rho=r / a_{0}$ :

$$
\left\langle\frac{1}{r^{3}}\right\rangle=\frac{1}{24 a_{0}^{3}} \int_{0}^{\infty} \rho e^{-\rho} d \rho
$$

Integrating by parts

$$
\int_{0}^{\infty} \rho e^{-\rho} d \rho=-\left.\rho e^{-\rho}\right|_{0} ^{\infty}-\int_{0}^{\infty}\left(-e^{-\rho}\right) d \rho
$$

The first term is zero and the second term integrates to unity. The answer is:

$$
\left\langle\frac{1}{r^{3}}\right\rangle=\frac{1}{24 a_{0}^{3}}
$$

9. Using the radial wave function from Table (4.2) for the $3 d$ state of hydrogen:

$$
P_{32}(r)=\sqrt{\frac{2}{15 a_{0}}} \frac{2}{81}\left(\frac{r}{a_{0}}\right)^{3} e^{-r / 3 a_{0}}
$$

Following example 4.4, the average value is:

$$
\langle r\rangle=\int_{0}^{\infty}\left|P_{32}(r)\right|^{2} r d r=\frac{C^{2}}{a_{0}} \int_{0}^{\infty}\left(\frac{r}{a_{0}}\right)^{6} e^{-2 r / 3 a_{0}} r d r
$$

where $C=\sqrt{2 / 15}(2 / 81)$ are the constants in $P_{32}(r)$. Substituting $\rho=r / a_{0}$ :

$$
\langle r\rangle=a_{0} C^{2} \int_{0}^{\infty} \rho^{7} e^{-2 \rho / 3} d \rho
$$

This integral can be evaluated by integrating by parts 7 times:

$$
\langle r\rangle=a_{0} C^{2}(7!)\left(\frac{3}{2}\right)^{7} \int_{0}^{\infty} e^{-2 \rho / 3} d \rho
$$

The integral is easily evaluated, giving another factor of $3 / 2$. Pluggin in $C^{2}$ :

$$
\begin{array}{r}
\langle r\rangle=a_{0}\left(\frac{2^{2}}{9^{4}} \frac{2}{15}\right)(7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2)\left(\frac{3}{2}\right)^{8} \\
=\frac{21}{2} a_{0}
\end{array}
$$

10. Following Example 4.1, for a given $n$-state, the possible values of $l$ are $\mathrm{n}-1, \mathrm{n}-2, \ldots 0$. Therefore, $n=5$ allows $l=0,1,2,3,4$. For a given $l$ value, the possible magnetic quantum numbers are $m_{l}=-l,(-l+1), \ldots 0,1, \ldots,(l-1), l$. For $n=5$ the results are:

$$
\begin{aligned}
l & =0: m=0 \\
l & =1: m=-1,0,1 \\
l & =2: m=-2,-1,0,1,2 \\
l & =3: m=-3,-2,-1,0,1,2,3 \\
l & =4: m=-4,-3,-2,-1,0,1,2,3,4
\end{aligned}
$$

11. Using Eq. (4.6), we have the relationship:

$$
n=l+\nu+1
$$

where $\nu$ is the number of nodes. Following Example 4.2, but for the $5 d$ state:

$$
5=2+\nu+1
$$

giving $\nu=2$ as the number of nodes in the wavefunction.
12. Using Eq. (4.4), a wave function is a product of radial and angular parts:

$$
\psi(r, \theta, \phi)=\frac{P_{n l}(r)}{r} \Theta_{l m_{l}}(\theta) \Phi(\phi)
$$

and for this problem, $\psi(r, \theta, \phi)=C \cos (\theta) r e^{-Z r / 2 a_{0}}$. For the angular part, $\cos (\theta)$ appears in Table 4.1 for the spherical harmonic corresponding to $l=1$ and $m_{l}=0$. The factor $C$ is just a normalization constant. For the radial part, from the LHS of Eq. (4.5):

$$
\frac{-\hbar^{2}}{2 m} \frac{d^{2}}{d r^{2}} P_{n l}(r)+\frac{\hbar^{2} l(l+1)}{2 m r^{2}} P_{n l}(r)-\frac{1}{4 \pi \epsilon_{0}} \frac{Z e^{2}}{r} P_{n l}(r)
$$

where $P_{n l}(r)=r^{2} e^{-Z r / 2 a_{0}}$. Taking the second derivative of the radial wave function:

$$
\frac{d^{2}}{d r^{2}} P_{n l}(r)=2 e^{-Z r / 2 a_{0}}-\frac{2 r Z}{a_{0}} e^{-Z r / 2 a_{0}}+\frac{Z^{2} r^{2}}{4 a_{0}} e^{-Z r / 2 a_{0}}
$$

Substituting in $l=1$ and collecting terms, the LHS of Eq. (4.5) becomes:

$$
\frac{\hbar^{2} r Z}{m a_{0}} e^{-Z r / 2 a_{0}}-\frac{Z e^{2} r}{4 \pi \epsilon_{0}} e^{-Z r / 2 a_{0}}+\frac{\hbar^{2} Z^{2} r^{2}}{8 m a_{0}} e^{-Z r / 2 a_{0}}
$$

Recall from Eq. (1.20) that the Bohr radius $a_{0}$ may expressed as follows:

$$
a_{0}=\frac{4 \pi \epsilon_{0} \hbar^{2}}{m e^{2}}
$$

Substituting this expression into the first term of the previous equation, the first two terms cancel. Completing Eq. (4.5):

$$
\frac{\hbar^{2} Z^{2}}{8 m a_{0}} r^{2} e^{-Z r / 2 a_{0}}=E P_{n l}(r)
$$

The radial wave function is in fact an eigenfunction of the Schrödinger equation with corresponding eigenvalue (energy):

$$
E=\frac{\hbar^{2} Z^{2}}{8 m a_{0}}
$$

13. Using the Coulomb energy levels given, with the constants evaluated:

$$
E_{n}=-13.6 \frac{Z^{2}}{n^{2}}
$$

Evaluating this for hydrogen with $n=1,2,3$ :

$$
E_{1}=-13.6 \mathrm{eV}, \quad E_{2}=-3.4 \mathrm{eV}, \quad E_{3}=-1.51 \mathrm{eV}
$$

For the $\mathrm{Ne}^{+9}$ nucleus with one electron, $Z=10$ and the energy levels are:

$$
E_{1}=-1360 \mathrm{eV}, \quad E_{2}=-340 \mathrm{eV}, \quad E_{3}=-151 \mathrm{eV}
$$

14. Using Eq. (4.5):

$$
\left(\frac{-\hbar^{2}}{2 m} \frac{d^{2}}{d r^{2}}+\frac{\hbar^{2} l(l+1)}{2 m r^{2}}-\frac{1}{4 \pi \epsilon_{0}} \frac{Z e^{2}}{r}\right) P_{n l}(r)=E P_{n l}(r)
$$

where $Z=1$ for hydrogen. From Eq. (1.20):

$$
a_{0}=\frac{4 \pi \epsilon_{0} \hbar^{2}}{m e^{2}}
$$

and substituting $r=a_{0} \rho$ :

$$
\left(\frac{-\hbar^{2}}{2 m} \frac{d^{2}}{d\left(\rho a_{0}\right)^{2}}+\frac{\hbar^{2} l(l+1)}{2 m\left(\rho a_{0}\right)^{2}}-\frac{\hbar^{2}}{m a_{0}} \frac{Z}{\left(\rho a_{0}\right)}\right) P_{n l}(r)=E P_{n l}(r)
$$

Factoring out the constant terms:

$$
\frac{\hbar^{2}}{m a_{0}^{2}}\left(-\frac{1}{2} \frac{d^{2}}{d \rho^{2}}+\frac{l(l+1)}{2 \rho^{2}}-\frac{Z}{\rho}\right) P_{n l}(r)=E P_{n l}(r)
$$

Substituting back for $a_{0}$, we get the desired result:

$$
\frac{1}{a_{0}} \frac{e^{2}}{4 \pi \epsilon_{0}}\left(-\frac{1}{2} \frac{d^{2}}{d \rho^{2}}+\frac{l(l+1)}{2 \rho^{2}}-\frac{1}{\rho}\right) P_{n l}(r)=E P_{n l}(r)
$$

15. a) Using $l=1$, this simplifies to:

$$
V_{1}(\rho)=\frac{1}{\rho^{2}}-\frac{1}{\rho}
$$

and a sketch can be easily made using standard plotting software.
b) Using $n=3$ from Problem 13, and $l=1$ :

$$
\frac{1}{\rho^{2}}-\frac{1}{\rho}=\frac{-1.5 \mathrm{eV}}{27.2 \mathrm{eV}}=-0.055
$$

Solving for rho gives a quadratic equation:

$$
-0.055 \rho^{2}+\rho-1=0
$$

with solutions $\rho=1.062$ and $\rho=17.12$. These are the classical turning points. c) From the sketch, we see that $V_{1}(\rho)-E$ is negative below the turning points, and positive outside. By the equality given in the previous problem, clearly the derivative term has the opposite sign. So the ratio $\left(\frac{d P_{31}}{d \rho^{2}}\right) / P_{31}$ is negative outside of the turning points and positive inside.
d) The radial function is given by Table 4.2:

$$
P_{31}(r)=\sqrt{\frac{2}{3 a_{0}}} \frac{4}{27}\left(\frac{r}{a_{0}}\right)^{2}\left(1-\frac{r}{6 a_{0}}\right) e^{-r / 3 a_{0}}
$$

or in terms of $\rho$ :

$$
P_{31}(r) \propto \rho^{2}\left(1-\frac{\rho}{6}\right) e^{-\rho / 3}
$$

This is easily plotted using standard plotting software. The constant terms can be ignored, since only the shape of the wave function is relevant here. The

shape can be seen in Fig. 4.7 (b) of the text. Outside of the turning points, the wavefunction quickly heads towards zero. This is expected, since it is outside the range where it is classically allowed. Inside the turning points, the wavefunction has the shape of an oscillation (a wave).
16. The problem follows the development of Section 2.5. Starting with Eq. (4.15):

$$
\left[\frac{\hbar^{2}}{2 m} \nabla^{2}+V(\mathbf{r}, t)\right] \psi=i \hbar \frac{\partial \psi}{\partial t}
$$

Substituting $\psi(\mathbf{r}, t)=\phi(\mathbf{r}) T(t)$ into Eq. (4.15):

$$
\mathbf{H} \phi(\mathbf{r}) T(t)=i \hbar \phi(\mathbf{r}) \frac{\partial T(t)}{\partial t}
$$

where $\mathbf{H}$ represents the operator in the square brackets. Since $\mathbf{r}$ and $t$ are independent and $\mathbf{H}$ operates only on $\mathbf{r}$ :

$$
\frac{\mathbf{H} \phi(\mathbf{r})}{\phi(\mathbf{r})}=\frac{i \hbar}{T(t)} \frac{\partial T(t)}{\partial t}
$$

Setting this equal to the separation constant $E$ :

$$
i \hbar\left(\frac{1}{T(t)} \frac{\partial T(t)}{\partial t}\right)=E
$$

Moving $d t$ to the RHS and integrating:

$$
\ln T(t)=-i \frac{E}{\hbar} t
$$

Setting $\omega=E / \hbar$ and solving for $T$ :

$$
T(t)=e^{-i \omega t}
$$

The solution for $\phi(\mathbf{r})$ is similarly obtained by solving the time-independent equation. The wavefunction is:

$$
\psi(\mathbf{r}, t)=\phi(\mathbf{r}) e^{-i \omega t}
$$

which is the desired result.
17. The transition integral is given by the integral in Eq. (4.21):

$$
\int \phi_{n_{1} l_{1} m_{l}^{1}}^{*}\left(\frac{z}{a_{0}}\right) \phi_{n_{2} l_{2} m_{l}^{2}} d V
$$

For the transition $3 d_{1} \rightarrow 2 p_{1}$, this integral becomes:

$$
\int \phi_{3,2,1}^{*}\left(\frac{z}{a_{0}}\right) \phi_{2,1,1} d V
$$

where $\phi_{n l m}$ is the spatial wavefunction for hydrogen. Using Tables 4.1 and 4.2 , and writing $\rho=r / a_{0}$ :

$$
\begin{aligned}
\phi_{3,2,1} & =\frac{P_{3,2}(r)}{r} Y_{2,1}(\theta, \phi) \\
& \frac{2 \sqrt{2}}{81 \sqrt{15}} \rho^{2} e^{-\rho / 3}\left(-\sqrt{\frac{15}{8 \pi}} \sin (\theta) \cos (\theta) e^{i \phi}\right) \\
\phi_{2,1,1} & =\frac{P_{2,1}(r)}{r} Y_{1,1}(\theta, \phi) \\
& =\frac{1}{2 \sqrt{6}} \rho e^{-\rho / 2}\left(-\sqrt{\frac{3}{8 \pi}} \sin (\theta) e^{i \phi}\right)
\end{aligned}
$$

where the factors $1 / \sqrt{a_{0}}$ in front of the constant terms from Table 4.2 have been absorbed into the $z / a_{0}$ term in the integral. Taking the complex conjugate of $\phi_{3,2,1}$, and converting $z=r \cos (\theta)$ to spherical coordinates:

$$
\begin{aligned}
\int \phi_{3,2,1}^{*} & \left(\frac{z}{a_{0}}\right) \phi_{2,1,1} d V=\frac{1}{648 \pi} \int \rho^{4} e^{-5 \rho / 6} \sin ^{2}(\theta) \cos ^{2}(\theta) d V \\
& =\frac{1}{648 \pi} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{2 \pi} \rho^{6} e^{-5 \rho / 6} \sin ^{3}(\theta) \cos ^{2}(\theta) d \rho d \theta d \phi
\end{aligned}
$$

Carrying out the integrations:

$$
\begin{array}{r}
\frac{1}{648 \pi} \int_{0}^{\infty} r^{6} e^{-5 r / 6} d r \int_{0}^{\pi} \sin ^{3} \theta \cos ^{2} \theta d \theta \int_{0}^{2 \pi} d \phi \\
\frac{2 \pi}{648 \pi} \int_{0}^{\infty} r^{6} e^{-5 r / 6} d r \int_{0}^{\pi}\left(1-\cos ^{2} \theta\right) \cos ^{2} \theta d(\cos \theta) \\
=\frac{1}{324}\left[6!\left(\frac{6}{5}\right)^{7}\right]\left(\frac{4}{15}\right)=2.123
\end{array}
$$

18. To find the transition coefficient for polarized light from hydrogen, use the results found in Appendix FF (online) along with Eqs. (4.20) and (4.21). According to the selection rules in Table 4.3, $\Delta m_{l}= \pm 1$ for x - and y -polarized light. Therefore, we must calculate the transition integrals for both the $2 p_{1} \rightarrow$ $1 s_{0}$ and $2 p_{-1} \rightarrow 1 s_{0}$ cases. As in Appendix FF, use the following in place of the $z$ operator in Eq. (4.21):

$$
\begin{aligned}
& x=\frac{1}{2}\left(r_{+}+r_{-}\right) \\
& y=\frac{1}{2 i}\left(r_{+}-r_{-}\right)
\end{aligned}
$$

For the case of $x$-polarized light:

$$
I_{12}=2\left(\left|\phi_{1 s_{0}}^{*} x \phi_{2 p_{1}}\right|^{2}+\left|\phi_{1 s_{0}}^{*} x \phi_{2 p-1}\right|^{2}\right)
$$

Substituting the above expression for $x$ :

$$
\begin{gathered}
\phi_{1 s_{0}}^{*} x \phi_{2 p_{1}}=\frac{1}{2}\left(\phi_{1 s_{0}}^{*} r_{+} \phi_{2 p_{1}}+\phi_{1 s_{0}}^{*} r_{-} \phi_{2 p_{1}}\right) \\
\phi_{1 s_{0}}^{*} x \phi_{2 p_{-1}}=\frac{1}{2}\left(\phi_{1 s_{0}}^{*} r_{+} \phi_{2 p-1}+\phi_{1 s_{0}}^{*} r_{-} \phi_{2 p-1}\right)
\end{gathered}
$$

where $\phi_{1 s_{0}}^{*} r_{+} \phi_{2 p_{1}}$ and $\phi_{1 s_{0}}^{*} r_{-} \phi_{2 p_{-1}}$ are both equal to zero. Using the results given in Appendix FF for the remaining terms:

$$
I_{12}=2\left(\frac{1}{6} R_{i}^{2}+\frac{1}{6} R_{i}^{2}\right)=\frac{2}{3} R_{i}^{2}
$$

Using the results of Eqs. (4.23) and (4.26):

$$
A_{21}=\frac{6.078 \times 10^{15}}{(121.6)^{3}} \frac{1.109}{6}=6.25 \times 10^{8} \text { per atom per second }
$$

The same procedure is used for y -polarized light. The transition integral is:

$$
I_{12}=2\left(\left|\phi_{1 s_{0}}^{*} y \phi_{2 p_{1}}\right|^{2}+\left|\phi_{1 s_{0}}^{*} y \phi_{2 p-1}\right|^{2}\right)
$$

Substituting for $y$ :

$$
\begin{aligned}
\phi_{1 s_{0}}^{*} y \phi_{2 p_{1}} & =\frac{1}{2 i}\left(\phi_{1 s_{0}}^{*} r_{+} \phi_{2 p_{1}}-\phi_{1 s_{0}}^{*} r_{-} \phi_{2 p_{1}}\right) \\
\phi_{1 s_{0}}^{*} y \phi_{2 p_{-1}} & =\frac{1}{2 i}\left(\phi_{1 s_{0}}^{*} r_{+} \phi_{2 p_{-1}}-\phi_{1 s_{0}}^{*} r_{-} \phi_{2 p_{-1}}\right)
\end{aligned}
$$

The nonzero terms give the transition integral:

$$
I_{12}=2\left(\frac{-1}{6} R_{i}^{2}+\frac{-1}{6} R_{i}^{2}\right)=\frac{-2}{3} R_{i}^{2}
$$

The result for y-polarized light is:

$$
A_{21}=\frac{6.078 \times 10^{15}}{(121.6)^{3}} \frac{-1.109}{6}=-6.25 \times 10^{8} \text { per atom per second }
$$

The minus sign can be ignored since by definition the integral in Eq. (4.21) is positive definite.
19. Using the selection rules from Table 4.3:

$$
\Delta l= \pm 1
$$

Hence, a $p$-state $(l=1)$ can decay to either a $d$-state or an $s$-state with lower $n$. The possible final states are: $3 d, 3 s, 2 s$ or $1 s$. Note that we require $l<n$ so there is no $d$-state for $n=1,2$ (as shown in Figure 4.5).
20.(a) Assuming that the angular momentum vector 1 lies on the surface of a cone as in Figure 4.16, the radius of the circle at the base of the cone is:

$$
r=|\mathbf{l}| \sin \theta=l \sin \theta
$$

And, for a change of the azimuthal angle $d \phi$, the distance that the tip of the angular momentum vector moves is given by:

$$
d \mathbf{l}=l \sin \theta d \phi
$$

b) Using the relationship of the torque to angular to momentum:

$$
\left|\frac{d \mathbf{l}}{d t}\right|=|\tau|
$$

Using Eq. (4.40) gives:

$$
\left|\frac{d \mathbf{l}}{d t}\right|=\frac{e}{2 m}|\mathbf{l} \times \mathbf{B}|
$$

The definition of the vector product gives:

$$
\left|\frac{d \mathbf{l}}{d t}\right|=\frac{e}{2 m} l B \sin (\theta)
$$

Substituting $d|\mathbf{l}|=l \sin \theta d \phi$ :

$$
l \sin (\theta) \frac{d \phi}{d t}=\frac{e}{2 m} l B \sin (\theta)
$$

This gives the Lamar frequency:

$$
\omega_{L}=\frac{d \phi}{d t}=\frac{e B}{2 m}
$$

21. From Section 4.3.4, for the $f$-state with $l=3$, the possible values of $m_{l}$ and $m_{s}$ are:

$$
\begin{array}{r}
m_{l}=-3,-2,-1,0,1,2,3 \\
m_{s}=-\frac{1}{2},+\frac{1}{2}
\end{array}
$$

22. The total angular momentum of the $4 f$ electron will is the vector sum of the electron's spin and its orbital angular momentum. Following Section 4.3.4:

$$
J=j_{1}+j_{2}, j_{1}+j_{2}-1, \ldots\left|j_{2}-j_{1}\right|
$$

Here, $j_{1}$ is the orbital angular momentum and $j_{2}$ is the spin. So for an electron in the $f$-state, $j_{1}=3$, with spin $j_{2}=1 / 2$, the possible values for $J$ are:

$$
J=\frac{7}{2}, \frac{5}{2}
$$

Using Eq. (4.50), the spin-orbit coupling energy is:

$$
\begin{array}{ll}
E_{s-o}=\frac{\zeta \hbar^{2}}{2} l=\frac{3 \zeta \hbar^{2}}{2} & \text { for } j=l+\frac{1}{2} \\
E_{s-o}=\frac{-\zeta \hbar^{2}}{2}(l+1)=-2 \zeta \hbar^{2} & \text { for } j=l-\frac{1}{2}
\end{array}
$$

Hence the levels are split by $\Delta E_{s-o}=(7 / 2) \zeta \hbar^{2}$.
23. An electron in the $2 p$ state, with $l=2$ and $s=1 / 2$, has possible values:

$$
j=\frac{3}{2}, \frac{1}{2}
$$

Using Eq. (4.56) and the equations that follow:

$$
g_{3 / 2}=\frac{4}{3} \text { and } g_{1 / 2}=\frac{2}{3}
$$

The splitting of the $m$-levels is:

$$
\Delta E=g_{j} \mu_{B} B m_{j}
$$

where $\mu_{B}$ is the Bohr magneton given in Appendix A and we are given $B=$ $5 T$. For $j=3 / 2$, the possible $m_{j}$ values and energy splittings $\Delta E$ are:

| $m_{j}$ | $\Delta E(\mathrm{eV})$ |
| :---: | :---: |
| $+(3 / 2)$ | $5.796 \times 10^{-4}$ |
| $+(1 / 2)$ | $1.932 \times 10^{-4}$ |
| $-(1 / 2)$ | $-1.932 \times 10^{-4}$ |
| $-(3 / 2)$ | $-5.796 \times 10^{-4}$ |

Similarly, for $j=1 / 2$, the energy splittings are $\Delta E= \pm 0.966 \times 10^{-4} \mathrm{eV}$ for $m_{j}= \pm 1 / 2$, respectively.
24. Using Eq. (4.50), the separation in energies due to spin-orbit coupling is:

$$
\Delta E=\frac{\zeta \hbar^{2}}{2} l-\left(\frac{-\zeta \hbar^{2}}{2}\right)(l+1)=\left(\frac{\zeta \hbar^{2}}{2}\right)(2 l+1)
$$

Since we are using the atomic system of units, $\hbar=1$ :

$$
\begin{equation*}
\Delta E=\frac{\zeta}{2}(2 l+1) \tag{1}
\end{equation*}
$$

For a $p$-state in $\mathrm{He}^{+}$with $l=1$ we are given in these units:

$$
\Delta E_{H e^{+}}=7.9 \times 10^{-6}
$$

which results in $\zeta_{H e}=5.27 \times 10^{-6}$. Using Eq. (4.51), the relationship between $\zeta_{\mathrm{He}}$ and $\zeta_{\mathrm{Ne}}$ just depends on $Z^{4}$. (Note that the average value in the brackets of Eq. (4.51) is the same in both cases.) This gives:

$$
\frac{\zeta_{N e}}{\zeta_{H e}}=\frac{10^{4}}{2^{4}}=625
$$

Plugging in the above value for $\zeta_{H e}$ gives:

$$
\zeta_{N e}=3.29 \times 10^{-3}
$$

The separation between the $3 p_{3 / 2}$ and $3 p_{1 / 2}$ levels is then:

$$
\Delta E=\frac{3.29 \times 10^{-3}}{2}(2 l+1)=4.94 \times 10^{-3}
$$

A comparison with the separation of the corresponding helium states reveals the vastly increased impact of spin-orbit coupling for neon.

