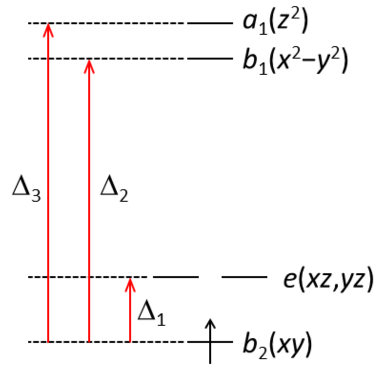
Problem Set 3
Ch153a – Winter 2026
Due: 30 January 2026

1. (10 points) Consider the ligand field energy diagram for a tetragonal d^1 metal-oxo complex. The two zero-order ground-state wave functions for this system are:



$$\left|\psi_A^{(0)}\right\rangle = |xy\rangle|\alpha\rangle$$

$$\left|\psi_B^{(0)}\right\rangle = |xy\rangle|\beta\rangle$$

where $|\alpha\rangle$ is the m_S = +1/2 spin function and $|\beta\rangle$ is the mS = −1/2 spin function. The spin-orbit coupling operator, $\widehat{H}_{SO} = \lambda\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ mixes the real *d*-orbitals.

The orbital angular momentum operators act on the *d*-orbitals according to the following table (the unit of angular momentum, $\hbar$, is taken to be equal to 1):

d-orbital	$\hat{\boldsymbol{L}}_x$	$\hat{\boldsymbol{L}}_y$	$\hat{\boldsymbol{L}}_z$
$\|x^2-y^2\rangle$	$-i\|yz\rangle$	$-i\|xz\rangle$	$2i\|xy\rangle$
$\|z^2\rangle$	$-i\sqrt{3}\|yz\rangle$	$i\sqrt{3}\|xz\rangle$	0
$\|xy\rangle$	$i\|xz\rangle$	$-i\|yz\rangle$	$-2i\|x^2-y^2\rangle$
$\|xz\rangle$	$-i\|xy\rangle$	$i\|x^2-y^2\rangle - i\sqrt{3}\|z^2\rangle$	$i\|yz\rangle$
$\|yz\rangle$	$i\|x^2-y^2\rangle + i\sqrt{3}\|z^2\rangle$	$i\|xy\rangle$	$-i\|xz\rangle$

The spin angular momentum operators act on the d-orbitals according to the following table (the unit of angular momentum, $\hbar$, is taken to be equal to 1):

	$\hat{\boldsymbol{S}}_x$	$\hat{\boldsymbol{S}}_y$	$\hat{\boldsymbol{S}}_z$
$\|\alpha\rangle$	$\frac{1}{2}\|\beta\rangle$	$\frac{i}{2}\|\beta\rangle$	$\frac{1}{2}\|\alpha\rangle$
$\|\beta\rangle$	$\frac{1}{2}\|\alpha\rangle$	$-\frac{i}{2}\|\alpha\rangle$	$-\frac{1}{2}\|\beta\rangle$

Perturbation theory gives the first order correction to the wavefunction as:

$$|\Psi_k\rangle = \left|\Psi_k^{(0)}\right\rangle - \sum_i{}' \frac{\left\langle \Psi_i^{(0)} \middle| \hat{H}_{SO} \middle| \Psi_k^{(0)} \right\rangle}{\left(E_i^{(0)} - E_k^{(0)}\right)} \left|\Psi_i^{(0)}\right\rangle$$

Find expressions for the ground-state wave functions corrected to first order, $|\Psi_A\rangle$ and $|\Psi_B\rangle$, (the energy gaps, taken to be positive, are defined in the energy level diagram and the summation runs over the other d-orbital wavefunctions, excluding $\left|\Psi_A^{(0)}\right\rangle$ and $\left|\Psi_B^{(0)}\right\rangle$).

2. (20 points) The Zeeman operator has the following form:

$$\hat{H}_Z = \beta_e \vec{\boldsymbol{B}} \cdot \left(\hat{\mathbf{L}} + g_e \hat{\mathbf{S}}\right)$$

   a. Write down the secular determinant using the first order wavefunctions from problem 1 and the Zeeman operator assuming that $\vec{\boldsymbol{B}} = \boldsymbol{B_z}$. That is, the magnetic field is parallel to the molecular *z*-axis. Solve the determinant to get the two eigenvalues in terms of β_e, $\boldsymbol{B_z}$, g_e, λ, and any energy gaps (Δ_1, Δ_2, or Δ_3). Only retain terms to the first power of the ratio (λ/Δ). What is the energy of an EPR transition with this magnetic field orientation?

   b. Write down the secular determinant using the first order wavefunctions from problem 1 and the Zeeman operator assuming that $\vec{\boldsymbol{B}} = \boldsymbol{B_x}$. That is, the magnetic field is parallel to the molecular *x*-axis. Solve the determinant to get the two eigenvalues in terms of β_e, $\boldsymbol{B_z}$, g_e, λ, and any energy gaps (Δ_1, Δ_2, or Δ_3). Only retain terms to the first power of the ratio (λ/Δ). What is the energy of an EPR transition with this magnetic field orientation?