CHEM 1410
HW # 7

P10.2) Classify the following functions as symmetric, antisymmetric, or neither in the exchange of electrons 1 and 2:

a) $\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$

$$\left[1s(2)2s(1)+2s(2)1s(1)\right]\left[\alpha(2)\beta(1)-\beta(2)\alpha(1)\right]=$$
$$-\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]$$

Therefore the function is antisymmetric in the exchange of electrons 1 and 2.

b) $\left[1s(1)2s(2)+2s(1)1s(2)\right]\alpha(1)\alpha(2)$

$$\left[1s(2)2s(1)+2s(2)1s(1)\right]\alpha(2)\alpha(1)=\left[1s(1)2s(2)+2s(1)1s(2)\right]\alpha(1)\alpha(2)$$

Therefore the function is symmetric in the exchange of electrons 1 and 2.

c) $\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$

$$\left[1s(2)2s(1)+2s(2)1s(1)\right]\left[\alpha(2)\beta(1)+\beta(2)\alpha(1)\right]$$
$$=\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

Therefore the function is symmetric in the exchange of electrons 1 and 2.

d) $\left[1s(1)2s(2)-2s(1)1s(2)\right]\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$

$$\left[1s(2)2s(1)-2s(2)1s(1)\right]\left[\alpha(2)\beta(1)+\beta(2)\alpha(1)\right]$$
$$=-\left[1s(1)2s(2)-2s(1)1s(2)\right]\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

Therefore the function is antisymmetric in the exchange of electrons 1 and 2.

e) $\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)+\alpha(1)\alpha(2)\right]$

$$\left[1s(1)2s(2)+2s(1)1s(2)\right]\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)+\alpha(1)\alpha(2)\right]$$
$$\neq\pm\left[1s(2)2s(1)+2s(2)1s(1)\right]\left[\alpha(2)\beta(1)-\beta(2)\alpha(1)+\alpha(2)\alpha(1)\right]$$

Therefore the function is neither symmetric or antisymmetric in the exchange of electrons 1 and 2.

P10.5) Show that the functions $\frac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}}$ and $\frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}$ are eigenfunctions of $\hat{S}^2_{total}$. What is the eigenvalue in each case?

Solve this equation by acting on $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ separately, and combining the results.

$$\begin{aligned}
&\hat{S}^2_{total}\alpha(1)\beta(2)\\
&=\hat{S}_1^2\alpha(1)\beta(2)+\hat{S}_2^2\alpha(1)\beta(2)+2\left(\hat{S}_{1x}\hat{S}_{2x}\alpha(1)\beta(2)+\hat{S}_{1y}\hat{S}_{2y}\alpha(1)\beta(2)+\hat{S}_{1z}\hat{S}_{2z}\alpha(1)\beta(2)\right)\\
&=\beta(2)\hat{S}_1^2\alpha(1)+\alpha(1)\hat{S}_2^2\beta(2)+2\left(\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2)+\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2)+\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2)\right)\\
&=\frac{3\hbar^2}{4}\alpha(1)\beta(2)+\frac{3\hbar^2}{4}\alpha(1)\beta(2)+2\left(\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\beta(2)+\hat{S}_{1y}\alpha(1)\hat{S}_{2y}\beta(2)+\hat{S}_{1z}\alpha(1)\hat{S}_{2z}\beta(2)\right)\\
&=\frac{3\hbar^2}{4}\alpha(1)\beta(2)+\frac{3\hbar^2}{4}\alpha(1)\beta(2)+2\times\frac{\hbar}{2}\left(\hat{S}_{1x}\alpha(1)\alpha(2)-i\hat{S}_{1y}\alpha(1)\alpha(2)-\hat{S}_{1z}\alpha(1)\beta(2)\right)\\
&=\frac{3\hbar^2}{4}\alpha(1)\beta(2)+\frac{3\hbar^2}{4}\alpha(1)\beta(2)+2\times\left(\frac{\hbar}{2}\right)^2\left(\beta(1)\alpha(2)-i^2\beta(1)\alpha(2)+\alpha(1)\beta(2)\right)\\
&=\frac{3\hbar^2}{2}\alpha(1)\beta(2)+\frac{\hbar^2}{2}\left(2\beta(1)\alpha(2)+\alpha(1)\beta(2)\right)\\
&=\hbar^2\alpha(1)\beta(2)+\hbar^2\beta(1)\alpha(2)
\end{aligned}$$

$$\begin{aligned}
&\hat{S}^2_{total}\beta(1)\alpha(2)\\
&=\hat{S}_1^2\beta(1)\alpha(2)+\hat{S}_2^2\beta(1)\alpha(2)+2\left(\hat{S}_{1x}\hat{S}_{2x}\beta(1)\alpha(2)+\hat{S}_{1y}\hat{S}_{2y}\beta(1)\alpha(2)+\hat{S}_{1z}\hat{S}_{2z}\beta(1)\alpha(2)\right)\\
&=\alpha(2)\hat{S}_1^2\beta(1)+\beta(1)\hat{S}_2^2\alpha(2)+2\left(\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2)+\hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2)+\hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2)\right)\\
&=\frac{3\hbar^2}{4}\beta(1)\alpha(2)+\frac{3\hbar^2}{4}\beta(1)\alpha(2)+2\left(\hat{S}_{1x}\beta(1)\hat{S}_{2x}\alpha(2)+\hat{S}_{1y}\beta(1)\hat{S}_{2y}\alpha(2)+\hat{S}_{1z}\beta(1)\hat{S}_{2z}\alpha(2)\right)\\
&=\frac{3\hbar^2}{4}\beta(1)\alpha(2)+\frac{3\hbar^2}{4}\beta(1)\alpha(2)+2\times\frac{\hbar}{2}\left(\hat{S}_{1x}\beta(1)\beta(2)+i\hat{S}_{1y}\beta(1)\beta(2)+\hat{S}_{1z}\beta(1)\alpha(2)\right)\\
&=\frac{3\hbar^2}{4}\beta(1)\alpha(2)+\frac{3\hbar^2}{4}\beta(1)\alpha(2)+2\times\left(\frac{\hbar}{2}\right)^2\left(\alpha(1)\beta(2)-i^2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right)\\
&=\frac{3\hbar^2}{2}\beta(1)\alpha(2)+\frac{\hbar^2}{2}\left(2\alpha(1)\beta(2)-\beta(1)\alpha(2)\right)\\
&=\hbar^2\alpha(1)\beta(2)+\hbar^2\beta(1)\alpha(2)
\end{aligned}$$

Therefore, $\hat{S}_{total}^2$ acting on $\dfrac{\alpha(1)\beta(2)+\beta(1)\alpha(2)}{\sqrt{2}}$ yields

$$\frac{1}{\sqrt{2}}\left[\hbar^2\alpha(1)\beta(2)+\hbar^2\beta(1)\alpha(2)+\hbar^2\alpha(1)\beta(2)+\hbar^2\beta(1)\alpha(2)\right]$$

$$=\frac{2\hbar^2}{\sqrt{2}}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

The eigenvalue is $2\hbar^2$.

$\hat{S}_{total}^2$ acting on $\dfrac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}$ yields

$$\frac{1}{\sqrt{2}}\left[\hbar^2\alpha(1)\beta(2)+\hbar^2\beta(1)\alpha(2)-\hbar^2\alpha(1)\beta(2)-\hbar^2\beta(1)\alpha(2)\right]$$

$$=\frac{1}{\sqrt{2}}\times 0\times\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]$$

The eigenvalue is 0.

P10.11) In this problem you will show that the charge density of the filled $n = 2$, $l = 1$ subshell is spherically symmetrical and that therefore $\mathbf{L} = 0$. The angular distribution of the electron charge is simply the sum of the squares of the magnitude of the angular part of the wave functions for $l = 1$ and $m_l = -1$, 0, and 1.

a) Given that the angular part of these wave functions is

$$Y_1^0(\theta,\phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^1(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\ e^{i\phi}$$

$$Y_1^{-1}(\theta,\phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\ e^{-i\phi}$$

write an expression for $\left|Y_1^0(\theta,\phi)\right|^2 + \left|Y_1^1(\theta,\phi)\right|^2 + \left|Y_1^{-1}(\theta,\phi)\right|^2$.

$$\left|Y_1^0(\theta,\phi)\right|^2 + \left|Y_1^1(\theta,\phi)\right|^2 + \left|Y_1^{-1}(\theta,\phi)\right|^2 = \frac{3}{4\pi}\cos^2\theta + \frac{3}{8\pi}\sin^2\theta + \frac{3}{8\pi}\sin^2\theta$$

b) Show that $\left|Y_1^0(\theta,\phi)\right|^2 + \left|Y_1^1(\theta,\phi)\right|^2 + \left|Y_1^{-1}(\theta,\phi)\right|^2$ does not depend on θ and ϕ.

$\frac{3}{4\pi}\cos^2\theta + \frac{3}{8\pi}\sin^2\theta + \frac{3}{8\pi}\sin^2\theta = \frac{3}{4\pi}\left(\cos^2\theta + \sin^2\theta\right) = \frac{3}{4\pi}$. This is not a function of θ and ϕ.

c) Why does this result show that the charge density for the filled $n = 2$, $l = 1$ subshell is spherically symmetrical?

If a function is independent of θ and ϕ, then it has the same value for all θ and ϕ. This is what we mean by being spherically symmetrical.

P10.15) Calculate the terms that can arise from the configuration $np^1n'p^1, n \neq n'$. Compare your results with those derived in the text for np^2. Which configuration has more terms and why?

Because the principle quantum number is different, any combination of m_l and m_s is allowed. Therefore, $S = 0$, 1 and $L = 0$, 1, and 2. Any combination of the two quantum numbers is allowed. This leads to ^{1}S, ^{1}P, and ^{1}D terms as well as ^{3}S, ^{3}P, and ^{3}D terms. The $np^1n'p^1, n \neq n'$ configuration has more terms because some of the possible terms listed above are not allowed if $n = n'$ because of the Pauli principle.

Using the method discussed in Example Problem 10.7, $M_{Lmax} = 6$ and $M_{Smax} = 3/2$. Therefore the ground state term is ^4I, which has $(2L + 1)(2S + 1) = (2\times6 + 1)(4) = 52$ states.

P10.17) How many ways are there to place three electrons into an f subshell? What is the ground-state term for the f^3 configuration, and how many states are associated with this term? See Problem P10.16.

The first electrons can have any combination of 7 m_l and 2 m_s values so that $n = 14$ and $m = 3$. The number of states is $\frac{14!}{3!(14-3)!} = 364$.

EXTRA PROBLEM

The energy levels of the hydrogen atom are given by $E = -\mu e^4/8h^2\varepsilon_0 n^2 = -13.60/n^2$. This is based on a reduced mass μ for the electron/proton system. For positronium the reduced mass is given by $\mu = m_e m_{pos}/(m_e + m_{pos}) = m_e m_e/(m_e + m_e) = m_e/2$. Thus, we can approximately give the energy level formula for the energy levels of positronium as $E = -6.80/n^2$. ($\mu \approx m_e$ for the H atom.) Therefore, $\Delta E \approx E_2 - E_1 = -1.7 - (-6.8) = 5.1$ eV.