

Density Function Theory (DFT) laboratory: Bonding and band-structure in Silicon

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Laboratory Objectives:

In this lab students will perform online Density Functional Theory (DFT) simulations of crystalline bulk Si structures with varying lattice constant parameters and analyze the results to:

- Developing understanding of variations in energy levels as a function of the interatomic distance, thereby understanding the effect of structure on electronic properties
- Determining the nature of the system (metallic, semiconducting or insulating)
- Interpreting the DFT band-structure results.

Background

Density Functional theory (DFT) is a unique and powerful technique to explore material properties from first principles. DFT simulations involve transforming the many body Schrodinger equation (SE) to much simpler Kohn Sham (KS) non interacting particles problem and solving these equations under certain approximations. Only by specifying the atomic coordinates of the system, we can get the total ground state energy and using which various mechanical, electronic and optical properties of the materials can be predicted. DFT simulations solve for the Kohn Sham energy eigen values, which are generally interpreted as band structure of the material. Though, these can be used as a qualitative reference for understanding physical phenomenon, it should be remembered that DFT accurately predicts only the ground state energies. More rigorous perturbation theory methods like GW approximation are required to obtain quantitative results of the band-structures.

Generally the approximations involved in the DFT simulations can be categorized into two major categories: (a) Physical (b) Numerical. It is important to understand the approximations you are using in the DFT simulations to meaningfully interpret the results. Physical approximations involve the choice of exchange-correlation functional involved in transforming the many-body SE to KS non interacting particle problem in an effective potential. Numerical approximations involve the choice of pseudo-potentials, type and number of basis functions used for representing the wave-functions, number of k-points and grid points etc. For a detailed review of the various approximations and their impact on the simulation results, reader is referred to a reference [3]. Those interested in learning more about DFT simulations will find the following resources useful:

- Computational Physics, J. M. Thijssen, Cambridge University Press, 2nd edition (April 9, 2007)
- Electronic Structure: Basic Theory and Practical Methods, Richard Martin, Cambridge University Press (April 26, 2004)

- Mattsson, Schultz, Desjarlais, Mattsson and Leung, “Designing meaningful DFT calculations in materials science”, MSMSE 13, R1-R31, 2005.

Procedure:

The following assignment should be performed individually or in small groups. The background and pre-lab lectures in this learning module provide the necessary background. The first user guide available <http://nanohub.org/resources/9269/supportingdocs> provides additional help for using the “DFT calculations with Quantum Espresso” tool on nanoHUB.org.

Assignment:

Follow the directions in the pre-lab lecture to perform your first DFT simulation of Si-band structure with the experimental lattice constant of 5.43 Å. Once the simulation is finished, explore the band structure plot and try comparing it to the experimental plot given in the prelab lecture. One should remember that what we get is the Kohn Sham energy eigen values at various k-points. . The Bandstructure/DOS tab allow you to set the parameters for the band structure calculation. Now repeat the simulations for different lattice parameters, say from 20Å to 5.43Å (equilibrium lattice parameter). In each case save the bandstructure plots, note the Fermi energy level and total energy from scf-output logs. Answer the following questions and make a report with appropriate plots pasted in a word or ppt document.

1. Convince yourself that the Bravais lattice with the two-atom basis set structure form a FCC lattice(diamond lattice). You can write a small matlab program to replicate the 2- atom unit cell in all directions using periodic boundary conditions (PBC).
2. Document all the relevant approximations mentioned in the pre-lab and background lectures. For the present simulations, these values are left at their default values. In real life, we should make sure that the choice of exchange-correlation functional, appropriate pseudo-potentials (replace core electrons), Kinetic energy cutoffs (this determines the size of basis set in plane wave calculations), number of bands (number of energy eigen values to solve for), number of k-points.
3. Include 6 Kohn Sham bandstructures for various lattice parameters in one page. For each plot, indicate the lattice parameter and the Fermi energy level. Also indicate the bandgap, (difference between the highest occupied energy level and lowest unoccupied energy level) . Try these estimating the values using the Fermi level and Bandstructure plot . They can also be found in the scf-output log. Indicate whether it is direct or indirect band-gap material.(If the highest occupied energy level and lowest unoccupied energy level correspond to same k-point, then it is direct band-gap material)
4. Plot the Kohn-Sham band gap as a function of the lattice parameter and indicate at each lattice parameter whether the gap is direct or indirect.
5. Compare the equilibrium band-structure with the experimental band structure of Si in L- Γ -K region. Document the differences you observe.

6. (Advanced) Characterize the bonding/anti-bonding splitting as a function of lattice parameters for s and p states (starting with a large lattice parameter you should be able to quantify this easily until the s and p bands mix).

Additional suggested activities:

1. Try the same problem for a metallic structure of your choice.
2. Try the same problem for GaAs structures
3. Expand or compress the lattice parameter slightly (0.2-0.3%) and observe the difference in bandstructure. Does this give you any insight about strained Si, used in all microelectronics now-a-days.
4. Read the assumptions details from Ref[3] and change the default values in tool. Observe the change in results.