29.2  (a) Longest wavelength implies lowest frequency and smallest energy:

the atom falls from \( n = 3 \) to \( n = 2 \) losing energy 

\[
\frac{13.6 \text{ eV}}{3^2} + \frac{13.6 \text{ eV}}{2^2} = 1.89 \text{ eV}
\]

The photon frequency is 

\[
f = \frac{\Delta E}{h}
\]

and its wavelength is 

\[
\lambda = \frac{c}{f} = \frac{hc}{\Delta E} = \left(\frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(1.89 \text{ eV})}\right) \left(\frac{\text{eV}}{1.60 \times 10^{-19} \text{ J}}\right)
\]

\[
\lambda = 656 \text{ nm}
\]

(b) The biggest energy loss is for an atom to fall from an ionized configuration, 

\( n = \infty \) to the \( n = 2 \) state

It loses energy 

\[
\frac{13.6 \text{ eV}}{\infty} + \frac{13.6 \text{ eV}}{2^2} = 3.40 \text{ eV}
\]

to emit light of wavelength 

\[
\lambda = \frac{hc}{\Delta E} = \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)(3.00 \times 10^8 \text{ m/s})}{(3.40 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \approx 365 \text{ nm}
\]

29.5  (a) The photon has energy 2.28 eV.

And \( (13.6 \text{ eV}) / 2^2 = 3.40 \text{ eV} \) is required to ionize a hydrogen atom from state \( n = 2 \). So while the photon cannot ionize a hydrogen atom pre-excited to \( n = 2 \), it can ionize a hydrogen atom in the \( n = 3 \) state, with energy 

\[
\frac{13.6 \text{ eV}}{3^2} = -1.51 \text{ eV}
\]

(b) The electron thus freed can have kinetic energy 

\[
K_e = 2.28 \text{ eV} - 1.51 \text{ eV} = 0.769 \text{ eV} = \frac{1}{2} m_e v^2
\]

Therefore,

\[
v = \sqrt{\frac{2(0.769)(1.60 \times 10^{-19}) \text{ J}}{9.11 \times 10^{-31} \text{ kg}}} \approx 520 \text{ km/s}
\]
29.6  (a) In the $3d$ subshell, $n = 3$ and $\ell = 2$,
we have 
\[
\begin{array}{cccccccccccc}
  n & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3 & 3 \\
  \ell & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 & 2 \\
  m_s & +2 & +2 & +1 & +1 & 0 & 0 & -1 & -1 & -2 & -2 \\
  m_l & +1/2 & -1/2 & +1/2 & -1/2 & +1/2 & -1/2 & +1/2 & -1/2 & -1/2 & -1/2 \\
\end{array}
\]
(A total of 10 states)

(b) In the $3p$ subshell, $n = 3$ and $\ell = 1$,
we have 
\[
\begin{array}{cccccccc}
  n & 3 & 3 & 3 & 3 & 3 & 3 & 3 \\
  \ell & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
  m_s & +1 & +1 & +0 & +0 & -1 & -1 & -1 \\
  m_l & +1/2 & -1/2 & +1/2 & -1/2 & +1/2 & -1/2 & -1/2 \\
\end{array}
\]
(A total of 6 states)

*29.7  (a) 
\[
\int |\psi|^2 dV = 4\pi \int_0^\infty r^2 |\psi|^2 r^2 dr = 4\pi \left( \frac{1}{\pi a_0^3} \right) \int_0^\infty r^2 e^{-2r/a_0} dr
\]

Using integral tables,
\[
\int |\psi|^2 dV = -\frac{2}{a_0^2} \left[ e^{-a_0 r} \left( r^2 + a_0 r + \frac{a_0^2}{2} \right) \right]_0^{+\infty} = \left( -\frac{2}{a_0^2} \right) \left( \frac{a_0^3}{2} \right) = 1
\]
so the wave function as given is normalized.

(b) 
\[
\int |\psi|^2 dV = 4\pi \int_{a_0/2}^{3a_0/2} r^2 dr = 4\pi \left( \frac{1}{\pi a_0^3} \right) \int_{a_0/2}^{3a_0/2} r^2 e^{-2r/a_0} dr
\]

Again, using integral tables,
\[
P_{a_0/2 \rightarrow 3a_0/2} = -\frac{2}{a_0^2} \left[ e^{-2r/a_0} \left( r^2 + a_0 r + \frac{a_0^2}{2} \right) \right]_{a_0/2}^{3a_0/2} = -\frac{2}{a_0^2} \left[ e^{3} \left( \frac{17a_0^2}{4} \right) \right] e^{-1} \left( \frac{5a_0^2}{4} \right) = 0.497
\]
\[ \psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

\[ \frac{2}{r} \frac{d\psi}{dr} = \frac{-2}{r \sqrt{\pi a_0^3}} e^{-r/a_0} = \frac{2}{r a_0} \psi \]

\[ \frac{d^2\psi}{dr^2} = \frac{1}{\sqrt{\pi a_0^7}} e^{-r/a_0} = \frac{1}{a_0^2} \psi \]

\[ -\frac{\hbar^2}{2m_e} \left( \frac{1}{a_0^2} - \frac{2}{r a_0} \right) \psi - \frac{e^2}{4\pi \epsilon_0 r} \psi = E \psi \]

But

\[ a_0 = \frac{\hbar^2 (4\pi \epsilon_0)}{m_e e^2} \]

so

\[ -\frac{\epsilon^2}{8\pi \epsilon_0 a_0} = E \]

or

\[ E = -\frac{k_e^2}{2a_0} \]

This is true, so the Schrödinger equation is satisfied.

\[ \psi = \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \]

so

\[ P_r = 4\pi r^2 \left| \psi^2 \right| = 4\pi r^2 \frac{r^2}{24a_0^5} e^{-r/a_0} \]

Set

\[ \frac{dP}{dr} = \frac{4\pi}{24a_0^5} \left[ 4r^2 e^{-r/a_0} + r^4 \left( -\frac{1}{a_0} \right) e^{-r/a_0} \right] = 0 \]

Solving for \( r \), this is a maximum at \( r = 4a_0 \).

\[ r_{av} = \int_0^\infty r P(r) dr = \int_0^\infty \left( \frac{4r^3}{a_0^3} \right) (e^{-2r/a_0}) dr \]

Make a change of variables with \( \frac{2r}{a_0} = x \) and \( dr = \frac{a_0}{2} dx \)

Then

\[ r_{av} = \frac{a_0}{4} \int_0^\infty x^3 e^{-x} dx = \frac{a_0}{4} \left[ -x^3 e^{-x} + 3\left(-x^2 e^{-x} + 2 e^{-x} (-x - 1)\right) \right]_0^\infty = \frac{3}{2}a_0 \]
\[ E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} = \Delta E \]

\( \lambda_1 = 310 \text{ nm}, \quad \text{so} \quad \Delta E_1 = 4.00 \text{ eV} \)

\( \lambda_2 = 400 \text{ nm}, \quad \Delta E_2 = 3.10 \text{ eV} \)

\( \lambda_3 = 1378 \text{ nm}, \quad \Delta E_3 = 0.900 \text{ eV} \)

and the ionization energy = 4.10 eV

The energy level diagram having the fewest levels and consistent with these energies is shown at the right.

29.12  
(a) For the d state, \( l = 2 \),  
\[ L = \sqrt{6} \hbar = 2.58 \times 10^{-34} \text{ J} \cdot \text{s} \]

(b) For the f state, \( l = 3 \),  
\[ L = \sqrt{l(l+1)} \hbar = \sqrt{12} \hbar = 3.65 \times 10^{-34} \text{ J} \cdot \text{s} \]

29.14  
In the N shell, \( n = 4 \). For \( n = 4 \), \( l \) can take on values of 0, 1, 2, and 3. For each value of \( l \), \( m_l \) can be \(-l\) to \( l\) in integral steps. Thus, the maximum value for \( m_l \) is 3. Since \( L_z = m_l \hbar \), the maximum value for \( L_z \) is \( L_z = 3\hbar \).

29.15  
The 5th excited state has \( n = 6 \), energy \[ \frac{-13.6 \text{ eV}}{36} = -0.378 \text{ eV} \]

The atom loses this much energy:  
\[ \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 3.00 \times 10^8 \text{ m/s}}{1.60 \times 10^{-19} \text{ J/ eV}} = 1.14 \text{ eV} \]

to end up with energy \[ -0.378 \text{ eV} - 1.14 \text{ eV} = -1.52 \text{ eV} \]

which is the energy in state 3: \[ \frac{-13.6 \text{ eV}}{3^3} = -1.51 \text{ eV} \]

While \( n = 3 \), \( l \) can be as large as 2, giving angular momentum \[ \sqrt{l(l+1)} \hbar = \sqrt{6} \hbar \]
29.17 (a) \( n = 1: \) For \( n = 1, \ell = 0, m_\ell = 0, m_s = \pm \frac{1}{2} \)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \ell )</th>
<th>( m_\ell )</th>
<th>( m_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>+1/2</td>
</tr>
</tbody>
</table>

Yields 2 sets; \( 2n^2 = 2(1)^2 = 2 \)

(b) \( n = 2: \) For \( n = 2, \)

we have

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \ell )</th>
<th>( m_\ell )</th>
<th>( m_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>±1/2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>±1/2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>±1/2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>±1/2</td>
</tr>
</tbody>
</table>

yields 8 sets; \( 2n^2 = 2(2)^2 = 8 \)

Note that the number is twice the number of \( m_\ell \) values. Also, for each \( \ell \) there are \((2\ell + 1)\) different \( m_\ell \) values. Finally, \( \ell \) can take on values ranging from 0 to \( n - 1 \).

So the general expression is

\[
\text{number} = \sum_{\ell=0}^{n-1} 2(2\ell + 1)
\]

The series is an arithmetic progression:

\[2 + 6 + 10 + 14 \ldots\]

the sum of which is

\[
\text{number} = \frac{n}{2} [4 + (n - 1)4] = 2n^2
\]

(c) \( n = 3: \) \( 2(1) + 2(3) + 2(5) = 2 + 6 + 10 = 18 \)

\( 2n^2 = 2(3)^2 = 18 \)

(d) \( n = 4: \) \( 2(1) + 2(3) + 2(5) + 2(7) = 32 \)

\( 2n^2 = 2(4)^2 = 32 \)

(e) \( n = 5: \) \( 32 + 2(9) = 32 + 18 = 50 \)

\( 2n^2 = 2(5)^2 = 50 \)

29.21 (a) \( 1s^2 2s^2 2p^4 \)

(b) For the 1s electrons, \( n = 1, \ell = 0, m_\ell = 0, m_s = \pm \frac{1}{2} \) and \(-\frac{1}{2}\)

For the two 2s electrons, \( n = 2, \ell = 0, m_\ell = 0, m_s = \pm \frac{1}{2} \) and \(-\frac{1}{2}\)

For the four 2p electrons, \( n = 2; \ell = 1; m_\ell = -1, 0, \text{ or } 1; \text{ and } m_s = \pm \frac{1}{2} \) or \(-\frac{1}{2}\)
29.24  (a) For electron one and also for electron two, \( n = 3 \) and \( \ell = 1 \). The possible states are listed here in columns giving the other quantum numbers:

<table>
<thead>
<tr>
<th>electron one</th>
<th>( m_l )</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>1</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_s )</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>electron two</td>
<td>( m_l )</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( m_s )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
</tr>
<tr>
<td>electron one</td>
<td>( m_l )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( m_s )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
<td>-( \frac{1}{2} )</td>
</tr>
<tr>
<td>electron two</td>
<td>( m_l )</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( m_s )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
<td>( -\frac{1}{2} )</td>
</tr>
</tbody>
</table>

There are thirty allowed states, since electron one can have any of three possible values for \( m_l \) for both spin up and spin down, amounting to six states, and the second electron can have any of the other five states.

(b) Were it not for the exclusion principle, there would be 36 possible states, six for each electron independently.

29.27  (a) \( n + \ell \)  
<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>subshell</td>
<td>1s</td>
<td>2s</td>
<td>2p, 3s</td>
<td>3p, 4s</td>
<td>3d, 4p, 5s</td>
<td>4d, 5p, 6s</td>
</tr>
</tbody>
</table>

(b) \( Z = 15 \): Filled subshells: 1s, 2s, 2p, 3s  
(12 electrons)  
Valence subshell: 3 electrons in 3p subshell  
Prediction: Valence = +3 or -5  
Element is phosphorus, Valence = +3 or -5 (Prediction correct)

\( Z = 47 \): Filled subshells: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s  
(38 electrons)  
Outer subshell: 9 electrons in 4d subshell  
Prediction: Valence = -1  
Element is silver, (Prediction fails) Valence is +1

\( Z = 86 \): Filled subshells: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p  
(86 electrons)  
Prediction Outer subshell is full: inert gas  
Element is radon, inert (Prediction correct)
29.45 We use \[ \psi_{2s}(r) = \frac{1}{4}(2\pi a_0^3)^{1/2} \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/2a_0} \]

By Equation 29.6, \( P(r) = 4\pi r^2 \psi^2 = \frac{1}{8} \left( \frac{r^2}{a_0^3} \right)^2 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} \)

(a) \[ \frac{dP(r)}{dr} = \frac{1}{8} \left[ \frac{2r^2}{a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 - 2\frac{2r^2}{a_0^3} \left( 1 - \frac{r}{a_0} \right) \left( 2 - \frac{r}{a_0} \right) - \frac{r^2}{a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 \left( \frac{2}{a_0} \right) \right] e^{-r/a_0} = 0 \]

or \[ \frac{1}{8} \left( \frac{r^2}{a_0^3} \right)^2 \left( 2 - \frac{r}{a_0} \right)^2 - 2\frac{2r^2}{a_0^3} \left( 1 - \frac{r}{a_0} \right) \left( 2 - \frac{r}{a_0} \right) - \frac{r^2}{a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 \left( \frac{2}{a_0} \right) \right] e^{-r/a_0} = 0 \]

The roots of \( \frac{dP}{dr} = 0 \) at \( r = 0, \quad r = 2a_0 \) and \( r = \infty \) are minima with \( P(r) = 0 \)

Therefore we require \[ \begin{align*} &4 - (6r/a_0) + (r/a_0)^2 = 0 \end{align*} \]

with solutions \[ r = (3 \pm \sqrt{5})a_0 \]

We substitute the last two roots into \( P(r) \) to determine the most probable value:

When \( r = (3 - \sqrt{5})a_0 = 0.7639a_0 \), \( P(r) = 0.0519/a_0 \)

When \( r = (3 + \sqrt{5})a_0 = 5.236a_0 \), \( P(r) = 0.191/a_0 \)

Therefore, the most probable value of \( r \) is \( (3 + \sqrt{5})a_0 = \boxed{5.236a_0} \)

(b) \[ \int_0^\infty P(r) dr = \int_0^\infty \frac{1}{8} \left( \frac{r^2}{a_0^3} \right)^2 \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} dr \]

Let \( u = \frac{r}{a_0}, \quad dr = a_0 du \),

\[ \int_0^\infty P(r) dr = \int_0^\infty \frac{1}{8} u^2 (4 - 4u + u^2) e^{-u} du = \int_0^\infty \frac{1}{8} (u^4 - 4u^3 + 4u^2) e^{-u} du = -\frac{1}{8} (u^4 + 4u^2 + 8u + 8) e^{-u} \bigg|_0^\infty = 1 \]

This is as desired.

29.50 \[ P = \int_{2.50a_0}^{\infty} \frac{4r^2}{a_0} e^{-2r/a_0} dr = \frac{1}{2} \int_{5.00}^{\infty} z^2 e^{-z} dz \quad \text{where} \quad z = \frac{2r}{a_0} \]

\[ P = -\frac{1}{2} \left[ z^2 + 2z + 2 \right] e^{-z} \bigg|_{5.00}^{\infty} = -\frac{1}{2} [0] + \frac{1}{2} [25.0 + 10.0 + 2.00] e^{-5} = \left( \frac{37}{2} \right) (0.00674) = 0.125 \]