1.

\[ \hat{\mathbf{V}} = \frac{\mathbf{r}}{r^3} \cdot \mathbf{E}_r \]

\[ u_{2s} = N \left( 2 - \frac{n}{a_0} \right) e^{-r/2a_0} \]

\[ u_{2s} = N \left( 2 - r \right) e^{-r/2} \]

\[ \frac{1}{4\sqrt{\pi}} \]

\[ \langle \mathbf{V} \rangle = \int u_{2s} \mathbf{V} \, d\mathbf{r} = \int \int \int N(2-n)e^{-\frac{r}{a_0}} (-\frac{1}{r}) N(2-n)e^{-\frac{r}{2a_0}} \, r \, dr \, dz \, dy \]

\[ = -4\pi N^2 \int_0^\infty r(2-r) e^{-r} \, dr \]

\[ = -4\pi N^2 \left[ 4 \int_0^\infty e^{-r} \, dr - 4 \int_0^\infty r^2 e^{-r} \, dr + \int_0^\infty r^3 e^{-r} \, dr \right] \]

\[ = -4\pi \left( \frac{1}{3r} \right) \left[ 4 \left( \frac{1}{1^2} \right) - 4 \left( \frac{2}{1^3} \right) + \frac{3!}{2!} \right] \]

\[ = -\frac{1}{8} \left( 4 - \frac{8}{9} \right) \]

\[ = -\frac{1}{4} a.u. \quad = -\frac{1}{4} E_h \quad = 1.09 eV \]

Recall \( \langle H \rangle \) (apart from \( \hbar^2 \)), \( \langle E \rangle = -\frac{1}{8} E_h \quad (=-\frac{1}{2}\hbar^2 E_h) \)

\[ \Rightarrow \langle T \rangle = \langle E \rangle - \langle V \rangle = +\frac{1}{8} E_h \quad \text{(kinetic plus potential)} \]
2. Atkins Exercise 9.12(b)

Orbital angular momentum is

\[ \langle \hat{L}^2 \rangle^{1/2} = \hbar(l(l + 1))^{1/2} \]

There are \( l \) angular nodes and \( n - l - 1 \) radial nodes.

(a) \( n = 4, \ l = 2 \), so \( \langle \hat{L}^2 \rangle^{1/2} = 6^{1/2} \hbar = \frac{2.45 \times 10^{-34}}{} \text{J s} \)

\[ 2 \text{ angular nodes} \quad 1 \text{ radial node} \]

(b) \( n = 2, \ l = 1 \), so \( \langle \hat{L}^2 \rangle^{1/2} = 2^{1/2} \hbar = \frac{1.49 \times 10^{-34}}{} \text{J s} \)

\[ 1 \text{ angular nodes} \quad 0 \text{ radial nodes} \]

(c) \( n = 3, \ l = 1 \), so \( \langle \hat{L}^2 \rangle^{1/2} = 2^{1/2} \hbar = \frac{1.49 \times 10^{-34}}{} \text{J s} \)

\[ 1 \text{ angular node} \quad 1 \text{ radial node} \]

3. Atkins Exercise 9.13(b)

See Figures 8.35 and 9.16 as well as Table 8.2 of the text. The number of angular nodes is the value of the quantum number \( l \), which for d orbitals is 2. Hence, each of the five d-orbitals has two angular nodes. To locate the angular nodes look for the values of \( \theta \) that make the wavefunction zero.

\( d_x^2 \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The nodal planes are difficult to picture. \[ \theta = 0.95532 \] is the angular node for both planes.

\( d_{xy} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( xz \) and \( yz \) planes, and \[ \theta = 0 \] is the angular node for both planes.

\( d_{yz} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( xz \) and \( xy \) planes, and \[ \theta = 0 \text{ and } \pi/2 \] respectively, are the angular nodes of these planes.

\( d_{xz} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes are the \( yz \) and \( xy \) planes, and \[ \theta = 0 \text{ and } \pi/2 \] respectively, are the angular nodes of these planes.

\( d_{x^2-y^2} \) orbital: see eqn 9.23, Table 8.2, and Figures 8.35 and 9.16. The two nodal planes at \( \phi = \pi/4 \) and \( \phi = 3\pi/4 \) respectively, and \[ \theta = 0 \] is the angular node of both of these planes.
4.

\[ \psi = N(27 - 18r + 2r^2) e^{-r/3} \]

(a) \# radial nodes = 2 (the solution to: \(27 - 18r + 2r^2 = 0\))

(b) \(l = 0, m = 0\) because the wavefunction has no angular dependence

(c) \(n = 3\) because total \# nodes = \(n - 1\)

(there are no angular nodes because \(l = 0\))

\[ F_n = \frac{\hbar^2}{2m} = -\frac{1}{18} \text{ a.u.} \]

\(n = 3\)

(d) Classical turning radius is value of \(r\) for which \(E = V\) (and consequently \(T = \text{kin. en.} = 0\)).

In atomic units, \(1 \text{ eV} = \frac{\hbar}{m} \)

\[ -\frac{1}{18} = -\frac{1}{r} \]

\(r = 18 \text{ a.u.} = 9.52 \text{ Å} \)

Atomic unit of length = \(a_0 = 0.529 \text{ Å}\)

5. Atkins Exercise 9.14(b)

(a) \(5d \rightarrow 2s\) is [not] an allowed transition, for \(\Delta l = -2\) (\(\Delta l\) must equal \(\pm 1\)).

(b) \(5p \rightarrow 3s\) is [allowed], since \(\Delta l = -1\).

(c) \(5p \rightarrow 3f\) is [not] allowed, for \(\Delta l = +2\) (\(\Delta l\) must equal \(\pm 1\)).
6. Atkins Problem 9.27

\[ E_n = \frac{-Z^2 e^4}{32 \pi^2 \hbar^2 n^2} \text{ where } Z = 2 \text{ (atomic number)} \]

\[ E_n = -\frac{e^4}{m_e n^2} \left( \frac{4 \pi^2}{32 \pi^2} \right) \]

\[ m_e = 9.10938 \times 10^{-31} \text{ kg} \]

\[ m_n = m_e + m_p = 2 (1.67493 + 1.67262) \times 10^{-27} \text{ kg} \]

\[ m_p = 6.656/20 \times 10^{-27} \]

\[ \frac{m_n}{m_e} = 9.999640 \times 10^{-1} = 0.9999640 \]

\[ m_3^3 = m_3^1 \times 2 + m_3^2 = 5.210170 \times 10^{-27} \text{ kg} \]

\[ \frac{m_3^3}{m_3^1} = 0.999946 \]

For \( n = 3 \rightarrow n = 2 \) transition, \( \delta = \frac{\hbar c}{\lambda} (E_3 - E_2) \)

\[ n = 2 \rightarrow n = 1 \]

\[ E_1^3 = 60958.5 \text{ cm}^{-1} \]

\[ E_1^1 = 60953.78 \text{ cm}^{-1} \]

\[ E_2^3 = 329165.26 \text{ cm}^{-1} \]

\[ E_2^1 = 329150.68 \text{ cm}^{-1} \]
Total wave function must be antisymmetric with respect to interchange of any two electrons.

\( \psi = |s(1) s(1)\rangle \) is symmetric

\( \Rightarrow \) spin part must be antisymmetric

\( |s(1) s(2)\rangle - |s(2) s(1)\rangle \) is antisymmetric

\( \Rightarrow \) spin part must be symmetric.

Then we form two-electron spin function that are symmetric or antisymmetric with respect to interchange of two electrons:

\[
\begin{align*}
&\frac{1}{\sqrt{2}} [\psi_1 \psi_1 + \psi_2 \psi_2] \\
&\frac{1}{\sqrt{2}} [\psi_1 \psi_2 - \psi_2 \psi_1]
\end{align*}
\]

\( \psi \) is antisymmetric

\( \frac{1}{\sqrt{2}} [\psi_1 \psi_2 - \psi_2 \psi_1] \) is antisymmetric.

Total wave function:

\[
\frac{1}{\sqrt{2}} [\psi_1 \psi_1 + \psi_2 \psi_2]
\]

\( \psi \) is symmetric

\( \frac{1}{\sqrt{2}} [\psi_1 \psi_2 - \psi_2 \psi_1] \) is antisymmetric.
If we ignore the electron repulsion, the energy of each electron is the same as in a hydrogenic (i.e., 
\text{hydrogen-like}) atom or ion with \( \ell = 3 \) (c). The total energy is the sum

\[
E_{\text{electron}} = -\frac{\epsilon^2}{\ell^2 n^2} \sum_{n=1}^{\ell=3} \quad = -\frac{9}{2} E_1
\]

\[
E_{\text{electron}} = -\frac{9}{2} E_1
\]

\[
E = -\frac{18}{2} E_1 = -9 E_1
\]

The actual energy will be higher because the electron repulsion energy, which we have ignored, is positive.