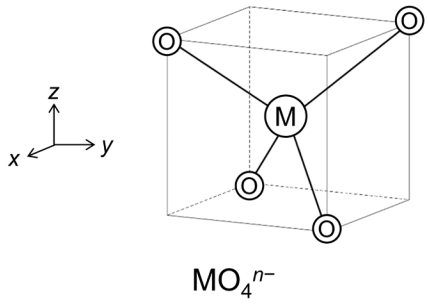
Problem Set 1
Ch153a – Winter 2023
Due: 6 January 2023

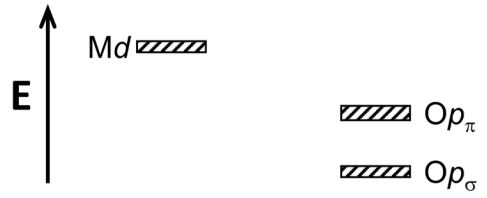
1. Consider the electronic structure of tetrahedral MO_4^{n-} anions using a basis set of five metal *d* orbitals and twelve oxygen 2*p* orbitals. A convenient configuration of the oxygen orbitals is one in which one 2*p* orbital on each O-atom is oriented parallel to the M−O bond ($2p_\sigma$), and two orbitals on each O-atom are oriented perpendicular to the M−O bond ($2p_\pi$). Recall that the matrix for a C_n rotation about the *z*-axis is:

$$\begin{bmatrix} \cos\left(\frac{2\pi}{n}\right) & \sin\left(\frac{2\pi}{n}\right) & 0 \\ -\sin\left(\frac{2\pi}{n}\right) & \cos\left(\frac{2\pi}{n}\right) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$



MO_4^{n-}

a. Complete the following table of *reducible* representations in the T_d point group for the three orbital sets M*d*, Op_σ, and Op_π.



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
M*d*					
Op_σ					
Op_π					

b. Decompose the M*d*, Op_σ, and Op_π reducible representations into their component irreducible representations.

c. Complete the qualitative molecular orbital diagram in the graphic for tetrahedral MO_4^{n-} anions using the M*d*, Op_σ, and Op_π basis set of orbitals. Label each orbital with its appropriate symmetry designation.

d. Suggest an explanation for the energy separation between the Op_σ and Op_π prior to bonding with the metal *d* orbitals.

e. For a d^0 metal center, consider the following one-electron excitations: HOMO→LUMO; HOMO→LUMO+1; HOMO−1→LUMO; HOMO−1→LUMO+1. List the term symbols of the excited states that arise from each of these excitations. Which of these transitions are electric-dipole and spin-allowed?