Exercises for

Computational Modeling of Quantum Materials

Dr. Dominik Juraschek

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Exercise 3: Monday, February 19th, 2024

1. Ferroelectric polarization

In this exercise, we compute the ferroelectric polarization of the prototypical perovskite-oxide compound barium titanate ($BaTiO_3$). When logged into the workstation, copy the BaTiO3_input_files folder from the /home/vasp_input directory to your Calculations folder. In the folder, you will find the regular VASP input files, INCAR, KPOINTS, and POTCAR, as well as two POSCAR files, one for the high-temperature cubic structure, and one for the low-temperature tetragonal structure. $BaTiO_3$ undergoes a paraelectric to ferroelectric phase transition when cooled below 120° C, where it turns from a centrosymmetric cubic phase into a noncentrosymmetric tetragonal phase. Due to the breaking of inversion symmetry, a ferroelectric polarization arises.

The ferroelectric polarization can be calculated by a sum over all individual dipole moments generated by the displaced ions in the unit cell,

$$P_i = \frac{1}{V_c} \sum_n Z^*_{n,ij} u_{n,j}. \tag{1}$$

The above equation is similar to that of the mode effective charge that you have encountered in exercise 2. Here, $u_{n,j}$ are the displacements of the ions in the tetragonal structure with respect to the cubic structure. V_c is the unit-cell volume and $Z^*_{n,ij}$ is the Born effective charge tensor of the tetragonal structure.

Task: Compute the Born effective charge tensor for the tetragonal structure with VASP. (You will need to adjust the INCAR file accordingly, as done in exercise 2.) Extract the displacement vectors of the ions by subtracting the direct coordinates of the ions in the cubic structure from those of the ions in the tetragonal structure. Compute the ferroelectric polarization in units of $\mu C/cm^2$ and compare it to values you can find for $BaTiO_3$ in literature. For all calculations, use the default values given for ENCUT and KPOINTS. (No convergence testing or structural optimization are necessary.)

2. Double-well potential

Starting from the cubic structure, the displacements of the ions along all spatial directions $(\pm x, \pm y, \pm z)$ are symmetrically equivalent and the energies of the respective tetragonal structures therefore degenerate. Along one particular spatial direction (in our case $\pm x$), the potential energy of the lattice forms a double-well potential, where the two minima corresponding to the $\pm x$ tetragonal structures are separated by an energy

barrier. The height of the energy barrier determines whether the electric polarization can be reversed through the application of an electric field or not. In a ferroelectric material, the direction of polarization can be switched, whereas in other polar materials a polarization may exist, but is locked in place. We will in the following map out the double-well potential of the crystal lattice. In order to do so, we will need to displace the ions along the tetragonal direction of the unit cell and compute the total energies and polarizations of the corresponding structures as a function of the displacement amplitude.

Task 1: Create a POSCAR with a switched ferroelectric polarization, by inversion of the ionic coordinates along the x axis with respect to the cubic coordinates. Then, create seven intermediate structures between the two states, so that the middle one contains exactly the cubic coordinates. Furthermore, create four structures with increased tetragonal displacements to each of the $\pm x$ directions. The ionic displacements in the resulting 17 structures (2 at minima, 7 intermediate, 2×4 with increased displacements) should be uniformly spaced. Hint: Work with a dimensionless displacement amplitude, Q, whose value is ± 1 at the respective minima structures and 0 at the cubic coordinates. The displacements of the individual ions are then given by $Qu_{n,j}$.

Task 2: Perform total-energy calculations for each of the structures with VASP. Plot the total energy (in eV) as a function of the ferroelectric polarization (in $\mu\mathrm{C/cm}^2$) (which in turn of course is a function of the dimensionless amplitude). Fit the curve to a polynomial function, $V = \alpha P^2 + \beta P^4$. Shift the energy scale such that the peak of the energy barrier is set to $V = 0$. Extract the signs and magnitudes of the coefficients from the fit. What is the height of the energy barrier in eV? Estimate the electric field strength (in V/m) that is necessary to overcome the barrier, by computing the electric dipole coupling $V_{\mathrm{edc}} = -p_x E$, where $p_x = P_x V_c$.