Chemistry 410A **Exam 4** **Fall 2008**

Solutions

1. **40 points.**

   (a) Draw a line through any of these integrals that approach zero when $R \to \infty$. **Solution:** Any term where the same electron is on two different nuclei goes to zero:

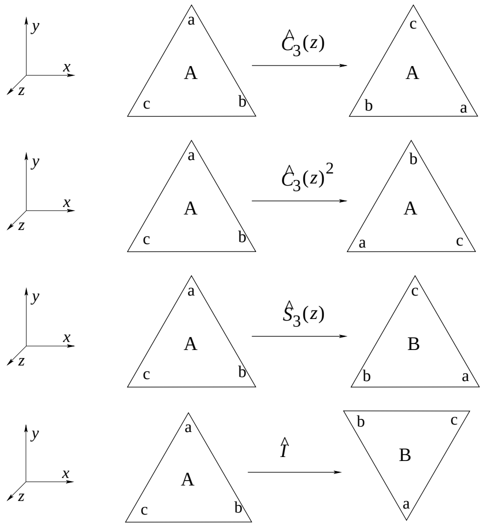
   $$i) \quad \int\int 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{A}}(2)\, 1s_{\mathrm{A}}(2)\, d\tau_1\, d\tau_2$$

   ~~$$ii) \quad \int\int 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{A}}(2)\, 1s_{\mathrm{B}}(2)\, d\tau_1\, d\tau_2$$~~

   $$iii) \quad \int\int 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{B}}(2)\, 1s_{\mathrm{B}}(2)\, d\tau_1\, d\tau_2$$

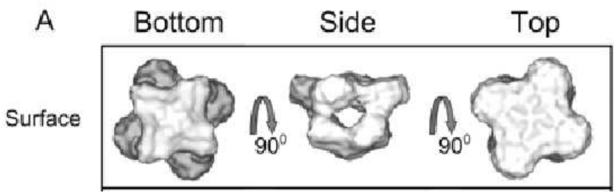
   ~~$$iv) \quad \int\int 1s_{\mathrm{A}}(1)\, 1s_{\mathrm{B}}(1)\, 1s_{\mathrm{A}}(2)\, 1s_{\mathrm{B}}(2)\, d\tau_1\, d\tau_2$$~~

   (b) The triangles below are labeled **A** on the top and **B** on the bottom. Draw the result of carrying each specified operation.



   (c) Find the direct product $a_{2g} \otimes a_{2u}$ in the point group D_{4h}. $\boxed{A_{1u}}$

2. Identify the point group of the protein Wza below.



$\boxed{C_4}$

3. Find all the representations of the electronic states resulting from the configuration $a_{1g}^2\, e_u^2$ in D_{4h}. **Solution:** The nondegenerate a_{1g} orbital is full with two electrons, but the doubly degenerate e_u is only partly full, so we take the direct product

$e_u \otimes e_u$:

D_{4h}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{C}_2'$	$2\hat{C}_2''$	$\hat{I}$	$2\hat{S}_4$	$\hat{\sigma}_h$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$
e_u	2	0	−2	0	0	−2	0	2	0	0
$e_u \otimes e_u$	4	0	4	0	0	4	0	4	0	0

The order of the group Q is 16. Now we need to decompose the reducible representation. The characters are all zero except for $\hat{E}$, $\hat{C}_2$, $\hat{I}$, and $\hat{\sigma}_h$. Therefore, we can ignore all the other terms in the sums that we use to find the coefficients for each irreducible representation. Another simplification is that we know only g representations can result from the product of two u functions, so we can ignore half the irreducible representations:

$$e_u \otimes e_u = a_1 A_{1g} \oplus a_2 A_{2g} \oplus a_3 B_{1g} \oplus a_4 B_{1g} \oplus a_5 E_g$$

$$a_1 = \frac{1}{16}\left[(4)(1) + (4)(1) + (4)(1) + (4)(1)\right] = 1$$

$$a_2 = \frac{1}{16}\left[(4)(1) + (4)(1) + (4)(1) + (4)(1)\right] = 1$$

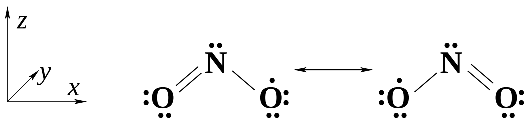
$$a_3 = \frac{1}{16}\left[(4)(1) + (4)(1) + (4)(1) + (4)(1)\right] = 1$$

$$a_4 = \frac{1}{16}\left[(4)(1) + (4)(1) + (4)(1) + (4)(1)\right] = 1$$

$$a_5 = \frac{1}{16}\left[(4)(2) + (4)(-2) + (4)(2) + (4)(-2)\right] = 0$$

$$e_u \otimes e_u = \boxed{A_{1g} \oplus A_{2g} \oplus B_{1g} \oplus B_{2g}}.$$

4. Determine the MO configuration for NO_2, a C_{2v} molecule with the resonance Lewis structures drawn below. Try to give the MO's for a given group of electrons in order of increasing energy, but don't worry about the ordering of different groups. Identify which orbitals correspond to which electron groups.



Solution: There are 7+2(8)=23 electrons in the molecule. They separate into groups that either lie in the xz plane, the plane of the molecule (core, σ bond, and lone pair electrons), or above and below the plane (π bond electrons, the unpaired electron). Those that lie in the xz plane must be symmetric under $\hat{\sigma}_{xz}$ and are either a_1 (no nodes) or b_1 (a node along the yz plane). The others are either b_2 (no yz node) or a_2 (with the yz node). Given the choice, the lowest energy one will be the one without the yz node. They break down as follows:

group	# electrons	Γ's	group	# electrons	Γ's
O $1s^2$ core	4	a_1,b_1	O lone pairs	8	a_1,b_1,a_1,b_1
N $1s^2$ core	2	a_1	N—O π bond	2	b_2
N—O σ bonds	4	a_1,b_1	O unpaired e^-	1	a_2
N lone pair	2	a_1			