# Mid-Term Examination

## Chemistry 3BB3

### Winter, 2005

## Part 1.  Thinking Problems.

### More on the Effective Nuclear Charge.

In class, we discussed the 2-electron atom in some detail.  In this problem, we will extend this result to the 3-electron atom.  Our approach to the problem will be as follows:  we will start by discussing the 2-electron system.  In order to decide whether the third electron goes into the 2s or 2p orbitals (which are degenerate in the Hydrogen atom), we need to examine the effective nuclear charge felt by the third electron.  Finally, we will approximate the energy of the 3-electron system.

Let us first examine the 2-electron system.  We know that the energy is given by Eq. (3.26) in the notes, namely

$$E_{2\,el.\,system}\left(\zeta\right) = -\zeta^2 + \frac{5}{8}\zeta + 2\zeta\left(\zeta - Z\right) \tag{1}$$

where $\zeta$ the effective nuclear charge.  With effective nuclear charge $\zeta$, form of the 1s, 2s, and $2p_0$ orbitals is

$$\psi_{1s}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{\pi}} \cdot e^{-\zeta r}$$

$$\psi_{2s}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{32\pi}} \cdot \left(2 - \zeta r\right) e^{-\zeta r/2} \tag{2}$$

$$\psi_{2p_0}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{32\pi}} \cdot \left(\zeta r\right) e^{-\zeta r/2} \cos\left(\theta\right)$$

Does the third electron go into the 2s orbital or the 2p orbital?  To understand this, consider the orbital energy of the third electron.  The energy of the 2s orbital is the sum of
   (a)  the kinetic energy of an electron in the 2s orbital

$$\left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} \right| \psi_{2s} \right\rangle = \frac{\zeta^2}{8} \tag{3}$$

   (b)  the electron-nuclear attraction energy of an electron in the 2s orbital

$$\left\langle \psi_{2s} \left| -\frac{Z}{r} \right| \psi_{2s} \right\rangle = -\frac{Z \cdot \zeta}{4} \tag{4}$$

   (c)  the electron-electron repulsion energy of an electron in the 2s orbital for the electrons in the 1s orbital.

This last term is, of course, difficult to compute.  However, we can imagine invoking a "mean field" approximation, and assuming that an electron in the 2s orbital does not feel the "detailed motion" of electrons in the 1s orbital, but only the "average" field due to the electrons in the 1s

orbital. That is, we neglect electron correlation between electrons in the 2s orbital and the 1s orbital. (This type of electron correlation is sometimes called "core-valence" electron correlation.)

*In class, we used the same idea to discuss the 2-electron atom, imagining that one of the 1s electrons felt the only the "average" effects of the other 1s electron. This led to the concept of the effective nuclear charge. Do you think the approximation we are making here is better than or worse than that one. That is:*

**PART A. (2 points) In general, is it more important to model electron correlation between**
   (a) two electrons in a 1s orbital.
   (b) one electron in a 1s orbital and another electron in a 2s orbital.

Within the mean-field model, then,

$$V_{ee}[\psi_{2s}] = \int \frac{2|\psi_{1s}(\boldsymbol{r}')|^2 |\psi_{2s}(\boldsymbol{r})|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' d\boldsymbol{r} \tag{5}$$

Equation (5) is simply the classical electrostatic repulsion between two charge distributions, one of which is due to 2 electrons in the 1s orbital $(2|\psi_{1s}(\boldsymbol{r}')|^2)$ and one of which is due to an electron in the 2s orbital $(|\psi_{2s}(\boldsymbol{r})|^2)$.

The orbital energy of an electron in the 2s orbital is then given by the formula

$$\varepsilon_{2s} = \left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \psi_{2s} \right\rangle + V_{ee}[\psi_{2s}]. \tag{6}$$

Similarly, the orbital energy of an electron in the 2p orbital is given by the formula

$$\varepsilon_{2p} = \left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \psi_{2p} \right\rangle + V_{ee}[\psi_{2p}] \tag{7}$$

where the key integrals are

$$\left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} \right| \psi_{2p} \right\rangle = \frac{\zeta^2}{8} \tag{8}$$

and

$$\left\langle \psi_{2p} \left| -\frac{Z}{r} \right| \psi_{2p} \right\rangle = -\frac{Z \cdot \zeta}{4}. \tag{9}$$

The energy of the 3-electron atom is then computed as

$$E_{3\,el.\,system} = E_{2\,el.\,system} + \varepsilon[\psi_{2s}] \tag{10}$$

or

$$E_{3\,el.\,system} = E_{2\,el.\,system} + \varepsilon[\psi_{2p}] \tag{11}$$

To go further, we must compare the effective nuclear charge felt by electrons in 2s and 2p orbitals. This is most easily done by defining the electrostatic potential due to the electrons in the 1s orbital:

$$\Phi(r) = \int \frac{2|\psi_{1s}(\boldsymbol{r}')|^2}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' = \frac{2}{r}\left[1 - e^{-2\zeta r}(\zeta r + 1)\right] \tag{12}$$

The 2s and 2p electrons then move in a potential that is the sum of the potential due to the nucleus and the potential from the 1s electrons. Thus, the orbital energy can be rewritten as

$$\varepsilon_{2s} = \left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} \right| \psi_{2s} \right\rangle + \int |\psi_{2s}(\boldsymbol{r})|^2 \left( \frac{-Z}{r} + \Phi(r) \right) d\boldsymbol{r}$$

$$\varepsilon_{2p} = \left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} \right| \psi_{2p} \right\rangle + \int |\psi_{2p}(\boldsymbol{r})|^2 \left( \frac{-Z}{r} + \Phi(r) \right) d\boldsymbol{r}$$

(13)

Based on this, we infer that the local effective nuclear charge for an electron in a 2s or a 2p orbital is

$$Z_{eff}(r) = Z - 2 + 2e^{-2\zeta r}(\zeta r + 1).$$

(14)

You will find the following integral to be helpful in the following parts of this problem.

$$\int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$$

(15)

**PART B. (4 points) For an electron in the 2s orbital, what is the "expected value" of the effective nuclear charge. That is, what is the "average" effective nuclear charge felt by an electron in a 2s orbital.**

**PART C.  (4 points)** For an electron in the 2p orbital, what is the "expected value" of the effective nuclear charge.  That is, what is the "average" effective nuclear charge felt by an electron in a 2p orbital.

**Part D.** (10 points) Approximate the energy of the three-electron system with an electron in the 2s orbital using the variational principle with respect to the effective nuclear charge. You may wish to compare your result to the accurate Hartree-Fock energy of the Lithium atom, $E_{HF}^{Li} = -7.433$ Hartree .

# Part 2.  Multiple Choice/Short Answer

**Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout Parts 2 and 3 of this exam.**

**1-2.  Write expressions for each of the following operators <u>in SI units</u>.**

| Quantity | Quantum-Mechanical Operator in <u>SI units</u> |
|---|---|
| nuclear kinetic energy, $\hat{T}_n$ | |
| electronic kinetic energy, $\hat{T}_e$ | |
| nuclear-electron attraction energy, $\hat{V}_{ne}$ | |
| nuclear-nuclear repulsion energy, $\hat{V}_{nn}$ | |
| electron-electron repulsion energy, $\hat{V}_{ee}$ | |

We wrote the "electronic" Schrödinger equation for the $P$-atom, $N$-electron molecule in the Born-Oppenheimer approximation as

$$\left( \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \right) \psi_e \left( \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N ; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P \right)$$
$$= U_{BO} \left( \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P \right) \psi_e \left( \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N ; \boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_P \right)$$

3.  **Using the above notation and the notation from problems 1 and 2, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.**

4.  **Let $\Psi \left( \boldsymbol{r}_1, \sigma_1 ; \boldsymbol{r}_2, \sigma_2 ; \ldots ; \boldsymbol{r}_N, \sigma_N \right)$ be antisymmetric with respect to exchange of any two electronic coordinates.  Show that the probability of two electrons with the same spin being at the same location is zero.**

5. **Which of the following statements are true.**
   (a) A Bohr is about .5 Angstroms.
   (b) An Angstrom is about .5 Bohr.
   (c) A Hartree is about 27 electron volts.
   (d) An electron volt is about 27 Hartree.
   (e) A Hartree is about 2,200 $cm^{-1}$.
   (f) An $cm^{-1}$ is about 2,200 Hartree.
   (g) A Hartree is about 2,600 kJ/mol.
   (h) A kJ/mol is about 2600 Hartree.

6. **Write the <u>radial</u> Schrödinger Equation for the one-electron atom with atomic number $Z$ and orbital angular momentum quantum number $l$ <u>in atomic units</u>.**

   In particle physics experiments, one often observes "exotic" atoms, where two particles bind to each other to form a hydrogen-like atom. In problems seven and eight, let's imagine an atom where the electron, $e^-$, was replaced by an antimuon, $\mu^+$. The antimuon has a charge of $+e$ (where e is the magnitude of the charge of the electron) and a mass that is 203 times the mass of the electron. According to the standard model of particle physics, the heaviest baryon (the proton is the lightest baryon) will have the quark configuration $(ttb)^+$, with mass about 700,000 times that of the electron. (By contrast, the mass of the proton is 1836 times that of the electron.) This "heavy baryon," which has not yet been observed experimentally, could be called the "top proton" (because it is similar to the normal proton, but with up and down quarks replaced by top and bottom quarks). The anti-top proton, $\overline{(ttb)}$ has a charge equal to that of the electron (-e), and the same mass as the "top proton." Summarizing, then, we have:

| | Hydrogen Atom | | Exotic "anti-top muon" hydrogen-like atom. | |
|---|---|---|---|---|
| particles | electron $(e^-)$ | proton $(p)$ | antimuon $(\mu^+)$ | anti-"top proton" $\overline{(ttb)}$ |
| charge | $-e$ | $+e$ | $+e$ | $-e$ |
| mass | $m_e$ | $1836\ m_e$ | $203\ m_e$ | $698,000\ m_e$ |

   For the purposes of questions seven and eight, ignore the effects of nuclear forces; we are only interested in the electrostatic interaction between the light particle (the electron or the antimuon) and the heavy particle (the proton or the anti-top proton).

7. **Using the Born-Oppenheimer Approximation, the ground-state electrostatic energy of the exotic "anti-top muon" hydrogen-like atom is:**

$$E_{\substack{\text{anti-top muon} \\ \text{exotic atom}}} = \underline{\hspace{3cm}} \quad \text{Hartree}$$

8. **The Born-Oppenheimer approximation is**
   (a) more accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom.
   (b) less accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom.

Usually the form of the wave function for a hydrogen-like atom is a rather complicated function of $r$, $\theta$, and $\phi$. However, for certain special values of the principle quantum number, $n$, and orbital angular momentum quantum number, $l$, the wave function takes a simple form. In problems 9 and 10, we will consider the lowest-energy $g$-orbital.

9. **For the one-electron atom with atomic number $Z$, the lowest-energy $g$ orbital is proportional to**

$$\psi_{\substack{\text{lowest energy} \\ \text{g orbital}}}(r,\theta,\phi) \propto$$

10. **The energy of the lowest-energy $g$ orbital is (in atomic units):**

$$E_{\substack{\text{lowest energy} \\ \text{g orbital}}} = \qquad\qquad \text{Hartree}$$

11-12. **For each of the following orbitals, write the appropriate eigenvalue. (If the orbital is not an eigenvalue of the operator in question, write "not an eigenvalue" (or something similar) to indicate this.)**

$\hat{L}^2\, \psi_{2p_x}(\boldsymbol{r}) = \qquad\qquad\qquad\qquad \psi_{2p_x}(\boldsymbol{r})$

$\hat{L}^2\, \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = \qquad\qquad\qquad \psi_{3d_{3z^2-r^2}}(\boldsymbol{r})$

$\hat{L}_z\, \psi_{2p_x}(\boldsymbol{r}) = \qquad\qquad\qquad\qquad \psi_{2p_x}(\boldsymbol{r})$

$\hat{L}_z\, \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = \qquad\qquad\qquad \psi_{3d_{3z^2-r^2}}(\boldsymbol{r})$

13-14. **The following statements pertain to the restricted-Hartree-Fock method (RHF) and the unrestricted Hartree-Fock method (UHF). Which of the following statements are true?**
   (a) The Hartree-Fock method includes the effects of electron correlation.
   (b) The RHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.
   (c) The UHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.
   (d) In an RHF wave function, $\alpha$-spin electrons and $\beta$-spin electrons occupy the same "spatial" orbitals.
   (e) In an UHF wave function, $\alpha$-spin electrons and $\beta$-spin electrons occupy the same "spatial" orbitals.
   (f) The UHF wave function is higher in energy than the RHF wave function.
   (g) The RHF wave function is higher in energy than the UHF wave function.
   (h) The RHF energy is greater than the exact energy.
   (i) The UHF energy is greater than the exact energy.

**15. Below, <u>sketch</u> the 1s, 2s, and 3s orbitals in the Hydrogen atom.**

As a very primitive model of the Helium atom, we computed the energy of the atom when we neglected the electron-electron repulsion entirely, obtaining an energy of -4 Hartree.

**16. Neglecting electron-electron repulsion, what is the energy of the Neon atom? (Write your answer in Hartree units.)**

**17. The answer in question 16 is**
(a) less than the exact ground-state energy of the Neon atom.
(b) greater than the exact ground-state energy of the Neon atom.

**18. Write an appropriate Slater determinant (include all the rows and all the columns) for a $^3S$ state with the $1s^2 2s^1 5s^1$ electron configuration. Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.**

| $M_S$ | $M_L$ | | | | | |
|---|---|---|---|---|---|---|
| | **5** | **4** | **3** | **2** | **1** | **0** |
| **3/2** | | | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_{-1}}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\alpha\|$ | $\|\psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-2}}\alpha\|$ |
| **1/2** | $\|\psi_{3d_2}\alpha\ \psi_{3d_2}\beta\ \psi_{3d_1}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_1}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_2}\beta\ \psi_{3d_0}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_0}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_0}\alpha\|$ <br> $\|\psi_{3d_2}\beta\ \psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_2}\beta\ \psi_{3d_{-1}}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_{-1}}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_2}\beta\ \psi_{3d_1}\alpha\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_2}\beta\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_0}\beta\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_0}\alpha\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\alpha\ \psi_{3d_{-2}}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\beta\ \psi_{3d_1}\alpha\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\beta\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_2}\beta\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_0}\beta\|$ | $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-2}}\beta\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_0}\beta\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\beta\ \psi_{3d_0}\alpha\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\beta\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_0}\beta\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_1}\beta\ \psi_{3d_0}\alpha\ \psi_{3d_{-1}}\alpha\|$ <br> $\|\psi_{3d_1}\alpha\ \psi_{3d_1}\beta\ \psi_{3d_{-2}}\alpha\|$ <br> $\|\psi_{3d_2}\alpha\ \psi_{3d_{-1}}\alpha\ \psi_{3d_{-1}}\beta\|$ |

19. **List all the terms associated with the ground state electron configuration of Vanadium, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. (You do not need to show the possible values of $J$ here.)**

20. **What is the term symbol for the ground state term of the Cobalt atom, which has electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$?**

21. **What are the possible values of $M_J$ in the ground state of the Cobalt atom?**

**22. We are interested in the** $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ **excited state of the Manganese atom. What are the possible terms?**

For each of the following, write the eigenvalue. (If there is no eigenvalue, write "no eigenvalue"; if there are multiple eigenvalues possible, write all the possibilities.) Here, the wave functions are denoted either by (a) a Slater determinant or (b) a term symbol. In each case, it is up to you to decipher the relevant quantum numbers.

**23.**

$$\hat{L}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{L}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{L}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

$$\hat{L}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

**24.**

$$\hat{S}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{S}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{S}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

$$\hat{S}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

**25.**

$$\hat{J}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{J}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

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$$\hat{J}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \qquad\qquad \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

# Part 3. Closed-Book Derivation

1. **Explain why $\hat{J}^2$ and $\hat{S}^2$ commute (7 points), but $\hat{J}^2$ and $\hat{S}_x$ do not (7 points).**

   *You cannot use results for commutators including $\hat{\boldsymbol{J}}$ ; that is the purpose of this problem!* Rather, you must rewrite terms containing $\hat{\boldsymbol{J}}$ in terms of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, and then use commutator identities (e.g., formulae for $\left[\hat{A},\hat{B}\hat{C}\right]$, $\left[\hat{A}\hat{B},\hat{C}\right]$, $\left[\hat{A},\hat{B}+\hat{C}\right]$, $\left[\hat{A}+\hat{B},\hat{C}\right]$) and known commutator relationships for the orbital angular momentum ($\hat{\boldsymbol{L}}=\left[\hat{L}_x,\hat{L}_y,\hat{L}_z\right]$, $\hat{L}^2 = \hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{L}}$) and the spin angular momentum ($\hat{\boldsymbol{S}}=\left[\hat{S}_x,\hat{S}_y,\hat{S}_z\right]$, $\hat{S}^2 = \hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{S}}$) or electrons to get the desired result.

   **You may find it helpful to recall that $\left[\hat{S}_x,\hat{S}_y\right]= i\hbar\hat{S}_z$, $\left[\hat{S}_y,\hat{S}_z\right]= i\hbar\hat{S}_x$, and $\left[\hat{S}_z,\hat{S}_x\right]= i\hbar\hat{S}_y$.**

Let $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)\,Y_l^m(\theta,\phi)$ denote the hydrogenic orbital $(Z=1)$ with principle quantum number $n$, orbital angular momentum quantum number $l$, and magnetic quantum number $m$.

## 2a. (10 points) Show that

$$\left\langle \psi_{n,l,m}\left|\frac{1}{r}\right|\psi_{n,l,m}\right\rangle = \frac{1}{n^2}\,.$$

Kramer's relation is a very useful formula for computing integrals of the form $\left\langle \psi_{n,l,m} \left| r^k \right| \psi_{n,l,m} \right\rangle$ for one-electron atoms. When applied to the Hydrogen atom, Kramer's formula is:

$$\tfrac{k+1}{n^2}\left\langle \psi_{n,l,m} \left| r^k \right| \psi_{n,l,m} \right\rangle = (2k+1)\left\langle \psi_{n,l,m} \left| r^{k-1} \right| \psi_{n,l,m} \right\rangle + k\left[\tfrac{1}{4}\left(k^2 - 1\right) - l\left(l+1\right)\right]\left\langle \psi_{n,l,m} \left| r^{k-2} \right| \psi_{n,l,m} \right\rangle$$

**2b. (6 points) What is the average (mean) distance from the nucleus of an electron in an _s_ orbital of the hydrogen atom? Compare this to the result for _p_ orbitals.**

# KEY Mid-Term Exam KEY

## Chemistry 3BB3

### Winter, 2005

## Part 1.  Thinking Problems.

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Let us first examine the 2-electron system.  We know that the energy is given by Eq. (3.26) in the notes, namely

$$E_{2\,el.\,system}\left(\zeta\right) = -\zeta^2 + \frac{5}{8}\zeta + 2\zeta\left(\zeta - Z\right) \tag{1}$$

where $\zeta$ the effective nuclear charge.  With effective nuclear charge $\zeta$, form of the 1s, 2s, and $2p_0$ orbitals is

$$\psi_{1s}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{\pi}} \cdot e^{-\zeta r}$$

$$\psi_{2s}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{32\pi}} \cdot \left(2 - \zeta r\right) e^{-\zeta r/2} \tag{2}$$

$$\psi_{2p_0}\left(\boldsymbol{r}\right) = \sqrt{\frac{\zeta^3}{32\pi}} \cdot \left(\zeta r\right) e^{-\zeta r/2} \cos\left(\theta\right)$$

Does the third electron go into the 2s orbital or the 2p orbital?  To understand this, consider the orbital energy of the third electron.  The energy of the 2s orbital is the sum of
   (a)  the kinetic energy of an electron in the 2s orbital

$$\left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} \right| \psi_{2s} \right\rangle = \frac{\zeta^2}{8} \tag{3}$$

   (b)  the electron-nuclear attraction energy of an electron in the 2s orbital

$$\left\langle \psi_{2s} \left| -\frac{Z}{r} \right| \psi_{2s} \right\rangle = -\frac{Z \cdot \zeta}{4} \tag{4}$$

   (c)  the electron-electron repulsion energy of an electron in the 2s orbital for the electrons in the 1s orbital.

This last term is, of course, difficult to compute.  However, we can imagine invoking a "mean field" approximation, and assuming that an electron in the 2s orbital does not feel the "detailed motion" of electrons in the 1s orbital, but only the "average" field due to the electrons in the 1s

orbital. That is, we neglect electron correlation between electrons in the 2s orbital and the 1s orbital. (This type of electron correlation is sometimes called "core-valence" electron correlation.)

***In class, we used the same idea to discuss the 2-electron atom, imagining that one of the 1s electrons felt the only the "average" effects of the other 1s electron. This led to the concept of the effective nuclear charge. Do you think the approximation we are making here is better than or worse than that one. That is:***

**PART A. (2 points) In general, is it more important to model electron correlation between**
   **(a) two electrons in a 1s orbital.**
   (b) one electron in a 1s orbital and another electron in a 2s orbital.

Within the mean-field model, then,

$$V_{ee}[\psi_{2s}] = \int \frac{2|\psi_{1s}(\mathbf{r}')|^2 |\psi_{2s}(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \tag{5}$$

Equation (5) is simply the classical electrostatic repulsion between two charge distributions, one of which is due to 2 electrons in the 1s orbital $(2|\psi_{1s}(\mathbf{r}')|^2)$ and one of which is due to an electron in the 2s orbital $(|\psi_{2s}(\mathbf{r})|^2)$.

The orbital energy of an electron in the 2s orbital is then given by the formula

$$\varepsilon_{2s} = \left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \psi_{2s} \right\rangle + V_{ee}[\psi_{2s}]. \tag{6}$$

Similarly, the orbital energy of an electron in the 2p orbital is given by the formula

$$\varepsilon_{2p} = \left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \psi_{2p} \right\rangle + V_{ee}[\psi_{2p}] \tag{7}$$

where the key integrals are

$$\left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} \right| \psi_{2p} \right\rangle = \frac{\zeta^2}{8} \tag{8}$$

and

$$\left\langle \psi_{2p} \left| -\frac{Z}{r} \right| \psi_{2p} \right\rangle = -\frac{Z \cdot \zeta}{4}. \tag{9}$$

The energy of the 3-electron atom is then computed as

$$E_{3\,el.\,system} = E_{2\,el.\,system} + \varepsilon[\psi_{2s}] \tag{10}$$

or

$$E_{3\,el.\,system} = E_{2\,el.\,system} + \varepsilon[\psi_{2p}] \tag{11}$$

To go further, we must compare the effective nuclear charge felt by electrons in 2s and 2p orbitals. This is most easily done by defining the electrostatic potential due to the electrons in the 1s orbital:

$$\Phi(r) = \int \frac{2|\psi_{1s}(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{2}{r}[1 - e^{-2\zeta r}(\zeta r + 1)] \tag{12}$$

The 2s and 2p electrons then move in a potential that is the sum of the potential due to the nucleus and the potential from the 1s electrons. Thus, the orbital energy can be rewritten as

$$\varepsilon_{2s} = \left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} \right| \psi_{2s} \right\rangle + \int |\psi_{2s}(\boldsymbol{r})|^2 \left[ \frac{-Z}{r} + \Phi(r) \right] d\boldsymbol{r}$$

$$\varepsilon_{2p} = \left\langle \psi_{2p} \left| -\frac{\nabla^2}{2} \right| \psi_{2p} \right\rangle + \int |\psi_{2p}(\boldsymbol{r})|^2 \left[ \frac{-Z}{r} + \Phi(r) \right] d\boldsymbol{r} \tag{13}$$

Based on this, we infer that the local effective nuclear charge for an electron in a 2s or a 2p orbital is

$$Z_{eff}(r) = Z - 2 + 2e^{-2\zeta r}(\zeta r + 1). \tag{14}$$

You will find the following integral to be helpful in the following parts of this problem.

$$\int_0^\infty r^n e^{-ar} dr = \frac{n!}{a^{n+1}} \tag{15}$$

**PART B. (4 points) For an electron in the 2s orbital, what is the "expected value" of the effective nuclear charge. That is, what is the "average" effective nuclear charge felt by an electron in a 2s orbital.**

The "average" effective nuclear charge will be

$$\begin{aligned}
\left\langle \psi_{2s} \left| Z_{eff}(r) \right| \psi_{2s} \right\rangle &= \left\langle \psi_{2s} \left| Z - 2 + 2e^{-2\zeta r}(\zeta r + 1) \right| \psi_{2s} \right\rangle \\
&= \left\langle \psi_{2s} |Z - 2| \psi_{2s} \right\rangle + \left\langle \psi_{2s} |2e^{-2\zeta r}\zeta r| \psi_{2s} \right\rangle + \left\langle \psi_{2s} |2e^{-2\zeta r}| \psi_{2s} \right\rangle \\
&= (Z - 2)\left\langle \psi_{2s} |\psi_{2s} \right\rangle + 2\left\langle \psi_{2s} |\zeta r e^{-2\zeta r}| \psi_{2s} \right\rangle + 2\left\langle \psi_{2s} |e^{-2\zeta r}| \psi_{2s} \right\rangle \\
&= Z - 2 + 2\zeta \int |\psi_{2s}(\boldsymbol{r})|^2 r e^{-2\zeta r} d\boldsymbol{r} + 2\int |\psi_{2s}(\boldsymbol{r})|^2 e^{-2\zeta r} d\boldsymbol{r}
\end{aligned} \tag{16}$$

Next, we compute the key integrals, which are

$$\begin{aligned}
\int |\psi_{2s}(\boldsymbol{r})|^2 r e^{-2\zeta r} d\boldsymbol{r} &= \int \frac{\zeta^3}{32\pi} \cdot (2 - \zeta r)^2 e^{-\zeta r} \left( r e^{-2\zeta r} \right) d\boldsymbol{r} \\
&= \frac{\zeta^3}{32\pi} \int_0^\infty \left( 4 - 4\zeta r + \zeta^2 r^2 \right) r e^{-3\zeta r} \left( 4\pi r^2 \right) dr \\
&= \frac{\zeta^3}{8} \int_0^\infty \left( 4r^3 - 4\zeta r^4 + \zeta^2 r^5 \right) e^{-3\zeta r} dr \\
&= \frac{\zeta^3}{8} \left( \frac{\zeta^2 5!}{(3\zeta)^6} - \frac{4\zeta \cdot 4!}{(3\zeta)^5} + \frac{4 \cdot 3!}{(3\zeta)^4} \right) \\
&= \left( \frac{\zeta^5 (5 \cdot 3)}{3^6 \zeta^6} - \frac{12\zeta^4}{3^5 \zeta^5} + \frac{3\zeta^3}{3^4 \zeta^4} \right) \\
&= \frac{1}{\zeta} \left( \frac{5}{3^5} - \frac{4}{3^4} + \frac{1}{3^3} \right) \\
&= \frac{1}{243\zeta} (5 - 12 + 9) \\
&= \frac{2}{243\zeta} \\
&= \frac{.00823}{\zeta}
\end{aligned} \tag{17}$$

and

$$\int |\psi_{2s}(\boldsymbol{r})|^2 \, e^{-2\zeta r} d\boldsymbol{r} = \int \frac{\zeta^3}{32\pi} \cdot (2 - \zeta r)^2 \, e^{-\zeta r} \left( e^{-2\zeta r} \right) d\boldsymbol{r}$$

$$= \frac{\zeta^3}{32\pi} \int\limits_{0}^{\infty} \left( 4 - 4\zeta r + \zeta^2 r^2 \right) e^{-3\zeta r} \left( 4\pi r^2 \right) dr$$

$$= \frac{\zeta^3}{8} \int\limits_{0}^{\infty} \left( 4r^2 - 4\zeta r^3 + \zeta^2 r^4 \right) e^{-3\zeta r} dr$$

$$= \left( \frac{\zeta^3}{8} \right) \left[ \frac{4 \cdot 2!}{(3\zeta)^3} - \frac{4\zeta \cdot 3!}{(3\zeta)^4} + \frac{\zeta^2 \cdot 4!}{(3\zeta)^5} \right] \tag{18}$$

$$= \left( \frac{1}{3^3} - \frac{1}{3^3} + \frac{1}{3^4} \right)$$

$$= \left( \frac{1}{81} \right)$$

$$= 0.0123$$

and so

$$\left\langle \psi_{2s} \left| Z_{\mathit{eff}}(r) \right| \psi_{2s} \right\rangle = Z - 2 + 2\zeta \left( \frac{2}{243\zeta} \right) + 2 \left( \frac{1}{81} \right)$$

$$= Z - 2 + \frac{4}{243} + \frac{2}{81}$$

$$= Z - 2 + \frac{4}{243} + \frac{6}{243} \tag{19}$$

$$= Z - 2 + \frac{10}{243}$$

$$= Z - \frac{476}{243}$$

$$= Z - 1.959$$

**PART C. (4 points) For an electron in the 2p orbital, what is the "expected value" of the effective nuclear charge. That is, what is the "average" effective nuclear charge felt by an electron in a 2p orbital.**

$$\left\langle \psi_{2p} \left| Z_{eff}\left(r\right) \right| \psi_{2p} \right\rangle = \left\langle \psi_{2p} \left| Z - 2 + 2e^{-2\zeta r}\left(\zeta r + 1\right) \right| \psi_{2p} \right\rangle$$

$$= Z - 2 + 2\zeta \int \left| \psi_{2p}\left(\boldsymbol{r}\right)\right|^2 re^{-2\zeta r}d\boldsymbol{r} + 2\int \left| \psi_{2p}\left(\boldsymbol{r}\right)\right|^2 e^{-2\zeta r}d\boldsymbol{r} \tag{20}$$

When evaluating the key integrals, we will observe that the integral

$$\int_0^\pi \cos^2\theta \sin\theta d\theta \tag{21}$$

recurs several times. To evaluate this integral, define a change of variables, with

$$
\begin{aligned}
u &= \cos\left(\theta\right) \\
du &= -\sin\left(\theta\right)d\theta \\
\theta &= 0 \rightarrow u = 1 \\
\theta &= \pi \rightarrow u = -1
\end{aligned} \tag{22}
$$

so that

$$\int_0^\pi \cos^2\theta \sin\theta d\theta = \int_1^{-1} u^2\left(-du\right) = \int_{-1}^1 u^2 du = \left[\frac{u^3}{3}\right]_{-1}^1 = \left(\frac{1}{3} - \frac{-1}{3}\right) = \frac{2}{3} \tag{23}$$

Now, returning to Eq. (20), we evaluate the key integrals as:

$$
\begin{aligned}
\int \left|\psi_{2p}\left(\boldsymbol{r}\right)\right|^2 re^{-2\zeta r}d\boldsymbol{r} &= \int \cdot \left(\zeta r\right)^2 e^{-\zeta r}\cos^2\left(\theta\right)re^{-2\zeta r}d\boldsymbol{r} \\
&= \frac{\zeta^5}{32\pi}\int_0^\infty\int_0^\pi\int_0^{2\pi}\left(r^3 e^{-3\zeta r}\cos^2\left(\theta\right)\right)r^2\sin\theta d\phi d\theta dr \\
&= \frac{\zeta^5\left(2\pi\right)}{32\pi}\int_0^\infty\int_0^\pi\left(r^5 e^{-3\zeta r}\right)\cos^2\left(\theta\right)\sin\theta d\theta dr \\
&= \frac{\zeta^5\left(2\pi\right)}{32\pi}\int_0^\infty r^5 e^{-3\zeta r}dr\int_0^\pi\cos^2\left(\theta\right)\sin\theta d\theta \\
&= \frac{\zeta^5\left(2\pi\right)}{32\pi}\left(\frac{5!}{\left(3\zeta\right)^6}\right)\left(\frac{2}{3}\right) \\
&= \frac{1}{\zeta}\left(\frac{5}{3^6}\right) \\
&= .006859\left(\frac{1}{\zeta}\right)
\end{aligned} \tag{24}
$$

and

$$\int \left| \psi_{2p}\left(\boldsymbol{r}\right)\right|^2 re^{-2\zeta r}d\boldsymbol{r} = \int \cdot\left(\zeta r\right)^2 e^{-\zeta r}\cos^2\left(\theta\right)e^{-2\zeta r}d\boldsymbol{r}$$

$$= \frac{\zeta^5}{32\pi}\int\limits_0^\infty\int\limits_0^\pi\int\limits_0^{2\pi}\left(r^2e^{-3\zeta r}\cos^2\left(\theta\right)\right)r^2\sin\theta d\phi d\theta dr$$

$$= \frac{\zeta^5\left(2\pi\right)}{32\pi}\int\limits_0^\infty\int\limits_0^\pi\left(r^4e^{-3\zeta r}\right)\cos^2\left(\theta\right)\sin\theta d\theta dr$$

$$= \frac{\zeta^5\left(2\pi\right)}{32\pi}\int\limits_0^\infty r^4e^{-3\zeta r}dr\int\limits_0^\pi\cos^2\left(\theta\right)\sin\theta d\theta \qquad (25)$$

$$= \frac{\zeta^5\left(2\pi\right)}{32\pi}\left(\frac{4!}{\left(3\zeta\right)^5}\right)\left(\frac{2}{3}\right)$$

$$= \left(\frac{1}{3^5}\right)$$

$$= .004115$$

and so

$$\left\langle \psi_{2p}\left|Z_{eff}\left(r\right)\right|\psi_{2p}\right\rangle = \left\langle \psi_{2p}\left|Z-2+2e^{-2\zeta r}\left(\zeta r+1\right)\right|\psi_{2p}\right\rangle$$

$$= Z-2+2\left(\frac{5}{3^6}\right)+2\left(\frac{1}{3^5}\right)$$

$$= Z-2+\frac{16}{3^6} \qquad (26)$$

$$= Z-\frac{1442}{729}$$

$$= Z-1.978$$

**Part D.**　　　**(10 points)　Approximate the energy of the three-electron system.　How could you improve your result?　(You may wish to compare your result to the accurate Hartree-Fock energy of the Lithium atom,** $E_{HF}^{Li} = -7.433$ Hartree **.)**

The energy of the $s$ orbital is given by Eq. (6), that is,

$$\varepsilon_{2s} = \left\langle \psi_{2s} \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \psi_{2s} \right\rangle + V_{ee}[\psi_{2s}] \tag{27}$$

Using Eqs. (3) and (4), we have that

$$\varepsilon_{2s} = \frac{\zeta^2}{8} - \frac{\zeta Z}{4} + V_{ee}[\psi_{2s}] \tag{28}$$

where

$$V_{ee}\left[\psi_{2s}\right] = \int \left|\psi_{2s}\left(\boldsymbol{r}\right)\right|^2 \Phi\left(r\right) d\boldsymbol{r}$$

$$= \int_0^\infty \left(\frac{\zeta^3}{32\pi}\right) \cdot \left(2 - \zeta r\right)^2 e^{-\zeta r} \left[\frac{2}{r}\left[1 - e^{-2\zeta r}\left(\zeta r + 1\right)\right]\right] 4\pi r^2 dr$$

$$= \left(\frac{\zeta^3}{4}\right) \int_0^\infty \left(4 - 4\zeta r + \zeta^2 r^2\right) e^{-\zeta r} \left(\left[1 - e^{-2\zeta r}\left(\zeta r + 1\right)\right]\right) r \, dr$$

$$= \left(\frac{\zeta^3}{4}\right)\begin{vmatrix} \int_0^\infty \left(4r - 4\zeta r^2 + \zeta^2 r^3\right) e^{-\zeta r} dr \\[2mm] -\zeta \int_0^\infty \left(4r - 4\zeta r^2 + \zeta^2 r^3\right) r e^{-3\zeta r} dr \\[2mm] -\int_0^\infty \left(4r - 4\zeta r^2 + \zeta^2 r^3\right) e^{-3\zeta r} dr \end{vmatrix}$$

$$= \left(\frac{\zeta^3}{4}\right)\begin{vmatrix} \dfrac{4\left(1!\right)}{\zeta^2} - \dfrac{4\zeta\left(2!\right)}{\zeta^3} + \dfrac{\zeta^2\left(3!\right)}{\zeta^4} \\[3mm] -\zeta\left(\dfrac{4\left(2!\right)}{\left(3\zeta\right)^3} - \dfrac{4\zeta\left(3!\right)}{\left(3\zeta\right)^4} + \dfrac{\zeta^2\left(4!\right)}{\left(3\zeta\right)^5}\right) dr \\[3mm] -\dfrac{4\left(1!\right)}{\left(3\zeta\right)^2} + \dfrac{4\zeta\left(2!\right)}{\left(3\zeta\right)^3} - \dfrac{\zeta^2\left(3!\right)}{\left(3\zeta\right)^4} \end{vmatrix}$$

$$= \left(\zeta\right)\left(\frac{1}{4}\right)\begin{vmatrix} 4 - 8 + 6 \\[2mm] -\dfrac{8}{3^3} + \dfrac{8}{3^3} - \dfrac{8}{3^4} \\[2mm] -\dfrac{4}{3^2} + \dfrac{8}{3^3} - \dfrac{6}{3^4} \end{vmatrix}$$

$$= \frac{\zeta}{4}\left(2 - \frac{14}{81} + \frac{8}{27} - \frac{4}{9}\right)$$

$$= \frac{\zeta}{4}\left(2 - \frac{14}{81} - \frac{4}{27}\right)$$

$$= \frac{\zeta}{4}\left(2 - \frac{26}{81}\right)$$

$$= \frac{\zeta}{4}\left(\frac{136}{81}\right) \tag{29}$$

$$= \frac{34\zeta}{81}$$

The total energy is given by Eq. (10) as

$$E_{3 \text{ el. system}} = E_{2 \text{ el. system}} + \varepsilon\left[\psi_{2s}\right]$$

$$= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta\left(\zeta - Z\right) + \frac{\zeta^2}{8} - \frac{\zeta Z}{4} + V_{ee}\left[\psi_{2s}\right]$$

$$= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta^2 - 2\zeta Z + \frac{\zeta^2}{8} - \frac{\zeta Z}{4} + \frac{34\zeta}{81} \tag{30}$$

$$= \frac{9}{8}\zeta^2 + \left(\frac{5}{8} + \frac{34}{81} - \frac{9Z}{4}\right)\zeta$$

$$= \frac{9}{8}\zeta^2 + \left(\frac{677}{648} - \frac{9Z}{4}\right)\zeta$$

Differentiating with respect to $\zeta$, we obtain

$$0 = \frac{\partial E_{3 \text{ el. system}}}{\partial \zeta} = \frac{9}{4}\zeta + \left(\frac{677}{648} - \frac{9Z}{4}\right)$$

$$\zeta = Z - \frac{677}{648}\left(\frac{4}{9}\right) \tag{31}$$

$$\zeta = Z - \frac{677}{1458}$$

$$\zeta = Z - .464$$

The energy of the 3-electron system is obtained by inserting this result back into Eq. (30) for the energy. Thus,

$$E_{3 \text{ el. system}} = \frac{9}{8}\zeta^2 + \left(\frac{677}{648} - \frac{9Z}{4}\right)\zeta \qquad\qquad \left(\zeta = Z - \frac{677}{1458}\right)$$

$$= \frac{9}{8}\left(Z - \frac{677}{1458}\right)^2 + \left(\frac{677}{648} - \frac{9Z}{4}\right)\left(Z - \frac{677}{1458}\right)$$

$$= \frac{9}{8}\left(Z^2 - \frac{677}{729}Z + \frac{677^2}{1458^2}\right) - \frac{9}{4}Z^2 + Z\left(\frac{9 \cdot 677}{4 \cdot 1458} + \frac{677}{648}\right) - \left(\frac{677^2}{648 \cdot 1458}\right)$$

$$= -\frac{9}{8}Z^2 + Z\left(-\frac{677}{648} + \frac{9 \cdot 677}{4 \cdot 1458} + \frac{677}{648}\right) + \frac{677^2}{1458}\left(\frac{9}{8 \cdot 1458} - \frac{1}{648}\right)$$

$$= -\frac{9}{8}Z^2 + Z\left(\frac{677}{648}\right) + \frac{677^2}{1458}\left(\frac{1}{2 \cdot 648} - \frac{1}{648}\right) \tag{32}$$

$$= -\frac{9}{8}Z^2 + Z\left(\frac{677}{648}\right) - \frac{677^2}{1458 \cdot 1296}$$

$$= -\frac{9}{8}Z^2 + \left(\frac{677}{648}\right)Z + -\frac{677^2}{1458 \cdot 1296}$$

$$= -\frac{9}{8}Z^2 + \left(\frac{677}{648}\right)Z - \frac{458329}{1889568}$$

$$= -1.125 \cdot Z^2 + 1.045 \cdot Z - .242$$

For Lithium ($Z = 3$) this gives an effective nuclear charge of $\zeta = 2.536$

$$E_{3 \text{ el. system}}^{Li} \approx -7.233 \;\; \text{Hartree} \tag{33}$$

This energy is quite high, mostly because we are forcing all three orbitals to have the same nuclear charge. As a result, the $2s$ orbital is assigned far too

high an effective nuclear charge, while the effective nuclear charge assigned to the $1s$ orbital is much too low. It should be noted that while I took great care to keep track of my fractions, it would be fine to replace fractions with their decimal approximations throughout (this would dramatically simplify some of the key formulae).

Also, there is no special need to reduce the expressions to their simplest form, though this is convenient (especially for the intermediate steps).

# Part 2. Multiple Choice/Short Answer

**Except when noted otherwise, you should use the Born-Oppenheimer approximation and atomic units throughout Parts 2 and 3 of this exam.**

**1-2. Write expressions for each of the following operators <u>in SI units</u>.**

| Quantity | Quantum-Mechanical Operator in <u>SI units</u> |
|---|---|
| nuclear kinetic energy, $\hat{T}_n$ | $\displaystyle\sum_{\alpha=1}^{P} -\frac{\hbar^2}{2m_\alpha}\nabla_\alpha^2$ |
| electronic kinetic energy, $\hat{T}_e$ | $\displaystyle\sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2$ |
| nuclear-electron attraction energy, $\hat{V}_{ne}$ | $\displaystyle\sum_{\alpha=1}^{P}\sum_{i=1}^{N}\frac{-Z_\alpha e^2}{4\pi\varepsilon_0\left\|r_i-R_\alpha\right\|}$ |
| nuclear-nuclear repulsion energy, $\hat{V}_{nn}$ | $\displaystyle\sum_{\alpha=1}^{P-1}\sum_{\beta=\alpha+1}^{P}\frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0\left\|R_\alpha-R_\beta\right\|}$ |
| electron-electron repulsion energy, $\hat{V}_{ee}$ | $\displaystyle\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{4\pi\varepsilon_0\left\|r_i-r_j\right\|}$ |

We wrote the "electronic" Schrödinger equation for the $P$-atom, $N$-electron molecule in the Born-Oppenheimer approximation as

$$\left(\hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}\right)\psi_e\left(r_1,r_2,\ldots,r_N;R_1,R_2,\ldots,R_P\right)$$

$$= U_{BO}\left(R_1,R_2,\ldots,R_P\right)\psi_e\left(r_1,r_2,\ldots,r_N;R_1,R_2,\ldots,R_P\right)$$

**3. Using the above notation and the notation from problems 1 and 2, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.**

$$\left(\hat{T}_n + U_{BO}\left(R_1,R_2,\ldots,R_P\right)\right)\chi_n\left(R_1,R_2,\ldots,R_P\right) = E_{BO}\ \chi_n\left(R_1,R_2,\ldots,R_P\right) \tag{34}$$

4. Let $\Psi\left(r_1,\sigma_1;r_2,\sigma_2;\ldots;r_N,\sigma_N\right)$ be **antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.**

The wave function is antisymmetric with respect to simultaneous exchange of space and spin coordinates, so

$$\Psi\left(r_1,\sigma_1;r_2,\sigma_2;\ldots;r_N,\sigma_N\right) = -\Psi\left(r_2,\sigma_2;r_1,\sigma_1;\ldots;r_N,\sigma_N\right)$$

If $r_1 = r_2$ and $\sigma_1 = \sigma_2$, then

$$\Psi\left(r_1,\sigma_1;r_1,\sigma_1;\ldots;r_N,\sigma_N\right) = -\Psi\left(r_1,\sigma_1;r_1,\sigma_1;\ldots;r_N,\sigma_N\right)$$
$$2\Psi\left(r_1,\sigma_1;r_1,\sigma_1;\ldots;r_N,\sigma_N\right) = 0$$
$$\Psi\left(r_1,\sigma_1;r_1,\sigma_1;\ldots;r_N,\sigma_N\right) = 0$$

Then

$$\left|\Psi\left(r_1,\sigma_1;r_1,\sigma_1;\ldots;r_N,\sigma_N\right)\right|^2 = 0$$

5. **Which of the following statements are true.**
   **(a) A Bohr is about .5 Angstroms.**
   (b) An Angstrom is about .5 Bohr.
   **(c) A Hartree is about 27 electron volts.**
   (d) An electron volt is about 27 Hartree.

   (e) A Hartree is about 2,200 $\text{cm}^{-1}$.
   (f) An $\text{cm}^{-1}$ is about 2,200 Hartree.
   **(g) A Hartree is about 2,600 kJ/mol.**
   (h) A kJ/mol is about 2600 Hartree.

6. **Write the** <u>radial</u> **Schrödinger Equation for the one-electron atom with atomic number** $Z$ **and orbital angular momentum quantum number** $l$ <u>**in atomic units**</u>**.**

$$\left(-\frac{1}{2r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}\right)R_{n,l}(r) = E\,R_{n,l}(r)$$

In particle physics experiments, one often observes "exotic" atoms, where two particles bind to each other to form a hydrogen-like atom. In problems seven and eight, let's imagine an atom where the electron, $e^-$, was replaced by an antimuon, $\mu^+$. The antimuon has a charge of $+e$ (where e is the magnitude of the charge of the electron) and a mass that is 203 times the mass of the electron. According to the standard model of particle physics, the heaviest baryon (the proton is the lightest baryon) will have the quark configuration $(ttb)^+$, with mass about 700,000 times that of the electron. (By contrast, the mass of the proton is 1836 times that of the electron.) This "heavy baryon," which has not yet been observed experimentally, could be called the "top proton" (because it is similar to the normal proton, but with up and down quarks replaced by top and bottom quarks). The anti-top proton, $\overline{(ttb)}$ has a charge equal to that of the electron (-e), and the same mass as the "top proton." Summarizing, then, we have:

| | Hydrogen Atom | | Exotic "anti-top muon" hydrogen-like atom. | |
|---|---|---|---|---|
| particles | electron ($e^-$) | proton ($p$) | antimuon ($\mu^+$) | anti-"top proton" $\overline{(ttb)}$ |
| charge | $-e$ | $+e$ | $+e$ | $-e$ |
| mass | $m_e$ | $1836\ m_e$ | $203\ m_e$ | $698,000\ m_e$ |

For the purposes of questions seven and eight, ignore the effects of nuclear forces; we are only interested in the electrostatic interaction between the light particle (the electron or the antimuon) and the heavy particle (the proton or the anti-top proton).

7. **Using the Born-Oppenheimer Approximation, the ground-state electrostatic energy of the exotic "anti-top muon" hydrogen-like atom is:**

$$E_{\substack{\text{anti-top muon} \\ \text{exotic atom}}} = \underline{\phantom{\dfrac{-203}{2}}} \quad \text{Hartree}$$

$$\dfrac{-203}{2}$$

8. **The Born-Oppenheimer approximation is**
   (a) more accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom.
   **(b) less accurate for the hydrogen atom than for the exotic "anti-top muon" hydrogen-like atom.** *[NOTE: This is true because the muon is "slow" compared to the anti-top proton. If it was not true that $\frac{203 m_e}{698,000 m_e} < \frac{1}{1836 m_e}$ then this __would not__ be true, and the answer would be (a).]*

Usually the form of the wave function for a hydrogen-like atom is a rather complicated function of $r$, $\theta$, and $\phi$. However, for certain special values of the principle quantum number, $n$, and orbital angular momentum quantum number, $l$, the wave function takes a simple form. In problems 9 and 10, we will consider the lowest-energy $g$-orbital.

9. **For the one-electron atom with atomic number $Z$, the lowest-energy $g$ orbital is proportional to**

$$\psi_{\substack{\text{lowest energy} \\ \text{g orbital}}} (r,\theta,\phi) \propto r^4 e^{-\left(\frac{Z}{5}\right)r} Y_4^m (\theta,\phi) \qquad (m = -4,-3,-2,\ldots 4)$$

10. **The energy of the lowest-energy _g_ orbital is (in atomic units):**

$$E_{\substack{\text{lowest energy} \\ \text{g orbital}}} = -\frac{Z^2}{2\left(5^2\right)} \qquad \text{Hartree}$$

$$= -\frac{Z^2}{50} \qquad \text{Hartree}$$

11-12. **For each of the following orbitals, write the appropriate eigenvalue. (If the orbital is not an eigenvalue of the operator in question, write "not an eigenvalue" (or something similar) to indicate this.)**

$\hat{L}^2 \, \psi_{2p_x}(\boldsymbol{r}) = 2 \, \psi_{2p_x}(\boldsymbol{r}) \quad \text{(in atomic units with } \hbar = m_e = 1\text{)}$

$\hat{L}^2 \, \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 6 \, \psi_{3d_{3z^2-r^2}}(\boldsymbol{r})$
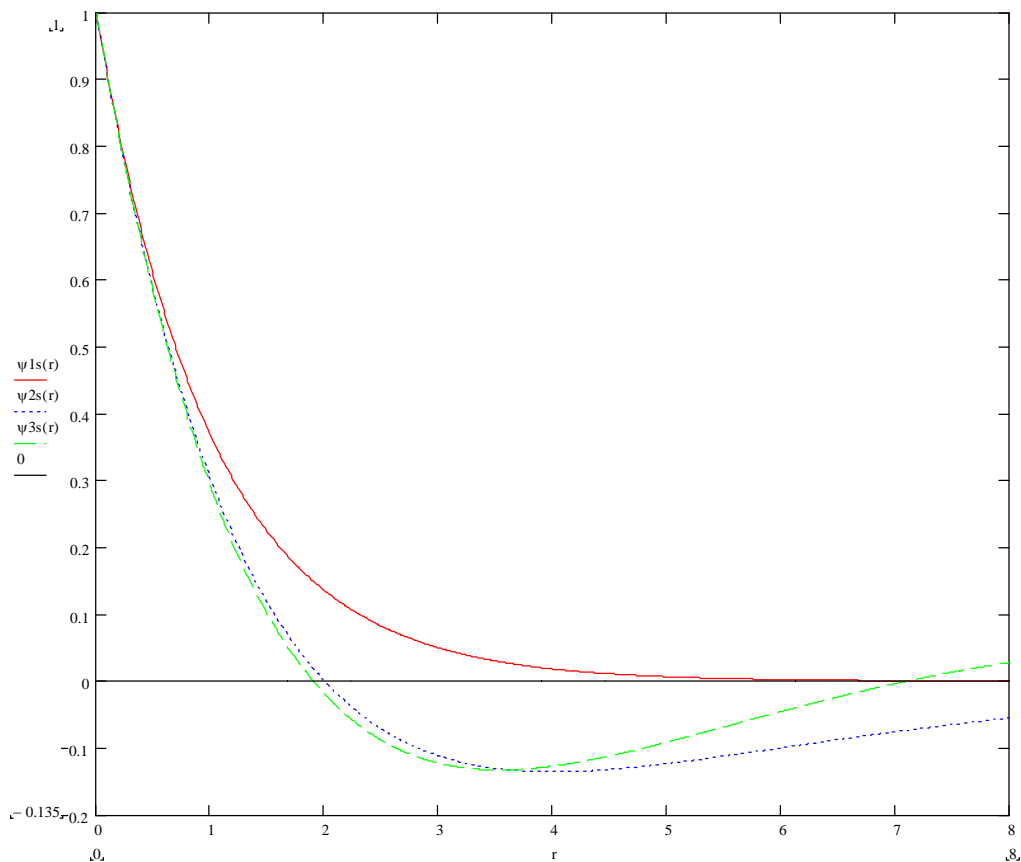
$\hat{L}_z \, \psi_{2p_x}(\boldsymbol{r}) = \left[\text{not an eigenfunction of } \hat{L}_z\right] \, \psi_{2p_x}(\boldsymbol{r})$

$\hat{L}_z \, \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 0 \cdot \psi_{3d_{3z^2-r^2}}(\boldsymbol{r}) = 0$

13-14. **The following statements pertain to the restricted-Hartree-Fock method (RHF) and the unrestricted Hartree-Fock method (UHF). Which of the following statements are true?**

(a) The Hartree-Fock method includes the effects of electron correlation.

**(b) The RHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.**

(c) The UHF wave function is usually chosen to be an eigenfunction of $\hat{S}^2$ and $\hat{L}^2$.

**(d) In an RHF wave function, $\alpha$-spin electrons and $\beta$-spin electrons occupy the same "spatial" orbitals.**

(e) In an UHF wave function, $\alpha$-spin electrons and $\beta$-spin electrons occupy the same "spatial" orbitals.

(f) The UHF wave function is higher in energy than the RHF wave function.

**(g) The RHF wave function is higher in energy than the UHF wave function.**

**(h) The RHF energy is greater than the exact energy.**

**(i) The UHF energy is greater than the exact energy.**

**15. Below, <u>sketch</u> the 1s, 2s, and 3s orbitals in the Hydrogen atom.**



As a very primitive model of the Helium atom, we computed the energy of the atom when we neglected the electron-electron repulsion entirely, obtaining an energy of -4 Hartree.

**16. Neglecting electron-electron repulsion, what is the energy of the Neon atom? (Write your answer in Hartree units.)**

In this case, the energy would be the sum of the orbital energies in the one-electron atom. So

$$
\begin{aligned}
E_{\substack{\text{no e-e} \\ \text{repulsion}}} &= (2 \text{ electrons})(1s \text{ orbital energy}) + (2 \text{ electrons})(2s \text{ orbital energy}) \\
&\quad + (6 \text{ electrons})(2p \text{ orbital energy}) \\
&= (2)\left(-\frac{(10)^2}{2}\right) + 2\left(\frac{-(10)^2}{2(2^2)}\right) + 6\left(\frac{-(10)^2}{2(2^2)}\right) \\
&= (10)^2\left(-1 - \tfrac{1}{4} - \tfrac{3}{4}\right) \\
&= -200 \text{ Hartree}
\end{aligned}
\tag{35}
$$

The actual energy is about -128 Hartree.

**17. The answer in question 16 is**
  **(a) less than the exact ground-state energy of the Neon atom.**
  (b) greater than the exact ground-state energy of the Neon atom.

**18.** Write an appropriate Slater determinant (include all the rows and all the columns) for a $^3S$ state with the $1s^2 2s^1 5s^1$ electron configuration. Remember to include the appropriate normalization constant for orthogonal and normalized orbitals.

$$\Psi_{1s^2 2s^1 5s^1} = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(\boldsymbol{r}_1)\alpha(1) & \psi_{1s}(\boldsymbol{r}_1)\beta(1) & \psi_{2s}(\boldsymbol{r}_1)\alpha(1) & \psi_{5s}(\boldsymbol{r}_1)\alpha(1) \\ \psi_{1s}(\boldsymbol{r}_2)\alpha(2) & \psi_{1s}(\boldsymbol{r}_2)\beta(2) & \psi_{2s}(\boldsymbol{r}_2)\alpha(2) & \psi_{5s}(\boldsymbol{r}_2)\alpha(2) \\ \psi_{1s}(\boldsymbol{r}_3)\alpha(3) & \psi_{1s}(\boldsymbol{r}_3)\beta(3) & \psi_{2s}(\boldsymbol{r}_3)\alpha(3) & \psi_{5s}(\boldsymbol{r}_3)\alpha(3) \\ \psi_{1s}(\boldsymbol{r}_4)\alpha(4) & \psi_{1s}(\boldsymbol{r}_4)\beta(4) & \psi_{2s}(\boldsymbol{r}_4)\alpha(4) & \psi_{5s}(\boldsymbol{r}_4)\alpha(4) \end{vmatrix}$$

**$M_L$**

### $M_S = 3/2$

| $M_L$ | 5 | 4 | 3 | 2 | 1 | 0 |
|---|---|---|---|---|---|---|
| | | | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_0}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_{-2}}\alpha|$ | $|\psi_{3d_1}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\alpha|$ |
| | | | | | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-2}}\alpha|$ |

### $M_S = 1/2$

| $M_L$ | 5 | 4 | 3 | 2 | 1 | 0 |
|---|---|---|---|---|---|---|
| | $|\psi_{3d_2}\alpha \ \psi_{3d_2}\beta \ \psi_{3d_1}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_1}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_0}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_{-1}}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\alpha \ \psi_{3d_{-2}}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-2}}\beta|$ |
| | | $|\psi_{3d_2}\alpha \ \psi_{3d_2}\beta \ \psi_{3d_0}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_0}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_{-2}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\beta \ \psi_{3d_{-2}}\alpha|$ |
| | | | $|\psi_{3d_2}\beta \ \psi_{3d_1}\alpha \ \psi_{3d_0}\alpha|$ | $|\psi_{3d_2}\beta \ \psi_{3d_1}\alpha \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_2}\beta \ \psi_{3d_1}\alpha \ \psi_{3d_{-2}}\alpha|$ | $|\psi_{3d_2}\beta \ \psi_{3d_0}\alpha \ \psi_{3d_{-2}}\alpha|$ |
| | | | $|\psi_{3d_2}\alpha \ \psi_{3d_2}\beta \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_2}\beta \ \psi_{3d_{-2}}\alpha|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\beta|$ | $|\psi_{3d_1}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\beta|$ |
| | | | | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_0}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_0}\beta \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_1}\alpha \ \psi_{3d_0}\beta \ \psi_{3d_{-1}}\alpha|$ |
| | | | | $|\psi_{3d_1}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_0}\alpha|$ | $|\psi_{3d_2}\beta \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_1}\beta \ \psi_{3d_0}\alpha \ \psi_{3d_{-1}}\alpha|$ |
| | | | | | $|\psi_{3d_1}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_{-1}}\alpha|$ | $|\psi_{3d_1}\alpha \ \psi_{3d_1}\beta \ \psi_{3d_{-2}}\alpha|$ |
| | | | | | $|\psi_{3d_1}\alpha \ \psi_{3d_0}\alpha \ \psi_{3d_0}\beta|$ | $|\psi_{3d_2}\alpha \ \psi_{3d_{-1}}\alpha \ \psi_{3d_{-1}}\beta|$ |

**19. List all the terms associated with the ground state electron configuration of Vanadium, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. (You do not need to show the possible values of $J$ here.)**

$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$

**20. What is the term symbol for the ground state term of the Cobalt atom, which has electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$?**

This is the same as the Vanadium case, but in this case we are dealing with "holes" instead of electrons. So the ground state term symbol is $^4F$. *However*, the best value of $J = L + S = 3 + \frac{3}{2} = \frac{9}{2}$ because in this case the shell is more than half-filled. (For Vanadium the best value of $J = |L - S| = |3 - \frac{3}{2}| = \frac{3}{2}$). So the ground state term symbol is $^4F_{9/2}$.

**21. What are the possible values of $M_J$ in the ground state of the Cobalt atom?**

$M_J = -\frac{9}{2}, -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$

**22.   We are interested in the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ excited state of the Manganese atom. What are the possible terms?**

There are a slew of different values—I should have counted the states before assigning this problem!

| $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ **Term** | **New range of L and S** | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3 4p^1$ **Term** |
|---|---|---|
| $^4F$ | $2 \le L \le 4; 1 \le S \le 2$ | $^5D, {}^5F, {}^5G; {}^3D, {}^3F, {}^3G$ |
| $^4P$ | $0 \le L \le 2; 1 \le S \le 2$ | $^5S, {}^5P, {}^5D; {}^3S, {}^3P, {}^3D$ |
| $^2H$ | $4 \le L \le 6; 0 \le S \le 1$ | $^3I, {}^3H, {}^3G; {}^1I, {}^1H, {}^1G$ |
| $^2G$ | $3 \le L \le 5; 0 \le S \le 1$ | $^3F, {}^3H, {}^3G; {}^1F, {}^1H, {}^1G$ |
| $^2F$ | $2 \le L \le 4; 0 \le S \le 1$ | $^3F, {}^3D, {}^3G; {}^1F, {}^1D, {}^1G$ |
| $^2D$ | $1 \le L \le 3; 0 \le S \le 1$ | $^3F, {}^3D, {}^3P; {}^1F, {}^1D, {}^1P$ |
| $^2D$ | $1 \le L \le 3; 0 \le S \le 1$ | $^3F, {}^3D, {}^3P; {}^1F, {}^1D, {}^1P$ |
| $^2P$ | $0 \le L \le 2; 0 \le S \le 1$ | $^3D, {}^3P, {}^3S; {}^1D, {}^1P, {}^1S$ |

For each of the following, write the eigenvalue. (If there is no eigenvalue, write "no eigenvalue"; if there are multiple eigenvalues possible, write all the possibilities.) Here, the wave functions are denoted either by (a) a Slater determinant or (b) a term symbol. In each case, it is up to you to decipher the relevant quantum numbers.

**23.**

$$\hat{L}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = 12 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{L}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = 3 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{L}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \begin{bmatrix} \text{not an eigenfunction} \\ \text{of } \hat{L}^2 \end{bmatrix} \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

$$\hat{L}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = 4 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

**24.**

$$\hat{S}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \frac{15}{4} \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{S}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right| = \frac{3}{2} \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha \right|$$

$$\hat{S}^2 \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \frac{3}{4} \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

$$\hat{S}_z \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right| = \frac{1}{2} \left| \psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta \right|$$

**25.**

$$\hat{J}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \begin{bmatrix} \text{not an eigenfunction since} \\ \left[\hat{J}^2, L_z\right] \neq 0; \left[\hat{J}^2, S_z\right] \neq 0 \end{bmatrix} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{J}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right| = \left(3 + \tfrac{3}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$= \tfrac{9}{2}\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_0}\alpha\right|$$

$$\hat{J}^2 \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \begin{bmatrix} \text{not an eigenfunction since} \\ \left[\hat{J}^2, L_z\right] \neq 0; \left[\hat{J}^2, S_z\right] \neq 0 \end{bmatrix} \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$\hat{J}_z \left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right| = \left(4 + \tfrac{1}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

$$= \left(\tfrac{9}{2}\right)\left|\psi_{3d_2}\alpha \quad \psi_{3d_1}\alpha \quad \psi_{3d_1}\beta\right|$$

# Part 3. Closed-Book Derivation

1. **Explain why $\hat{J}^2$ and $\hat{S}^2$ commute (7 points), but $\hat{J}^2$ and $\hat{S}_x$ do not (7 points).**

*You cannot use results for commutators including $\hat{\boldsymbol{J}}$ ; that is the purpose of this problem!* Rather, you must rewrite terms containing $\hat{\boldsymbol{J}}$ in terms of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$, and then use commutator identities (e.g., formulae for $\left[\hat{A},\hat{B}\hat{C}\right]$, $\left[\hat{A}\hat{B},\hat{C}\right]$, $\left[\hat{A},\hat{B}+\hat{C}\right]$, $\left[\hat{A}+\hat{B},\hat{C}\right]$) and known commutator relationships for the orbital angular momentum $(\hat{\boldsymbol{L}}=\left[\hat{L}_x,\hat{L}_y,\hat{L}_z\right]$, $\hat{L}^2=\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{L}})$ and the spin angular momentum $(\hat{\boldsymbol{S}}=\left[\hat{S}_x,\hat{S}_y,\hat{S}_z\right]$, $\hat{S}^2=\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{S}})$ or electrons to get the desired result.

**You may find it helpful to recall that $\left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z$, $\left[\hat{S}_y,\hat{S}_z\right]=i\hbar\hat{S}_x$, and $\left[\hat{S}_z,\hat{S}_x\right]=i\hbar\hat{S}_y$.**

$$
\begin{aligned}
\left[\hat{J}^2,\hat{S}^2\right] &= \left[\hat{\boldsymbol{J}}\cdot\boldsymbol{J},\hat{S}^2\right] \\
&= \left[\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right),\hat{S}^2\right] \\
&= \left[\hat{L}^2+\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}+\hat{S}^2,\hat{S}^2\right] \\
&= \left[\hat{L}^2+2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{S}^2,\hat{S}^2\right] && \begin{pmatrix}\text{because spin and orbital angular}\\ \text{momenta commute}\end{pmatrix} \\
&= \left[\hat{L}^2,\hat{S}^2\right]+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+\left[\hat{S}^2,\hat{S}^2\right] && \begin{pmatrix}\text{because the commutator of a sum}\\ \text{is the sum of the commutators}\end{pmatrix} \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+\left[\hat{S}^2,\hat{S}^2\right] && (\text{$L$ and $S$ are both good quantum numbers!}) \\
&= 0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}^2\right]+0 && (\text{every operator commutes with itself}) \\
&= 2\hat{\boldsymbol{S}}\cdot\left[\hat{\boldsymbol{L}},\hat{S}^2\right]+2\left[\hat{\boldsymbol{S}},\hat{S}^2\right]\cdot\hat{\boldsymbol{L}} && (\text{use identity for the commutator of a product}) \\
&= 0+2\left[\hat{\boldsymbol{S}},\hat{S}^2\right]\cdot\hat{\boldsymbol{L}} && \begin{pmatrix}\text{because spin and orbital angular}\\ \text{momenta commute}\end{pmatrix} \\
&= 2\left[\hat{S}_x,\hat{S}^2\right]\hat{L}_x+2\left[\hat{S}_y,\hat{S}^2\right]\hat{L}_y && (\text{definition of the dot product}) \\
&\quad +2\left[\hat{S}_z,\hat{S}^2\right]\hat{L}_z \\
&= 2(0)\hat{L}_x+2(0)\hat{L}_y+2(0)\hat{L}_z && \begin{pmatrix}\hat{S}^2\text{ commutes with every component of the spin}\\ \text{angular momentum}\end{pmatrix} \\
&= 0
\end{aligned}
$$

$$\left[\hat{J}^2,\hat{S}_x\right]=\left[\hat{\boldsymbol{J}}\cdot\boldsymbol{J},\hat{S}_x\right]$$

$$=\left[\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right)\cdot\left(\hat{\boldsymbol{L}}+\hat{\boldsymbol{S}}\right),\hat{S}_x\right]$$

$$=\left[\hat{L}^2+\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}+\hat{S}^2,\hat{S}_x\right]$$

$$=\left[\hat{L}^2+2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}}+\hat{S}^2,\hat{S}_x\right] \qquad \left(\begin{array}{l}\text{because spin and orbital angular}\\ \text{momenta commute}\end{array}\right)$$

$$=\left[\hat{L}^2,\hat{S}_x\right]+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+\left[\hat{S}^2,\hat{S}_x\right] \qquad \left(\begin{array}{l}\text{because the commutator of a sum}\\ \text{is the sum of the commutators}\end{array}\right)$$

$$=0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+\left[\hat{S}^2,\hat{S}_x\right] \qquad (L\text{ and }S\text{ are both good quantum numbers!})$$

$$=0+\left[2\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{L}},\hat{S}_x\right]+0 \qquad \left(\begin{array}{l}\hat{S}^2\text{ commutes with every component of the spin}\\ \text{angular momentum}\end{array}\right)$$

$$=2\hat{\boldsymbol{S}}\cdot\left[\hat{\boldsymbol{L}},\hat{S}_x\right]+2\left[\hat{\boldsymbol{S}},\hat{S}_x\right]\cdot\hat{\boldsymbol{L}} \qquad (\text{use identity for the commutator of a product})$$

$$=0+2\left[\hat{\boldsymbol{S}},\hat{S}_x\right]\cdot\hat{\boldsymbol{L}} \qquad \left(\begin{array}{l}\text{because spin and orbital angular}\\ \text{momenta commute}\end{array}\right)$$

$$=2\left[\hat{S}_x,\hat{S}_x\right]\hat{L}_x+2\left[\hat{S}_y,\hat{S}_x\right]\hat{L}_y \qquad (\text{definition of the dot product})$$
$$+2\left[\hat{S}_z,\hat{S}_x\right]\hat{L}_z$$

$$=0+2\left[\hat{S}_y,\hat{S}_x\right]\hat{L}_y+2\left[\hat{S}_z,\hat{S}_x\right]\hat{L}_z \qquad (\text{every operator commutes with itself})$$

$$=2\left(-i\hbar\hat{S}_z\right)\hat{L}_y+2\left(i\hbar\hat{S}_y\right)\hat{L}_z \qquad \left(\begin{array}{l}\left[\hat{S}_x,\hat{S}_y\right]=i\hbar\hat{S}_z\rightarrow\left[\hat{S}_y,\hat{S}_x\right]=-i\hbar\hat{S}_z\\ \left[\hat{S}_z,\hat{S}_x\right]=i\hbar\hat{S}_y\end{array}\right)$$

$$=2i\hbar\left(\hat{S}_y\hat{L}_z-\hat{S}_z\hat{L}_y\right)$$

$$\neq 0$$

Let $\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r)Y_l^m(\theta,\phi)$ denote the hydrogenic orbital $(Z=1)$ with principle quantum number $n$, orbital angular momentum quantum number $l$, and magnetic quantum number $m$.

## 2a. (10 points) Show that

$$\left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle = \frac{1}{n^2}.$$

Write the general Hamiltonian for the one-electron atom,

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{Z}{r} \tag{36}$$

Use the Hellmann-Feynman Theorem,

$$\left. \frac{\partial E}{\partial Z} \right|_{Z=1} = \left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \left. \frac{\partial \hat{H}}{\partial Z} \right|_{Z=1} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle$$

$$\left. \frac{\partial E}{\partial Z} \right|_{Z=1} = \left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \frac{-1}{r} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle \tag{37}$$

$$\left. \frac{\partial E}{\partial Z} \right|_{Z=1} = -\left\langle \psi_{n,l,m}(\boldsymbol{r}) \left| \frac{1}{r} \right| \psi_{n,l,m}(\boldsymbol{r}) \right\rangle$$

But, from the energy of the one-electron atom, we know that

$$\left. \frac{\partial E}{\partial Z} \right|_{Z=1} = \left. \frac{\partial \left( \frac{-Z^2}{2n^2} \right)}{\partial Z} \right|_{Z=1} = \left. \frac{-2Z}{2n^2} \right|_{Z=1} = -\frac{1}{n^2} \tag{38}$$

Substituting into Eq. (37) we get

$$-\frac{1}{n^2} = -\left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle$$

$$\frac{1}{n^2} = \left\langle \psi_{n,l,m} \left| \frac{1}{r} \right| \psi_{n,l,m} \right\rangle \tag{39}$$

Kramer's relation is a very useful formula for computing integrals of the form $\langle \psi_{n,l,m} | r^k | \psi_{n,l,m} \rangle$

for one-electron atoms. When applied to the Hydrogen atom, Kramer's formula is:

$$\frac{k+1}{n^2} \langle \psi_{n,l,m} | r^k | \psi_{n,l,m} \rangle = (2k+1) \langle \psi_{n,l,m} | r^{k-1} | \psi_{n,l,m} \rangle + k \left[ \frac{1}{4}(k^2-1) - l(l+1) \right] \langle \psi_{n,l,m} | r^{k-2} | \psi_{n,l,m} \rangle$$

## 2b. (6 points) What is the average (mean) distance from the nucleus of an electron in an *s* orbital of the hydrogen atom? Compare this to the result for *p* orbitals.

We need the formula with $k=1$, because we want to know the mean distance, which is given by the expression

$$\langle \psi_{n,l,m} | r | \psi_{n,l,m} \rangle = \text{mean distance} \tag{40}$$

We know

$$\langle \psi_{n,l,m} | r^{1-2} | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | r^{-1} | \psi_{n,l,m} \rangle = \frac{1}{n^2} \tag{41}$$

from 2a. We know that

$$\langle \psi_{n,l,m} | r^{2-2} | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | r^0 | \psi_{n,l,m} \rangle = \langle \psi_{n,l,m} | \psi_{n,l,m} \rangle = 1 \tag{42}$$

because wave functions are normalized. So, we have that

$$\frac{1+1}{n^2} \langle \psi_{n,l,m} | r^1 | \psi_{n,l,m} \rangle = (2(1)+1) \langle \psi_{n,l,m} | r^0 | \psi_{n,l,m} \rangle$$
$$+ 1 \left[ \frac{1}{4}(1^2-1) - l(l+1) \right] \langle \psi_{n,l,m} | r^{-1} | \psi_{n,l,m} \rangle$$
$$\frac{2}{n^2} \langle \psi_{n,l,m} | r | \psi_{n,l,m} \rangle = 3 + 1 \left[ \frac{1}{4}(0) - l(l+1) \right] \frac{1}{n^2} \tag{43}$$
$$\langle \psi_{n,l,m} | r | \psi_{n,l,m} \rangle = \frac{1}{2} \left( 3n^2 - l(l+1) \right)$$

For an *s* orbital, $l=0$ and so

$$\langle \psi_{n,0,0} | r | \psi_{n,0,0} \rangle = \frac{3}{2} n^2 \tag{44}$$

while for a *p* orbital $l=1$ and so

$$\langle \psi_{n,1,m} | r | \psi_{n,1,m} \rangle = \frac{3}{2} n^2 - 1 \tag{45}$$

Note that for a given value of the principle quantum number, $n$, an electron in a *p* orbital is actually closer, on average, to the nucleus than an electron in an *s* orbital.