Problem Set 1

Practice problems:
Do these to learn the material. Check your answers against those in the back of the book or against your friends’ answers, or bring questions to office hours.

1-68, 2-15, 2-32, 2-74, 3-41, 3-44, 4-46, 4-49, 5-5, 5-6, 5-19, 5-32, 5-44

Discussion problems:
We will discuss these in class (3:30) on Wednesday the 2nd. Be prepared to present answers to and to discuss any of these up at the blackboard.

1. Use the periodic table on page 159 and find each instance where elements in the same column do not have analogous ground-state electronic structures. Can you come up with any general rules as to when this occurs, and any general ideas as to why? (You can ignore the lanthanides and actinides.)

2. Study the plots and diagrams of hydrogen orbitals on pages 141 and 143.
   (a) Sketch the $\psi^2_{2p}$-versus-$r$ plot, along a line that goes up and down on the page (for the orbital as drawn).
   (b) Sketch a stippled representation of the 3p orbital as well as a plot of $\psi^2_{3p}$ versus $r$. Remember that the 3p orbital has one radial (like the 2s) and one angular (like the 2p) node.
   (c) For the 2s orbital, figure out the following, qualitatively, in relation to the provided picture:
      - The single most likely point for finding a 2s electron.
      - The most likely distance from the nucleus (the most likely radius) at which a 2s electron would be found.
      - The average distance of a 2s electron from the nucleus.
3. The first through sixth ionization energies of carbon, in attojoules (1 aJ = 10^{-18} J) are:

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>I_1</th>
<th>I_2</th>
<th>I_3</th>
<th>I_4</th>
<th>I_5</th>
<th>I_6</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>C</td>
<td>1.81</td>
<td>3.90</td>
<td>7.67</td>
<td>10.3</td>
<td>62.8</td>
<td>78.5</td>
</tr>
</tbody>
</table>

In photoelectron spectroscopy, a single photon detaches an electron from an atom A:

$$A + \text{photon} \rightarrow A^+ + e^- \text{ (with kinetic energy)}$$

Don’t consider processes where one photon comes in and two or more electrons come out (this is possible, but quite uncommon) and assume none of the photon’s energy remains in the atom (also mostly true).

The ionization energies given above are useful and relevant, but they only indirectly give you the information you need to solve the problem. Thinking and (educated) guessing will be necessary.

(a) Carbon has 1s, 2s, and 2p electrons. Which of these can be detached using light with wavelength $\lambda = 100$ nm? Explain your answer.

(b) What is the maximum speed for an electron detached with 100 nm light?

(c) Which electrons (1s, 2s, and/or 2p) can be detached using 28 nm light? Explain your answer.

(d) Assume no energy is lost as heat or remains in the atom; that is, all excess energy goes into kinetic energy. If light with a wavelength of 2 nm is used, how many different electron speeds will be observed? (Explain your answer.)

**Graded problem:**

This should be written up and handed in before class begins on Wednesday the 2nd. This problem may also be discussed in class.

1. Look at the atomic emission spectra on page 117 of your text. The wavelength of every bright line in a given spectrum is determined by the energy difference between an initial (higher energy) state and a final (lower energy) state.
(a) Which initial and final states are responsible for each of the bright lines in
the spectrum of hydrogen shown? Also explain why there are no transitions
with energies that would put them in the dark regions of the hydrogen
spectrum. (In other words, how do you know that this region doesn’t
contain lines for \( n = 13 \) to \( n = 4 \), or \( n = 89 \) to \( n = 3 \), or any other
combination of \( n \) values except the ones you listed?)

(b) Not every combination of initial and final energy levels will result in emis-
sion, however: the process is subject to the selection rule:

\[
\Delta \ell = \pm 1
\]

This means that transitions can occur where an electron moves between \( p \)
(\( \ell = 1 \)) and \( s \) (\( \ell = 0 \)) orbitals, or between \( p \) (\( \ell = 1 \)) and \( d \) (\( \ell = 2 \)) orbitals,
but not between \( p \) and \( p \) (\( \Delta \ell = 0 \)) or \( s \) and \( d \) (\( \Delta \ell = 2 \)).

Why do we not need to consider selection rules to understand the hydrogen
spectrum? (Note that the selection rules are still true for hydrogen—a 2s
atom will not emit light at all to get back to the 1s ground state—but
hydrogen is special because the selection rules don’t actually change the
spectrum.)

(c) Come up with a plausible explanation for the energy levels involved for
each of the bright lines in the spectrum for lithium and for sodium. The
spectra in your text don’t show some faint lines; you can also use:

Again, also explain why regions of the spectrum that are dark have no
transitions. The cartoon diagram on page 150 may be helpful in guiding
your intuition.