EXAM SOLUTIONS

1) The states are eigenstates of L^2, S^2, J^2 and J_z. For 3d in hydrogen $l=2$ and $s=\frac{1}{2}$ so $j=\frac{5}{2},\frac{3}{2}$.

To evaluate $\langle \vec{L}\cdot\vec{S}\rangle$ write

$$\vec{J}=\vec{L}+\vec{S}$$

$$J^2=\vec{J}\cdot\vec{J}=(\vec{L}+\vec{S})\cdot(\vec{L}+\vec{S})=L^2+S^2+2\vec{L}\cdot\vec{S}$$

$$\vec{L}\cdot\vec{S}=\frac{1}{2}\left[J^2-L^2-S^2\right]$$

so

$$\langle \vec{L}\cdot\vec{S}\rangle=\frac{1}{2}\left[j(j+1)\hbar^2-l(l+1)\hbar^2-s(s+1)\hbar^2\right]$$

$j=\frac{5}{2}$:
$$\langle \vec{L}\cdot\vec{S}\rangle=\frac{1}{2}\left[\frac{5}{2}\cdot\frac{7}{2}-2(3)-\frac{1}{2}\left(\frac{3}{2}\right)\right]\hbar^2=\frac{1}{2}\left[\frac{35-24-3}{4}\right]\hbar^2$$
$$=\underline{\underline{+\hbar^2}}$$

$j=\frac{3}{2}$:
$$\langle \vec{L}\cdot\vec{S}\rangle=\frac{1}{2}\left[\frac{3}{2}\cdot\frac{5}{2}-2(3)-\frac{1}{2}\left(\frac{3}{2}\right)\right]\hbar^2=\frac{1}{2}\left[\frac{15-24-3}{4}\right]\hbar^2$$
$$=\underline{\underline{-\tfrac{3}{2}\hbar^2}}$$

The energy shift is $E^{(1)}=\langle V_{LS}\rangle=(g-1)\frac{e^2}{4\pi\epsilon_0}\frac{1}{2m^2c^2}\left\langle\frac{1}{r^3}\right\rangle\langle\vec{L}\cdot\vec{S}\rangle$

$$E^{(1)}=(g-1)\frac{e^2}{4\pi\epsilon_0}\frac{1}{\cancel{2}m^2c^2}\frac{\cancel{2}}{l(l+1)(2l+1)}\frac{1}{(na_0)^3}\langle\vec{L}\cdot\vec{S}\rangle \qquad \begin{matrix} n=3\\ l=2\end{matrix}$$

$$=(1)\frac{e^2}{4\pi\epsilon_0}\frac{1}{m^2c^2}\left(\frac{1}{a_0}\right)^3\frac{\langle\vec{L}\cdot\vec{S}\rangle}{(2)(3)(5)(3)^3}$$

$$=\frac{e^2}{4\pi\epsilon_0}\frac{1}{m^2c^2}\left[\frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m}\right]^{-3}\frac{\langle\vec{L}\cdot\vec{S}\rangle}{810}$$

$$=\frac{1}{810}mc^2\left(\frac{e^2}{4\pi\epsilon_0}\cdot\frac{1}{\hbar c}\right)^4\frac{\langle\vec{L}\cdot\vec{S}\rangle}{\hbar^2}$$

$j=\frac{5}{2}$	$E^{(1)}=1.789\times10^{-6}\,eV$
$j=\frac{3}{2}$	$E^{(1)}=-2.683\times10^{-6}\,eV$

2) (a) (1s) thru (3s) are filled and $\therefore$ irrelevant (only 1 possible state). $(3p)^2$ has $6 \cdot 5/2 = \boxed{15 \text{ states}}$

(b) We need the wave function to be antisymmetric.

$S=1$ symmetric $\qquad L=2,0$ symmetric

$S=0$ antisymmetric $\qquad L=1$ antisymmetric

$$\boxed{{}^1S_0 \quad {}^1D_2 \quad {}^3P_0,\ {}^3P_1,\ {}^3P_2}$$

(c) $\vec{F} = \vec{J} + \vec{I}$ where $i = \frac{1}{2}$. In general $f = |j-i|, \cdots, j+i$

STATE	${}^1S_0$	${}^1D_2$	${}^3P_0$	${}^3P_1$	${}^3P_2$
f values	$1/2$	$3/2,\ 5/2$	$1/2$	$1/2,\ 3/2$	$3/2,\ 5/2$

Check by counting total states. Expect 15×2

$$2+4+6+2+2+4+4+6 = 30 \checkmark$$

3) (a) Since the fermions are in different space quantum states we can have both symmetric and antisymmetric spin functions; ie. both singlets and triplets are allowed.

$\#$ of states $= 4$

(b) $\psi_1 = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) + \phi_2(x_1)\phi_1(x_2)\right] \cdot \frac{1}{\sqrt{2}}\left[\chi_1^+\chi_2^- - \chi_1^-\chi_2^+\right]$

$\psi_2 = \frac{1}{\sqrt{2}}\left[\phi_1(x_1)\phi_2(x_2) - \phi_2(x_1)\phi_1(x_2)\right] \chi_1^+\chi_2^-$

$\psi_3 = \frac{1}{\sqrt{2}}\left[\ " \quad - \quad " \ \right] \frac{1}{\sqrt{2}}\left[\chi_1^+\chi_2^- + \chi_1^-\chi_2^+\right]$

$\psi_4 = \frac{1}{\sqrt{2}}\left[\ " \quad - \quad " \ \right] \chi_1^-\chi_2^-$

(c) H_1 is spin independent so the spin functions give $\langle \chi_s^{m_s} | \chi_s^{m_s} \rangle = 1$ for each state. The singlet state (ψ_1) has a different space wave function than the triplets (ψ_2, ψ_3, ψ_4), so the triplets and singlet will have different energies.

H_1 is positive so all states shift up in energy. The triplet states shift up more because (with the antisymmetric space wave function) the particles are farther apart.

Prediction: —— TRIPLETS (3 states)
—— SINGLET (1 state)

(d) $E^{(1)} = \langle \psi | H_1 | \psi \rangle$ where

$$\psi = \frac{1}{\sqrt{2}} \left[\phi_1(x_1)\phi_2(x_2) \pm \phi_2(x_1)\phi_1(x_2) \right]$$

so

$$E^{(1)} = \frac{1}{2} \Big\{ \langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \rangle + \langle \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle$$
$$\pm \left[\langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle + \langle \phi_2(x_1)\phi_1(x_2) | H_1 | \phi_1(x_1)\phi_2(x_2) \rangle \right]$$

$$= E_{DIRECT} \pm E_{EXCHANGE} \quad \begin{cases} + & \text{singlets} \\ - & \text{triplets} \end{cases}$$

The energy difference between the $S=0$ and $S=1$ states is

$$\Delta E \equiv E_{SINGLET} - E_{TRIPLET}$$
$$\Delta E = 2E_{EXCH.} = 2 \langle \phi_1(x_1)\phi_2(x_2) | H_1 | \phi_2(x_1)\phi_1(x_2) \rangle$$

$$= 2 \langle \phi_1(x_1)\phi_2(x_2) | \tfrac{1}{2}k\left(x_1^2 - 2x_1x_2 + x_2^2\right) | \phi_2(x_1)\phi_1(x_2) \rangle$$

Now take each term of H_1 and write out the separate x_1 and x_2 integrals:

$$\Delta E = k\left\{\left(\int_{-\infty}^{\infty}\phi_1^*(x_1)\cancelto{0}{x_1^2}\,\phi_2(x_1)\,dx_1\right)\cdot\left(\int_{-\infty}^{\infty}\cancelto{0}{\phi_2^*(x_2)}\,\phi_1(x_2)\,dx_2\right)\right.$$

$$-2\left(\int_{-\infty}^{\infty}\phi_1^*(x_1)\,x_1\,\phi_2(x_1)\,dx_1\right)\cdot\left(\int_{-\infty}^{\infty}\phi_2^*(x_2)\,x_2\,\phi_1(x_2)\,dx_2\right)$$

$$\left.+\left(\int_{-\infty}^{\infty}\cancelto{0}{\phi_1^*(x_1)}\,\phi_2(x_1)\,dx_1\right)\cdot\left(\int_{-\infty}^{\infty}\phi_2^*\cancelto{0}{(x_2)\,x_2^2}\,\phi_1(x_2)\,dx_2\right)\right\}$$

$$\boxed{\Delta E = -2k\,\langle\phi_1|x|\phi_2\rangle\langle\phi_2|x|\phi_1\rangle}$$

This is a negative ΔE $\Rightarrow$

$E_{s=0} - E_{s=1}$ = negative $\Rightarrow$ $S=1$ is above $s=0$.