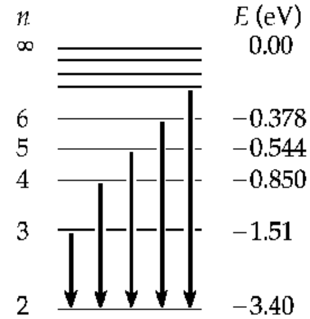
29.2 (a) Longest wavelength implies lowest frequency and smallest energy:



Balmer Series

the atom falls from $n = 3$

to $n = 2$

losing energy $-\dfrac{13.6\text{ eV}}{3^2} + \dfrac{13.6\text{ eV}}{2^2} = \boxed{1.89\text{ eV}}$

The photon frequency is $f = \dfrac{\Delta E}{h}$

and its wavelength is $\lambda = \dfrac{c}{f} = \dfrac{hc}{\Delta E} = \dfrac{\left(6.626\times10^{-34}\text{ J}\cdot\text{s}\right)\left(3.00\times10^{8}\text{ m/s}\right)}{(1.89\text{ eV})}\left(\dfrac{\text{eV}}{1.60\times10^{-19}\text{ J}}\right)$

$\lambda = \boxed{656\text{ nm}}$

(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 $-\dfrac{13.6\text{ eV}}{\infty} + \dfrac{13.6\text{ eV}}{2^2} = \boxed{3.40\text{ eV}}$

to emit light of wavelength $\lambda = \dfrac{hc}{\Delta E} = \dfrac{\left(6.626\times10^{-34}\text{ J}\cdot\text{s}\right)\left(3.00\times10^{8}\text{ m/s}\right)}{(3.40\text{ eV})\left(1.60\times10^{-19}\text{ J/eV}\right)} = \boxed{365\text{ nm}}$

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 $n = \boxed{3}$ 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, $v = \sqrt{\dfrac{2(0.769)\left(1.60\times10^{-19}\right)\text{ J}}{9.11\times10^{-31}\text{ kg}}} = \boxed{520\text{ km/s}}$

29.6 (a) In the $3d$ subshell, $n = 3$ and $\ell = 2$,

we have

n	3	3	3	3	3	3	3	3	3	3
ℓ	2	2	2	2	2	2	2	2	2	2
m_ℓ	+2	+2	+1	+1	0	0	–1	–1	–2	–2
m_s	+1/2	–1/2	+1/2	–1/2	+1/2	–1/2	+1/2	–1/2	+1/2	–1/2

(A total of 10 states)

(b) In the $3p$ subshell, $n = 3$ and $\ell = 1$,

we have

n	3	3	3	3	3	3
ℓ	1	1	1	1	1	1
m_ℓ	+1	+1	+0	+0	–1	–1
m_s	+1/2	–1/2	+1/2	–1/2	+1/2	–1/2

(A total of 6 states)

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

Using integral tables, $\int |\psi|^2 dV = -\frac{2}{a_0^2}\left[e^{-2r/a_0}\left(r^2 + a_0 r + \frac{a_0^2}{2}\right)\right]_0^\infty = \left(-\frac{2}{a_0^2}\right)\left(-\frac{a_0^2}{2}\right) = \boxed{1}$

so the wave function as given is normalized.

(b) $P_{a_0/2\to 3a_0/2} = 4\pi\int_{a_0/2}^{3a_0/2} |\psi|^2 r^2\,dr = 4\pi\left(\frac{1}{\pi a_0^3}\right)\int_{a_0/2}^{3a_0/2} r^2 e^{-2r/a_0}\,dr$

Again, using integral tables,

$$P_{a_0/2\to 3a_0/2} = -\frac{2}{a_0^2}\left[e^{-2r/a_0}\left(r^2 + a_0 r + \frac{a_0^2}{2}\right)\right]_{a_0/2}^{3a_0/2} = -\frac{2}{a_0^2}\left[e^{-3}\left(\frac{17a_0^2}{4}\right) - e^{-1}\left(\frac{5a_0^2}{4}\right)\right] = \boxed{0.497}$$

29.9

$$\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \qquad \frac{2}{r}\frac{d\psi}{dr} = \frac{-2}{r\sqrt{\pi a_0^5}} e^{-r/a_0} = \frac{2}{r a_0}\psi$$

$$\frac{d^2\psi}{dr^2} = \frac{1}{\sqrt{\pi a_0^7}} e^{-r/a_0} = \frac{1}{a_0^2}\psi \qquad -\frac{\hbar^2}{2m_e}\left(\frac{1}{a_0^2} - \frac{2}{r a_0}\right)\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

But $a_0 = \dfrac{\hbar^2(4\pi\epsilon_0)}{m_e e^2}$

so $-\dfrac{e^2}{8\pi\epsilon_0 a_0} = E$

or $\boxed{E = -\dfrac{k_e e^2}{2a_0}}$

This is true, so the Schrödinger equation is satisfied.

29.10

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

so $P_r = 4\pi r^2 \left|\psi^2\right| = 4\pi r^2 \dfrac{r^2}{24 a_0^5} e^{-r/a_0}$

Set $\dfrac{dP}{dr} = \dfrac{4\pi}{24 a_0^5}\left[4r^3 e^{-r/a_0} + r^4\left(-\dfrac{1}{a_0}\right)e^{-r/a_0}\right] = 0$

Solving for r, this is a maximum at $\boxed{r = 4a_0}$.

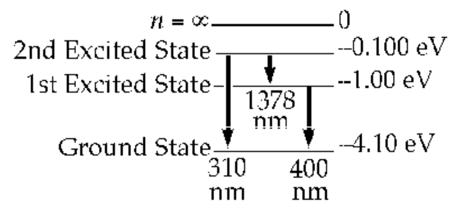
29.41

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

Make a change of variables with $\dfrac{2r}{a_0} = x$ and $dr = \dfrac{a_0}{2}dx$

Then $r_{av} = \dfrac{a_0}{4}\displaystyle\int_0^\infty x^3 e^{-x}dx = \dfrac{a_0}{4}\left[-x^3e^{-x} + 3\left(-x^2e^{-x} + 2e^{-x}(-x-1)\right)\right]\Big|_0^\infty = \boxed{\tfrac{3}{2}a_0}$

29.48 $E = \frac{hc}{\lambda} = \frac{1240\text{ eV}\cdot\text{nm}}{\lambda} = \Delta E$



$\lambda_1 = 310\text{ nm},$ so $\Delta E_1 = 4.00\text{ eV}$

$\lambda_2 = 400\text{ nm},$ $\Delta E_2 = 3.10\text{ eV}$

$\lambda_3 = 1378\text{ nm},$ $\Delta E_3 = 0.900\text{ eV}$

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, $\ell = 2$, $L = \boxed{\sqrt{6}\hbar} = 2.58\times10^{-34}\text{ J}\cdot\text{s}$

(b) For the f state, $\ell = 3$, $L = \sqrt{\ell(\ell+1)}\hbar = \boxed{\sqrt{12}\hbar} = 3.65\times10^{-34}\text{ J}\cdot\text{s}$

***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 $-\ell$ to ℓ in integral steps. Thus, the maximum value for m_ℓ is 3. Since $L_z = m_\ell\hbar$, the maximum value for L_z is $L_z = \boxed{3\hbar}$.

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: $\frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\text{ J}\cdot\text{s})(3.00\times10^{8}\text{ m/s})}{(1090\times10^{-9}\text{ m})(1.60\times10^{-19}\text{ J/eV})} = 1.14\text{ eV}$

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 $\sqrt{\ell(\ell+1)}\hbar = \boxed{\sqrt{6}\hbar}$

29.17 (a) $n = 1$: For $n = 1$, $\ell = 0$, $m_\ell = 0$, $m_s = \pm\frac{1}{2}$

n	ℓ	m_ℓ	m_s
1	0	0	–1/2
1	0	0	+1/2

Yields 2 sets; $2n^2 = 2(1)^2 = \boxed{2}$

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

we have

n	ℓ	m_ℓ	m_s
2	0	0	±1/2
2	1	–1	±1/2
2	1	0	±1/2
2	1	1	±1/2

yields 8 sets; $2n^2 = 2(2)^2 = \boxed{8}$

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

So the general expression is number $= \sum_{0}^{n-1} 2(2\ell + 1)$

The series is an arithmetic progression: $2 + 6 + 10 + 14 \ldots$

the sum of which is number $= \frac{n}{2}[2a + (n-1)d]$

where $a = 2$, $d = 4$: number $= \frac{n}{2}[4 + (n-1)4] = 2n^2$

(c) $n = 3$: $2(1) + 2(3) + 2(5) = 2 + 6 + 10 = 18$ $2n^2 = 2(3)^2 = \boxed{18}$

(d) $n = 4$: $2(1) + 2(3) + 2(5) + 2(7) = 32$ $2n^2 = 2(4)^2 = \boxed{32}$

(e) $n = 5$: $32 + 2(9) = 32 + 18 = 50$ $2n^2 = 2(5)^2 = \boxed{50}$

29.21 (a) $\boxed{1s^2 2s^2 2p^4}$

(b) For the 1s electrons, $n = 1$, $\ell = 0$, $m_\ell = 0$, $m_s = +1/2$ and $-1/2$
For the two 2s electrons, $n = 2$, $\ell = 0$, $m_\ell = 0$, $m_s = +1/2$ and $-1/2$
For the four 2p electrons, $n = 2$; $\ell = 1$; $m_\ell = -1, 0$, or 1; and $m_s = +1/2$ or $-1/2$

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:

electron one	m_ℓ	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0
	m_s	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
electron two	m_ℓ	1	0	0	–1	–1	1	0	0	–1	–1	1	1	0	–1	–1
	m_s	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$

electron one	m_ℓ	0	0	0	0	0	–1	–1	–1	–1	–1	–1	–1	–1	–1	–1
	m_s	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
electron two	m_ℓ	1	1	0	–1	–1	1	1	0	0	–1	1	1	0	0	–1
	m_s	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$

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)

$n + \ell$	1	2	3	4	5	6	7
subshell	$1s$	$2s$	$2p$, $3s$	$3p$, $4s$	$3d$, $4p$, $5s$	$4d$, $5p$, $6s$	$4f$, $5d$, $6p$, $7s$

(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 $\psi_{2s}(r) = \frac{1}{4}\left(2\pi a_0{}^3\right)^{-1/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$

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

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

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

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

Therefore we require $[\,.\,.\,.\,.\,.\,] = 4 - (6r/a_0) + (r/a_0)^2 = 0$

with solutions $r = \left(3 \pm \sqrt{5}\right)a_0$

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

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

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

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

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

Let $u = \frac{r}{a_0}$, $dr = a_0\,du$,

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

$\boxed{\text{This is as desired}}$.

29.50 $$P = \int_{2.50a_0}^\infty \frac{4r^2}{a_0{}^3}e^{-2r/a_0}\,dr = \frac{1}{2}\int_{5.00}^\infty z^2 e^{-z}\,dz \text{ where } z \equiv \frac{2r}{a_0}$$

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