

# DFT study of Lithium

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## Abstract

We perform a simple study of metallic Lithium via DFT calculations using a plane wave basis set. The equilibrium lattice constant, Density of States and band structure are calculated. Additionally, an AE isolated atom simulation is performed in order to compute the photoemission energy of a 1s electron.

## 1 Introduction

Lithium and its electronic properties have been the subject of extensive studies both experimentally and theoretically, making it a suitable test case for various types of Density Functional Theory (DFT) calculations. This present study is meant as an exercise in DFT computational methods on solid bcc Lithium. Firstly, a convergence study is performed on self consistent field computation parameters. The equilibrium lattice constant is thus estimated with scf calculations, comparing the results obtained using different exchange-correlation functionals. Non-self-consistent calculations are then carried out to obtain the Density of States and the band structure. Lastly, through All Electron calculations on the isolated Li atom we calculate the charge density function and the photoemission energy for a 1s electron with a comparison between different methods for obtaining such energy.

## 2 Method and Computational Parameters

The computational tool used in this study is Quantum Espresso, a plane wave based suite for electronic structure calculations [1]. Self-consistent field simulations for bcc Lithium are performed using the following parameters:

- Exchange-Correlation functional: PBE (Perdew-Burke-Ernzerhof [2], a GGA functional).
- Pseudopotential: Norm-Conserving PBE pseudopotential available from Quantum Espresso FHI pseudopotential library.
- Smearing: Methfessel-Paxton [3], 0.01 Ry.
- Lattice constant:  $a = 6.5$  Bohr, compatible with values from in-depth computational studies [4].
- Wavefunction kinetic energy cutoff *ecutwfc*.
- Charge density cutoff *ecutrho*.
- Size of Monkhorst-Pack [5]  $k$  points grid  $n_k$ .

We search for appropriate values of wavefunction kinetic energy cutoff  $ecutwfc$  and  $k$  space grid size, that is values that allow the total energy to converge within a 0.001 Ry threshold.

Firstly, simulations are performed over a range of  $ecutwfc$  values with a fixed  $4 \times 4 \times 4$  ( $n_k = 4$ ) Monkhorst-Pack grid, with results shown in Fig. 1. The choice of wavefunction cutoff sets the size of the basis set  $\{\psi_i\}$  and is thus essential in ensuring the eigenfunctions of the Kohn-Sham problem are correctly described. Since the pseudopotential is norm-conserving, the standard value  $ecutrho = 4 * ecutwfc$  is adopted.

Having fixed the wavefunction cutoff, we perform simulations using different  $n_k$  and similarly track the total energy per atom (Fig. 2). We settle for values  $ecutwfc = 20$  and  $n_k = 10$ , both well within the convergence region. Notice how the total energy is decreasing with increasing cutoff, as the dependence of the energy w.r.t. cutoff (i.e. w.r.t. the size of the PW basis set) is variational, while the same does not apply to the  $k$  grid size.

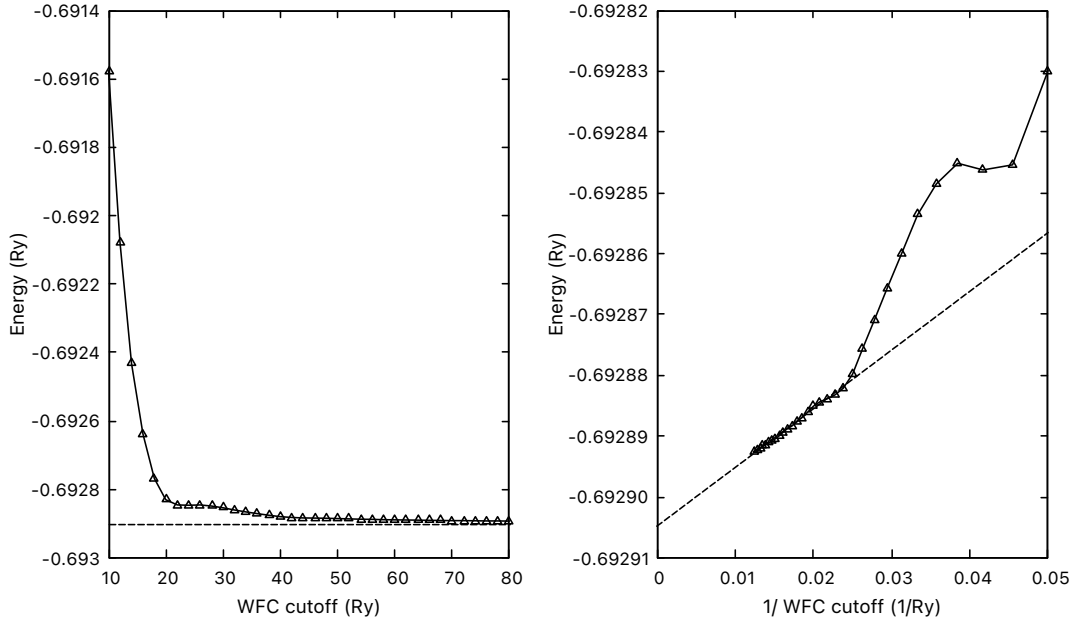


Figure 1: Total energy per atom as function of WFC cutoff (left) and  $1/(\text{WFC cutoff})$  (right). A linear fit was performed on the energy w.r.t.  $1/(\text{WFC cutoff})$  as shown by dashed line in right panel in order to extrapolate a converged value. Dashed line in left panel indicates extrapolated value from the fit.  $ecutwfc = 20$  is well within the required convergence region.

### 3 Equilibrium lattice constant

We calculate the equilibrium lattice constant for bcc Li by performing scf calculations at different input lattice spacings and finding the value that minimizes the total energy per atom. Additionally, the same calculations are performed forcing a LDA PZ (Perdew-Zunger [6]) exchange-correlation functional. Fig. 3 compares the resulting curves fitted with a Murnaghan equation of state [7].

We observe that LDA exchange-correlation functional underestimates the equilibrium lattice constant and the binding energy, with respect to both the GGA result (PBE) and

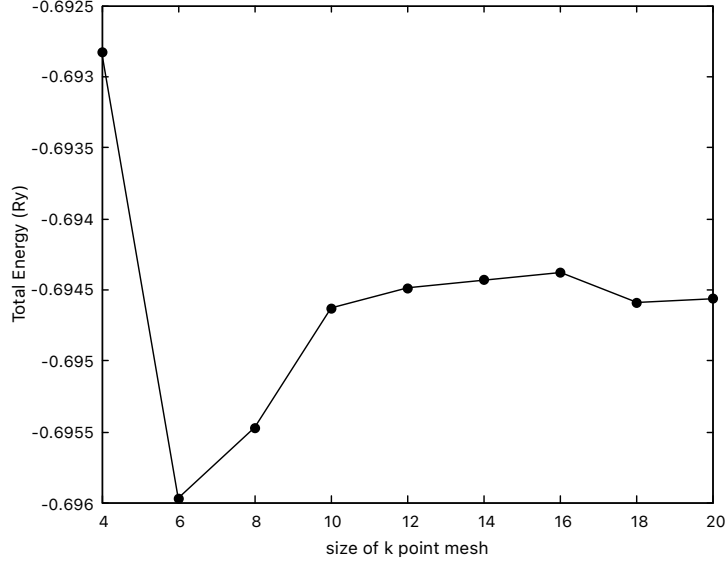


Figure 2: Total energy per atom as function of k points grid size.  $n_k = 10$  is considered converged.

expected values from the literature [4], in agreement with results from in-depth comparative studies between XC functionals [8].

XC functional	$a$ (Bohr)
GGA (PBE)	6.432
LDA (PZ)	6.313

Table 1: Comparison of calculated equilibrium lattice constants.

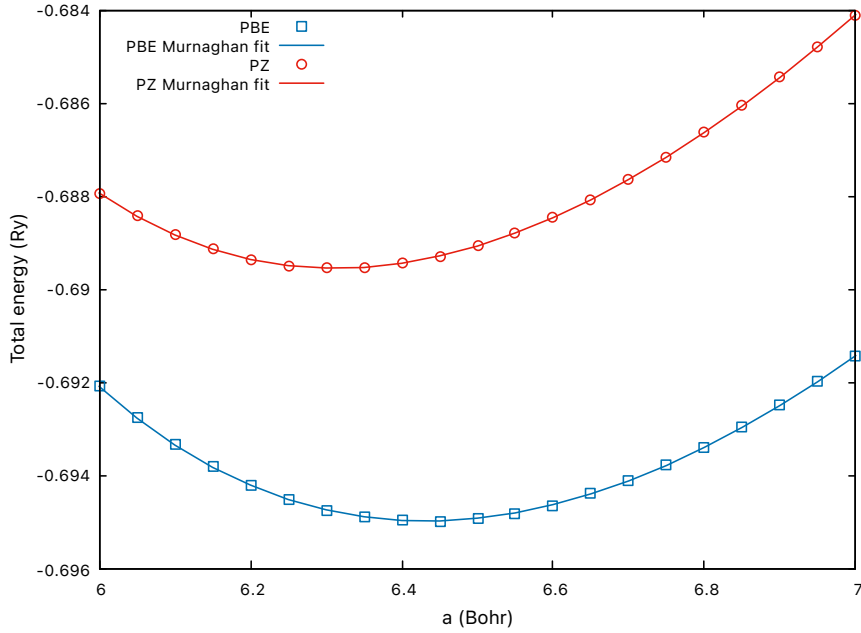


Figure 3: Total energy per atom as function of lattice spacing  $a$  for both PBE and PZ exchange-correlation functionals. Results are fitted with a Murnaghan equation of state.

## 4 DOS and band structure

The Density of States (DOS) is computed via nscf calculations, as well as the Projected Density of States (PDOS) defined as:

$$PDOS_{\alpha}(E) = \sum_{n,\mathbf{k}} w_{\mathbf{k}} |\langle \phi_{\alpha} | \psi_{n\mathbf{k}} \rangle|^2 \delta(E - \varepsilon_{n\mathbf{k}}) \quad (1)$$

where  $\alpha = Inlm$  identifies the atomic wavefunctions  $|\phi_{\alpha}\rangle$  on which the Kohn-Sham eigenfunctions  $|\psi_{n\mathbf{k}}\rangle$  are projected.

This is a task that requires a denser  $k$  grid than scf calculations in order to sample the Brillouin Zone with precision. We map the DOS via nscf calculations with increasing values of  $n_k$  and assess the convergence "visually" i.e. by checking the stability of the positions and the number of peaks. A smearing is also needed to properly compute the DOS as well as the Fermi energy. We similarly keep track of the shape as we vary the smearing in order to find an adequate broadening value.

The calculation is thus carried out with a fine grid of size  $n_k = 20$  and 0.03 Ry Gaussian broadening. See Fig. 4 for the resulting DOS and PDOS on atomic wavefunctions calculated with 8 bands.

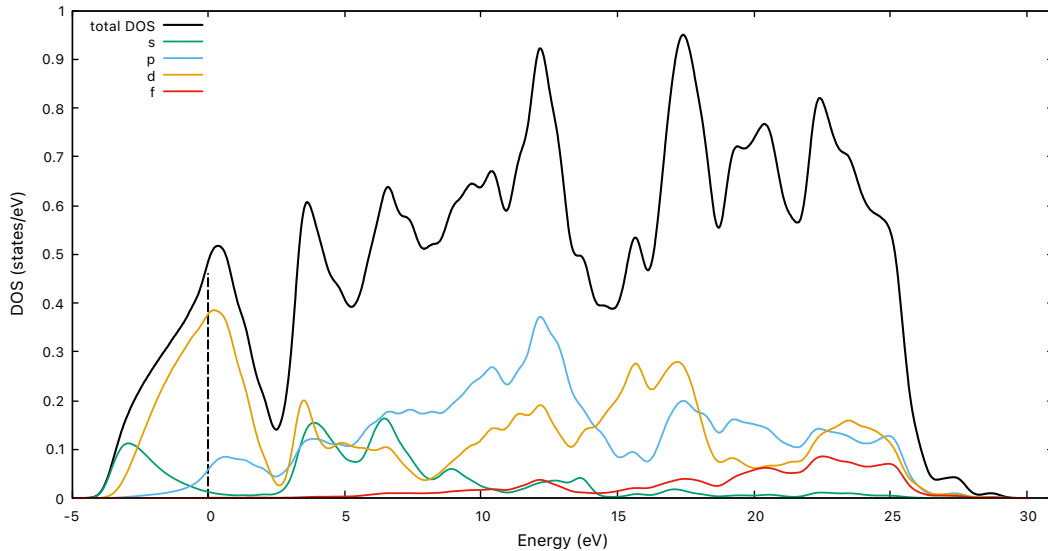


Figure 4: Density of States and atomic wavefunctions PDOS. Reference energy value is the estimated Fermi energy.

Sampling the band structure requires the definition of a path along the irreducible Brillouin Zone along directions of high symmetry. Fig. 5 shows a  $\Gamma - H - N - \Gamma - P - H$  path in a bcc lattice.

The band structure is thus calculated using 8 bands, as displayed in Fig. 6. The lower bands appear to be in satisfactory agreement with previous studies [9, 10].

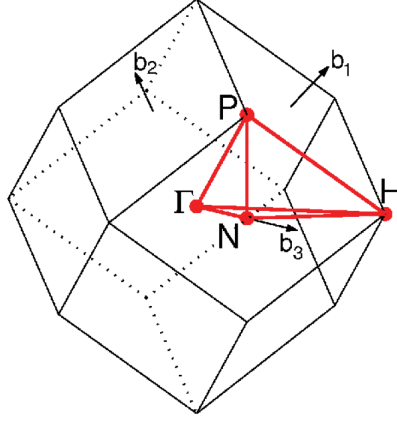


Figure 5: Brillouin zone of bcc lattice with relevant points and  $k$ -path highlighted.

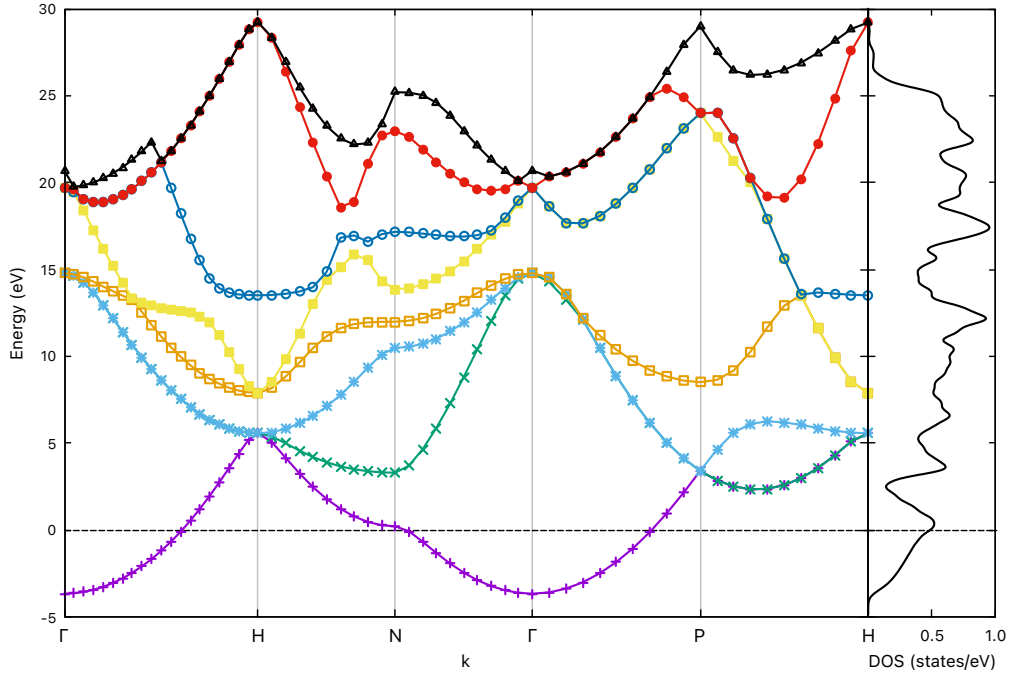


Figure 6: Band structure of bcc Lithium shown alongside the DOS, calculated using 8 bands. Reference energy value is the estimated Fermi energy.

## 5 Isolated atom calculations

We perform an All Electron (AE) calculation on the isolated Lithium atom. The total charge density distribution is shown in Fig. 7 along with its separated components associated with the atomic orbitals  $1s$  and  $2s$ .

The photoemission energy of a  $1s$  electron can be accessed via a few different methods. Here we compare the results obtained with two. The first is by simply computing the total energy difference between the neutral atomic configuration  $1s^2 2s^1$  and the ionized  $1s^1 2s^1$  atom. The second is by means of Janak's theorem, which states that for a Kohn-Sham state  $i$  the eigenvalue is equal to the derivative of the total energy with respect to the

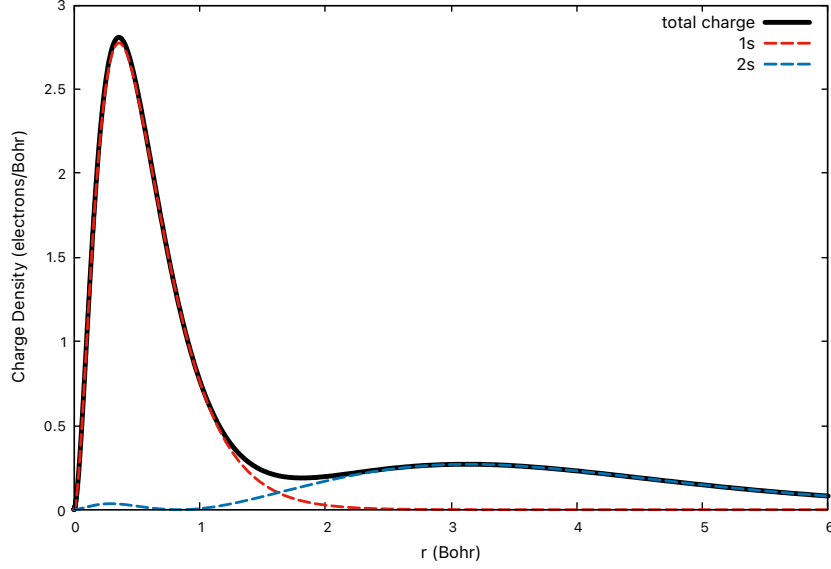


Figure 7: Charge density distribution and its atomic orbitals components.

occupation of such state:

$$\epsilon_i = \frac{dE_{total}}{dn_i} \quad (2)$$

Using Janak's theorem, the difference in energy between the  $1s^1$  and the  $1s^2$  states can be approximated

$$-E(1s^1) + E(1s^2...) = \int_1^2 dq \frac{\partial E_{total}(n_{1s} = q)}{\partial q} = \int_1^2 dq \epsilon_{1s}(n_{1s} = q) \approx \epsilon_{1s}(n_{1s} = 3/2) \quad (3)$$

where the last step assumes a linear dependence of  $\epsilon$  with respect to the occupation  $q$ . Computing the photoemission energy can thus be achieved with a calculation on a fictitious configuration  $1s^{1.5}2s^1$ .

Results are reported in Table 2. The two methods produce similar results; however, both are significantly off compared to the experimental value 54.7 eV [11].

Method	Photoemission energy (eV)
Tot. energy difference	68.401
Janak theorem	68.144

Table 2: Comparison of calculated photoemission energies for a 1s electron.

Obtaining values closer to experiment likely requires to account for the possibility of magnetization and to include relativistic corrections, as well as a systematic study of different exchange-correlation functionals.

## 6 Conclusion

In this study we have computed basic properties of Lithium crystal via DFT calculations. We have tested the total energy convergence with respect to computational parameters and estimated the equilibrium lattice constant which is compatible with values found in

literature. In doing so we found that an LDA exchange-correlation functional underestimates the lattice constant compared to a PBE (GGA) functional. The DOS and band structure have been calculated, with the lower bands being in satisfactory (for the scope of this work) agreement with the structure calculated in previous studies. Focusing on the isolated atom, we mapped the charge density and its orbital wavefunction components and computed the photoemission energy of a  $1s$  electron, which significantly differs from the experimental value.

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