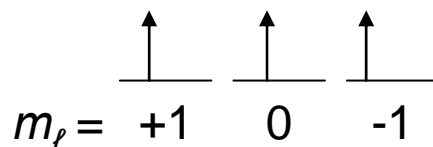


**Quiz 9**  
**CHEM 325**  
**Spring 2009**

Name: \_\_\_\_\_

1a. (7 Points) What is the ground state term symbol for N (include  $J$ )? You are given that the electronic configuration of N is  $[\text{He}] 2s^2 2p^3$ . Hint: use the shortcut method discussed in class.

**Using the short cut method (and labeling the orbitals as shown), gives the following microstate.**



**For this microstate  $M_L = 0$  and  $M_S = 3/2$ . This can only arise from a term with  $L = 0$  and  $S = 3/2$ , which is  $^4\text{S}$ .**

**The possible  $J$  values are  $L + S, L + S - 1, \dots, |L - S|$ , which in this case is  $3/2$  (since  $L + S = |L - S| = 3/2$ ). The ground state is therefore  $^4\text{S}_{3/2}$ .**

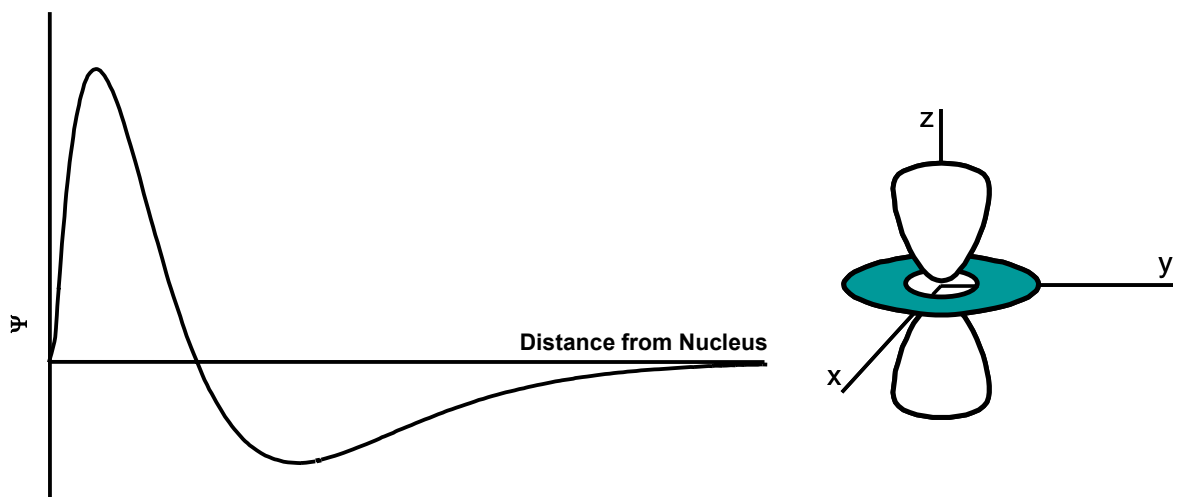
b. (4 Points) The other two terms that arise from nitrogen's electronic configuration are  $^2\text{P}$  and  $^2\text{D}$ . Which one is lower in energy? Why?

**Hunds's Rules predict that when two states have the same spin (multiplicity) the one with the largest  $L$  is lowest in energy as this minimizes  $e^-e^-$  interactions. In this case it is  $^2\text{D}$ .**

c. (4 Points) Is a transition from the ground state to either the  $^2\text{P}$  or to the  $^2\text{D}$  state allowed? Why? If you did not get an answer for part *a*, list the criteria for a transition to be allowed and state which one will be the most important. For this analysis you may ignore  $J$ .

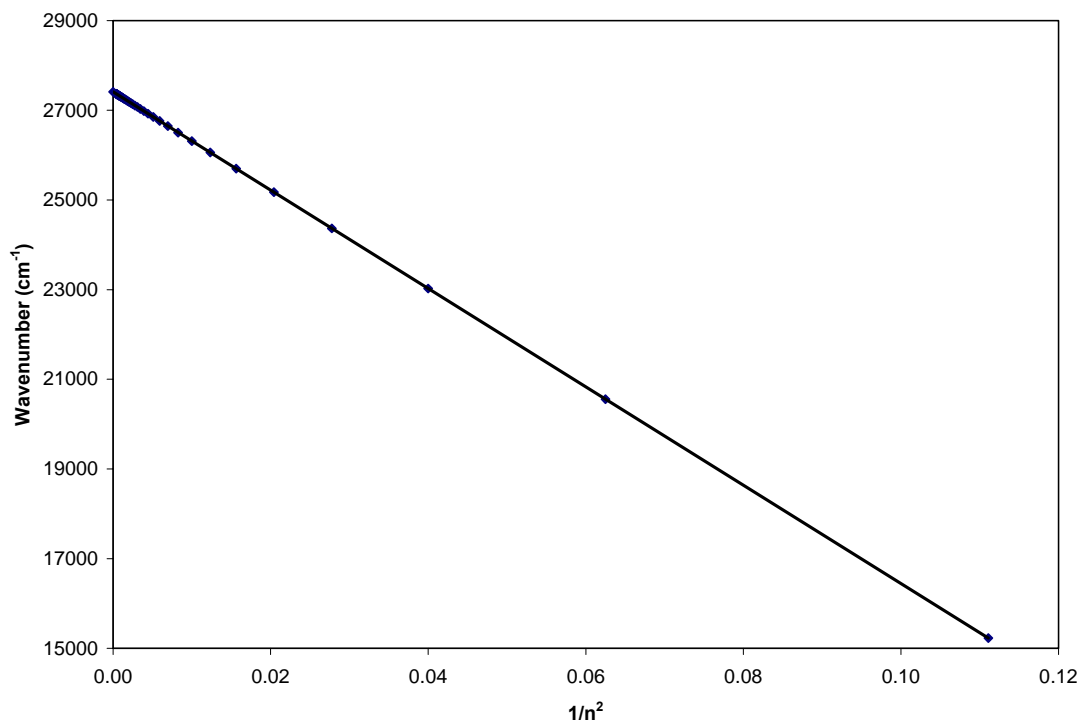
**Since the ground state is  $^4\text{S}$  and the excited states are  $^2\text{P}$  and  $^2\text{D}$ , the two possible transitions ( $^2\text{D} \leftarrow ^4\text{S}$  and  $^2\text{P} \leftarrow ^4\text{S}$ ) are both spin forbidden ( $\Delta S \neq 0$ ). Although the  $^2\text{P} \leftarrow ^4\text{S}$  transition would be orbitally allowed ( $\Delta L = +1$ ), it would not be expected to be observed because for atomic system being spin forbidden dominates all other considerations. So at best, the  $^2\text{P} \leftarrow ^4\text{S}$  transition would be extremely weak.**

2. (10 Points) The radial and angular portions of a certain hydrogen wavefunction are shown below.



- The number of radial nodes is/are **1**.
- The number of angular nodes is/are **2**.
- For this orbital  $\ell$  equals **2**.
- The possible  $m_\ell$  value/s for this  $\ell$  is/are  **$\pm 2, \pm 1, 0$** .
- The actual value of  $m_\ell$  for this orbital is **0**.
- For this orbital  $n$  equals **4**.
- The name of this orbital is  **$4d_{z^2}$** .
- When compared to an s orbital of the same  $n$  in the hydrogen atom, this orbital's energy is greater than    less than    **the same as**    the s orbital's energy. (circle one)
- When compared to an s orbital of the same  $n$  in the iron atom, this orbital's energy is **greater than**    less than    the same as    the s orbital's energy. (circle one)

3. (8 Points) When the energy of a particular series of lines in the H atom absorption spectrum are graphed as a function of  $1/n^2$ , where  $n$  is an integer, the data can be fit to a straight line with a slope of  $-109642.89 \text{ cm}^{-1}$  and an intercept of  $27410.72 \text{ cm}^{-1}$ , as shown below. Determine the value of  $R_H$  and the value of the  $n$  for the other term involved in the transition.



The term energy in the hydrogen atom is given by the equation  $E_n = -\frac{R_H Z^2}{n^2}$ . Since a transition requires a change in energy on the atom's part, it must result from the single electron moving from a term with some  $n_{\text{initial}}$  to a term with some  $n_{\text{final}}$ . Thus, we may write  $\Delta E = E_{\text{final}} - E_{\text{initial}} = \left( -\frac{R_H Z^2}{n_{\text{final}}^2} \right) - \left( -\frac{R_H Z^2}{n_{\text{initial}}^2} \right)$ , where  $n_{\text{final}} > n_{\text{initial}}$  for absorption. Since

$Z = 1$ , we can simplify this to  $\Delta E = \frac{R_H}{n_{\text{initial}}^2} - \frac{R_H}{n_{\text{final}}^2}$ . A given series of lines in the hydrogen

absorption spectrum are transitions from the same  $n_{\text{initial}}$  to different  $n_{\text{final}}$  values. This means that  $n_{\text{initial}}$  is a constant and the changing  $n^2$  in the graph shown above is due to

$n_{\text{final}}$ . Thus, the equation  $\Delta E = \frac{R_H}{n_{\text{initial}}^2} - \frac{R_H}{n_{\text{final}}^2}$  is in the form of a straight line with a slope

of  $-R_H$  and  $\frac{R_H}{n_{\text{initial}}^2} = \text{intercept}$ , or  $n_{\text{initial}} = \sqrt{\frac{R_H}{\text{intercept}}}$ . Therefore  $R_H = 109642.89 \text{ cm}^{-1}$  and

$$n_{\text{initial}} = \sqrt{\frac{R_H}{\text{intercept}}} = \sqrt{\frac{109642.89 \text{ cm}^{-1}}{27410.72 \text{ cm}^{-1}}} = 2.$$