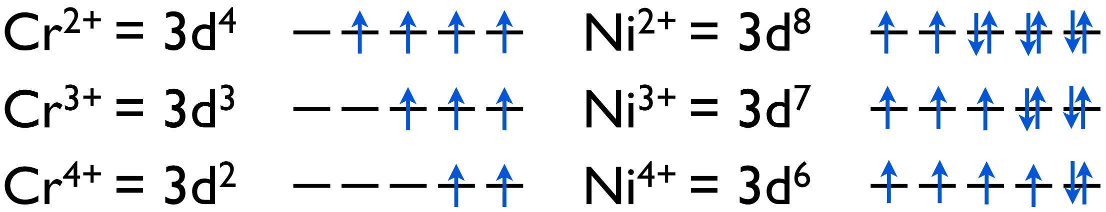
Physics 223B: Homework 2

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.



The electronic configurations are shown in the figure. It is straightforward to read off S and L from these diagrams. The results are shown in the following table.

ion	S	L	J
Cr^{2+}	2	2	0
Cr^{3+}	3/2	3	3/2
Cr^{4+}	1	3	2
Ni^{2+}	1	3	4
Ni^{3+}	3/2	3	9/2
Ni^{4+}	2	2	4

Table 1: Magnetic quantum numbers

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.

   Let us first imagine $\vec{L}$ were a classical (axial) vector, rather than an operator. It transforms just like any other vector under the rotations of the cubic group. It is also odd under time reversal, which immediately implies that the Hamiltonian must be an even function of $\vec{L}$. Consider expanding H in a Taylor series, i.e. $H = \sum_{abc} A_{abc} L_x^a L_y^b L_z^c$. Since all the cubic rotations are linear operations, terms of a given order $(a+b+c=n)$ do not mix. Let's look at second order first. First consider the simplest rotations by π around a principle axis (x, y, or z). This changes the sign of two of three components of $\vec{L}$, and we can choose any two by choice of axis. This immediately requires, at second order, only the diagonal terms L_x^2, L_y^2, L_z^2. Now consider the 3-fold rotation about the (111) axis. This cyclically permutes the x, y, and z axes. Invariance under this therefore forces the coefficients of the three diagonal terms to be equal, leaving only the sum $L_x^2 + L_y^2 + L_z^2 = \vec{L} \cdot \vec{L}$. This has full spherical symmetry so is obviously fully cubic invariant.

Now let us go to fourth order. All possible terms are of the form L_x^4, $L_x^3 L_y$, $L_x^2 L_y^2$, $L_x L_y L_z^2$, and permutations of the indices. Using the π rotations, only the L_x^4 and $L_x^2 L_y^2$ terms (and permutations) are allowed. Now adding in the cyclic permutations, we are left with just two terms, $L_x^4 + L_y^4 + L_z^4$ and $L_x^2 L_y^2 + L_x^2 L_z^2 + L_y^2 L_z^2$. Both are indeed cubic invariant, as we can easily check.

So classically we conclude that

$$H = c_0 + c_1 \vec{L} \cdot \vec{L} + c_2 (L_x^4 + L_y^4 + L_z^4) + c_3 (L_x^2 L_y^2 + L_x^2 L_z^2 + L_y^2 L_z^2) \tag{1}$$

gives the form up to fourth order in $\vec{L}$. Now let us take into account the form of the $\ell = 2$ operators. First, for these operators $\vec{L} \cdot \vec{L} = \ell(\ell+1) = 6$ is a trivial constant. So the c_1 term can be absorbed into c_0. Moreover, it is straightforward to see that $(\vec{L} \cdot \vec{L})^2 = L_x^4 + L_y^4 + L_z^4 + 2(L_x^2 L_y^2 + L_x^2 L_z^2 + L_y^2 L_z^2)$, which allows the c_3 term to also be absorbed into c_2 and c_0. So to fourth order, by a redefinition, we have

$$H = c_0 + c_1 (L_x^4 + L_y^4 + L_z^4). \tag{2}$$

Now in fact this is the *full* answer. The reason is that any higher terms of order $n \geq 5$ can rewritten in terms of lower order terms. Let us imagine writing any given polynomial interaction in terms of L_z, and $L_\pm = L_x \pm i L_y$. By commuting these around, we can always eliminate pairs of L_+ and L_- in favor of L_z, and so generally consider terms of the form $L_z^a L_+^b$ or $L_z^a L_-^b$. Consider the former. Within the $\ell = 2$ states, we must have $b \leq 4$, otherwise L_+^b simply annihilates all the states, as there is no level which can be raised more than 4 times. Now whatever b is, after acting b times on a state, the L_z eigenvalue must be at least $-2+b$. That means the total number of possible eigenvalues of L_z acting after L_+^b is $2-(-2+b)+1 = 5-b$. For example, if $b=4$, then there is only one choice, $L_z = +2$, after the action of L_+^4. So we can just set $L_z = 2$ in such a term,i.e. $L_z L_+^4 = 2 L_+^4$. For smaller b, where there are $5-b$ eigenvalues of L_z, we can always write L_z^a in terms of a linear combination of $1, L_z, \cdots, L_z^{4-b}$. Thus in general the only terms we need to consider are those with $a \leq 4-b$. Then the total powers of L are $n = a+b \leq 4$. The same reasoning applies to the L_- terms. Thus only terms up to overall fourth order in L_μ need be included, so Eq. (2) is the full answer.

(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.

We just have to diagonalize H in Eq. (2). Looking up the forms of the spin operators and using a little algebra, we obtain (dropping the overall constant c_0)

$$H = c_1 \begin{pmatrix} 21 & 0 & 0 & 0 & 3 \\ 0 & 18 & 0 & 0 & 0 \\ 0 & 0 & 24 & 0 & 0 \\ 0 & 0 & 0 & 18 & 0 \\ 3 & 0 & 0 & 0 & 21 \end{pmatrix}, \tag{3}$$

which is in the usual basis of L_z eigenstates. It is very easy to diagonalize this. There are two states with energy $24c_0$, a basis of which is

$$|m=0\rangle, \qquad \frac{1}{\sqrt{2}}\left(|m=2\rangle + |m=-2\rangle\right), \tag{4}$$

while the other three states have energy $18c_0$, for which we can choose the basis

$$|m=1\rangle, \qquad |m=-1\rangle, \qquad \frac{1}{\sqrt{2}}\left(|m=2\rangle - |m=-2\rangle\right). \tag{5}$$

Now we should rewrite this answer in terms of polynomials of x, y, z as requested. This is just a matter of noting that the states represent spherical harmonics, i.e. $|m\rangle \propto Y_{2m}(\theta,\phi)$ and using the known forms for these, rewriting using $\sin\theta e^{\pm i\phi} = (x \pm iy)/r$ and $\cos\theta = z/r$. For example, $Y_{22} \sim \sin^2\theta e^{2i\phi} \sim (x+iy)^2/r^2$. We do not care about the overall radial dependence, so it is convenient to multiply everything by a factor of r^2 to obtain simple polynomials. Then $|\pm 2\rangle \sim (x \pm iy)^2$, $|\pm 1\rangle \sim z(x \pm iy)$ and $0\rangle \sim 3z^2 - r^2 \sim 2z^2 - x^2 - y^2$. Using these relations we find that the doublet of levels is spanned by the two states

$$|e_g, 1\rangle \sim 2z^2 - x^2 - y^2, \qquad |e_g, 2\rangle \sim x^2 - y^2, \tag{6}$$

and the triplet is spanned by

$$|t_{2g}, 1\rangle \sim yz, \qquad |t_{2g}, 2\rangle \sim xz, \qquad |t_{2g}, 3\rangle \sim yz. \tag{7}$$

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

$$H = \frac{\Delta}{2}\left[\sum_{a=4}^{5} n_a - \sum_{a=1}^{3} n_a\right] + U\sum_a n_{a\uparrow}n_{a\downarrow} - J_H \sum_{a<b} \vec{S}_a \cdot \vec{S}_b, \tag{8}$$

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.

Here there is a competition between the e_g-t_{2g} splitting Δ, which favors filling the t_{2g} shell, and U and J_H, which favor unpaired electrons, which are forced into the e_g levels. We need to compare their energies. First consider the state with the filled t_{2g} shell. The spin is zero for all orbitals in this case, so we have

$$E_{S=0} = -3\Delta + 3U. \tag{9}$$

Now we can consider the states with two unpaired electrons. We place one electron in the e_g shell. To minimize the Hund's coupling, we should put the two unpaired electrons in a triplet state. For the two unpaired electrons, there is a term $-J_H \vec{S}_1 \cdot \vec{S}_2 = -\frac{J_H}{2}(\vec{S}_1 + \vec{S}_2)^2 + \frac{3}{4}J_H = -J_H + \frac{3}{4}J_H = -J_H/4$. Hence

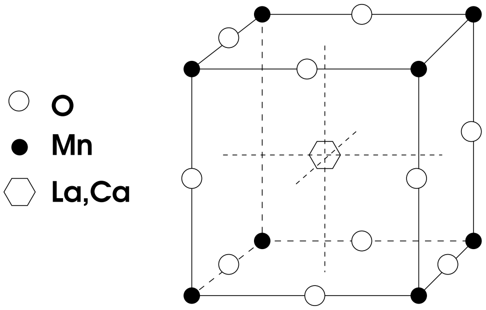
$$E_{S=1} = -2\Delta + 2U - \frac{1}{4}J_H. \tag{10}$$

Finally, we can have four unpaired electrons, placing two in the e_g shell, and aligning all spins into an $S = 2$ state. The Hund's term in this case is $-J_H \sum_{a>b=2}^{5} \vec{S}_a \cdot \vec{S}_b = -\frac{J_H}{2}(\sum_{a=2}^{5} \vec{S}_a)^2 + 2J_H \times \frac{3}{4} = -3J_H + \frac{3}{2}J_H = -\frac{3}{2}J_H$. Hence

$$E_{S=2} = -\Delta + U - \frac{3}{2}J_H. \tag{11}$$

Now we can compare energies. The $S = 0$ level is lower than both other levels if $\Delta > U + 3/4J_H$. The $S = 2$ level is lowest if $\Delta < U + 3/4J_H$. One can check that the $S = 1$ level is never the ground state.

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.

   Well, it is pretty clear that in this way the x and y axes become different from the z axis. So a term of the form L_z^2 would become allowed. Looking back at the e_g eigenstates in Eq. (4), it is clear this will split them. Another way to see this is to recognize that the $x^2 - y^2$ and $2z^2 - x^2 - y^2$ states are equivalent in energy because of rotations which mix x, y with z. These are all removed by the distortion. Many other arguments could be given here.

(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.

If the splitting of the two orbitals is λu, then the energy is lowered by the absolute value of this since the lower energy is occupied (actually we may not be sure where the energy zero is, so if we really want to, we can multiply this by some fractional factor $c < 1$). The total energy becomes

$$E_{tot} = -c\lambda|u| + \frac{1}{2}ku^2. \tag{12}$$

Minimizing this gives

$$E_{tot} = -\frac{c^2\lambda^2}{2k} < 0. \tag{13}$$

The lattice would distort when $T \sim \frac{c^2\lambda^2}{2kk_B}$.