5.61 Fall 2017
Problem Set #7

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.

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

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

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

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

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

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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.

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

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

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.]

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?

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?

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.

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

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 $3d$.]

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?

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 $\psi_{\text{space}}\psi_{\text{spin}}$.

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

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

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.

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

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.

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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):

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

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?

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?

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?

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.

E. Within the IPM, what is the energy difference between a closed shell $1s^22s^22p_x^2$ configuration and a high spin $1s^22s^{\uparrow}2p_x^{\uparrow}2p_y^{\uparrow}2p_z^{\uparrow}$ configuration for carbon? Does this agree with your intuition?

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