DFT Calculations of the Lattice Constant, Stable Atomic Structure and the Ground State Total Energy of Silicon

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Abstract

The all-electron, full potential FHI-aims DFT code was used to predict the stable structure and the theoretical lattice constant of Silicon. These were compared with the frozen-core, pseudopotential results [1] and known experimental structure and lattice constant of Silicon. Results obtained showed that the most stable structure of Silicon is the diamond structure which is in complete agreement with experiment. The calculated lattice constant of the stable structure is 5.42 Å which is 99.998% of the 5.43 Å experimental value. The calculated ground state total energy of the stable structure is - 7874.1127 eV per atom.

Keywords: Density functional theory, DFT, total energy minimisation, lattice constant, Silicon, atomic structure.

1.0   Introduction

One of the most profound scientific advances of the twentieth century was the development of quantum mechanics and the repeated experimental observations that confirmed that this theory of matter describes, with astonishing accuracy, the universe in which we live [2]. Density Functional Theory, DFT [3,4], is a phenomenally successful approach to finding solutions to the fundamental equation that describes the quantum behavior of atoms and molecules, the Schrodinger equation, in settings of practical value. This approach has rapidly grown from being a specialized art practiced by a small number of physicists and chemists at the cutting edge of quantum mechanical theory to a tool that is used regularly by large numbers of researchers in chemistry, physics, materials science, chemical engineering, geology, and other disciplines.

In this research work, the DFT code FHI-aims was used to predict the stable structure and then compute the lattice constant and ground state total energy of Silicon.

2.0   Theoretical Analysis

The formalism of DFT was introduced by Hohenberg and Kohn in 1964 [5]. In 1965, Kohn and Sham [6] presented a scheme to treat approximately the interacting electron system within this formalism. It is currently the most popular and successful method for studying the ground state electronic structures. Although far from a panacea for all physical problems in this domain, very accurate calculations can be performed with reasonable computational costs. With this formulation, the many-body problem is mapped onto an effective single particle problem. Kohn and Sham thus established that for any real (interacting) system with ground-state density n(r) there always exists a non-interacting system with the same ground state density n(r). This leads to the famous Kohn-Sham equation,

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}\right)\psi_i = \varepsilon_i\psi_i \qquad (1)$$

where ψ_i and ε_i are the single particle wavefunction and eigenvalue, respectively. The density of the non-interacting system

$$n(r) = \sum_{i=1}^{N}|\psi_i(r)|^2 \qquad (2)$$

will reproduce the exact density of the fully interacting system. Moreover the energy of the non-interacting system reproduces the exact ground state energy of the interacting system. The existence of such a potential is fascinating but the

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utility of DFT is dependent on one finding a decent approximation for V_{eff} that can be used in practical simulations [4]. Typically, V_{eff} is separated into an electron-nuclear (V_{en}), classical (Hartree) electron-electron interaction (V_H) and the remaining exchange-correlation potential (V_{xc});

$$V_{eff} = V_{en} + V_H + V_{xc} \qquad (3)$$

where,

$$V_H(r) = \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \qquad (4)$$

The Kohn-Sham approach is in principle exact! The approximation only enters when we have to decide on an explicit form for the unknown functional for the exchange-correlation energy E_{xc} and its corresponding potential V_{xc}. The central goal of modern DFT is therefore to find better and better approximations to these two quantities.

A great variety of different approximations to V_{xc} have been developed. For many years the local density approximation (LDA) has been used. In the LDA the exchange correlation energy density at a point in space is taken to be that of the homogeneous electron gas with the local electron density, $\varepsilon_{xc}(n)$. Thus the total exchange correlation energy functional is approximated as,

$$E_{xc}^{LDA} = \int n(\vec{r}) \, \varepsilon_{xc}\big(n(\vec{r})\big) d\vec{r} \qquad (5)$$

from which the potential is obtained as,

$$V_{xc} = \frac{\delta E_{xc}}{\delta n} \qquad (6)$$

The LDA has proven to be a remarkably fruitful approximation. Properties such as structure, vibrational frequencies, elastic moduli and phase stability (of similar structures) are described very reliably for many systems. However, in computing energy differences between rather different structures the LDA can have significant errors. For instance, the binding energy of many systems is overestimated and energy barriers in diffusion or chemical reactions may be too small or absent. Currently, effective potentials that depend both on the local density and the magnitude of its local gradient – so called, generalized gradient functionals (GGA's) - are widely used [7]. The GGA approach in its various forms goes some way to correcting the problems seen in LDA calculations. There are many GGA versions.

Hybrid functionals are now available and are widely used in chemical applications with the B3LYP functional being the most notable. Computed binding energies, geometries and frequencies are systematically more reliable than the best GGA functionals. In addition the description of the energies of non-equilibrium geometries are improved. The implementation of hybrid functionals requires the calculation of the non-local exchange operator and is thus somewhat problematic within the plane wave formalism. However, in a local orbital basis set the operator can be evaluated efficiently in direct space.

FHI-aims, the "Fritz Haber Institute ab initio molecular simulations", is an all-electron, full-potential computer program package for computational materials science based only on quantum-mechanical first principles [8]. The main production method is DFT to compute the total energy and derived quantities of molecular or solid condensed matter in its electronic ground state. In addition, FHI-aims allows to describe electronic single-quasiparticle excitations in molecules using different self-energy formalisms, and wave-function based molecular total energy calculation based on Hartree-Fock (HF) and many-body perturbation theory (MP2 and MP4).

Preconstructed hierarchical basis sets allow one to move from qualitative tight-binding like accuracy to meV-level total energy convergence with the basis set. For LDA and GGA DFT, periodic and cluster-type geometries are supported, including relaxation and ab initio molecular dynamics. The basis sets allow one to access all elements from light to heavy. A low-communication based algorithms and ScaLapack-based linear algebra for all matrix operations guarantee efficient scaling (CPU time and memory) up to massively parallel computer systems with thousands of CPUs [9].

FHI-aims version 071711_5 (released on July 17, 2011; upgrade 5) was used for all computations. It only works on Unix [10] or Linux [11,12] operating systems.

FHI-aims is distributed in source code form, thus the first task is to compile an executable program. For this, the following mandatory prerequisites are needed and must be installed before compiling FHI-aims:

(i)   A working Unix or Unix-based (Linux) operating system (Ubuntu 11.04 in this work).

(ii)   A working Fortran 95 (or later) compiler. A good example for x86 type computers is Intel's ifort compiler (Composerxe 2011.5.220 installed for this work). Other free but significantly slower compilers for all platforms are gfortran from the GNU compiler collection and the g95 compiler.

(iii) A compiled version of the lapack library, and a library providing optimized basic linear algebra subroutines (BLAS). Standard libraries such as Intel's mkl or IBM's essl provide both lapack and BLAS support. Intel's Compoerserxe 2011.5.220 comes with mkl.

Computations can only be carried out after successfully building an executable program. FHI-aims requires two input files - control.in (which contains all runtime-specific information) and geometry.in (which contains information directly related to the atomic structure for a given calculation). The two input files must be placed in the same directory from where the FHI-aims binary is invoked at the command line.

3.0   Results and Discussion

Silicon bulk total energies per atom at several lattice constants were computed for three possible structures – BCC, FCC and Diamond. Results obtained were then plotted, using the plotting software *Origin 5.0.*

Table 1: Computed Ground State Total Energy of Silicon

Lattice Constant (Å)	TOTAL ENERGY PER ATOM (eV)		
	BCC	FCC	Diamond
2.80	-7873.2768	-7865.8438	-7805.1694
2.90	-7873.5296	-7868.0302	-7815.0762
3.00	-7873.6441	-7869.6871	-7823.6340
3.10	-7873.6531	-7870.9197	-7831.0478
3.20	-7873.5949	-7871.8269	-7837.4542
3.30	-7873.4751	-7872.4818	-7842.9856
3.50	-7873.1302	-7873.2599	-7851.9168
3.60	-7872.9288	-7873.4629	-7855.4719
3.70	-7872.7190	-7873.5847	-7858.5463
3.80	-7872.5041	-7873.6362	-7861.2038
3.90	-7872.2927	-7873.6295	-7863.4854
4.00	-7872.0816	-7873.5808	-7865.4297
4.10	-7871.8737	-7873.5010	-7867.0818
5.10	-7870.0692	-7872.002	-7873.8916
5.20	-7869.9296	-7871.8374	-7874.0161
5.30	-7869.8067	-7871.6776	-7874.0869
5.40	-7869.6916	-7871.5185	-7874.1123
5.41	-7869.6801	-7871.5028	-7874.1126
5.42	-7869.6685	-7871.4872	-7874.1127
5.43	-7869.6569	-7871.4715	-7874.1123
5.44	-7869.6454	-7871.4558	-7874.1116
5.45	-7869.6337	-7871.4401	-7874.1106
5.50	-7869.5748	-7871.3613	-7874.1005
5.60	-7869.4553	-7871.2033	-7874.0583
5.70	-7869.3383	-7871.0488	-7873.9918

Figure 1: Silicon Structure and Lattice Constant using FHI-aims

From Figure 1 above, FHI-aims predicts that the most stable structure of Silicon is the diamond structure which is in complete agreement with experiment. The calculated lattice constant of the stable structure is 5.42 Å. This is 99.998% of the 5.43 Å experimental value. On the other hand, Stekolnikov et al [1], using a frozen-core pseudopotential code (VASP code) calculated a value of 5.398 Å as the lattice constant of the diamond structure of Silicon. This clearly illustrates that all-electron, full potential DFT [13] is more accurate than frozen-core, pseudopotential DFT.

4.0   Conclusion

Using the all electron, full potential FHI-aims code, the most stable structure of Silicon was predicted to be the diamond structure with a lattice constant of 5.42 Å. These are in excellent agreement with experiment. A value of 5.398 Å was calculated as the lattice constant of Silicon using the frozen-core, pseudopotential VASP code. Hence, all electron, full potential DFT calculations appear to be more accurate than frozen-core, pseudopotential calculations, at least for the study carried out on silicon.

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