CHEM 4PB3/6PB3 **Assignment 1** OUT: Tue 31-Jan-17
(4PB3-17-A1.doc) DUE: Tue 14-Feb-17

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

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

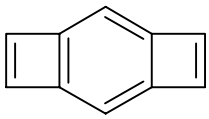
2. Of the atoms with Z <11 which have ground states of odd parity ?

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 ?

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 $\mathbf{L \times L} = i\hbar\mathbf{L}$
b Evaluate $[L_x^2, L_y]$.

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

6. For the molecule below, use **π- Hückel MO theory** to deduce the **MO energy diagram** for the π electrons. NB in Hückel treatments, the z-direction is always along the 2pπ axis. Use a right handed co-ordinate system (+z out-of-plane toward you, +x to right, +y upward).



tricyclo[6.2.0.$0^{3,6}$]deca-1(8),2,4,6,9-pentaene

a) Identify the subsets of symmetry-equivalent orbitals and determine the irreducible representations spanning each subset.
b) Use projection operators to determine normalized SALCs.
c) Within the Hückel approximations, set up and **solve the secular determinant(s)** to find the π MO energies. Prepare a π-energy level diagram. Use a quantitative vertical scale (units of β).
d) Indicate the ground state electronic configuration and give its correct state symbol.
e) Determine the symmetry(s) of the state(s) arising from HOMO→LUMO π→π* excitations (consider all possible electronic excitations involving HOMO(s) & LUMO(s) and all possible spin arrangements).
f) Determine the dipole-allowed or dipole-forbidden character of all possible HOMO → LUMO pure electronic transition(s) (v'=0 → v"=0). If forbidden, what vibrational modes could generate allowed vibronic transitions (combined electronic & vibrational changes) ?

If you want to experience more of how pencil & paper can be used for MO calculations (& earn **BONUS MARKS**)

g) Solve for the MO coefficients and sketch the MOs.
h) Deduce the π bond order between each pair of C atoms.
i)Calculate the delocalization energy - are you surprised ?

To make your life a little easier, you can get the solutions for cubic polynomial equations using the cubic equation solver at http://www.wolframalpha.com/widgets/

POINT GROUP for D_{2h}

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	