Exercises for

Computational Modeling of Quantum Materials

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Exercise 4: Monday, March 4th, 2024

1. Exchange interaction

In this exercise, we compute the magnetic ground state and the exchange interaction of the perovskite-oxide compound strontium manganite ($SrMnO_3$), which possesses a rich strain- and temperature-dependent magnetic phase diagram. When logged into the workstation, copy the SrMnO3_input_files folder from the /home/vasp_input directory to your Calculations folder. $SrMnO_3$ is an antiferromagnetic insulator at low temperatures, where the $3d$ spins of the manganese ions start ordering below the Neél temperature of $T_N = 175$ K. We will perform spin-polarized calculations, which we switch on by adding the following flags to the INCAR file:

```
### Spin polarization

ISPIN   =  2
MAGMOM  =  2*0 -3  3  6*0
```

ISPIN=2 switches on spin-polarized calculations and MAGMOM determines the number of unpaired spins on each of the ions. MAGMOM takes as many entries as there are atoms in the unit cell. Check the orbital configuration of the ions in the compound (e.g. using ptable.org → electrons) and verify that the values specified for MAGMOM above reflect the correct ionic configuration.

In order to improve the quality of the calculations, we will apply the Perdew-Burke-Ernzerhof implementation of the generalized gradiant approximation revised for solids (PBEsol), which we do using the GGA flag. Furthermore, we need to add a non-spherical gradient contribution, which is important for an accurate description of $3d$ elements, and which we set using the LASPH tag. The INCAR therefore further contains the following lines:

```
### GGA

GGA    =  PS
LASPH  =  .TRUE.
```

$SrMnO_3$ is a strongly correlated material, due to the localized manganese $3d$ orbitals. We therefore require a DFT+U treatment of the antiferromagnetic insulating state, as discussed in the lecture. In order to activate DFT+U in VASP, we need to set the following flags in the INCAR file:

```
### DFT+U

LDAU      = .TRUE.
LDAUTYPE  = 1
LDAUL     = -1  2 -1
LDAUU     =  0.0  3.0  0.0
LDAUJ     =  0.0  0.0  0.0
LDAUPRINT = 1
LMAXMIX   = 6
```

LDAU switches on the Hubbard correction and LDAUTYPE chooses the type of implementation, which here is the rotationally invariant formalism according to Liechtenstein et al. LDAUL chooses to which orbital on which ion the Hubbard correction is added. The three columns represent the three types of ions in the unit cell, Sr, Mn, and O, and the assigned values determine the orbitals ($s = 0$, $p = 1$, $d = 2$, and -1 means no correction added). LDAUU and LDAUJ determines the magnitude of the U and J parameters (in eV) that are added to the respective orbitals. We follow previous studies, for example Edström & Ederer (2018) (reference on the Moodle), and set a correction of $U = 3$ eV on the Mn $3d$ orbital. LDAUPRINT specifies how much information about the spins is printed in the OUTCAR file and LMAXMIX is a parameter specifying the treatment of the orbital-dependent charge densities.

Task 1: First, we will verify that the antiferromagnetic spin configuration really describes the ground state. Perform a total-energy calculation with VASP for the antiferromagnetic state, the ferromagnetic state, and the nonmagnetic state. For the ferromagnetic state, you will need to adjust the MAGMOM flag accordingly. For the nonmagnetic state, you can simply switch off the spin-polarized calculation by setting ISPIN=1. Which state has the lowest energy?

The Heisenberg model describes the magnetic state of a material through the exchange interaction and the corresponding Hamiltonian can be written as

$$H = \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j. \tag{1}$$

$J > 0$ supports antiferromagnetic ordering of the spins, whereas $J < 0$ supports ferromagnetic ordering. In principle, the indices i and j run over all pairs of Mn ions in the crystal, but we will limit ourselves to the dominant contribution of nearest-neighbor interaction here, $J_{12} \equiv J$. Each Mn ion has 6 nearest neighbors, and the Heisenberg model yields the following energies for the antiferromagnetic and ferromagnetic states (assuming normalized classical spins, $|\mathbf{S}_i| = 1$):

$$E_{\text{AFM}} = -6J, \quad E_{\text{FM}} = 6J. \tag{2}$$

We can therefore extract the exchange interaction by computing the total energies of the two states as

$$J = \frac{E_{\text{FM}} - E_{\text{AFM}}}{12}. \tag{3}$$

Task 2: Compute the exchange interaction J for $SrMnO_3$ and compare it to values found in literature, for example in Edström & Ederer (2018). What parts are we missing in our simplified calculation?

2. Strain-dependent magnetic order

Perovskite oxides possess rich phase diagrams as a function of strain, pressure, and temperature. Strain can be induced by growing the material onto a substrate with a different lattice constant, therefore forcing the grown material into a different geometry than it would prefer on its own. This method provides a powerful tool to control the properties of materials through modifications of the symmetry and geometry of the crystal lattice. In this part of the exercise, we will compute the exchange interaction in $SrMnO_3$ as a function of an applied tensile strain. (Tensile strain leads to an increase of the lattice constant, whereas compressive strain leads to a reduction.) In the simplest approximation, the effect of tensile strain can be considered as an increase of the lattice constant of the cubic crystal.

Task: Create ten structures with a strain, ϵ, varying from 0% to 5% (meaning a 5% increase of the lattice constant) and compute the exchange interaction for each one of them. Plot the energies of the antiferromagnetic and ferromagnetic states, as well as the exchange interaction as a function of the strain, $E_{\mathrm{AFM}}(\epsilon)$, $E_{\mathrm{FM}}(\epsilon)$, and $J(\epsilon)$. At which magnitude of strain does the material undergo a phase transition from the antiferromagnetic to the ferromagnetic state?