Physics 223B: Homework 2

due January 31, 10am in Prof. Balents' mailbox at the KITP

1. **Hund's rules:** In this problem, please apply the Hund's rule analysis given in class.
   (a) Find the expected magnetic state (i.e. S, L, J quantum numbers) for Cr^{2+}, Cr^{3+}, and Cr^{4+} ions in free space, supposing the first electron is always removed from the $4s$ shell.
   (b) Repeat for Ni^{2+}, Ni^{3+} and Ni^{4+}, assuming the the two $4s$ electrons are the first to go.

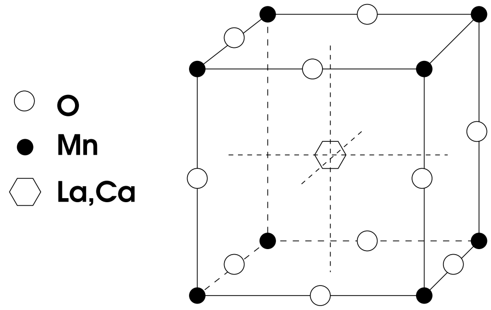
2. **Orbitals with cubic symmetry:** Consider the effect of cubic crystal fields on the five-fold degenerate d orbitals. The single particle potential on an electron, projected into this quintuplet, can in general be expressed as a function of the 3 orbital angular momentum operators, L_x, L_y, L_z, which are 5×5 matrices, since $\vec{L} \cdot \vec{L} = \ell(\ell+1)$ with $\ell = 2$.
   (a) Find the general form of the Hamiltonian as a function of $\vec{L}$, assuming cubic symmetry – that is the symmetries are those of a cube with corners at $(\pm 1, \pm 1, \pm 1)$ and the atomic nucleus at its center. Apart from a trivial constant, there should be only one free parameter not fixed by symmetry.
   (b) Show that the 5 levels split into a triplet and a doublet. Find a basis for each which is real, by using instead of spherical harmonic functions of angle, second order polynomials in x, y, z. The triplet and doublet states are called t_{2g} and e_g orbitals, respectively.

3. **Spin state transition:** Consider the cubic situation of the previous problem. Let us denote by $a = 1, 2, 3$ the t_{2g} orbitals and $a = 4, 5$ the e_g orbitals. Consider the single-ion Hamiltonian

$$H = \frac{\Delta}{2}\left[\sum_{a=4}^{5} n_a - \sum_{a=1}^{3} n_a\right] + U \sum_a n_{a\uparrow} n_{a\downarrow} - J_H \sum_{a<b} \vec{S}_a \cdot \vec{S}_b, \tag{1}$$

   where n_a is the number of electrons in orbital a, $n_{a\alpha}$ is the number with spin $\alpha = \uparrow, \downarrow$, and the sums, unless otherwise specified, are over all five orbitals. Assuming U, Δ, J_H are all positive, find the ground state spin as a function of these parameters, for the Co^{3+} ion which has 6 d electrons.

4. **Jahn-Teller effect:** The Jahn-Teller effect occurs for atoms having partially filled shells with an orbital degeneracy, for instance in $LaMnO_3$, where there is one electron in each pair of orbitally degenerate e_g levels. The "Jahn-Teller theorem" states that, if hopping of these e_g electrons from atom to atom is negligible, the crystal will distort at sufficiently low temperature and lift this orbital degeneracy.
   (a) Suppose the two nearest neighbor oxygens along the x-axis in the figure move toward the Mn a small distance u, while those along the y-axis move away from the Mn the same distance. Show that the symmetry arguments of the previous problem no longer imply orbital degeneracy for the e_g levels.



(b) If the orbital splitting after the distortion is λu, where λ is a Jahn-Teller coupling strength, argue that the total energy of the system (i.e. electronic energy plus lattice elastic energy $\frac{1}{2}ku^2$) is always lowered by making $u \neq 0$ at low enough temperature. Give a rough estimate (in terms of the parameters of the problem) of the temperature below which the lattice will distort, by equating $k_B T$ with the energy gain.