5.61 Fall 2017
Problem Set #7 Solutions

1. Hydrogenic Systems.

In each of the following cases, state which of the two quantities is larger. Justify your answers. You do not need to do any integrals here. Some equations on page 333 of McQuarrie might be helpful.

A. The average value of r for a 2s electron *versus* a 2p electron.

Solution:

The average value of $\langle r \rangle$ is larger for a 2s electron than a 2p electron.

B. The average value of $1/r$ for a 2s electron *versus* a 2p electron.

Solution:

$\left\langle \frac{1}{r} \right\rangle$ is $\frac{Z}{4a_0}$ for both the 2s and 2p cases. We can confirm this since we have derived an expression for $\left\langle \frac{1}{r} \right\rangle$ from the virial theorem in Question 4, and have proved that it is independent of the ℓ value.

C. The average value of r for a 2s electron in He^+ *versus* a 1s electron in H.

Solution:

$\langle r \rangle$ for 2s He^+ is $3a_0$ and for 1s Hydrogen it's $\frac{3}{2}a_0$. It makes sense that $\langle r \rangle$ of the electron in the He^+ 2s would be double the distance (on average) than that of the 1s electron.

D. The average value of r for a 3d electron in Fe^{25+} versus a 1s electron in C^{5+}.

Solution:

$\langle r \rangle$ for the 3d electron of Fe^{25+} is $\approx 0.4a_0$, whereas for the 1s electron of C^{5+} it is $0.25a_0$. It is expected that, although the nucleus of Fe^{25+} has a larger positive charge and would therefore pull its electron in the 3d shell closer, it's still not as close to the nucleus as the 1s electron of C^{5+}.

E. The number of *radial* nodes in an 8g orbital *versus* the number of *angular* nodes in an 8g orbital.

Solution:

The number of radial nodes is given as $n - \ell + 1$ while the number of angular nodes is given by ℓ. Therefore 8g has 3 radial nodes and 4 angular nodes.

F. The spacing between the radial nodes for a 14s orbital *versus* the spacing between the radial nodes for a 16d orbital.

Solution:

Both have the same number of nodes, but in general since the 16d electron will have a larger $\langle r \rangle$ value, we can expect that the node spacing should be larger for this case.

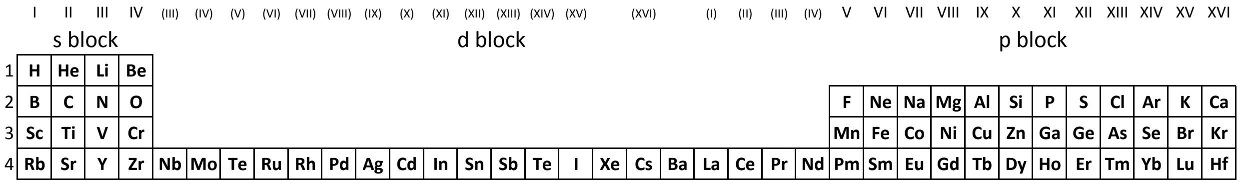
NOTE: Atomic properties such as the relative $n\ell$ orbital energies, $E_{n\ell}$, and radii, $\langle r^n \rangle_{n\ell}$, atomic ionization energy and electron affinity, and the dependence of these properties on electron configuration are explained by the systematic shielding of the $+Z$ nuclear charge experienced by an electron in the $n\ell$ atomic orbital by all of the electrons in the other occupied $n'\ell'$ atomic orbitals. One computes the effective nuclear charge experienced by an electron in the $n\ell$ orbital due to shielding by all of the other electrons in the electronic configuration, $Z_{n\ell}^{\text{eff}}(\textit{configuration})$. This effective nuclear charge is inserted in the standard hydrogenic formulas for orbital energy, $E_{n\ell}$, orbital radius, $\langle r \rangle_{n\ell}$, and other integer powers of r, $\langle r^n \rangle_{n\ell}$. *The Periodic Table is explained by shielding*! A table of these inter-orbital shielding effects, sometimes known as Burns' rules, is given in a paper by Gerald Burns, "Atomic Shielding Parameters," *J. Chem. Phys.* **41**, 1521-1522 (1964), https://doi.org/10.1063/1.1726113.

2. Spin 3/2 Periodic Table

Consider a universe where the electron has spin 3/2 instead of spin 1/2.

A. Draw the periodic table (up to Hafnium) in this alternate universe.

Solution: If the electron were to have $s = 3/2$, then there would be four possible m_s values, $m_s = +3/2, +1/2, -1/2, -3/2$, instead of the usual two. This means that each atomic orbital can be occupied by four electrons and still satisfy the Pauli exclusion principle (anti-symmetrization). s–orbitals can hold 4, p–orbitals can hold 12, etc. We build up the periodic table in the same way we are used to, adding electrons to shells as we go. The modified table (up to Hf) is shown in Figure 1.



	I	II	III	IV	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)	(XV)		(XVI)		(I)	(II)	(III)	(IV)	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
	s block				d block																				p block											
1	H	He	Li	Be																																
2	B	C	N	O																					F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca
3	Sc	Ti	V	Cr																					Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
4	Rb	Sr	Y	Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf

Figure 1: One reasonable ordering for a spin-3/2 periodic table.

That the $3d$ block should come after the $4s$ block isn't obvious (and may not even be true for a spin 3/2 table). In the real table, this lower energy for 4s rather than 3d occurs because e-e repulsion is significantly reduced for $4s$ electrons (which are much further from the core electrons), than for $3d$ electrons. Even though the one-electron orbital energy for $4s$ levels is higher than $3d$ levels, this reduction in e-e repulsion in many-electron atoms causes the reordering. We assume the same trend will exist here. There are 3 radial nodes for 4s and zero radial nodes for 3d.

B. Which elements would be "noble gases"? Which would be alkaline earth elements? Which elements would be in the same period as carbon?

Solution:

The analog of the "noble gases" would be those with complete n–shells, namely Be, Ca, Kr, and Hf. With regard to the "alkaline earth metals," we could argue that any element with an incomplete s–shell would count, which includes groups I-III. You might argue that only $(ns)^1$ configurations should count, in which case you consider only group I elements. In the real table, there is no ambiguity because the only incompletely filled s–shells have 1 electron anyway. For $S = 3/2$, carbon is in the second period, along with elements with $Z = 5 - 20$ (B through Ca).

C. What would the bond order of He_2 be in this universe? What about O_2?

Solution:

Since each MO can also be filled with 4 electrons now, the bond order of He_2 would be 4(!). O_2, on the other hand, now has a bond order of 0 (the two σ and two σ^* orbitals from the O $1s$ and $2s$ orbitals are each completely filled with 16 electrons). You should be realizing just how important the electron's spin is in determining the chemical structure and patterns of the universe.

D. What would the equivalent of the octet rule be in this alternate universe?

[**NOTE**: you could spend *a lot of time* answering this last question. It is intended to be fun. When it stops being fun, your answer is long enough.]

Solution:

The octet rule is based on having complete n-shells. It should be clear that the simplest analog in the spin 3/2 table is the "hexadectet" rule, i.e. $n = 2$ and 3 orbitals prefer to have 16 electrons in their outer shells (4 in s and 12 in p).

3. Rydberg States of a Many-Electron Atom.

The subject of this problem is potassium, which has a closed-shell ion-core:

$$K(1s^2 2s^2 2p^6 3s^2 3p^6)n^*\ell$$

The ionization energy (in cm^{-1} units) from the "4s" electronic ground state is 35009.78 cm^{-1}. The Rydberg constant for K is $\Re = 109737.32\text{cm}^{-1}$.

A. Why is it reasonable to ignore the anti-symmetrization requirement for Rydberg states of this 19 electron atom?

Solution:

We approximate the K atom as a K^+ core and an electron. As the K^+ core is complete (all filled shells), anti-symmetrization between the core and the single valence electron has a negligible effect, so we ignore it.

B. Consider three consecutive members of the ns, np, and nd Rydberg series:

n	**s-series**	**n**	**p-series**	**n**	**d-series**
8	31764.95 cm^{-1}	40	34934.97 cm^{-1}	9	33572.11 cm^{-1}
9	32648.17 cm^{-1}	41	34938.72 cm^{-1}	10	33851.76 cm^{-1}
10	33214.39 cm^{-1}	42	34942.20 cm^{-1}	11	34056.90 cm^{-1}

Compute n^*-values for all 9 of the tabulated energy levels. Do the n^* levels increase in steps of $\sim$1.00?

Solution:

We are provided with excitation energies from the ground state. To convert to energies under ionization, we use $E_{n^*} = E_{\text{ionization}} - E_{\text{state}}$. We combine this with

$$E_{n*} = -\frac{\Re}{n^{*2}}.$$

Thus

$$n^* = \sqrt{\frac{\Re}{E_{\text{state}} - E_{\text{ionization}}}}.$$

Plugging in the tabulated values,

ns	n*	δ_s	np	n*	δ_p	ns	n*	δ_s
8	5.815	2.185	40	38.300	1.700	9	8.737	0.263
9	6.817	2.183	41	39.297	1.703	10	9.735	0.265
10	7.818	2.182	42	40.297	1.703	11	10.731	0.269

C. The quantum defects, δ_ℓ, are defined as $n - n^*$. Compute the approximately n-independent quantum defects for the s, p, and d series of K.

Solution:

See above table. $\delta_\ell = n - n^*$. We see that the defect for ns is about 2.2, for np is about 1.7, and for nd is about 0.3.

D. Suggest a reason why $\delta_s \gg \delta_p > \delta_d$.

Solution:

s orbitals penetrate further into the inner core than orbitals with higher angular momentum. From this we expect $\delta_s \gg \delta_p \gg \delta_d \approx 0$.

E. The n^* values you have determined from real spectroscopic data may be considered "experimentally measured." But the tabulated integer n quantum numbers are not measured. They are inferred from some sort of physical argument. Can you suggest what this argument is?

[**HINT**: the lowest s, p, and d states of K are called $4s, 4p$, and $3d$.]

Solution:

The quantum defects above are correct, even down to the $4s$, $4p$, and $4d$ states, to within 0.1. We don't record n^* because, to an excellent approximation, it increases in steps of 1.

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4. Two Electron Wavefunctions: Spin.

For two electrons, the total z component of the spin angular momentum for the system is

$$\widehat{S}_{z,\text{ total}} = \widehat{S}_{z_1} + \widehat{S}_{z_2}$$

while the total spin operator is given by

$$\widehat{S}^2_{\text{total}} = \widehat{S}^2_{x,\text{ total}} + \widehat{S}^2_{y,\text{ total}} + \widehat{S}^2_{z,\text{ total}} + \left(\widehat{S}_{x_1} + \widehat{S}_{x_2}\right)^2 + \left(\widehat{S}_{y_1} + \widehat{S}_{y_2}\right)^2 + \left(\widehat{S}_{z_1} + \widehat{S}_{z_2}\right)^2$$

A. Show that both

$$\psi_{\alpha\beta} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 2s\beta(1) \\ 1s\alpha(2) & 2s\beta(2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}} \left(2s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2)\right)$$

and

$$\psi_{\beta\alpha} = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta(1) & 2s\alpha(1) \\ 1s\beta(2) & 2s\alpha(2) \end{vmatrix} \equiv \frac{1}{\sqrt{2}} \left(1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)\right)$$

are antisymmetric.

Show also that $\psi_{\alpha\beta}$ and $\psi_{\beta\alpha}$ are eigenfunctions of $\widehat{S}_{z,\text{ total}}$. What are the eigenvalues in each case?

Solution:

$$\Psi_{\alpha\beta} = \frac{1}{\sqrt{2}}[1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2)]$$

switching 1 and 2 by the $\hat{P}_{12}$ permutation operator

$$\begin{aligned} \hat{P}_{12}\Psi_{\alpha\beta} &= \frac{1}{\sqrt{2}}[1s\alpha(2)2s\beta(1) - 2s\beta(2)1s\alpha(1)] \\ &= -\frac{1}{\sqrt{2}}[2s\beta(2)1s\alpha(1) - 1s\beta(1)1s\alpha(2)] \\ &= -\Psi_{\alpha\beta}. \end{aligned}$$

This indicates that $\Psi_{\alpha\beta}$ is anti-symmetric:

$$\Psi_{\beta\alpha} = \frac{1}{\sqrt{2}}[1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)]$$

switching 1 and 2 by $\hat{P}_{12}$

$$\begin{aligned} \hat{P}_{12}\Psi_{\beta\alpha} &= \frac{1}{\sqrt{2}}[1s\beta(2)2s\alpha(1) - 2s\alpha(2)1s\beta(1)] \\ &= -\frac{1}{\sqrt{2}}[2s\alpha(2)1s\beta(1) - 1s\beta(2)2s\alpha(1)] \\ &= -\Psi_{\beta\alpha}. \end{aligned}$$

This indicates that $\Psi_{\beta\alpha}$ is anti-symmetric.

Now the eigenvalue for $\Psi_{\alpha\beta}$:

$$\begin{aligned} \widehat{S}_{z,\text{ total}} &= \widehat{S}_{z1} + \widehat{S}_{z2} \\ \widehat{S}_{z,\text{ total}}\Psi_{\alpha\beta} &= \left(\widehat{S}_{z1} + \widehat{S}_{z2}\right)\Psi_{\alpha\beta} \\ &= \frac{1}{\sqrt{2}}\left[\widehat{S}_{z1}\{1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2)\} + \widehat{S}_{z2}\{1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2)\}\right] \\ &= \frac{1}{\sqrt{2}}\left[\left(\frac{\hbar}{2}\right)1s\alpha(1)2s\beta(2) - \left(-\frac{\hbar}{2}\right)2s\beta(1)1s\alpha(2)\right. \\ &\quad \left. + \left(-\frac{\hbar}{2}\right)1s\alpha(1)2s\beta(2) - \left(\frac{\hbar}{2}\right)2s\beta(1)1s\alpha(2)\right] \\ &= 0 \end{aligned}$$

Now the eigenvalue for $\Psi_{\beta\alpha}$:

$$\begin{aligned}
\widehat{S}_{z,\text{ total}}\Psi_{\beta\alpha} &= \left(\widehat{S}_{z1} + \widehat{S}_{z2}\right)\Psi_{\beta\alpha} \\
&= \frac{1}{\sqrt{2}}\left[\widehat{S}_{z1}\{1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)\} + \widehat{S}_{z2}\{1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)\}\right] \\
&= \frac{1}{\sqrt{2}}\left[\left(-\frac{\hbar}{2}\right)1s\beta(1)2s\alpha(2) - \left(\frac{\hbar}{2}\right)2s\alpha(1)1s\beta(2)\right. \\
&\quad \left. + \left(\frac{\hbar}{2}\right)\{1s\beta(1)2s\alpha(2) - \left(-\frac{\hbar}{2}\right)2s\alpha(1)1s\beta(2)\right] \\
&= 0
\end{aligned}$$

This indicates that both $\Psi_{\alpha\beta}$ and $\Psi_{\beta\alpha}$ are eigenfunctions of $\widehat{S}_{z,\text{ total}}$, both with eigenvalues of 0.

B. Show that, while $\psi_{\alpha\beta}$ and $\psi_{\beta\alpha}$ cannot be written in the form $\psi_{\text{space}}\psi_{\text{spin}}$, the combinations of $\psi_{\alpha\beta} \pm \psi_{\beta\alpha}$ can both be cast in the form $\psi_{\text{space}}\psi_{\text{spin}}$.

Solution:

$$\begin{aligned}
\Psi_{\alpha\beta} &= \frac{1}{\sqrt{2}}[1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2)] \\
&= \frac{1}{\sqrt{2}}[(1s(1)2s(2)\alpha(1)\beta(2)) - (2s(1)1s(2)\beta(1)\alpha(2))] \\
&\neq \Psi_{\text{spin}}\Psi_{\text{space}} \\
\Psi_{\beta\alpha} &= \frac{1}{\sqrt{2}}[1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)] \\
&= \frac{1}{\sqrt{2}}[(1s(1)2s(2)\beta(1)\alpha(2)) - (2s(1)1s(2)\alpha(1)\beta(2))] \\
&\neq \Psi_{\text{spin}}\Psi_{\text{space}}.
\end{aligned}$$

However

$$\begin{aligned}
\Psi_{\alpha\beta} + \Psi_{\beta\alpha} &= \frac{1}{\sqrt{2}}[1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2) + 1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)] \\
&= \frac{1}{\sqrt{2}}[\{1s(1)2s(2)\alpha(1)\beta(2)\} - \{2s(1)1s(2)\beta(1)\alpha(2)\} \\
&\quad + \{1s(1)2s(2)\beta(1)\alpha(2)\} - \{2s(1)1s(2)\alpha(1)\beta(2)\}] \\
&= \frac{1}{\sqrt{2}}\{1s(1)2s(2) - 2s(1)1s(2)\}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \\
&= \frac{1}{\sqrt{2}}\Psi_{\text{space}} \cdot \Psi_{\text{spin}}.
\end{aligned}$$

Similarly,

$$
\begin{aligned}
\Psi_{\alpha\beta} - \Psi_{\beta\alpha} &= \frac{1}{\sqrt{2}}[1s\alpha(1)2s\beta(2) - 2s\beta(1)1s\alpha(2) - 1s\beta(1)2s\alpha(2) + 2s\alpha(1)1s\beta(2)] \\
&= \frac{1}{\sqrt{2}}[\{1s(1)2s(2)\alpha(1)\beta(2)\} - \{2s(1)1s(2)\beta(1)\alpha(2)\} \\
&\quad - \{1s(1)2s(2)\beta(1)\alpha(2)\} + \{2s(1)1s(2)\alpha(1)\beta(2)\}] \\
&= \frac{1}{\sqrt{2}}\{1s(1)2s(2) + 2s(1)1s(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \\
&= \frac{1}{\sqrt{2}}\Psi_{\text{space}} \cdot \Psi_{\text{spin}}.
\end{aligned}
$$

C. Verify that the total spin operator can be re-written in terms of raising and lowering operators:

$$\widehat{S}^2_{\text{total}} = \widehat{S}^2_1 + \widehat{S}^2_2 + 2\widehat{S}_{1_z}\widehat{S}_{2_z} + \left(\widehat{S}_{1+}\widehat{S}_{2-} + \widehat{S}_{1-}\widehat{S}_{2+}\right).$$

<u>Solution:</u>

$$
\begin{aligned}
\widehat{S}^2_{\text{total}} &= (\widehat{S}_1 + \widehat{S}_2)(\widehat{S}_1 + \widehat{S}_2) = \widehat{S}_1{}^2 + \widehat{S}_1\widehat{S}_2 + \widehat{S}_2\widehat{S}_1 + \widehat{S}_2{}^2 \\
&= \widehat{S}^1_1 + \widehat{S}^2_2 + 2(\widehat{S}_1\widehat{S}_2) \\
&= \widehat{S}^2_1 + \widehat{S}^2_2 + 2(\widehat{S}_{x_1}\widehat{S}_{x_2} + \widehat{S}_{y_1}\widehat{S}_{y_2} + \widehat{S}_{z_1}\widehat{S}_{z_2}) \\
&= \widehat{S}^2_1 + \widehat{S}^2_2 + 2\widehat{S}_{z_1}\widehat{S}_{z_2} + 2\left[\left(\frac{\widehat{S}_{+1} + \widehat{S}_{-1}}{2}\frac{\widehat{S}_{+2} + \widehat{S}_{-2}}{2}\right) + \left(\frac{\widehat{S}_{+1} - \widehat{S}_{-1}}{2i}\frac{\widehat{S}_{+2} - \widehat{S}_{-2}}{2i}\right)\right] \\
&= \widehat{S}^2_1 + \widehat{S}^2_2 + 2\widehat{S}_{z_1}\widehat{S}_{z_2} + \frac{1}{2}\Big[\widehat{S}_{+1}\widehat{S}_{+2} + \widehat{S}_{+1}\widehat{S}_{-2} + \widehat{S}_{-1}\widehat{S}_{+2} + \widehat{S}_{-1}\widehat{S}_{-2} - \widehat{S}_{+1}\widehat{S}_{+2} + \widehat{S}_{+1}\widehat{S}_{-2} \\
&\quad + \widehat{S}_{-1}\widehat{S}_{+2} - \widehat{S}_{-1}\widehat{S}_{-2}\Big] \\
&= \widehat{S}^2_1 + \widehat{S}^2_2 + 2\widehat{S}_{z_1}\widehat{S}_{z_2} + (\widehat{S}_{+1}\widehat{S}_{-2} + \widehat{S}_{-1}\widehat{S}_{+2})
\end{aligned}
$$

D. Show that neither $\psi_{\alpha\beta}$ nor $\psi_{\beta\alpha}$ is an eigenfunction of $\widehat{S}^2_{\text{total}}$. That is to say, show that neither of these wavefunctions is a total spin eigenstate.

Solution:

$$\begin{aligned}
\widehat{S}^2_{\text{total}}\Psi_{\alpha\beta} &= \left[\widehat{S}_1^2 + \widehat{S}_2^2 + 2\widehat{S}_{z_1}\widehat{S}_{z_2} + \widehat{S}_{+1}\widehat{S}_{-2} + \widehat{S}_{-1}\widehat{S}_{+2}\right]\Psi_{\alpha\beta} \\
\widehat{S}_1^2\Psi_{\alpha\beta} &= \frac{3}{4}\hbar^2\Psi_{\alpha\beta} \quad \widehat{S}_2^2\Psi_{\alpha\beta} = \frac{3}{4}\hbar^2\Psi_{\alpha\beta} \\
2\widehat{S}_{z_1}\widehat{S}_{z_2}\Psi_{\alpha\beta} &= \frac{2}{\sqrt{2}}\widehat{S}_{z_1}\left[\left(-\frac{\hbar}{2}\right)1s\alpha(1)2s\beta(2) - \left(\frac{\hbar}{2}\right)2s\beta(1)1s\alpha(2)\right] \\
&= -\frac{\hbar}{\sqrt{2}}\left[\left(\frac{\hbar}{2}\right)1s\alpha(1)2s\beta(2) + \left(-\frac{\hbar}{2}\right)2s\beta(1)1s\alpha(2)\right] \\
&= -\frac{\hbar^2}{2}\Psi_{\alpha\beta} \\
\widehat{S}_{+1}\widehat{S}_{-2}\Psi_{\alpha\beta} &= \frac{1}{\sqrt{2}}\widehat{S}_{+1}\left[0 - \hbar\sqrt{\frac{3}{4}+\frac{1}{4}}2s\beta(1)1s\beta(2)\right] \\
&= -\frac{\hbar}{\sqrt{2}}\cdot\hbar\sqrt{\frac{3}{4}+\frac{1}{4}}2s\alpha(1)1s\beta(2) \\
&= -\frac{\hbar^2}{\sqrt{2}}2s\alpha(1)1s\beta(2) \\
\widehat{S}_{-1}\widehat{S}_{+2}\Psi_{\alpha\beta} &= \frac{1}{\sqrt{2}}\widehat{S}_{-1}\left[\hbar\sqrt{\frac{3}{4}+\frac{1}{4}}1s\alpha(1)2s\alpha(2) + 0\right] \\
&= \frac{\hbar}{\sqrt{2}}\cdot\hbar 1s\beta(1)2s\alpha(2) \\
&= \frac{\hbar^2}{\sqrt{2}}1s\beta(1)2s\alpha(2)
\end{aligned}$$

Therefore, summing over all the terms gives

$$\begin{aligned}
\widehat{S}^2_{\text{total}}\Psi_{\alpha\beta} &= \hbar^2\Psi_{\alpha\beta} + \frac{\hbar^2}{\sqrt{2}}[1s\beta(1)2s\alpha(2) - 2s\alpha(1)1s\beta(2)] \\
&= \hbar^2[\Psi_{\alpha\beta} + \Psi_{\beta\alpha}]
\end{aligned}$$

Repeating similar steps for $\Psi_{\beta\alpha}$ gives

$$\widehat{S}^2_{\text{total}}\Psi_{\beta\alpha} = \hbar^2[\Psi_{\alpha\beta} + \Psi_{\beta\alpha}].$$

Therefore, neither $\Psi_{\alpha\beta}$ nor $\Psi_{\beta\alpha}$ is an eigenfunction of $\widehat{S}^2_{\text{total}}$.

E. Finally, show that the combinations $\psi_{\alpha\beta} \pm \psi_{\beta\alpha}$ are eigenfunctions of both $\widehat{S}_{z,\text{ total}}$ and $\widehat{S}^2_{\text{total}}$.

Solution:

$$\begin{aligned}
\widehat{S}_{z,\text{ total}}\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} \pm \Psi_{\beta\alpha}) &= \frac{1}{\sqrt{2}}(0 \pm 0) = 0 \\
\widehat{S}^2_{\text{total}}\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} + \Psi_{\beta\alpha}) &= \frac{\hbar^2}{\sqrt{2}}(\Psi_{\alpha\beta} + \Psi_{\beta\alpha} + \Psi_{\alpha\beta} + \Psi_{\beta\alpha}) \\
&= 2\hbar^2\left[\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} + \Psi_{\beta\alpha})\right] \\
\widehat{S}^2_{\text{total}}\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} - \Psi_{\beta\alpha}) &= \frac{\hbar^2}{\sqrt{2}}(\Psi_{\alpha\beta} + \Psi_{\beta\alpha} - \Psi_{\alpha\beta} - \Psi_{\beta\alpha}) \\
&= 0
\end{aligned}$$

F. Note that $\psi_{\alpha\beta}$, $\psi_{\beta\alpha}$, and $\psi_{\alpha\beta} \pm \psi_{\beta\alpha}$ are all degenerate states within the non-interacting electron picture. Comment on why your work above shows that $\psi_{\alpha\beta} \pm \psi_{\beta\alpha}$ are more realistic eigenstates of the Hamiltonian.

Solution:

We note that $\widehat{S}^2$ and $\widehat{S}_z$ correspond to the magnitude squared of the spin and its projection onto the z–axis, and therefore it would be more realistic if our wavefunctions are eigenfunctions of these operators. Since $\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} + \Psi_{\beta\alpha})$ and $\frac{1}{\sqrt{2}}(\Psi_{\alpha\beta} - \Psi_{\beta\alpha})$ are in fact eigenfunctions of our operators, they are more realistic than either $\Psi_{\alpha\beta}$ or $\Psi_{\beta\alpha}$ (which are not eigenfunctions of $\widehat{S}^2$ and $\widehat{S}_z$.

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5. Independent Particle Model.

The following concern the independent particle mode. You may find the following set of Coulomb and exchange integrals useful (energies in eV):

$\text{J}_{1s1s} = 17.0\ Z$	$\text{J}_{1s2s} = 4.8\ Z$	$\text{K}_{1s2s} = 0.9\ Z$	$\text{J}_{2s2s} = 3.5\ Z$
$\text{J}_{1s2p} = 6.6\ Z$	$\text{K}_{1s2p} = 0.5\ Z$	$\text{J}_{2s2p} = 4.4\ Z$	$\text{K}_{2s2p} = 0.8\ Z$
$\text{J}_{2p_i,2p_i} = 3.9\ Z$	$\text{J}_{2p_i,2p_k} = 3.5\ Z$	$\text{K}_{2p_i,2p_k} = 0.2\ Z\ i \neq k$	

A. Using the independent particle model discussed in class, what is the energy difference between the $1s^2px^2$ configuration and the $1s^22s^2$ configuration? How do you justify your result?

Solution:

We are asked to calculate the enregy difference between a $1s^22p_x^2$ and a $1s^22s^2$ configuration. Let's compute the energy for each using the independent particle model

$$\begin{aligned}
E[1s^22p_x^2] &= \sum_i E_i + \sum_{i,j}^{i>j} \widetilde{J}_{ij} - \widetilde{K}_{ij} \\
&= 2E_{1s} + 2E_{2p} \\
&\quad + \widetilde{J}_{1s\alpha,1s\beta} + \widetilde{J}_{1s\alpha,2p_x\alpha} + \widetilde{J}_{1s\alpha,2p_x\beta} + \widetilde{J}_{1s\beta,2p_x\alpha} + \widetilde{J}_{1s\beta,2p_x\beta} + \widetilde{J}_{2p_x\alpha,2p_x\beta} \\
&\quad - \widetilde{K}_{1s\alpha,1s\beta} - \widetilde{K}_{1s\alpha,2p_x\alpha} - \widetilde{K}_{1s\alpha,2p_x\beta} - \widetilde{K}_{1s\beta,2p_x\alpha} - \widetilde{K}_{1s\beta,2p_x\beta} - \widetilde{K}_{2p_x\alpha,2p_x\beta} \\
&= 2E_{1s} + 2E_{2p} + J_{1s,1s} + 4J_{1s,2p} + J_{2p_i,2p_i} - 2K_{1s,2p} \qquad (5.1)
\end{aligned}$$

$$E[1s^22s^2] = 2E_{1s} + 2E_{2s} + J_{1s,1s} + 4J_{1s,2s} + J_{2s,2s} - 2K_{1s,2s} \qquad (5.2)$$

$$\begin{aligned}
\Rightarrow \Delta E &= 4(J_{1s,2p} - J_{1s,2s}) + (J_{2p_i,2p_i} - J_{2s,2s}) - 2(K_{1s,2p} - K_{1s,2s}) \\
&= Z[4(6.6 - 4.8) - (3.9 - 3.5) - 2(0.5 - 0.9)] \\
&= +7.6Z\ eV \qquad (5.3)
\end{aligned}$$

B. What is the energy difference between the ground state of Lithium and the spin polarized $1s^\uparrow 2s^\uparrow 2pz^\uparrow$ state? Is this energy about the size you expected?

Solution:

$$\begin{aligned}
E[1s^22s^1] &= 2E_{1s} + E_{2s} + J_{1s1s} + 2J_{1s2s} - K_{1s2s} \\
&= -\frac{Z^2}{2}\left(\frac{2}{1^2} + \frac{1}{2^2}\right)(27.2\ eV) + Z(17.0 + 2\cdot 4.8 - 0.9) \\
&= -3^2(9/8)(27.2) + 3(25.7) = -198.3\ eV \qquad (5.4) \\
E[1s^\uparrow 2s^\uparrow 2p_x^\uparrow] &= E_{1s} + E_{2s} + E_{2p} + J_{1s2s} + J_{1s2p} + J_{2s2p} - K_{1s2s} - K_{1s2p} - K_{2s2p} \\
&= -\frac{Z^2}{2}\left(\frac{1}{1^2} + \frac{2}{2^2}\right)(27.2\ eV) + Z(4.8 + 6.6 + 4.4 - 0.9 - 0.5 - 0.8) \\
&= -3^2(3/4)(27.2) + 3(13.6) = -142.8\ eV \qquad (5.5) \\
\Rightarrow \Delta E &= -142.8 + 198.3 = 55.5\ eV \qquad (5.6)
\end{aligned}$$

Consulting the NIST Atomic Spectra Database [physics.nist.gov/cgi-bin/ASD], we find that the high-spin $1s2s2p$ state lies 57.469 eV above the ground state. Our IPM prediction is remarkably close given we've only included first order e-e repulsion corrections!

C. Use the IPM To compute the ionization potential of B (Boron): IP = E(B^+) − E(B). Compare your boron result with the ionization potential of Lithium within the IPM. Does this agree with periodic trends?

Solution:

No solution given.

D. Finally, compare the ionization potentials computed in part **C.** with the experimental results [IP(Li) = 5.4eV, IP(B) = 8.3eV] and the answer you would have gotten if you had assumed that the electrons do not interact.

Solution:

First, we calculate the ionization energy of Be:

$$\begin{aligned}
E[\text{Be} \to 1s^2 2s^2] &= 2E_{1s} + 2E_{2s} + J_{1s1s} + 4J_{1s2s} + J_{2s2s} - 2K_{1s2s} \\
&= -\frac{Z^2}{2}\left(\frac{2}{1^2} + \frac{2}{2^2}\right)(27.2\ eV) + Z(17.0 + 4 \times 4.8 + 3.5 - 2 \times 0.9) \\
&= -4^2(5/4)(27.2) + 4(37.9) = -392.4\ eV \qquad (5.7) \\
E[\text{Be}^+ \to 1s^2 2s] &= 2E_{1s} + E_{2s} + J_{1s1s} + 2J_{1s2s} - K_{1s2s} \\
&= -\frac{Z^2}{2}\left(\frac{2}{1^2} + \frac{2}{2^2}\right)(27.2\ eV) + Z(17.0 + 2 \times 4.8 - 0.9) \\
&= -4^2(9/8)(27.2) + 4(25.7) = -386.8\ eV \qquad (5.8)
\end{aligned}$$

$$\Rightarrow \text{IE} = \Delta E = -386.8 + 392.4 = 5.6\ eV \qquad (5.9)$$

Now, we do the same for Li. Note the ground state for Li is the same as Be^+ with $Z = 4 \to Z = 3$.

$$\begin{aligned}
E[\text{Li} \to 1s^2 2s] &= -3^2(9/8)(27.2) + 3(25.7) = -198.3\ eV \qquad (5.10) \\
E[\text{Li}^+ \to 1s^2] &= 2E_{1s} + J_{1s1s} \\
&= -\frac{Z^2}{2}\left(\frac{2}{1^2}\right)(27.2\ eV) + Z(17.0) = -193.8\ eV \qquad (5.11) \\
\Rightarrow \text{IE} &= \Delta E = -193.8 + 198.3 = 4.5\ eV \qquad (5.12)
\end{aligned}$$

The experimental IEs for Be and Li are 9.32 and 5.39 eV, respectively (NIST ASD). Though the IPM values are significantly off in magnitude, they reproduce the correct periodic trend: elements in the same period have increasing IEs from left to right.

In the absence of *e*-*e* interactions, the IEs would be the energies of the vacated one-electron orbitals. In each case this is a 2s orbital. The energy for Be would be $4^2/2(2^2) \times 27.2 = 54.4$ eV and for Li,

$3^2/2(2^2) \times 27.2 = 30.6$ eV. These values are extremely high! Even though the IPM predictions are not quantitatively correct, we see that they do account for the majority of the effects caused by *e*-*e* interactions.

E. Within the IPM, what is the energy difference between a closed shell $1s^2 2s^2 2p_x^2$ configuration and a high spin $1s^2 2s^\uparrow 2p_x^\uparrow 2p_y^\uparrow 2p_z^\uparrow$ configuration for carbon? Does this agree with your intuition?

Solution: Our final problem is comparing closed-shell and high-spin configurations for carbon, $Z = 6$.

$$\begin{aligned} E[1s^2 2s^2 2p_x^2] &= 2E_{1s} + 2E_{2s} + 2E_{2p} \\ &\quad + J_{1s1s} + 4J_{1s2s} + 4J_{1s2p} + J_{2s2s} + 4J_{2s2p} + J_{2p_x 2p_x} \\ &\quad - 2K_{1s2s} - 2K_{1s2p} - 2K_{2s2p} \\ &= -\frac{Z^2}{2}\left(\frac{2}{1^2} + \frac{4}{2^2}\right)(27.2\ eV) + Z(83.2) \\ &= 969.6\ eV \end{aligned} \tag{5.13}$$

$$\begin{aligned} E[1s^2 2s^\uparrow 2p_x^\uparrow 2p_y^\uparrow 2p_z^\uparrow] &= 2E_{1s} + 1E_{2s} + 3E_{2p} \\ &\quad + J_{1s1s} + 2J_{1s2s} + 6J_{1s2p} + 3J_{2s2p} + 3J_{2p_i 2p_k} \\ &\quad + K_{1s2s} - 3K_{1s2p} - 3K_{2s2p} - 3K_{2p_i 2p_k} \\ &= -\frac{Z^2}{2}\left(\frac{2}{1^2} + \frac{4}{2^2}\right)(27.2\ eV) + Z(84.5) \\ &= -961.8\ eV \end{aligned} \tag{5.14}$$

$$\Rightarrow E[\text{high spin}] - E[\text{closed shell}] = \Delta E = 7.8\ eV. \tag{5.15}$$

This agrees with our chemical intuition, where we expect closed shell configurations to be the most stable.

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