ICMEd Summer School DFT Module

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**Summer School for Integrated Computational Education**

**DFT Module Problems**

The purpose of this exercise is to get hands-on experience on running a density functional theory calculation and to compute values for the equilibrium lattice parameter, bulk modulus, and two single-crystal elastic constants.

One of the key concepts to be learned is the consideration of precision and accuracy. Higher numerical precision is expected for larger plane-wave cutoff and/or larger k-point mesh. However, even if the calculation is well converged numerically, it need not be highly accurate. The accuracy is limited by the approximations made in deriving the theoretical formulation of the exchange-correlation energy. In this exercise you will determine numerical convergence by running calculations for different k-point and plane-wave settings, and you will assess the accuracy of the converged results by comparing to experimental measurements.

1. (Basic) At atmospheric pressure the stable crystal structure of Si is diamond cubic. Your first task in this assignment is to compute the equation of state of diamond-cubic Si using Quantum Espresso on nanoHUB. Specifically, you will compute the equilibrium volume and the bulk modulus using pressure-volume relations as described below. In this exercise, you will be using the description of the crystal structure given in Fig. 1 below

1. Using a plane-wave cutoff of 24 Ry and a k-point mesh of 6x6x6, compute the energy and pressure as a function of volume over the range of lattice-constant values given in Table 1. Compute (i) the equilibrium lattice constant, and (ii) the bulk modulus. The equilibrium lattice constant can be estimated by interpolating the calculated results to zero pressure, and the bulk modulus can be estimated using the following approximate finite-difference expression:



**Fig. 1**: The conventional unit cell of the diamond-cubic crystal structure is shown on the left (taken from <http://math.ucr.edu/home/baez/week262.html>). On the right is the Cartesian vectors describing the primitive translation vectors that will be used in solving problem 1, as well as the positions of the basis atoms in fractional coordinates.



where *a0* is your estimated equilibrium lattice constant, *a1* and *a2* are two values of the lattice constant on either side of this equilibrium value, and *P1* and *P2* are the values of the pressure corresponding to *a1* and *a2*, respectively.

b. Next estimate the *numerical precision* of your results for lattice constant and bulk modulus obtained in part (a). To do this, repeat the calculations using two additional settings: (i) a 28 Ry cutoff and a 6x6x6 kpoint mesh, and (ii) a 24 Ry cutoff and an 8x8x8 kpoint mesh. Record the results in Tables 2 and 3. Calculate the percentage difference in lattice constant and bulk modulus relative to the answers you obtained in part (a). Based on these results, do you believe the calculation of lattice parameter is numerically converged? What about bulk modulus?

c. Finally, assess the *accuracy* of your LDA results by comparing your computed results from parts (a) and (b) with the experimentally measured values of 5.43 Å and 976 kBar (= 97.6 GPa), for the lattice constant and bulk modulus, respectively.

d. Repeat part (a) using GGA. You can use Table 1 again to record the answers. Indicate the values for GGA in parentheses next to the values for LDA. How do the results from GGA compare with those from LDA? Which exchange-correlation potential gives better agreement with experimental measurements?

2. (Intermediate) As a second exercise, you will calculate the single-crystal elastic constants *C11* and *C12* by computing the stresses resulting from a homogeneous tensile strain of the Si structure along the [001] direction. Specifically, you will use the mathematical relationship between the tensile strain that you impose (**= *33*) and the resulting stress that you will calculate (*  **33*):

**= *C11* **

*22*= *C12* **

1. Using the parameters from part 1(a), compute stress for the values of the strain given in Table 4 using LDA. To impose a given strain value, you will need to proceed as follows. Under the “Input Geometry” tab choose the “Determine unitcell (free)” option under “Structure type”. Under cell vectors, change the values to:

 -*a*/2 *a*/2 0

 -*a*/2 0 *a*(1 + **)/2

 0 *a*/2 *a*(1 + **)/2

where *a* is the LDA zero-pressure lattice constant derived in problem 1. The values of *22* and *33* can be obtained as the negative of the *22* and *33* elements of the pressure tensor recorded under the “Data” selection of “Result” menu.

1. Using the results from part 2(a), compute *C11* and *C12* using the formula *C11* ≈ **33 / ** = [**(** = 0.01) – **(** = -0.01)] / 0.02. A similar relationship can be used to compute *C12*. How do your results compare to the experimental values of *C11* = 1660 kBar (166 GPa) and *C12* = 640 kBar (64 GPa)?
2. The approach that you have used to compute the elastic constants in this problem implicitly assumes that the imposed strains are small enough for the material to behave as a linear-elastic solid. You can check the accuracy of this assumption by using a larger range of strain compared with that used in part 2(b), and comparing results. Specifically, compute *C11*from the values of the strain ** = -2 % and +2 % using the relation: *C11* ≈ [**(** = 0.02) – **(** = -0.02)] / 0.04, and similarly for *C12*. Record your results and compare with the value obtained in part (b). Is the linear-elasticity assumption valid?
3. Repeat parts 2(a) and 2(b) using GGA. How do the results from LDA and GGA compare? Which exchange-correlation potential gives better agreement with experimental measurements?

**Table 1**: Calculate the energies and pressures for diamond-cubic Si using the LDA (GGA) with a 24 Ry plane-wave cutoff and a 6x6x6 kpoint mesh. The first column lists the lattice constant, the second the total energy, and the third the pressure. Fill in the results for energy and pressure using Quantum Espresso on the nanoHUB to complete Problem 1a (and 1c).

|  |  |  |
| --- | --- | --- |
| Lattice Constant (Angstroms) | Energy(Ry) | Pressure(kBar) |
| 5.35 |  |  |
| 5.37 |  |  |
| 5.39 |  |  |
| 5.41 |  |  |
| 5.43 |  |  |
| 5.45 |  |  |
| 5.47 |  |  |
| 5.49 |  |  |
| 5.51 |  |  |

LDA Equilibrium Lattice Constant:

LDA Bulk Modulus:

GGA Equilibrium Lattice Constant:

GGA Bulk Modulus:

**Table 2**: Calculate the energies and pressures for diamond-cubic Si using the LDA with a 28 Ry plane-wave cutoff and a 6x6x6 kpoint mesh. The first column lists the lattice constant, the second the total energy, and the third the pressure. Fill in the results for energy and pressure using Quantum Espresso on the nanoHUB to complete Part (b) of Problem 1.

|  |  |  |
| --- | --- | --- |
| Lattice Constant (Angstroms) | Energy(Ry) | Pressure(kBar) |
| 5.35 |  |  |
| 5.37 |  |  |
| 5.39 |  |  |
| 5.41 |  |  |
| 5.43 |  |  |
| 5.45 |  |  |

Equilibrium Lattice Constant:

Bulk Modulus:

**Table 3**: Calculate the energies and pressures for diamond-cubic Si using the LDA with a 24 Ry plane-wave cutoff and an 8x8x8 kpoint mesh. The first column lists the lattice constant, the second the total energy, and the third the pressure. Fill in the results for energy and pressure using Quantum Espresso on the nanoHUB to complete Part (b) of Problem 1.

|  |  |  |
| --- | --- | --- |
| Lattice Constant (Angstroms) | Energy(Ry) | Pressure(kBar) |
| 5.35 |  |  |
| 5.37 |  |  |
| 5.39 |  |  |
| 5.41 |  |  |
| 5.43 |  |  |
| 5.45 |  |  |

Equilibrium Lattice Constant:

Bulk Modulus:

**Table 4**: Calculate the stress as a function of tetragonal strain for diamond-cubic Si using the LDA with a 24 Ry plane-wave cutoff and a 6x6x6 kpoint mesh. Use the procedure described in problem 2 to impose a given value of the strain. The first column lists the strain value in percent, the second the *22* component of the stress tensor, and the third the *33* component of the stress tensor. Fill in the results for stress using Quantum Espresso on the nanoHUB to complete Problem 2. List the values of the elastic moduli below the table.

|  |  |  |
| --- | --- | --- |
| Strain (**)(percent) | *22*(kBar) | *33*(kBar) |
| -2 |  |  |
| -1 |  |  |
| 0 |  |  |
| 1 |  |  |
| 2 |  |  |

*C11* and *C12* Derived from strains of -1 and +1 %:

*C11* and *C12* Derived from strains of -2 and +2 %: