SOLUTIONS

PROBLEM SET 7

CHM 3411, Dr. Chatfield

1. Li $1s^2 2s^1$

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) & \psi_{1s}(3)\alpha(3) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) & \psi_{1s}(3)\beta(3) \\ \psi_{2s}(1)\alpha(1) & \psi_{2s}(2)\alpha(2) & \psi_{2s}(3)\beta(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}} \Big[\psi_{1s}(1)\alpha(1)\big(\psi_{1s}(2)\beta(2)\,\psi_{2s}(3)\beta(3) - \psi_{2s}(2)\alpha(2)\,\psi_{1s}(3)\beta(3)\big)$$
$$- \psi_{1s}(2)\alpha(2)\big(\psi_{1s}(1)\beta(1)\,\psi_{2s}(3)\beta(3) - \psi_{2s}(1)\alpha(1)\,\psi_{1s}(3)\beta(3)\big)$$
$$+ \psi_{1s}(3)\alpha(3)\big(\psi_{1s}(1)\beta(1)\,\psi_{2s}(2)\alpha(2) - \psi_{2s}(1)\alpha(1)\,\psi_{1s}(2)\beta(2)\big) \Big]$$

$$= \frac{1}{\sqrt{6}} \Big(\boxed{\psi_{1s}(1)\alpha(1)\psi_{1s}(2)\beta(2)\psi_{2s}(3)\beta(3)} \boxed{- \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\alpha(2)\psi_{1s}(3)\beta(3)}$$
$$\boxed{- \psi_{1s}(2)\alpha(2)\psi_{1s}(1)\beta(1)\psi_{2s}(3)\beta(3)} \boxed{+ \psi_{1s}(2)\alpha(2)\psi_{2s}(1)\alpha(1)\psi_{1s}(3)\beta(3)}$$
$$\boxed{+ \psi_{1s}(3)\alpha(3)\psi_{1s}(1)\beta(1)\psi_{2s}(2)\alpha(2)} \boxed{- \psi_{1s}(3)\alpha(3)\psi_{2s}(1)\alpha(1)\psi_{1s}(2)\beta(2)} \Big)$$

Suppose we swap electrons 1 & 2, for example. Then

$$\Psi(2,1,3) = \frac{1}{\sqrt{6}} \Big(\boxed{\psi_{1s}(2)\alpha(2)\psi_{1s}(1)\beta(1)\psi_{2s}(3)\beta(3)} \boxed{- \psi_{1s}(2)\alpha(2)\psi_{2s}(1)\alpha(1)\psi_{1s}(3)\beta(3)}$$
$$\boxed{- \psi_{1s}(1)\alpha(1)\psi_{1s}(2)\beta(2)\psi_{2s}(3)\beta(3)} \boxed{+ \psi_{1s}(1)\alpha(1)\psi_{2s}(2)\alpha(2)\psi_{1s}(3)\beta(3)}$$
$$\boxed{+ \psi_{1s}(3)\alpha(3)\psi_{1s}(2)\beta(2)\psi_{2s}(1)\alpha(1)} \boxed{- \psi_{1s}(3)\alpha(3)\psi_{2s}(2)\alpha(2)\psi_{1s}(1)\beta(1)} \Big)$$

Now we cross out like terms in the expression for $\Psi(1,2,3)$ and $\Psi(2,1,3)$ above. Each such pair is cirled above with a unique outline in color or solid/dashed. The members of each pair have opposite sign. Therefore $\Psi(1,2,3) = -\Psi(2,1,3)$, satisfying the antisymmetry requirement.

2. Calculating the HF/6-31G* energy for a neon atom with Spartan yields

Total energy = -128.4744066 Hartrees

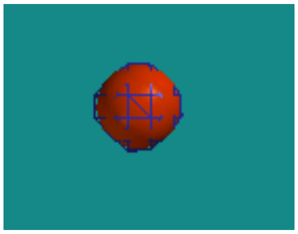
Energies of 5 lowest orbitals (in Hartrees), followed by the orbital we would expect from the Aufbau principle:

1. -32.76107 (1s)
2. -1.91071 (2s)
3. -0.83023 (2p)
4. -0.83023 (2p)
5. -0.83023 (2p)

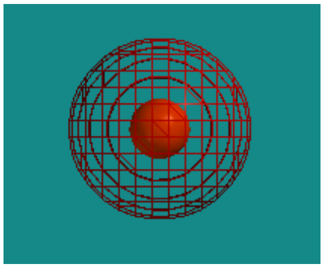
Note that the last three orbitals are degenerate, as expected for the three 2p orbitals. They are the p_x, p_y, and p_z (other information in the output can be used to identify which is which).

Images of the orbitals are below. Note that the 1s is very compact. One of the 2p orbitals was rotated slightly to show its shape.

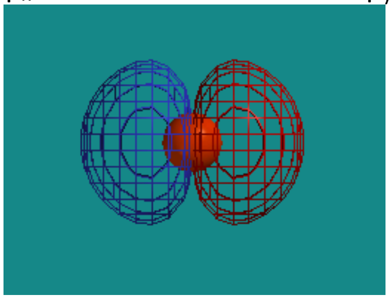
1s



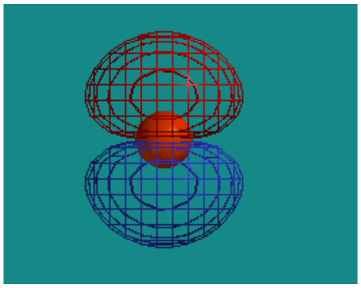
2s



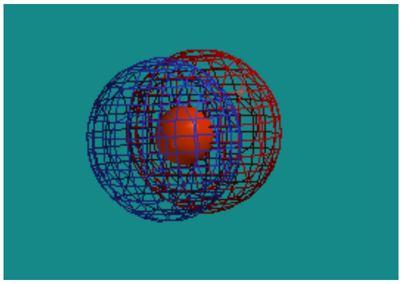
$2p_x$



$2p_y$



$2p_z$



We can determine Z_{eff} from $E = \frac{-Z_{eff}^2}{n^2}$ which becomes, rearranged: $Z_{eff} = \sqrt{-2n^2E}$. (This assumes E is in Hartrees.) Also, note that the shielding constant, is determined from: $Z_{eff} = Z - \sigma$ which becomes, rearranged, $\sigma = Z - Z_{eff}$.

orbital	E	Z_{eff}	σ
1s	-32.76107	8.06	1.94
2s	-1.91071	3.93	6.07
2p	-0.83023	2.61	7.39

As expected, the 2s and 2p are more highly shielded than the 1s (the 2p slightly more than the 2s). Also note that Z = 10, so the Z_{eff} experienced by the 1s orbital is only slightly reduced from Z. Also note that the three 2p orbitals are shielded to the same extent, so we do not distinguish them from each other. Finally, note that the calculated energies are approximate, and they include spin correlation as well as shielding, and the so these numbers are approximate.

3.

Spin correlation is an odd attribute that electrons. You are probably familiar with the idea of charge. Electrons have negative charge, and so two electrons tend to repel each other and "don't like" to be close to each other on account of charge.

Electrons also possess another property, spin. You can imagine a little charged particle spinning on its axis, although that image is only a "helper" and isn't perfect. It turns out that electrons can spin in only two senses; we call one "spin up" and the other "spin down." It has been found that two electrons with the same spin (both up or both down) cannot be in the same place at the same time – but electrons with opposite spin can be! (Or rather, spin doesn't prevent opposite-spin particles from being at the same place at the same time, although Coulombic repulsion does – it becomes infinitely large as the distance between the electrons approaches zero.) Extending this idea, for two electrons with the same spin to be very close (even if not quite at the same place) is highly unlikely. Spin, then, is effectively causing like-spin particles to stay farther apart –that is, relative position is correlated with spin.

In summary, then, there are at least TWO factors that tend to keep electrons away from each other. One is charge-charge repulsion. The other is spin correlation. If you look into it deeply, it turns out that spin correlation comes from the fact that electrons are indistinguishable – you can't tell one from another. But that is a story for another day.

4. The principle here is conservation of energy. When the photon is absorbed, its energy is used to ionize the atom, with any excess energy then imparted to the ionized electron as kinetic energy:

$$E_{photon} = I + E_K$$

$$E_{photon} = h\nu = \frac{hc}{\lambda} = 3.40\times10^{-18}\ \mathrm{J}$$

$$E_K = \tfrac{1}{2}m_e(1.79\times10^{6}\ \mathrm{ms^{-1}})^2 = 1.46\times10^{-18}\ \mathrm{J}$$

$$I = E_{photon} - E_K = 1.94\times10^{-18}\ \mathrm{J} = 1{,}170\ \mathrm{kJ/mol}$$

5. (i) p electron

$l=1 \quad s=\frac{1}{2} \qquad j=l+s, \ldots, |l-s| = \frac{3}{2}, \frac{1}{2}$

(ii) h electron $\left(\begin{array}{cccccc} l: 0 & 1 & 2 & 3 & 4 & 5 \\ s & p & d & f & g & h \end{array}\right)$

$l=5 \quad s=\frac{1}{2} \qquad j=\frac{11}{2}, \frac{9}{2}$

6. Possible term symbols for:

(i) Sc $[Ar]3d^1 4s^2$ 4s subshell filled $\Rightarrow$ no contribution

$3d^1$ $s = \frac{1}{2} = S = \frac{1}{2}, M = 2S+1 = 2 \quad L = 2 \Rightarrow D$

$J = 2+\frac{1}{2}, \ldots |2-\frac{1}{2}| = \frac{5}{2}, \frac{3}{2} \Rightarrow {}^2D_{5/2} \quad {}^2D_{3/2}$

(ii) Br $[Ar]3d^{10}4s^2 4p^5$

We only need to be concerned with the partially filled subshell, $4p^5$. Recall that a subshell missing one electron (the case here) is analyzed like a subshell containing one electron, i.e., $4p^5$ will have the same term symbol as $4p^1$

$$\overset{\overset{M=2}{\Uparrow}}{S} = \frac{1}{2} \quad \overset{\overset{P}{\Uparrow}}{L} = 1 \quad J = 1+\frac{1}{2}, \ldots \overbrace{|1-\tfrac{1}{2}|}^{\frac{1}{2}} = \frac{3}{2}, \frac{1}{2}$$

Term Symbols: ${}^2P_{3/2} \quad {}^2P_{1/2}$

7. Which transitions are allowed?

(i) $^2P_{3/2} \rightarrow {}^2S_{1/2}$ $\Delta S = 0$ ✓ $\Delta L = -1$ ✓ $\Delta J = -1$ ✓ allowed

(ii) $^3P_0 \rightarrow {}^3S_1$ $\Delta S = 0$ ✓ $\Delta L = -1$ ✓ $\Delta J = 1$ ✓ allowed

(iii) $^3D_3 \rightarrow {}^1P_1$ $\Delta S = -1$ ✗ $\Delta L = -1$ ✓ $\Delta J = -2$ ✗ forbidden (2 reasons)

8.

All lines in the hydrogen spectrum fit the Rydberg formula

$$\frac{1}{\lambda}=\tilde{R}_{\mathrm{H}}\left(\tfrac{1}{n_1^2}-\tfrac{1}{n_2^2}\right)\left[9\mathrm{A}.1,\ \text{with } \tilde{\nu}=\frac{1}{\lambda}\right]\qquad \tilde{R}_{\mathrm{H}}=109\ 677\,\mathrm{cm}^{-1}$$

Find n_1 from the value of $\lambda_{\max}$, which arises from the transition $n_1+1\rightarrow n_1$

$$\frac{1}{\lambda_{\max}\tilde{R}_{\mathrm{H}}}=\frac{1}{n_1^2}-\frac{1}{(n_1+1)^2}=\frac{2n_1+1}{n_1^2(n_1+1)^2}$$

$$\lambda_{\max}\tilde{R}_{\mathrm{H}}=\frac{n_1^2(n_1+1)^2}{2n_1+1}=(656.46\times10^{-9}\,\mathrm{m})\times(109677\times10^{2}\,\mathrm{m}^{-1})=7.20$$

and hence $n_1=2$, as determined by trial and error substitution. Therefore, the transitions are given by

$$\tilde{\nu}=\frac{1}{\lambda}=(109677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4}-\frac{1}{n_2^2}\right),\quad n_2=3,4,5,6$$

The next line has $n_2=7$, and occurs at

$$\tilde{\nu}=\frac{1}{\lambda}=(109677\,\mathrm{cm}^{-1})\times\left(\frac{1}{4}-\frac{1}{49}\right)=\boxed{397.13\,\mathrm{nm}}$$

The energy required to ionize the atom is obtained by letting $n_2\rightarrow\infty$. Then

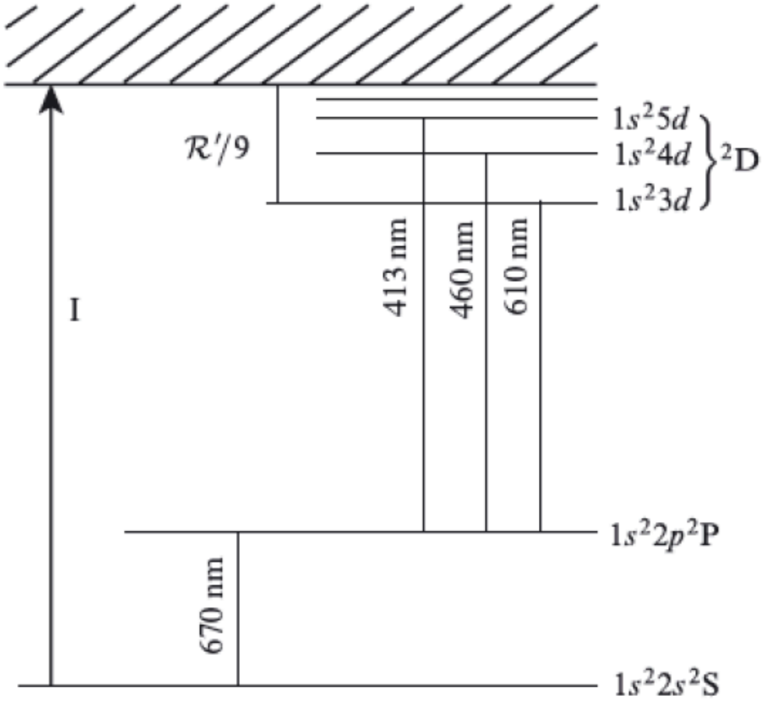
$$\tilde{\nu}_{\infty}=\frac{1}{\lambda_{\infty}}=(109677\ \mathrm{cm}^{-1})\times\left(\frac{1}{4}-0\right)=27419\ \mathrm{cm}^{-1},\quad \text{or}\quad \boxed{3.40\ \mathrm{eV}}$$

(The answer, $3.40\ \mathrm{eV}$, is the ionization energy of an H atom that is already in an excited state, with $n=2$.)

Comment. The series with $n_1=2$ is the Balmer series.

9.

The lowest possible value of n in $1s^2nd^1$ is 3; thus the series of ^2D terms correspond to $1s^2 3d$, $1s^2 4d$, etc. Figure 9C.1 is a description consistent with the data in the problem statement.



If we assume that the energies of the d orbitals are hydrogenic we may write

$$E(1s^2nd^1, {}^2D) = -\frac{hc\tilde{R}_{Li}}{n^2} \quad [n = 3, 4, 5, \cdots]$$

Then for the $^2D \rightarrow {}^2P$ transitions

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{|E(1s^2 2p^1, {}^2P)|}{hc} - \frac{\tilde{R}_{Li}}{n^2} \qquad \left[\Delta E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu},\ \tilde{\nu} = \frac{\Delta E}{hc}\right]$$

from which we can write

$$\frac{|E(1s^2 2p^1, {}^2P)|}{hc} = \frac{1}{\lambda} + \frac{\tilde{R}_{Li}}{n^2} = \begin{cases} \dfrac{1}{610.36 \times 10^{-7}\ \text{cm}} + \dfrac{\tilde{R}_{Li}}{9} & \text{(a)} \\ \dfrac{1}{460.29 \times 10^{-7}\ \text{cm}} + \dfrac{\tilde{R}_{Li}}{16} & \text{(b)} \\ \dfrac{1}{413.23 \times 10^{-7}\ \text{cm}} + \dfrac{\tilde{R}_{Li}}{25} & \text{(c)} \end{cases}$$

$$\text{Then}\ \left.\begin{array}{l} \text{(b)} - \text{(a) solves to } \tilde{R}_{Li} = 109886\ \text{cm}^{-1} \\ \text{(a)} - \text{(c) solves to } \tilde{R}_{Li} = 109910\ \text{cm}^{-1} \\ \text{(b)} - \text{(c) solves to } \tilde{R}_{Li} = 109963\ \text{cm}^{-1} \end{array}\right\} \text{Mean} = 109920\ \text{cm}^{-1}$$

The binding energies are therefore

$$E(1s^2\,3d^1,\,{}^2D) = -\frac{\widetilde{R}_{\mathrm{Li}}}{9} = -12213\,\mathrm{cm}^{-1}$$

$$E(1s^2\,2p^1,\,{}^2P) = -\frac{1}{610.36\times10^{-7}\ \mathrm{cm}} - 12213\ \mathrm{cm}^{-1} = -28597\ \mathrm{cm}^{-1}$$

$$E(1s^2\,2s^1,\,{}^2S) = -\frac{1}{670.78\times10^{-7}\ \mathrm{cm}} - 28597\ \mathrm{cm}^{-1} = -43505\ \mathrm{cm}^{-1}$$

Therefore, the ionisation energy is

$$I(1s^2\,2s^1,\,{}^2S) = 43505\ \mathrm{cm}^{-1}, \quad \text{or} \quad \boxed{5.39\ \mathrm{eV}}$$