CHEM 4PB3 **Solutions to Assignment 1** OUT: Thu 7 Feb 2019
DUE: Fri 15 Feb 2019

1. What are the eigenvalues of S^2 and S_z for the spin function

$(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3))/\sqrt{3}$ ** normalization function wrong in question

S	M_S	*Spin Adapted Configuration*
3/2	+ 3/2	${}^4\Phi_{3/2} = \alpha\alpha\alpha$
3/2	+ 1/2	${}^4\Phi_{1/2} = 1/3^{1/2}(\alpha\beta\alpha + \beta\alpha\alpha + \alpha\alpha\beta)$
3/2	− 1/2	${}^4\Phi_{-1/2} = 1/3^{1/2}(\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha)$
3/2	− 3/2	${}^4\Phi_{-3/2} = \beta\beta\beta$
1/2	+ 1/2	${}^2\Phi_{1/2} = 1/6^{1/2}(\alpha\beta\alpha + \beta\alpha\alpha - 2\alpha\alpha\beta)$
1/2	+ 1/2	${}^2\Phi_{1/2} = 1/2^{1/2}(\beta\alpha\alpha - \alpha\beta\alpha)$
1/2	− 1/2	${}^2\Phi_{-1/2} = 1/6^{1/2}(\beta\alpha\beta + \beta\beta\alpha - 2\alpha\beta\beta)$
1/2	− 1/2	${}^2\Phi_{-1/2} = 1/2^{1/2}(\beta\beta\alpha - \beta\alpha\beta)$

are the **set of spin functions for 3 electrons which are in separate space orbitals** (e.g. $1s^1 2s^1 2p^1$ configuration of excited Li)

The goal of the problem is to show that the values of S, M_S for the ${}^4\Phi_{1/2}$ spin state are (3/2, +1/2)
i.e $S^2\, {}^4\Phi_{1/2} = S(S+1)\, {}^4\Phi_{1/2} = (3/2)*(5/2)\, {}^4\Phi_{1/2} = 15/4\, {}^4\Phi_{1/2}$ and
$S_Z\, {}^4\Phi_{1/2} = M_S\, {}^4\Phi_{1/2} = (+1/2)\, {}^4\Phi_{1/2}$

$$
\begin{aligned}
S^2 &= (S_1 + S_2 + S_3)\cdot(S_1 + S_2 + S_3) = S_1^{\,2} + S_2^{\,2} + S_3^{\,2} + 2(S_1\cdot S_2 + S_1\cdot S_3 + S_2\cdot S_3) \\
&= S_1^{\,2} + S_2^{\,2} + S_3^{\,2} + 2(S_{1x}\cdot S_{2x} + S_{1y}\cdot S_{2y} + S_{1z}\cdot S_{2z} + S_{1x}\cdot S_{3x} + S_{1y}\cdot S_{3y} + S_{1z}\cdot S_{3z} \\
&\qquad + S_{2x}\cdot S_{3x} + S_{2y}\cdot S_{3y} + S_{2z}\cdot S_{3z})
\end{aligned}
$$

And one can show using ladder operators (see Levine, Quantum Chem. (1991) p277)
$S_x\alpha = +1/2\beta$ and $S_y\alpha = +1/2\beta$ and $S_x\beta = +1/2\alpha$ and $S_y\beta = -1/2\alpha$
using these results and applying the operators for the i^{th} spin ONLY to the i^{th} spin function gives

$$\Phi = \{\alpha(1)\,\alpha(2)\,\beta(3) + \alpha(1)\,\beta(2)\,\alpha(3) + \beta(1)\,\alpha(2)\,\beta(3)\}/\sqrt{3}$$

Q 1 $\hat{S}^2 = (\hat{S}_1 + \hat{S}_2 + \hat{S}_3)\cdot(\hat{S}_1 + \hat{S}_2 + \hat{S}_3)$ where S_i act only on spin $|i\rangle$

$$= \hat{S}_1^2 + \hat{S}_2^2 + \hat{S}_3^2 + 2\cdot(S_1\cdot S_2 + S_1\cdot S_3 + S_2\cdot S_3)$$

and $S_i\cdot S_j = S_{i_x}|i\rangle S_{j_x}|j\rangle + S_{i_y}|i\rangle S_{j_y}|j\rangle + S_{i_z}|i\rangle S_{j_z}|j\rangle$

and $\hat{S}_x\,\alpha = \beta/2$ $\quad \hat{S}_x\,\beta = \alpha/2$ $\quad \hat{S}_z\,\alpha = \alpha/2$

$\hat{S}_y\,\alpha = -i\beta/2$ $\quad \hat{S}_y\,\beta = -i\alpha/2$ $\quad S_z\,\beta = -\beta/2$

$\hat{S}_i^2\,\alpha = 3\alpha/4$ $\quad \hat{S}^2\,\beta = 3\beta/4$

here $i = \sqrt{-1}$, $\hbar = 1$

$\hat{S}^2(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$ – use position to identify spin index

12 TERMS each 3 outcomes	①②③ $\alpha\alpha\beta$	①②③ $\alpha\beta\alpha$	①②③ $\beta\alpha\beta$	TOTAL
$\hat{S}_1^2$	$\frac{3}{4}\,\alpha\alpha\beta$	$\frac{3}{4}\,\alpha\beta\alpha$	$\frac{3}{4}\,\beta\alpha\beta$	$\frac{3}{4}\,\Psi$
$\hat{S}_2^2$	$\frac{3}{4}\,\alpha\alpha\beta$	$\frac{3}{4}\,\alpha\beta\alpha$	$\frac{3}{4}\,\beta\alpha\beta$	$\frac{3}{4}\,\Psi$
$\hat{S}_3^2$	$\frac{3}{4}\,\alpha\alpha\beta$	$\frac{3}{4}\,\alpha\beta\alpha$	$\frac{3}{4}\,\beta\alpha\beta$	$\frac{3}{4}\,\Psi$
$S_{1x}S_{2x}$	$(\beta/2)(\beta/2)\,\beta$	$(\beta/2)(\alpha/2)\,\alpha$	$(\alpha/2)(\beta/2)\,\beta$	$\frac{1}{4}(\cancel{\beta\beta\beta} + \cancel{\beta\alpha\alpha} + \cancel{\alpha\beta\beta})$
$S_{1y}S_{2y}$	$(-i\beta/2)(-i\beta/2)\,\beta$	$(-i\beta/2)(-i\alpha/2)\,\alpha$	$(-i\alpha/2)(-i\beta/2)\,\beta$	$\frac{1}{4}(\cancel{-\beta\beta\beta} \cancel{-\beta\alpha\alpha} \cancel{-\alpha\beta\beta})$
$S_{1z}S_{2z}$	$(\frac{\alpha}{2})(\frac{\alpha}{2})\,\beta$	$(\frac{\alpha}{2})(\beta/2)\,\alpha$	$(\beta/2)(\alpha/2)\,\beta$	$\frac{1}{4}\,\Psi$
$S_{1x}S_{3x}$	$(\beta/2)\,\alpha\,(\frac{\alpha}{2})$	$(\frac{\beta}{2})\,\beta\,(\frac{\beta}{2})$	$(\frac{\alpha}{2})\,\alpha\,(\frac{\alpha}{2})$	$\frac{1}{4}(\cancel{\beta\alpha\alpha} + \cancel{\beta\beta\beta} + \cancel{\alpha\alpha\alpha})$
$S_{1y}S_{3y}$	$(-i\beta/2)\,\alpha\,(-i\alpha/2)$	$(-i\beta/2)\,\beta\,(-i\beta/2)$	$(-\frac{i\alpha}{2})\,\alpha\,(-\frac{i\alpha}{2})$	$\frac{1}{4}(\cancel{-\beta\alpha\alpha} \cancel{-\beta\beta\beta} \cancel{-\alpha\alpha\alpha})$
$S_{1z}S_{3z}$	$(\frac{\alpha}{2})\,\alpha\,(\beta/2)$	$(\frac{\alpha}{2})\,\beta\,(\frac{\alpha}{2})$	$(\beta/2)\,\alpha\,(\beta/2)$	$\frac{1}{4}\,\Psi$
$S_{2x}S_{3x}$	$\alpha\,(\beta/2)(\frac{\alpha}{2})$	$\alpha\,(\frac{\alpha}{2})(\frac{\beta}{2})$	$\beta\,(\frac{\beta}{2})(\frac{\alpha}{2})$	$\frac{1}{4}(\cancel{\alpha\beta\alpha} + \cancel{\alpha\alpha\beta} + \cancel{\beta\beta\alpha})$
$S_{2y}S_{3y}$	$\alpha\,(-i\beta/2)(-\frac{i\alpha}{2})$	$\alpha\,(-\frac{i\alpha}{2})(-i\beta/2)$	$\beta\,(-i\beta/2)(-\frac{i\alpha}{2})$	$\frac{1}{4}(\cancel{-\alpha\beta\alpha} \cancel{-\alpha\alpha\beta} \cancel{-\beta\beta\alpha})$
$S_{2z}S_{3z}$	$\alpha\,(\frac{\alpha}{2})(\beta/2)$	$\alpha\,(\beta/2)(\frac{\alpha}{2})$	$\beta\,(\frac{\alpha}{2})(\frac{\beta}{2})$	$\frac{1}{4}\,\Psi$

$$\hat{S}^2\,\Psi = \frac{9}{4}\,\Psi + 2\left(\frac{3}{4}\right)\Psi = \frac{15}{4}\,\Psi = \left(\frac{3}{2}\right)\left(\frac{5}{2}\right)\Psi \implies S = 3/2$$

Spin state is a QUARTET $\left|\frac{3}{2},\frac{1}{2}\right\rangle$ $\quad (|S, M_s\rangle)$

(The $(S_{ix}S_{ix}$ and $S_{iy}S_{iy})$ generate transformed spin states that CANCEL)

1a) What is the conserved component S_z ?

$S_z = s_{z1} + s_{z2} + s_{z3}$ where the small s_z act only on the spin of the i[th] electron

so $S_z\,[(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3))/\sqrt{3}] =$

$$
\begin{aligned}
S_z = \; & s_{z1}(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)) \\
& + s_{z2}(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)) \\
& + s_{z3}(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)) \\
= \; & \left(\frac{1}{2}\right)\alpha(1)\alpha(2)\beta(3) + \left(\frac{1}{2}\right)\alpha(1)\beta(2)\alpha(3) + \left(\frac{-1}{2}\right)\beta(1)\alpha(2)\alpha(3) \\
& + \left(\frac{1}{2}\right)\alpha(1)\alpha(2)\beta(3) + \left(\frac{-1}{2}\right)\alpha(1)\beta(2)\alpha(3) + \left(\frac{1}{2}\right)\beta(1)\alpha(2)\alpha(3) \\
& + \left(\frac{-1}{2}\right)\alpha(1)\alpha(2)\beta(3) + \left(\frac{1}{2}\right)\alpha(1)\beta(2)\alpha(3) + \left(\frac{1}{2}\right)\beta(1)\alpha(2)\alpha(3) \\
= \; & \left(\frac{1}{2}\right)(\alpha(1)\alpha(2)\beta(3) + \alpha(1)\beta(2)\alpha(3) + \beta(1)\alpha(2)\alpha(3)) \; = \; \left(\frac{1}{2}\right)^4\Phi_2
\end{aligned}
$$

1b) See additional page for solution of $S^2\,{}^4\Phi_{1/2} = S(S+1)\,{}^4\Phi_{1/2} = (3/2)*(5/2)\,{}^4\Phi_{1/2} = 15/4\,{}^4\Phi_{1/2}$

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2. Of the atoms with Z <11 which have ground states of odd parity ?

(2.) PARITY is symmetry w.r.t inversion

$(x_i, y_i, z_i) \longrightarrow (-x_i, -y_i, -z_i)$

if $\hat{\Pi}_i \Psi(i) = +1\,\Psi(i)$ — state is even (gerade)

if $\hat{\Pi}_i \Psi(i) = -1\,\Psi(i)$ — state is ODD (ungerade)

For ATOMIC TERMS, the eigenvalue for a term with multiple un-paired spins is $(-1)^{\Sigma_i l_i}$

where l_i is the orbital ang momentum of unpaired spin i

Thus if all EVEN number of unpaired e^-'s $\longrightarrow$ EVEN

S[illegible] with ODD " " " " $\longrightarrow$ ODD

H 1s[1]	$\Sigma l_i = 0$	g	He $1s^2$		g
Li $1s^2 2s$	$\Sigma l_i = 0$	g	Be $1s^2 2s^2$		g
B 2p	$\Sigma l_i = 1$	u	C .. $2p^2$	$\Sigma l_i = 2$	g
N $2p^3$	$\Sigma l_i = 3$	u	O $2p^4$	$\Sigma_i = 2$	g
F $2p^5$	$\Sigma l_i = 1$	u	Ne $2p^6$	$\Sigma_0 = 0$	g

3. Why is it incorrect to calculate the experimental ground state energy of lithium as $E_{2s} + 2*E_{1s}$, where E_{2s} and E_{1s} are the experimental binding energies of the 1s and 2s electrons ?

ANSWER: Because after removing the outermost 2s electron the remaining two electrons are more tightly bound. Similarly, after removing 2 electrons the last electron is more tightly bound.

E_{2s} is energy of Li $1s^22s^1 \rightarrow$ Li $1s^22s^0$ + e- (~5 eV)
E_{1s} is energy of Li $1s^22s^1 \rightarrow$ Li $1s^12s^1$ + e- (~55 eV)

But true experimental ground state energy is energy for the process Li $1s^22s^1 \rightarrow Li^{3+}$ + 3 e-

4a. Show that the commutation relations:

$[L_x, L_y] = i\hbar L_z$ with x,y,z cyclically permuted

are equivalent to the single relationship $\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}$

(hats left off for clarity)

$$\hat{L} \times \hat{L} = \begin{vmatrix} \underline{i} & \underline{j} & \underline{k} \\ L_x & L_y & L_z \\ L_x & L_y & L_z \end{vmatrix} = (L_y L_z - L_z L_y)\,\underline{i} + (L_z L_x - L_x L_z)\,\underline{j} + (L_x L_y - L_y L_x)\,\underline{k}$$

$$= [L_y, L_z]\,\underline{i} + [L_z, L_x]\,\underline{j} + [L_x, L_y]\,\underline{k}$$

Since $[L_x, L_y] = i\hbar L_z$ cyclically the

$$\hat{L} \times \hat{L} = i\hbar\,[L_x \underline{i} + L_y \underline{j} + L_z \underline{k}] = i\hbar\,\hat{L}$$ a.e.d.

4.b Evaluate $[L_x^2, L_y]$.

4). $[\hat{L}_x^2, L_y] = (L_x \underline{L_x L_y} - \underline{L_y L_x} L_x)$ → evaluate from commutation

and $[L_x, L_y] = i\hbar L_z = L_x L_y - L_y L_x$

so $L_x L_y = i\hbar L_z + L_y L_x$ and $L_y L_x = L_x L_y - i\hbar L_z$

Thus

$$[L_x^2, L_y] = \{L_x(i\hbar L_z - L_y L_x) - (L_x L_y - i\hbar L_z) L_x\}$$

$$= i\hbar L_x L_z + L_x L_y L_x - L_x L_y L_x + i\hbar L_z L_x$$

$$= i\hbar(L_x L_z + L_z L_x)$$

5. Show that $|n,t\rangle = e^{-iE_n t/\hbar}|n\rangle$ is a valid solution of the time dependent Schroedinger equation.

$$\hat{H}(t)\,|n,t\rangle = -\frac{\hbar}{i}\frac{\partial |n,t\rangle}{\partial t}$$

$$\hat{H}(t)\,e^{-iE_n t/\hbar}|n\rangle = -\frac{\hbar}{i}\frac{\partial}{\partial t}\left[e^{-iE_n t/\hbar}|n\rangle\right]$$

and $|n\rangle$ is not f(t)

$e^{-iE_n t/\hbar}$ is a phase

so $\hat{H}(t)$ does not depend

$$e^{-iE_n t/\hbar}\,\hat{H}\,|n\rangle = -\frac{\hbar}{i}|n\rangle\frac{d}{dt}\left(e^{-iE_n t/\hbar}\right)$$

$$\cancel{e^{-iE_n t/\hbar}}\,\hat{H}\,|n\rangle = -\frac{\hbar}{i}|n\rangle\left(\frac{-iE_n}{\hbar}\right)\cancel{e^{-iE_n t/\hbar}}$$

$$\frac{\partial}{\partial x}e^{ax} = \left(\frac{da}{dx}\right)e^{ax}$$

$$\hat{H}\,|n\rangle = E_n\,|n\rangle$$

time Independent S.E.