Exercises for

Computational Modeling of Quantum Materials

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Exercise 2: Monday, January 29th, 2024

1. Convergence and geometric optimization

When logged into the workstation, copy the MgO_input_files folder from the /home/ vasp_input directory to your Calculations folder. In there, you will find the input files, INCAR, KPOINTS, POSCAR, and POTCAR for magnesium oxide (MgO). As you have learned from the previous exercise, before we proceed to the actual calculations of physical properties, we need to perform a convergence test for the ENCUT and KPOINTS parameters, as well as a geometric optimization in order to obtain the ground-state MgO structure. You will note that the INCAR file contains additional lines:

```
### Accuracy

PREC    =  Accurate
ADDGRID = .TRUE.
```

These enhance the grid density for the internal Fast Fourier Transform (FFT) routine from real to reciprocal lattice and are recommended for accurate calculations of forces that we will need for the calculations of phonon modes.

Task: Redo tasks 2. (convergence testing) and 3. (geometric optimization) as in exercise 1, now for MgO. Reuse and adapt the scripts you've created for Si. The relaxed structure that you obtain here will serve as the basis for the next calculations.

2. Lattice dynamics

Last week, we computed the electronic band structure and density of states. In this exercise, we will compute phononic properties, including phonon eigenfrequencies and eigenvectors. For simplicity, we will focus only on the center of the Brillouin zone (Γ point). Even the knowledge of just the Γ-point phonons can tell us a lot about the properties of a material, such as the interaction with light in the infrared spectral region. The momentum of light is negligible compared to the crystal momentum of lattice vibrations (up to the x-ray spectrum), and all interaction therefore happens close to or approximately at the Brillouin-zone center.

The potential energy around the equilibrium position of the atoms can be regarded as harmonic. This allows us to describe the motion of the atoms as harmonic oscillators in the simplest approximation, with a linear restoring force. Remember the harmonic oscillator of a spring pendulum in 1D. The kinetic and potential energies are given by

$$T(\dot{x}) = \frac{1}{2}M\dot{x}^2, \quad V(x) = \frac{1}{2}Kx^2, \tag{1}$$

where M is the mass of the pendulum and K is the spring constant. The restoring force is given by $F = -V'(x) = -Kx$ and the spring constant is given by $K = -V''(x)$. At the same time, the force is given by $F = M\ddot{x}$, resulting in the equation

$$M\ddot{x} + Kx = 0. \tag{2}$$

We can solve this equation by the ansatz $x(t) = A\exp(i\omega t)$, which yields

$$\underbrace{\frac{K}{M}}_{\equiv D} - \omega = 0. \tag{3}$$

Now let us extend this to three dimensions, $\mathbf{u} = (u_x, u_y, u_z)$, and multiple connected springs. The kinetic and potential energies are then given by

$$T(\dot{u}) = \frac{1}{2}\sum_{ni} M_n \dot{u}_{ni}^2, \quad V(u) = \frac{1}{2}\sum_{ni,mj} \Phi_{ni,mj} u_{ni} u_{mj}. \tag{4}$$

Here, indices n and m run over all atoms in the unit cell and indices i and j denote spatial coordinates. M_n is the atomic mass, generally given in atomic mass units. Φ is called the force-constant matrix and the component $\Phi_{ni,mj}$ describes the force that an atom n experiences in direction i, when another atom m is displaced along direction j. The restoring force is given, equivalently to the 1D case, by $F_{ni} = -\partial V(u)/(\partial u_{ni}) = -\sum_{mj}\Phi_{ni,mj}u_{mj}$, and so is the force constant, $\Phi_{ni,mj} = -\partial^2 V(u)/(\partial u_{ni}\partial u_{mj})$. The equation of motion therefore reads

$$M_n\ddot{u}_{ni} + \sum_{mj}\Phi_{ni,mj}u_{mj} = 0. \tag{5}$$

It can be solved by an ansatz $u_{ni} = q_{ni}\exp(i\omega t)/\sqrt{M_n}$, which leads to the secular equation for lattice vibrations,

$$\sum_{mj}\underbrace{\frac{\Phi_{ni,mj}}{\sqrt{M_n M_m}}}_{D_{ni,mj}} q_{mj} - \omega^2 q_{ni} = 0, \tag{6}$$

where D is called the dynamical matrix. Diagonalization of the dynamical matrix will give us the eigenvalues ω^2, as well as the eigenvectors, q_{ni}, of the phonon modes.

In a regular total-energy calculation, VASP automatically computes the forces between the atoms (in units of eV/Å), which can be found in the OUTCAR file:

```
POSITION                                        TOTAL-FORCE (eV/Angst)
-----------------------------------------------------------------
0.00000    0.00000    0.00000    -0.000000   -0.000000   -0.000000
2.10000    2.10000    2.10000     0.000000    0.000000    0.000000
-----------------------------------------------------------------
```

The first three columns contain the positions of the ions in Cartesian coordinates and the next three columns contain the forces acting on the individual ions, (F_{nx}, F_{ny}, F_{nz}). There are two rows for the two atoms in the MgO unit cell. Because our system has perfect cubic symmetry, the forces are zero by construction, when the ions sit on their respective equilibrium positions.

We will construct the force-constant matrix (and accordingly the dynamical matrix) using a finite-differences approach: displace each of the atoms in the unit cell in each Cartesian direction and perform a total-energy calculation for each of the configurations to obtain the forces from the OUTCAR file. To make your life easier in this process, you may want to convert the POSCAR file to Cartesian coordinates. In order to do so, replace "Direct" by "Cartesian" in the POSCAR and replace the respective atomic coordinates below with the Cartesian values. You can either compute those values yourself or take them directly from the OUTCAR (see above).

We can compute the force constant upon displacement of a single atom in one Cartesian direction as

$$\Phi_{ni,mj} = -\frac{F_{ni}}{u_{mj}}. \tag{7}$$

For each of the atoms, choose a displacement of $u_{mj} = 0.01$ Å. Assuming there are N atoms in the unit cell, the force-constant matrix reads

$$\Phi = \begin{pmatrix} \Phi_{1x,1x} & \Phi_{1x,1y} & \Phi_{1x,1z} & \Phi_{1x,2x} & \cdots & \Phi_{1x,Nz} \\ \Phi_{1y,1x} & \Phi_{1y,1y} & & & & \vdots \\ \Phi_{1z,1x} & & \ddots & & & \vdots \\ \Phi_{2x,1x} & & & \ddots & & \vdots \\ \vdots & & & & \ddots & \vdots \\ \Phi_{Nz,1x} & \cdots & \cdots & \cdots & \cdots & \Phi_{Nz,Nz} \end{pmatrix}. \tag{8}$$

Take a moment to understand how the indices increase with rows and columns. From the force-constant matrix, you can directly construct the dynamical matrix as

$$\begin{pmatrix} \frac{\Phi_{1x,1x}}{\sqrt{M_1 M_1}} & \cdots & \cdots & \cdots & \cdots & \frac{\Phi_{1x,Nz}}{\sqrt{M_1 M_N}} \\ \vdots & \ddots & & & & \vdots \\ \vdots & & \ddots & & & \vdots \\ \vdots & & & \ddots & & \vdots \\ \vdots & & & & \ddots & \vdots \\ \frac{\Phi_{Nz,1x}}{\sqrt{M_N M_1}} & \cdots & \cdots & \cdots & \cdots & \frac{\Phi_{Nz,Nz}}{\sqrt{M_N M_N}} \end{pmatrix}. \tag{9}$$

Task: Perform the force calculations for the displaced structures in VASP and compute the force constants. Then, construct the dynamical matrix and calculate the phonon eigenfrequencies, $\Omega/(2\pi)$, in units of THz, as well as the eigenvectors by numerically diagonalizing it.

3. Dielectric properties

The electric susceptibility describes the response of a material to an externally applied electric field. In metals, this will result in an electrical current, whereas in semiconductors and insulators, such as MgO, this will result in a dielectric displacement of charges. The electric field can be static, such as generated by a capacitor, or time dependent, such as the electric field component of light. The frequency-dependent electric susceptibility, $\chi(\omega)$, is therefore a central quantity of interest for the description of light-matter interactions in solids. The susceptibility is defined by how much of an electric polarization is induced by the applied electric field,

$$\mathbf{P}(\omega) = \varepsilon_0\chi(\omega)\mathbf{E}(\omega). \tag{10}$$

The polarization, $\mathbf{P}$, and the electric field, $\mathbf{E}$, are both vectors, whereas the susceptibility is a tensor. All quantities (except the vacuum permittivity, ε_0, which is a natural constant) are generally frequency dependent. The limit $\omega \to 0$ is described by the static electric susceptibility, $\chi(0)$.

There are two major contributions to the electric susceptibility: 1) a polarization can arise from a deformation of the electron cloud around the nucleus, and 2) a polarization can arise from a displacement of the ions from their equilibrium positions. Both contributions occur simultaneously, but can be described independently in linear order. The electric susceptibility therefore consists of two parts: the electronic contribution, χ_{el}, and the lattice contribution, χ^{lat}, with

$$\chi(\omega) = \chi^{\text{el}}(\omega) + \chi^{\text{lat}}(\omega). \tag{11}$$

We will in the following compute $\chi(\omega)$ for MgO.

3.1 Electronic contribution to the electric susceptibility

First, we will compute the frequency-dependent electronic contribution to the electric susceptibility, $\chi^{\text{el}}(\omega)$. The internal VASP routine that we will be using calculates the dielectric function instead - do you remember how the dielectric function and the electric susceptibility are connected? The response of the material to a time-dependent electric field can be described in terms of (virtual) transitions of electrons between the valence and conduction bands, such as upon absorption of a photon. Therefore, the frequency-dependent electric susceptibility/dielectric function are often called *optical* susceptibility/dielectric function. The imaginary part of the dielectric function, $\varepsilon^{(2)}$, is computed through a summation over these transitions,

$$\varepsilon^{(2)}(\omega) \propto \sum_{v,c,\mathbf{k}} 2\omega_{\mathbf{k}}\delta(\epsilon_{c,\mathbf{k}+\mathbf{q}} - \epsilon_{c,\mathbf{k}} - \omega)|\langle u_{c,\mathbf{k}+\mathbf{q}}|u_{v,\mathbf{k}}\rangle|^2, \tag{12}$$

where $u_{v,\mathbf{k}}$ and $u_{c,\mathbf{k}+\mathbf{q}}$ denote valence and conduction states of the lattice-periodic part of the Kohn-Sham orbitals, and $\mathbf{k}$ and $\mathbf{q}$ are wavevectors. $\epsilon_{v,\mathbf{k}}$ and $\epsilon_{c,\mathbf{k}+\mathbf{q}}$ denote the corresponding band energy eigenvalues. In the evaluation, the limit $|\mathbf{q}| \to 0$ is taken, due to the vanishingly small momentum of light compared to the crystal momentum.

The real part of the dielectric function is then obtained through the Kramers-Kronig relations,

$$\varepsilon^{(1)} = 1 + \frac{2}{\pi} \mathcal{P} \int\limits_{0}^{\infty} d\omega' \frac{\varepsilon^{(2)}(\omega')\omega'}{\omega'^2 - \omega^2},\tag{13}$$

where $\mathcal{P}$ is the principal value of the integral.

In order to run the calculation with VASP, we will have to make the following changes to the INCAR file:

```
### Bands and DOS

LORBIT   =   11
NEDOS    =   2001

### Dielectric properties

LOPTICS  =  .TRUE.
NBANDS   =  ???
```

You already know the flags LORBIT and NEDOS from the previous exercise. For our purpose, NEDOS also sets the number of frequency steps, at which the dielectric function is evaluated. LOPTICS switches on the summation over the transition elements. By default, VASP only calculates the occupied valence bands, but in order to compute the transition elements, we also need to take (some of) the unoccupied conduction states into account. We therefore have to increase the number of bands using the flag NBANDS. How many bands are included in your standard calculation for MgO? Search for the flag in the OUTCAR file of one of the total energy runs you have done before, or count the number of valence electrons (flag ZVAL) in the POTCAR file. Set the NBANDS flag to three times that number and run the calculation.

As a result, the OUTCAR will show the following output:

```
(...)

frequency dependent IMAGINARY DIELECTRIC FUNCTION (...) density-density
E(ev)      X          Y          Z          XY         YZ         ZX
   ----------------------------------------------------------------
0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
0.042490  0.000163  0.000163  0.000163  0.000000  0.000000 -0.000000
0.084980  0.000327  0.000327  0.000327  0.000000  0.000000 -0.000000

(...)

frequency dependent       REAL DIELECTRIC FUNCTION (...) density-density
E(ev)      X          Y          Z          XY         YZ         ZX
```

```
   ----------------------------------------------------------------
0.000000   3.140009   3.140009   3.140009  -0.000000   0.000000  -0.000000
0.042490   3.140044   3.140044   3.140044  -0.000000   0.000000  -0.000000
0.084980   3.140148   3.140148   3.140148  -0.000000   0.000000  -0.000000


(...)
```

The first column contains the energy (and therefore frequency), at which the dielectric function was evaluated, followed by the six independent components of the symmetric tensor. Why do the diagonal components all have the same value? Note that after these entries, there is also a current-current evaluation of the dielectric tensor. You can ignore that output for our purpose.

Task: Plot one diagonal component of both the real and imaginary parts of the electric susceptibility as a function of frequency, $\chi^{\mathrm{el}}(\omega)$.

3.2 Lattice contribution to the electric susceptibility

Displacements of the ions from their equilibrium positions can be described by lattice vibrations (phonon modes), which you have computed in task 2. We now need to find a way to connect these to the dielectric susceptibility. The electric field can couple to the electric dipole moment of an optical phonon mode, $\mathbf{p}_{ph}$, where the interaction potential can be written as

$$V_{\mathrm{int}} = -\mathbf{p}_{ph} \cdot \mathbf{E}. \tag{14}$$

The electric dipole moment is given by a product of charge and displacement, specifically $\mathbf{p}_{ph} = \mathbf{Z}Q$, where $\mathbf{Z}$ is the so-called mode effective charge vector of the phonon and Q is the phonon amplitude. A common (and confusing) convention for phonons has the vector components Z_i given in units of $e/\sqrt{\mathrm{amu}}$, where e is the elementary charge and amu is the atomic mass unit, and Q in units of $\mathrm{\mathring{A}}\sqrt{\mathrm{amu}}$.

The lattice dynamics in response to an electric field can be described by a driven harmonic oscillator,

$$\ddot{Q}(t) + \kappa \dot{Q}(t) + \Omega^2 Q(t) = \sum_i Z_i E_i(t), \tag{15}$$

where we've written the scalar product from Eq. (14) in component notation. κ is the linewidth (damping) of the phonon mode.

Task: From the equation of motion, derive an analytical expression of the phonon amplitude in terms of the electric field, using the ansatz $Q(t) = Q_\omega e^{-i\omega t}$ and $E(t) = E_\omega e^{-i\omega t}$. Plug the solution into the expression for the electric dipole moment of the phonon mode, $\mathbf{p}_{ph}$, and identify the electric susceptibility that the phonon mode induces by comparison with Eq. (10). It is easiest to work in component notation for the vectors. Note that for the total expression of $\chi^{\mathrm{lat}}(\omega)$, you will need to sum over all phonon modes in the system.

We have already computed the phonon frequencies in task 2. In order to evaluate the expression you have obtained for $\chi^{\mathrm{lat}}(\omega)$, we still need to compute the mode effective

charge. The mode effective charge is given by the dipole moments generated by the displacements of all ions in the unit cell along the eigenvectors of the optical phonon mode,

$$Z_i = \sum_n Z_{n,ij}^* \frac{q_{n,j}}{\sqrt{M_n}}, \tag{16}$$

where $q_{n,j}$ is the eigenvector of ion n along direction i, M_n is the atomic mass, and the index n runs over all ions in the unit cell. You have calculated $q_{n,j}$ in task 2. We now have to calculate $Z_{n,ij}^*$, which is the Born effective charge tensor of ion n. The Born effective charge tensor is defined as $Z_{n,ij}^* = V_c \partial P_i/(\partial r_{n,j})$, where V_c is the volume of the unit cell. It describes the polarization that is induced along direction i when ion n is displaced along direction j. The Born effective charge of the ion may differ from its formal charge, for example when the displacement of the ion leads to a reconfiguration of the bond chemistry.

We will use a VASP-internal routine based on density functional perturbation theory (DFPT) to compute $Z_{n,ij}^*$. In order to do so, we will have to make the following changes to the INCAR file:

```
NCORE    =  1

(...)

### Dielectric properties

LEPSILON = .TRUE.
```

Note that NCORE is set to 1. This is required, because the internal routine changes the k-points set, which is not compatible with NCORE>1. Now run VASP and have a look at the output. (You can still execute mpirun with two cores.) The static electronic dielectric tensor is printed in the OUTCAR file:

```
 MACROSCOPIC STATIC DIELECTRIC TENSOR (including local field (...))
 ------------------------------------------------------------
         3.119253     -0.000000     -0.000000
        -0.000000      3.119253      0.000000
        -0.000000      0.000000      3.119253
 ------------------------------------------------------------
```

as well as the Born effective charge tensors:

```
 BORN EFFECTIVE CHARGES (including local field effects) (in |e|, (...))
 ---------------------------------------------------
 ion    1
    1      1.96590     -0.00000     -0.00000
    2     -0.00000      1.96590      0.00000
    3     -0.00000      0.00000      1.96590
 ion    2
```

1	-1.96590	0.00000	0.00000
2	-0.00000	-1.96590	-0.00000
3	0.00000	-0.00000	-1.96590

Do the effective charges that you obtain vary from the formal charges?

   Task: Compute the mode effective charge vectors for the three optical phonon modes in MgO. Plot the real and imaginary parts of the lattice contribution to the electric susceptibility as a function of frequency, $\chi_{ij}^{\text{lat}}(\omega)$, assuming a phonon linewidth of $\kappa = 0.1 \times \Omega/(2\pi)$.