Advanced solid state physics student project

Phonon dispersion and phonon-DOS calculation of ZnO in zincblende, rocksalt and wurtzite structure

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1 Overview

This Quantum Espresso simulation uses Density-Functional Theory to calculate Interatomic Force Constants(IFC's), the phonon dispersion and phonon-density of states of ZnO in zincblende, rocksalt and wurtzite structure. IFC's are calculated in these three steps:
1.) scf-calculation to get the energy of the ground state of the unperturbated system.
2.) calculation of phonons and dynamical matrices on a grid of q-vectors
3.) calculation of IFC's in real space Using the IFC's, phonons at any q-vector can be calculated and plotted. A detailed tutorial we used can be found here: `http://www.fisica.uniud.it/~giannozz/QE-Tutorial/tutorial_disp.html`

2 Procedure for ZnO in zincblende structure

The program pwgui(`http://www-k3.ijs.si/kokalj/pwgui/`) is very helpful to create input files. The self-consistent-field(scf) is calculated using the pw.x routine. This routine needs the following input parameters: lattice type(ibrav), lattice parameters(celldm), number of atoms in the unit cell(nat), number of types of atoms(ntyp), electron cutoff- frequency(ecutwfc), convergence threshold(conv_thr) atomic mass of the atoms, filename of the pseudo potentials, positions in the unit cell. A sufficient number of k-points is crucial to get reasonable results. Pseudopotentials can be found here: `http://www.quantum-espresso.org/pseudopotentials/`

2.1 pw.x example for zincblende structure

```
 &CONTROL
                 calculation = 'scf' ,
                restart_mode = 'from_scratch' ,
                      outdir = '\folder ' , !output directory
                  pseudo_dir = '\folder ' , !pseudopotential directory
                      prefix = 'zb' , !prefix of filenames
                     tstress = .true. , !calculate stress: true/false NOT REQUIRED
                     tprnfor = .true. , !calculate forces: true/false NOT REQUIRED
 /
 &SYSTEM
                       ibrav = 2, !lattice type, 2 = fcc
                   celldm(1) = 8.73, !lattice constant
                         nat = 2, !number of atoms in the unit cell
                        ntyp = 2, !number of types of atoms in the unit cell
                     ecutwfc = 42.0 , ! kinetic energy cutoff (Ry) for wavefunctions
 /
 &ELECTRONS
                    conv_thr = 1.0d-12, ! Convergence threshold for selfconsistency
                 mixing_beta = 0.7 , ! mixing factor for self-consistency
 /
ATOMIC_SPECIES
    O   16.00000  O.bp-van_ak.UPF !Name mass pseudopotential-file of atom 1
   Zn   65.40000  Zn.bp-van_ak.UPF !Name mass pseudopotential-file of atom 2
ATOMIC_POSITIONS alat
!alat: atomic positions in units of the lattice parameter celldm(1)
```

```
    O      0.000000000    0.000000000    0.000000000    !Name and position of Atom 1
   Zn      0.250000000    0.250000000    0.250000000    !Name and position of Atom 2
K_POINTS automatic !number of k-points and grid offset
3 3 3 1 1 1
```

2.2 ph.x example for zincblende structure

Next the program ph.x uses the output of the scf calculation and generates dynamical matrices on a grid of q-vectors. Again the number of q-points is crucial for reasonable results.

```
phonons of zb !title
&INPUTPH
                     outdir = '\folder' , !output folder
                     prefix = 'zb' , !prefix of filenames
                     fildyn = 'zb.dyn' , !filenames of dynamical matrices
                      ldisp = .true., !dispersion calculation
                   amass(1) = 16, !mass of atom 1
                   amass(2) = 65.4, !mass of atom 2
                     tr2_ph = 1.0d-12 , !threshold for self consistency
                        nq1 = 4 , !number of q-points
                        nq2 = 4 ,
                        nq3 = 4 ,
/
```

2.3 IFC calculation using q2r.x

Finally the dynamical matrices are Fourier transformed and IFC's are calculated using the program q2r.x. q2r.x needs the input(fildyn) and output(flfrc) filenames. It is recommended to use an acoustic sum rule (zasr='simple'/'crystal').

```
&input fildyn='zb.dyn', zasr='simple', flfrc='zb.fc' /
```

2.4 phonon dispersion relation

Now matdyn.x calculates phonons at any q-vector using the IFC's. matdyn.x needs the type of acoustic sum rule (asr), the atomic masses (amass), the q-vectors (e.g. q in band form, or arbitrary points) and input and output filenames. You must check, if the ouput of ph.x and matdyn.x match for a certain unused q-vector. If not, a denser grid or stronger convergence criteria may help.

```
&input
   asr='simple',  amass(1)=16, amass(2)=65.4,
   flfrc='zb.fc', flfrq='zb.freq', q_in_band_form=.true.,
/
5 !number of high symmetry points
 gG    40 !Gamma the 'g' stands for greek  40 points to the next high symmetry point
 X     40
 W     40
 gG    40
 L     40
```

Using the routine plotband.x the frequenies can be converted into a plotable format.

```
plotband.x zb.freq
```

2.5 phonon DOS

Using matdyn.x the phonon density of states is calculated aswell ('dos=.true.', number of k-points must be set ('nk1= ','nk2= ', 'nk3= ', fldos = output file).

```
 &input
   asr='simple', dos=.true.   amass(1)=16, amass(2)=65.4,
   flfrc='zb.fc', fldos='zb.phdos_out', nk1=12,nk2=12,nk3=12
/
```

The phonon density of states and the dispersion relation can be plotted using xmgrace, etc.

3 Comments on the procedure for other structures

3.1 rocksalt structure

Since rocksalt has a fcc-basis as zincblende. The calculation is analog with different atomic positions in the crystal basis.

3.2 wurtzite structure

To get reasonable results for the ground state energy of wurtzite, the pw.x routine had to use a relaxtion calculation. Thus the values of the high symmetry points mismatch with literature values. The following steps(ph.x, q2r.x,...) are analogue to zincblende and rocksalt.

pw.x relaxation input file:

```
# self-consistent calculation for Wurtzite (ZnO)
 &CONTROL
                 calculation = 'relax' , !relaxation calculation
                     outdir = '\folder' ,
                  pseudo_dir = '\folder' ,
                     prefix = 'wz' ,
 /
 &SYSTEM
                       ibrav = 4,
                   celldm(1) = 6.200,
                   celldm(3) = 1.61,
                         nat = 4,
                        ntyp = 2,
                     ecutwfc = 25 ,
                     ecutrho = 1000 ,
                 occupations = 'smearing' ,
                     degauss = 0.02 ,
                    smearing = 'gaussian' ,
 /
 &ELECTRONS
                    conv_thr = 1.0d-14 ,
                 mixing_beta = 0.7 ,
 /
 &IONS
 /
```

```
 &CELL
 /
ATOMIC_SPECIES
   Zn   65.40900  Zn.bp-van_ak.UPF
    O   15.99900  O.bp-van_ak.UPF
ATOMIC_POSITIONS crystal
   Zn      0.000000000    0.000000000    0.000000000
   Zn      0.333333333    0.666666667    0.500000000
    O      0.000000000    0.000000000    0.378000000
    O      0.333333333    0.666666667    0.878000000
K_POINTS automatic
  8 8 8   0 0 0
```