CHM 3411 – Problem Set 6
Due date: Wednesday, February 27th
Do all of the following problems. Show your work.

1) Just as we can construct p orbitals out of the $\ell = 1$ set of spherical harmonics, we can construct d orbitals out of the $\ell = 2$ set of spherical harmonics.
    One of the d orbitals for hydrogen has the following form

$$d(\theta,\phi) = N \sin\theta \cos\theta \cos\phi \qquad (1.1)$$

    a) For what value of N will the above d orbital be normalized?
    b) For what value(s) of θ and ϕ does the above d orbital have its maximum magnitude? Based on your answer, identify the d orbital. (Hint: $P(\theta,\phi) = \sin\theta \; [d(\theta,\phi)]^2 \; d\theta \; d\phi$. Pictures of the d orbitals are given in Fig 9A.16 of Atkins).

2) The first excited electronic state for the helium atom has the electron configuration He $1s^1 \, 2s^1$. The wavefunction for this state is $\Psi(1,2)$. In the orbital approximation, we expect to be able to write $\Psi(1,2)$ in terms of the space wavefunctions ψ_{1s} and ψ_{2s}, and the spin wavefunctions α and β. These are individually normalized, that is

$$\int \psi_{1s}^* \, \psi_{1s} \, d\tau_i = \int \psi_{2s}^* \, \psi_{2s} \, d\tau_i = \int \alpha^* \, \alpha \, d\tau_i = \int \beta^* \, \beta \, d\tau_i = 1 \qquad (2.1)$$

where the integrals are either over the coordinates of electron 1 or electron 2. Recall that $\Psi(1,2)$ must be antisymmetric with respect to the exchange (permutation) operator $P(1,2)$, that is

$$P(1,2) \, \Psi(1,2) = \Psi(2,1) = -\Psi(1,2) \qquad (2.2)$$

    Consider the space wavefunction $\psi(1,2) = \psi_{1s}(1) \, \psi_{2s}(2)$.

    a) Is $\psi(1,2)$ an eigenfunction of $P(1,2)$? If your answer is yes, is the eigenvalue for $\psi(1,2)$ equal to +1 (symmetric) or -1 (antisymmetric)?
    b) Consider the following two space wavefunctions that are linear combinations of ψ_{1s} and ψ_{2s}.

$$\psi_+ = N_+ \, [\psi_{1s}(1) \, \psi_{2s}(2) + \psi_{2s}(1) \, \psi_{1s}(2) \,] \qquad (2.3)$$

$$\psi_- = N_- \, [\psi_{1s}(1) \, \psi_{2s}(2) - \psi_{2s}(1) \, \psi_{1s}(2) \,] \qquad (2.4)$$

What values for the normalization constants N_+ and N_- make ψ_+ and ψ_- normalized space wavefunctions?
    c) Is ψ_+ an eigenfunction of $P(1,2)$? If your answer is yes, is the eigenvalue for ψ_+ equal to +1 (symmetric) or -1 (antisymmetric)?
    d) Is ψ_- an eigenfunction of $P(1,2)$? If your answer is yes, is the eigenvalue for ψ_- equal to +1 (symmetric) or -1 (antisymmetric)?
    e) As discussed in class, the four possible combinations of spin wavefunctions for two electrons, and their symmetries with respect to $P(1,2)$, are

$\alpha(1)\alpha(2)$	symmetric (eigenvalue = +1)	(2.5)
$\sigma_+ = (1/2)^{1/2} \, [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	symmetric (eigenvalue = +1)	(2.6)
$\beta(1)\beta(2)$	symmetric (eigenvalue = +1)	(2.7)
$\sigma_- = (1/2)^{1/2} \, [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	antisymmetric (eigenvalue = -1)	(2.8)

Which of the possible combinations of space wavefunction (ψ_+ or ψ_-) and spin wavefunctions (given in 2.5 – 2.8) satisfy the antisymmetry requirement of eq 2.2? What are the values for M_L and M_S for these states? What term symbols describe these wavefunctions?

3) Without using any summation symbols write the hamiltonian operator for a beryllium atom (Z = 4, 4 electrons).

4) Find all of the term symbols corresponding to np^3, that is, having three electrons in a set of p-orbitals. Include the possible values for the quantum number J (the quantum number for spin-orbit coupling) in your answer.

5) The configuration for the lowest energy arrangement of electrons for a titanium atom is

Ti(22 e⁻):   [Ar] $4s^2 3d^2$

The table of possible M_L and M_S values for this electron configuration is given below. Note there are 10!/8!2! = 45 entries in the table, each represented by a vertical line.

	M_L	4	3	2	1	0	-1	-2	-3	-4
M_S										
1										
0										
-1										

	M_L	4	3	2	1	0	-1	-2	-3	-4
M_S										
1			|	|	||	||	||	|	|	
0		|	||	|||	||||	|||||	||||	|||	||	|
-1			|	|	||	||	||	|	|	

Find all of the term symbols (electronic states) corresponding to this electron configuration, and rank them in order from lowest to highest energy. You do not have to give values for the quantum number J in your term symbols.

6) The energy of the ground and first several excited electronic states of the potassium atom are given below, relative to the lowest energy electronic state. Note that the actual energies are known to 2-3 more significant figures than in the data table.

Configuration	Term symbol	Energy (cm⁻¹)
[Ar] $4s^1$	$^2S_{1/2}$	0.
[Ar] $4p^1$	$^2P_{1/2}$	12985.
	$^2P_{3/2}$	13042.
[Ar] $3d^1$	$^2D_{5/2}$	21535.
	$^2D_{3/2}$	21537.
[Ar] $5p^1$	$^2P_{1/2}$	24701.
	$^2P_{3/2}$	24720.

    a) Using the selection rules for allowed transitions in atomic spectroscopy, identify all of the allowed transitions between the above electronic states of potassium. Give the energy for each transition (in cm⁻¹) and the wavelength at which each transition is expected to be observed.

    b) The following strong light emissions are seen when an electrical discharge is passed through a vapor of potassium atoms.

404.41 nm	766.49 nm	1169.0 nm
404.72 nm	769.90 nm	1177.0 nm
		1177.3 nm

Identify each of these emission lines with the appropriate atomic transitions in potassium. Note that there will be small differences between the observed wavelengths for the transitions and those calculated from the energy values in the table of energy levels. This is due to the experimental values being measured in air, which causes the wavelengths to be slightly different than they would be if measured under vacuum conditions.