CHEM 4PB3 **Solutions to Assignment 1** OUT: **31 Jan 2017**
DUE: **14 Feb 2017**

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. $1s^12s^12p^1$ 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
$S_Z\,{}^4\Phi_{1/2} = M_S\,{}^4\Phi_{1/2} = (+1/2)\,{}^4\Phi_{1/2}$

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

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 ith spin ONLY to the ith spin function gives

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

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

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

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

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

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

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

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 $(-1)^{\sum_i l_i}$

where l_i is the orbital ang momentum of unpaired spin i

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

Some with ODD " " " " $\longrightarrow$ ODD

H 1s[1] $\sum l_i = \emptyset$ g | He 1s[2] g

Li 1s[2]2s $\sum l_i = \emptyset$ g | Be 1s[2]2s[2] g

B 2p $\sum l_i = 1$ u | C .. 2p[2] $\sum l_i = 2$ g

N 2p[3] $\sum l_i = 3$ u | O 2p[4] $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$ $\sum l_i = 2$ g

F 2p[5] $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$ $\sum l_i = 1$ u | Ne 2p[6] $\sum l_i = 0$ 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 $1s^2 2s^1 \rightarrow$ Li $1s^2 2s^0$ + e- (~5 eV)
E_{1s} is energy of Li $1s^2 2s^1 \rightarrow$ Li $1s^1 2s^1$ + e- (~55 eV)

But true experimental ground state energy is energy for the process Li $1s^2 2s^1 \rightarrow Li^{3+}$ + 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 $[L_x, L_y] = i\hbar L_z$ cycling them

$$\hat{L} \times \hat{L} = i\hbar\,[L_x \underline{i} + L_y \underline{j} + L_z \underline{k}] = i\hbar \hat{\mathbf{L}}$$ QED

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

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

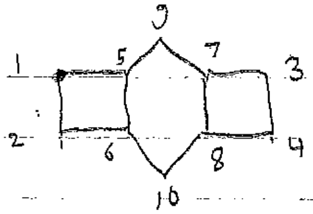
$$\cancel{e^{-iE_n t/\hbar}}\,\hat{H}\,|n\rangle = -\frac{\hbar}{i}|n\rangle\left(\frac{-iE_n}{\hbar}\right)\cancel{e^{-iE_n t/\hbar}}$$

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

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

time Independent S.E.

⑥ Hückel planar π



$z \odot \rightarrow x$, $\uparrow y$ D_{2h}

ⓐ symmetry sets (1,2,3,4) A
(5,6,7,8) B
(9,10) C

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	σxz	σyz
Γ_A	4	0	0	0	0	-4	0	0
Γ_B	4	0	0	0	0	-4	0	0
Γ_C	2	0	-2	0	0	-2	0	2

	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
$\Gamma_{A,B}$ =	0	0	1	1	1	1	0	0
Γ_C =	0	0	0	1	0	1	0	0

ⓑ SALC's

B_{2g} (2) χ_1 $\phi_1 - \phi_4 - \phi_3 + \phi_2 - \phi_4 + \phi_1 + \phi_2 - \phi_3 = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/2$
χ_2 $(\phi_5 + \phi_6 - \phi_7 - \phi_8)/2$

B_{3g} (3): χ_3 $\phi_1 - \phi_4 + \phi_3 - \phi_2 - \phi_4 + \phi_1 - \phi_2 + \phi_3 = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$
χ_4 $\frac{1}{2}(\phi_5 - \phi_6 + \phi_7 - \phi_8)$
χ_5 $\frac{1}{\sqrt{2}}(\phi_9 - \phi_{10}$

A_u (2) χ_6 $\phi_1 + \phi_4 - \phi_3 - \phi_2 + \phi_4 + \phi_1 - \phi_2 - \phi_3 = \frac{1}{2}[\phi_1 - \phi_2 - \phi_3 + \phi_4]$
χ_7 $\frac{1}{2}[\phi_5 - \phi_6 - \phi_7 + \phi_8]$

B_{1u} (3): χ_8 $\phi_1 + \phi_4 + \phi_3 + \phi_2 + \phi_4 + \phi_1 + \phi_2 + \phi_3 = \frac{1}{2}[\phi_1 + \phi_2 + \phi_3 + \phi_4]$
χ_9 $\frac{1}{2}[\phi_5 + \phi_6 + \phi_7 + \phi_8]$

χ_{10} $\frac{1}{\sqrt{2}}(\phi_9 + \phi_{10})$

ⓒ Secular Determinants

$\boxed{B_{2g}}$

$$\begin{array}{c} \chi_1 \\ \chi_2 \end{array} \begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = \begin{vmatrix} \alpha+\beta-E & \beta \\ \beta & \alpha+\beta-E \end{vmatrix} = \begin{vmatrix} x+1 & 1 \\ 1 & x+1 \end{vmatrix} = (x+1)^2 - 1 = 0$$

$H_{ii} = \alpha$

h_{ij} i,j adjacent $= \beta$

i,j not adj $\emptyset$

$H_{11} = \frac{1}{4}(\phi_1 + \phi_2 - \phi_3 - \phi_4) H (\phi_1 + \phi_2 - \phi_3 - \phi_4) = \frac{1}{4}(\alpha + \beta + \beta + \alpha + \alpha + \beta + \beta + \alpha)$
$= \alpha + \beta$

$x = (\alpha - E)/\beta$
$E = \alpha - \beta x$

$H_{22} = \frac{1}{4}(\phi_5 + \phi_6 - \phi_7 - \phi_8) = \alpha + \beta$

$H_{12} = \frac{1}{2}[(\phi_1 + \phi_2 - \phi_3 - \phi_4) H (\phi_5 + \phi_6 - \phi_7 - \phi_8) = \frac{1}{4}(\beta + \beta + \beta + \beta) = \beta$

$x^2 + 2x = 0 \Rightarrow x(x+2) = 0$ $\begin{pmatrix} x = 0 \\ x = -2 \end{pmatrix}$

E_1 =	α
E_2 =	$\alpha + 2\beta$

$\boxed{A_u}$ $\begin{vmatrix} H_{66}-E & H_{67} \\ H_{76} & H_{77}-E \end{vmatrix} = \begin{vmatrix} \alpha-\beta-E & \beta \\ \beta & \alpha-\beta-E \end{vmatrix} = \begin{vmatrix} x-1 & 1 \\ 1 & x-1 \end{vmatrix} = 0$

$H_{66} = \frac{1}{4}[(\phi_1-\phi_2-\phi_3+\phi_4) H (\phi_1-\phi_2-\phi_3+\phi_4) = \frac{1}{4}(\alpha-\beta-\beta+\alpha+\alpha-\beta-\beta+\alpha)$

$= \alpha-\beta$

$H_{67} = \frac{1}{4}(\phi_1-\phi_2-\phi_3+\phi_4)\hat{H}(\phi_5-\phi_6-\phi_7+\phi_8) = \frac{1}{4}(\beta+\beta+\beta+\beta = \beta$

$H_{77} = \frac{1}{4}(\phi_5-\phi_6-\phi_7+\phi_8)\hat{H}(\phi_5-\phi_6-\phi_7+\phi_8) = \frac{1}{4}(\alpha-\beta-\beta+\alpha+\alpha-\beta-\beta+\alpha) = \frac{1}{4}\alpha-\beta$

$(x-1)^2-1 = x^2-2x+1-1 = x^2-2x = 0 \rightarrow x=0$ $\boxed{E_6=\alpha}$

$x(x-2)$ $x=+2$ $\boxed{E_7 = \alpha-2\beta}$

$\boxed{B_{3g}}$ $\begin{vmatrix} H_{33}-E & H_{34} & H_{35} \\ H_{43} & H_{44}-E & H_{45} \\ H_{53} & H_{54} & H_{55}-E \end{vmatrix} = \begin{vmatrix} \alpha-\beta-E & \beta & 0 \\ \beta & \alpha-\beta-E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha-E \end{vmatrix} = \begin{vmatrix} x-1 & 1 & 0 \\ 1 & x-1 & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} =$

$H_{33} = \frac{1}{4}(\phi_1-\phi_2+\phi_3-\phi_4)H(\phi_1-\phi_2+\phi_3-\phi_4) = \frac{1}{4}(\alpha-\beta+\alpha-\beta+\alpha-\beta-\beta+\alpha) = \alpha-\beta$

$H_{44} = \frac{1}{4}(\phi_5-\phi_6+\phi_7-\phi_8)H(\phi_5-\phi_6+\phi_7-\phi_8) = \frac{1}{4}(\alpha-\beta+\beta-\alpha+\alpha-\beta-\beta+\alpha) = \alpha-\beta$

$H_{55} = \frac{1}{2}(\phi_9-\phi_{10})H(\phi_9-\phi_{10}) = \frac{1}{2}(\alpha+\alpha) = \alpha$

$H_{34} = \frac{1}{4}(\phi_1-\phi_2+\phi_3-\phi_4)H(\phi_5-\phi_6+\phi_7-\phi_8) = \frac{1}{4}(\beta+\beta+\beta-\beta) = \beta$

$H_{35} = \frac{1}{2\sqrt{2}}(\phi_1-\phi_2+\phi_3-\phi_4)H(\phi_9-\phi_{10}) = 0$

$H_{45} = \frac{\sqrt{2}}{4}(\phi_5-\phi_6+\phi_7-\phi_8)H(\phi_9-\phi_{10}) = \beta+\beta+\beta\ \beta = \sqrt{2}\beta$ NORM?

$(x-1)\begin{vmatrix} x-1 & \sqrt{2} \\ \sqrt{2} & x \end{vmatrix} - \begin{vmatrix} 1 & 0 \\ \sqrt{2} & x \end{vmatrix} = (x-1)[x(x-1)-2] - x = 0$

$(x-1)(x^2-x-2)-x = x^3-x^2-2x-x^2+x+2-x = 0$

x $\quad = x^3-2x^2-2x+2 = 0$

Roots from -1.17	$E_3 = \alpha+1.17\beta$
Wolfram α: 0.69	$E_4 = \alpha-0.69\beta$
2.48	$E_5 = \alpha-2.48\beta$

$\boxed{B_{1g}}$

$$\begin{vmatrix} H_{88}-E & H_{89} & H_{8\,10} \\ H_{98} & H_{99}-E & H_{9,10} \\ H_{10,8} & H_{10,9} & H_{10,10}-E \end{vmatrix} = \begin{vmatrix} \alpha+\beta-E & \beta & 0 \\ \beta & \alpha+\beta-E & \sqrt{2}\beta \\ 0 & \sqrt{2}\beta & \alpha-E \end{vmatrix} = \begin{vmatrix} x+1 & 1 & 0 \\ 1 & x+1 & \sqrt{2} \\ 0 & \sqrt{2} & x \end{vmatrix} =$$

$$H_{88} = \tfrac{1}{4}(\phi_1+\phi_2+\phi_3+\phi_4) H (+ \; + \; + \; +) = \tfrac{1}{4}(\alpha+\beta \ldots) = \alpha+\beta$$
$$H_{99} = \tfrac{1}{4}(\phi_5+\phi_6+\phi_7+\phi_8) H (+ \; + \; + \; +) = \tfrac{1}{4}(\alpha+\beta \cdots) = \alpha+\beta$$
$$H_{10,10} = \tfrac{1}{2}(\phi_9+\phi_{10}) H (\phi_9+\phi_{10}) = \tfrac{1}{2}(\alpha+\alpha) = \alpha$$
$$H_{89} = \tfrac{1}{4}(\phi_1+\phi_2+\phi_3+\phi_4) \hat{H} (\phi_5+\phi_6+\phi_7+\phi_8) = \tfrac{1}{2}(\beta+\beta+\beta+\beta) = \beta$$
$$H_{8\,10} = \tfrac{1}{4}(\phi_1+\phi_2+\phi_3+\phi_4) H (\phi_9+\phi_{10}) = 0$$
$$H_{10,9} = \tfrac{\sqrt{2}}{24}[\phi_5+\phi_6+\phi_7+\phi_8] H (\phi_9+\phi_{10}) = \tfrac{\sqrt{2}}{4}(\beta+\beta+\beta+\beta) = \sqrt{2}\beta$$

$$(x+1)\begin{vmatrix} x+1 & \sqrt{2} \\ \sqrt{2} & x \end{vmatrix} - \begin{vmatrix} 1 & 0 \\ \sqrt{2} & x \end{vmatrix} = (x+1)\left[x(x+1)-2\right] - x = 0$$

$$(x+1)(x^2+x-2) - x = x^3+x^2-2x+x^2+x-2-x = 0$$

$$x^3+2x^2-2x-2 = 0$$

x	
-2.48	$E_8 = \alpha + 2.48\beta$
-0.69	$E_9 = \alpha + 0.69\beta$
$+1.17$	$E_{10} = \alpha - 1.17\beta$

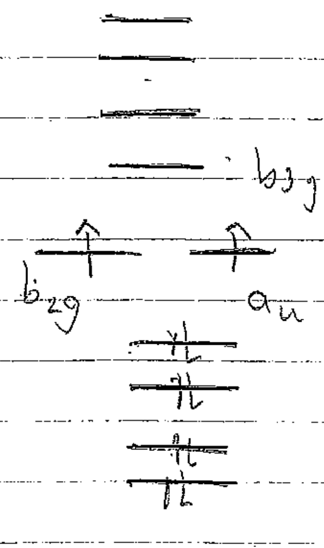
1 -1 -1 1 -1 1 1 -1 b_{3g} a_u

1 -1 -1 +1 1 -1 -1 +1 b_{3g}

1 -1 1 -1 +1 -1 +1 -1 ~~au~~ b_{2g}

1 +1 -1 -1 +1 1 -1 -1 b_{2g} a_u

(e) gs $b_{2g}^1 a_u^1 = {}^3B_{2u}$ ✓



(f) es

$b_{2g} \to b_{3g} \to (a_u^1 b_{3g}^1) \to {}^{1,3}B_{3u}$

$a_u \to b_{3g} \to (b_{2g}, b_{3g}) \to {}^{1,3}B_{1g}$

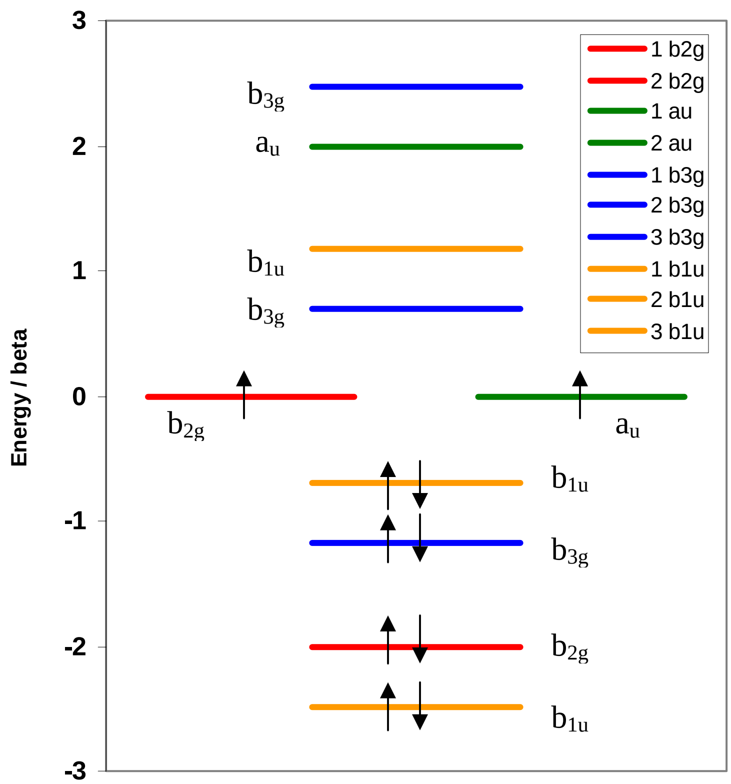
${}^3B_{2u} \to {}^3B_{3u}$ $\Gamma_{TM} = B_{1g}$ forbidden

$\boxed{{}^3B_{2u} \to {}^3B_{1g}}$ $\Gamma_{TM} = B_{3u}$ allowed

$\boxed{{}^3B_{2u} \to {}^3B_{3g}}$ can be VIBRONICALLY ALLOWED IF 1 mode of a_u, b_{2u} or b_{3u} vibrations is excited.

Ass#1 question #6

c) Quantitative energy level diagram for the pi system (Hückel, $\alpha = 0$, β is unit of E)



d) Lowest energy configuration is $(1b_{1u})^2\ (1b_{2g})^2\ (1b_{3g})^2\ (2b_{1u})^2\ (1b_{2g})^1\ (1a_u)^1$

the corresponding STATES will have symmetries from $1b_{2g} \otimes 1a_u = B_{2u}$
and the spins can be arranged either parallel (triplet) or antiparallel (singlet) ➔ $^3B_{2u}$ and $^1B_{2u}$
For states from the SAME configuration, the state with highest multiplicity is the lowest in energy, since this minimizes the electron repulsion (one of the Hund's rules)

Thus the **ground STATE** is $^3\mathbf{B_{2u}}$

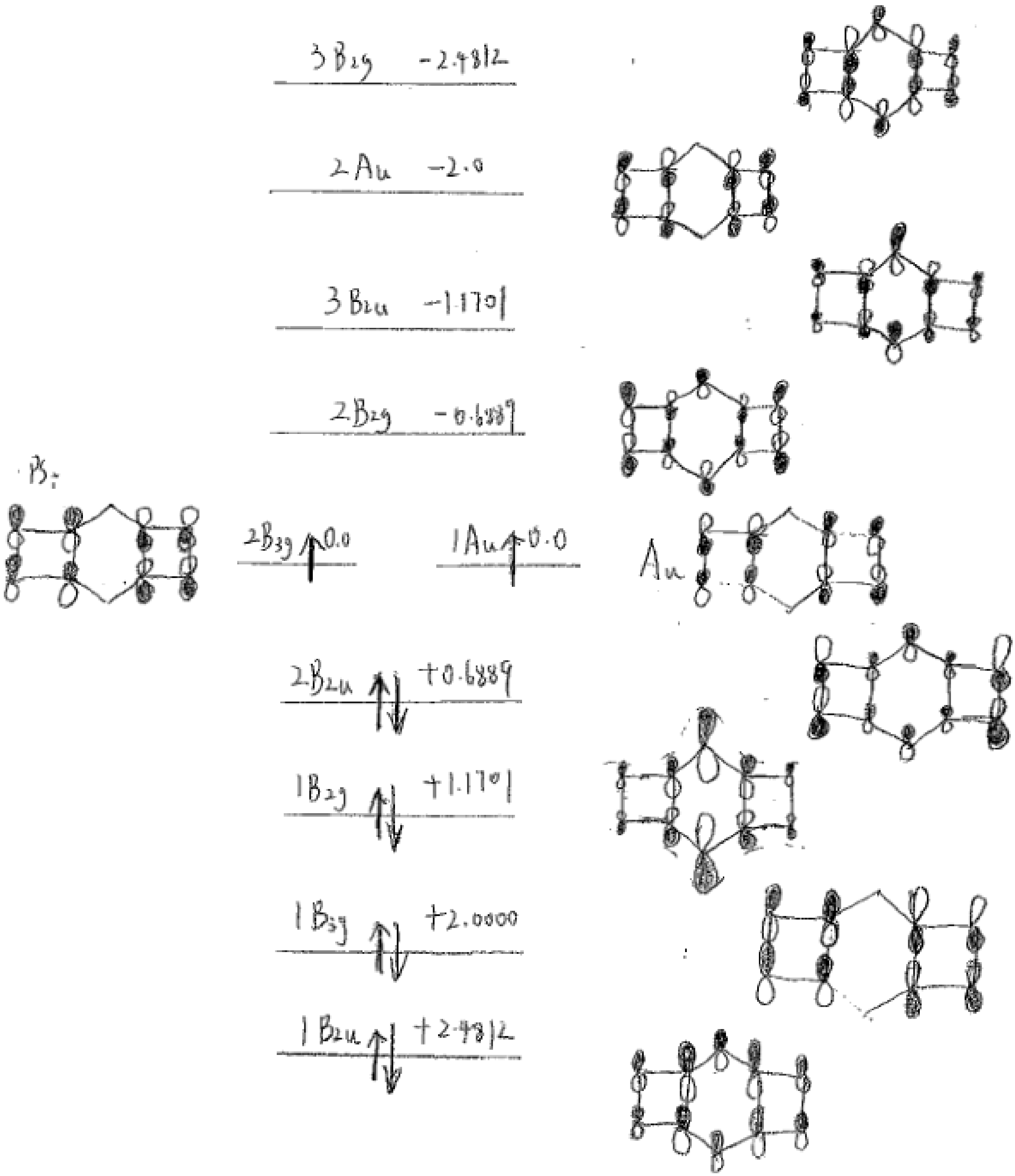
e) HOMO → LUMO can be either $b_{2g} \rightarrow b_{3g}$ OR $a_u \rightarrow b_{3g}$

$b_{2g} \rightarrow b_{3g}$ ➔ $(a_u{}^1,\ b_{3g}{}^1)$ configuration has states $^3B_{3u}$ and $^1B_{3u}$
$a_u \rightarrow b_{3g}$ ➔ $(b_{2g}{}^1,\ b_{3g}{}^1)$ configuration has states $^3B_{1g}$ and $^1B_{1g}$

f) transitions

$^3\mathbf{B_{2u}} \rightarrow {}^3B_{3u}$ has a transition symmetry of $b_{2u} \otimes b_{3u} = B_{1g}$ FORBIDDEN
$^3\mathbf{B_{2u}} \rightarrow {}^3B_{1g}$ has a transition symmetry of $b_{2u} \otimes b_{1g} = B_{3u}$ ALLOWED
DIPOLE allowed transitions (i) conserve spin multiplicity; (ii) have TM $\subset b_{1u}$, b_{2u} or b_{3u}
Only transitions to the triplet states are allowed. $^3\mathbf{B_{2u}} \rightarrow {}^1B_{3u}$ and $^3\mathbf{B_{2u}} \rightarrow {}^1B_{1g}$ are FORBIDDEN

The $^3\mathbf{B_{2u}} \rightarrow {}^3B_{3u}$ can be made into an allowed vibronic transition if an odd number of quanta of vibrational modes of a_u, b_{2u} OR b_{3u} is created in the excited state.
(NB g-modes do not work; $b_{1g} \otimes b_{1u} = a_u$ to which (x,y,z) do NOT belong)



3B2g -2.4812
2Au -2.0
3B2u -1.1701
2B2g -0.6889
B3:
2B3g 0.0
1Au 0.0
Au
2B2u +0.6889
1B2g +1.1701
1B3g +2.0000
1B2u +2.4812