Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 16 **Name:** _____

1. Show the following properties of commutators: (a) $[A, B] = -[B, A]$, (b) $[A^n, A^m] = 0$ for all n and m, (c) $[A^2, B] = A[A, B] + [A, B]A$, (d) $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$.

2. It is more convenient to express the momentum operators using ladder operators,

$$\hat{M}_+ = \hat{M}_x + i\hat{M}_y \qquad \hat{M}_- = \hat{M}_x - i\hat{M}_y.$$

Here, $\hat{M} = \hat{L}, \hat{S}$, and they give to following eigenvalues for the spherical harmonics,

$$\hat{M}_+ Y_l^m = \hbar\sqrt{l(l+1) - m(m+1)}\, Y_l^{m+1}$$

$$\hat{M}_- Y_l^m = \hbar\sqrt{l(l+1) - m(m-1)}\, Y_l^{m-1}.$$

   (a) Express the operators $\hat{M}_x$ and $\hat{M}_y$ in terms of the ladder operators.

   (b) Prove that $\hat{M}^2 = \frac{1}{2}\left(\hat{M}_+\hat{M}_- + \hat{M}_-\hat{M}_+\right) + \hat{M}_z^2$.

   (c) Show that $[\hat{M}_+, \hat{M}_-] = 2\hbar\hat{M}_z$.

   (d) Do the ladder operators commute with the total angular momentum and its individual components?

   (e) What does $\hat{M}^2 |Y_l^m\rangle$ yield?

   (f) Calculate the values of the following integrals: (i) $\left\langle p_x \middle| \hat{L}_z \middle| p_y \right\rangle$, (ii) $\left\langle p_x \middle| \hat{L}_+ \middle| p_y \right\rangle$, (iii) $\left\langle p_z \middle| \hat{L}_y \middle| p_x \right\rangle$, (iv) $\left\langle p_z \middle| \hat{L}_x \middle| p_y \right\rangle$, (iiv) $\left\langle p_z \middle| \hat{L}_x \middle| p_x \right\rangle$. Remember that $p_z = p_0$, $p_x = \frac{1}{\sqrt{2}}(p_{-1} - p_{+1})$, and $p_y = \frac{i}{\sqrt{2}}(p_{-1} + p_{+1})$.

3. What are the term symbols associated with the ground state electron configuration of the Vanadium atom, [Ar]$4s^2 3d^3$? You do not need to show the "J labels".

   (a) According to Hund's Rules, what is the ground-state term symbol for Vanadium?

   (b) For the ground state term symbol from (a), what are the possible values of J? List these in order of increasing energy.