Ch153a
Winter 2019
Due 11 January, 2019

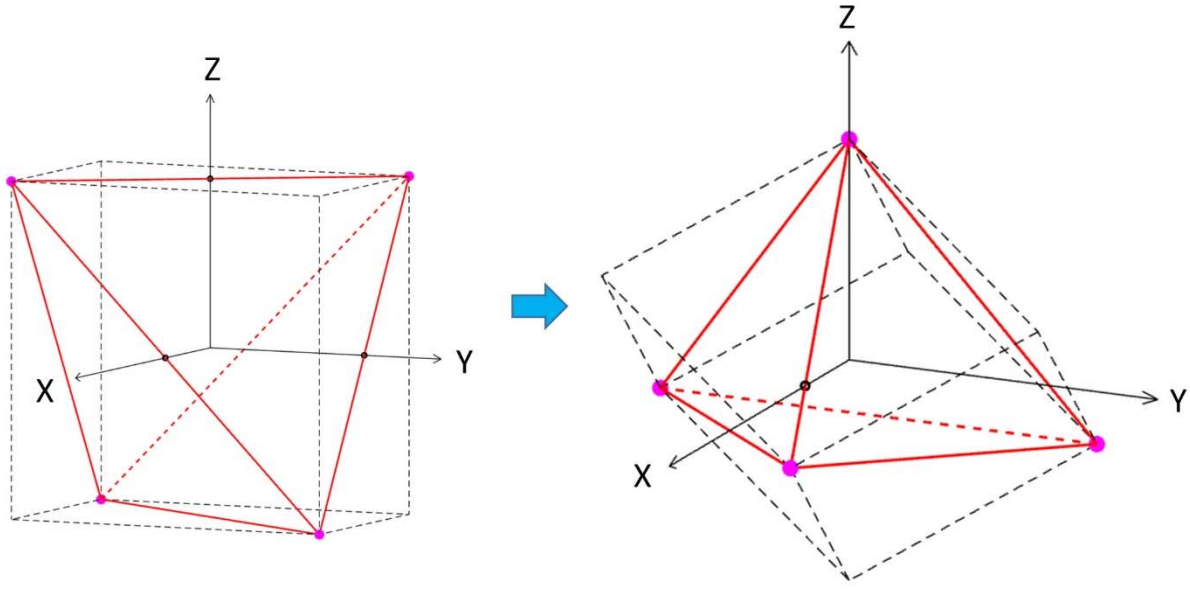
Problem Set 1

(1) In the typical representation of the tetrahedral (T_d) point group, the axis of quantization (*i.e.*, *z*-axis) is chosen to coincide with one of the three C_2 rotation axes, and the *x*- and *y*-axes coincide with the two remaining C_2 rotation axes. In this coordinate system, the real *d*-orbital wave functions form bases for the *E* and T_2 irreducible representations as follows:

$$E \quad \tfrac{1}{2}\left(2z^2 - x^2 - y^2\right) \sim d_{z^2}$$
$$\tfrac{\sqrt{3}}{2}\left(x^2 - y^2\right) \sim d_{x^2-y^2}$$

$$T_2 \quad \sqrt{3}\,(xy) \sim d_{xy}$$
$$\sqrt{3}\,(xz) \sim d_{xz}$$
$$\sqrt{3}\,(yz) \sim d_{yz}$$

In considerations of molecular electronic structure, the choice of coordinate system is arbitrary. An alternative T_d coordinate system has the z-axis coincide with one of the C_3 axes, and one edge of the tetrahedron lying in the *xz* plane as shown below.



This transformation of the tetrahedron can be accomplished by two sequential rotations: (1) a positive rotation about the *z*-axis (counterclockwise, viewed from the positive z-direction looking toward the origin); and (2) a positive rotation of $\frac{1}{2}\theta_T$ about the y-axis (where the tetrahedral angle $\theta_T \approx 109.5°$ and $\cos(\theta_T) = -\frac{1}{3}$).

The matrices for rotation of a function by θ about the three Cartesian axes are:

$$R_x = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}; \quad R_y = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}; \quad R_z = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

(a) Derive the two rotation matrices (R_1, R_2) that will transform the tetrahedron as described above, and the single matrix (R_{21}) that will accomplish this transformation.

(b) Apply the R_{21} transformation to the five real *d*-orbital functions to obtain five new functions ($\phi_{1\text{-}5}$) of the rotated tetrahedron.

(c) Determine to which irreducible representation each rotated orbital belongs (Hint: consider the σ_{xz} and $C_3(z)$ operations).

(d) Make linear combinations of the *E* and T_2 functions that give the simplest forms for the basis functions in the rotated coordinate system.

(2) Consider the tetrahedral anion MnO_4^-.

(a) Working in the T_d point group in which the *z*-axis coincides with a C_3 rotation, construct a molecular orbital diagram for MnO_4^- using the following basis orbitals: five Mn 3*d* orbitals; four O $2p_\sigma$ orbitals; and eight O $2p_\pi$ orbitals.

(b) Specify your choice (*e*, t_2, or both) of π bonding orbitals for MnO_4^-, then determine the Mn-oxo bond order.

(c) Draw Lewis structures for MnO_4^- that are consistent with your π-bonding model.

(d) Use your molecular orbital model to identify all of the electric-dipole allowed electronic transitions expected in MnO_4^-.