Worksheet 2
Properties of fermions and Density Functional Theory

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Important remarks

- Due date: **Tuesday, May 6th, 2014, 10:00**
- You can either send a PDF file to Bibek Adhikari (adbibek@icp.uni-stuttgart) or submit a hand-written copy.
- Hints for the solution and an introduction to SIESTA will be given on Wednesday, 30th, 2014, 8:00 (CIP-Pool)
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart) or Bibek Adhikari (adbibek@icp.uni-stuttgart.de)

Short Questions - Short Answers (5 points)

1. Q1: Explain the difference between the LDA and GGA approach in your own words.
2. Q2: What is the Born-Oppenheimer approximation?
3. Q3: What are the simplifications of the Hartree-Fock approach? - Short answer in your own words.
4. Q4: What does the Kohn-Sham equation describe?

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5. Q5: When is it useful to use DFT compared to Hartree-Fock? - Give reasons for your choice.

Theoretical Task: Fermi energy and partition sums (5 points)

T1: Grand canonical partition sum for bosons and electrons

The grand canonical partition sum is given by

$$Z_{GC} = Tr(\exp(-\beta(H - \mu N))) \tag{1}$$

with the inverse thermal energy $\beta = 1/k_B T$, the Hamilton function H, the chemical potential μ and the particle number N. Please calculate the partition sum for fermions (antisymmetric) and bosons (symmetric).

T2: Average occupation of a state

The average occupation of a state is given by

$$< n_i >= \frac{1}{Z_{GC}} Tr(\exp(-\beta(H - \mu N))n_i). \tag{2}$$

Please calculate the average occupation of states for fermions and bosons and draw your results.

T3: Fermi energy

For a maximum degeneracy, the chemical potential is given by $\mu \to \infty$. The energy distribution for fermions is given by $n\epsilon = 1/(exp(\beta(\epsilon - \mu)) - 1)$. Calculate the Fermi energy ϵ_F by integrating

$$N = V \int d\epsilon \; n(\epsilon) \; \mathcal{D}(\epsilon) \tag{3}$$

where $\mathcal{D}(\epsilon)$ is given by $\mathcal{D}(\epsilon) = (4\pi/2)(2s + 1)(2m/h^2)^{3/2}\epsilon^{1/2}$ with the spin s, the mass m, Planck's constant h and the volume V.

Computational Task: DFT simulations of silicon (10 points)

In this exercise we will simulate bulk silicon. The input file for silicon si.fdf, can also be found on the course website. The respective pseudopotentials should be downloaded from the website http://icmab.cat/leem/siesta/Databases/Pseudopotentials/periodictable-intro.html. The unit cell for silicon will be used for the calculations. The tasks are split into three distinct levels:

T1 Energy vs. volume: For this task we will calculate the lattice constant which leads to the lowest energy with DFT and compare this with the experimental lattice constant (5.43).

T2 The electronic density of states (eDOS) for bulk silicon will be analyzed.

T3 Band structure calculation for bulk silicon, along specified k-point directions.

The program SIESTA can be run with

```
/group/allatom/siesta/siesta-parallel
```

and the "eig2dos" and "gnubands" utilities can be found in the SIESTA distribution. Get the source files from the following paths:

```
/group/allatom/siesta/eig2dos.x
/group/allatom/siesta/gnubands.x
```

and compile these.

T1: Energy-Volume curve and lattice constant

The goal is to plot the energy vs. volume vurve for bulk silicon. For this a few simulations will be needed for which a different lattice constant will be used. Perform only an energy minimization (no k-points, bands etc. are needed here, and should also not be used here).

- Perform the first simulation using the experimental lattice constant for bulk silicon (5.43). Get the total energy from the simulation.
- Continue along the same line as above, for other lattice constants. Each time, change only the value of the LatticeConstant tag in the input file. Take approximately 10 values, 5 smaller and 5 larger than the experimental lattice constant, with an increment of 0.1.
- For each of the lattice constants used, get the total energy written in the output file.
- Plot the total energy vs. volume curve (note that the lattice is not cubic!).
- From the plot get the lattice constant which corresponds to the lowest total energy and compare with the experimental lattice constant. From this comparison, provide the error in the calculation of the lattice constant.

T2: Density of States bulk Silicon

- First of all modify the si.EIG file
- Follow the instuctions provided in the attached eig2dos.pdf to correctly estimate the DOS.
- Edit the fdf file, changing MeshCutoff to 100, 120, 180 and 260 Ry
- Write down the total energies.

- Check in the output file and Plot the Energy vs. MeshCutoff to see the convergence.

- Run the simulation with different kgrid cutoff. Edit the fdf, changing kgrid cutoff to 30 , 35, 40 and 45 bohr. Write down the total energies.

- Check in the output file for the number of k-points used in each calculation.

- Plot the Energy vs. k-points, to see the convergence.

- to use eig2dos utility:
  >> ./eig2dos.h < si.EIG | tee dos.dat
  You may plot the results using gnuplot or grace program:
  xmgrace dos.dat

- Calculate

T2: Band Sructure Analysis of Bulk Silicon

- Copy the *si.fdf* file. The initial coordinate along with some basic parameters has been already supplied in this file. Fill in the empty spaces with suitable parameters in the input file.

- The theoretical prediction has to be done for two flavors of xc functional namely :
  1. LDA (CA)
  2. GGA (PBE)

- Download the pseudo-potential files for each flavors of XC functional.

- Run the siesta calculation >> ./siesta < si.fdf | tee si.out

- Find the file si.bands

- Plot band structure using gnupbands.x
  >> ./gnubands.x < si.bands | tee bands.dat

- Plot bands.dat using xmgrace or gnuplot
  >> xmgrace bands.dat

- Select correct range of energies.

- Make a comparison for GGA and LDA

As a final step, search for the experimental energy bandgap for bulk silicon and compare this to the one from the DFT simulations. Specifically, from the eDOS and/or band structure in T2/T3 extract the theoretical bandgap. Do this for both GGA and LDA calculations. Compare these values with the experimental one and give the amount of error.