Lithium Local Pseudopotential Using DFT

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Overview

- Theoretical Background
  - Density Functional Theory
  - Pseudopotentials
- Build Lithium LPS
- Test Lithium LPS

Density Functional Theory (DFT)

- Successful quantum mechanical approach to matter
- Energy is a functional of the density[1], Use electron density as the basic quantity
  - Only three spatial variables

1. P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

Density Functional Theory (DFT)

- Different approaches to DFT
  - Kohn-Sham[1] DFT
    - Set of equations that make use of single particle orbitals
    - Many-body effects are in the exchange-correlation (xc) energy (use LDA[2,3])

$$E[\rho] = T_s[\{\phi_i[\rho]\}] + U_H[\rho] + E_{xc}[\rho] + V[\rho]$$

    - KS-DFT is a self-consistent cycle

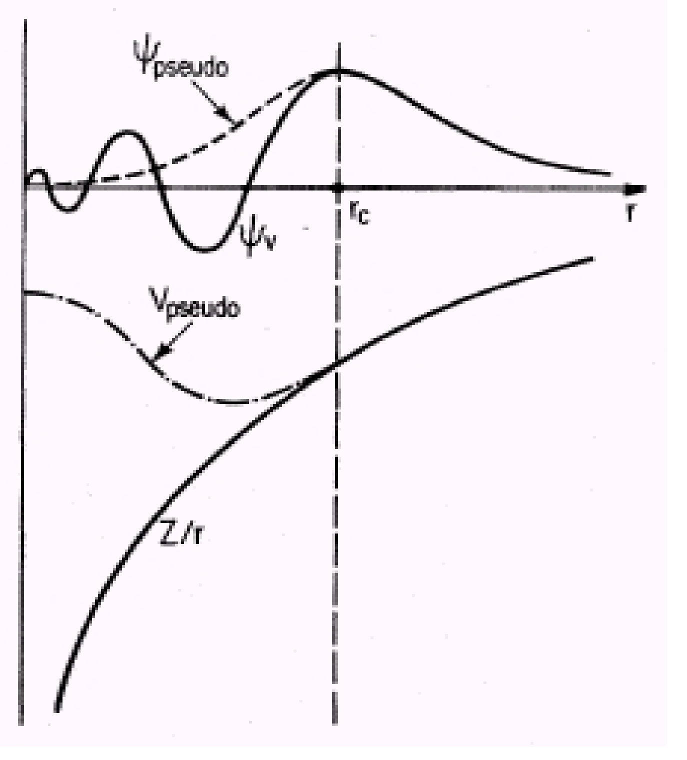
1. W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)
2. J.P. Perdew and A. Zunger, Phys. Rev. B, 1981, 23, 5048
3. D.M. Ceperley and B.J. Alder, Phys. Rev. Lett., 1980, 45, 566

Density Functional Theory (DFT)

- Orbital-Free DFT (OF-DFT)
  - Requires less computational time
  - Uses Local Pseudopotentials
  - This uses a Kinetic Energy Density Functional (KEDF) instead of KS kinetic energy operator

Pseudopotentials (PS)

- Replace the core electrons with an effective potential
  - Norm conserving[1]
  - Same after cut-off radius
  - Pseudo Wavefunction is nodeless for smooth potential
- Local and Nonlocal PS
  - Nonlocal – projected on to each angular momentum channel
  - Local – the same for different angular momentum cahnnels



1. D.R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. 43, 20 (1979)

Building LPS for Lithium

- Create a LPS using NLPS density for Lithium

- Test LPS by comparing Bulk Modulus, equilibrium lattice constant, and energy difference using KS-DFT

- Test Surface Energies for Lithium

Procedure

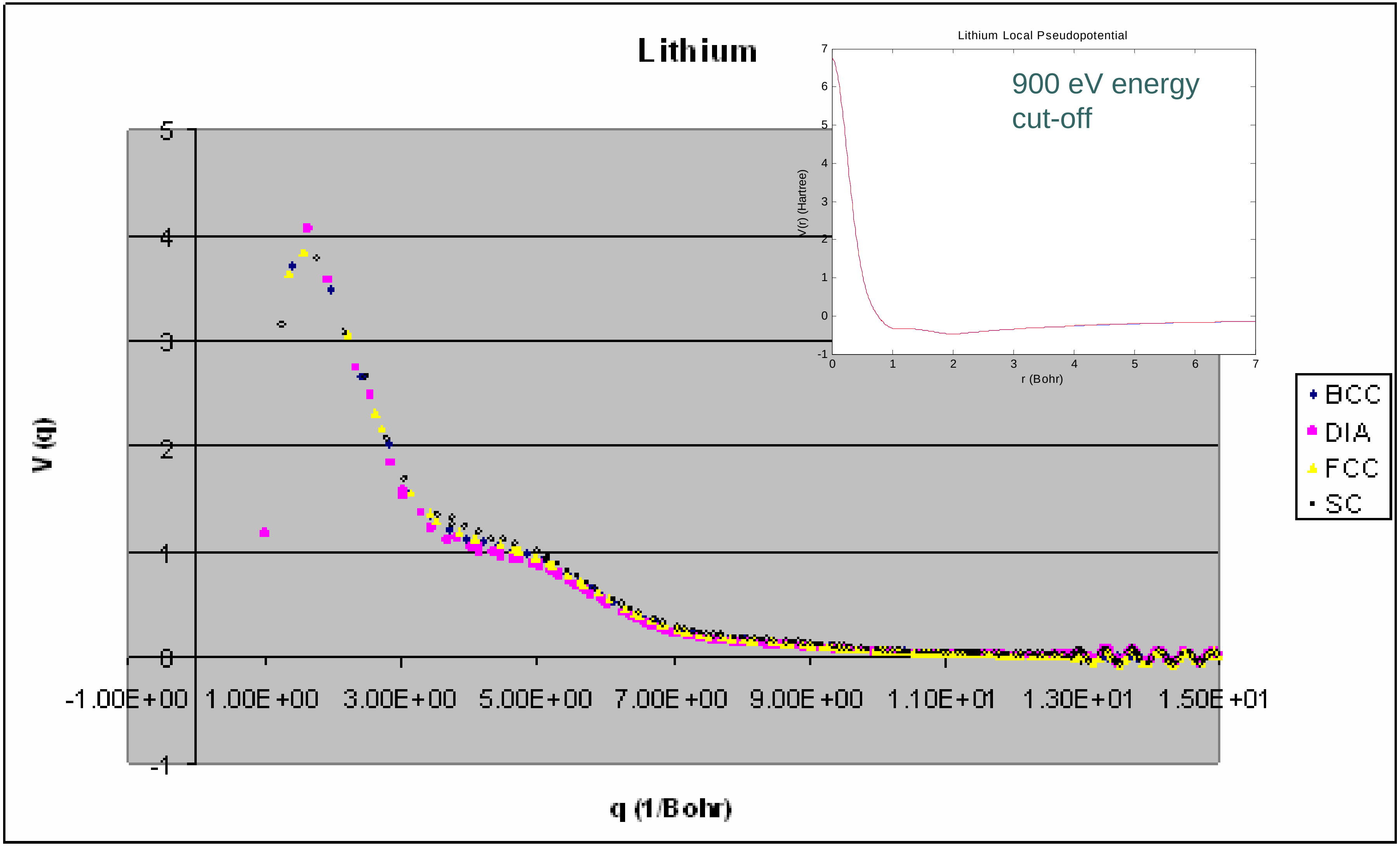
- Bulk densities for BCC, DIA, FCC, and SC structures
  - Using Troullier-Martins[1] NLPS for KS -DFT calculations

- Invert KS equations to obtain the local KS pseudopotential, using Wu-Yang[2] method.

$$W[v_{eff}(r), \rho_0(r)] = T_s[v_{eff}(r)] + \int dr(\rho(r) - \rho_0(r))v_{eff}(r)$$

1. N. Troullier, J.L. Martins, Phys. Rev. B 43, 3 (1991).
2. Q. Wu and W. Yang, *The Journal of Chemical Physics,* 2003, 118, 2498-2509.

Lithium LPS


Lithium
V (q)
q (1/Bohr)
5
4
3
2
1
0
-1
-1.00E+00
1.00E+00
3.00E+00
5.00E+00
7.00E+00
9.00E+00
1.10E+01
1.30E+01
1.50E+01
BCC
DIA
FCC
SC
Lithium Local Pseudopotential
V(r) (Hartree)
r (Bohr)
900 eV energy cut-off

Lithium Bulk Properties

Energy/atom Difference, $\Delta E = E_{BCC} - E_{DIA}$

cut-off radius (a.u.)	ΔE, Local (Ha)	ΔE, Nonlocal (Ha)	Difference (mHa)
2.5	0.012887	0.019437	6.6
3.0	0.014432	0.019437	5.0
3.5	0.015690	0.019437	3.7
4.0	0.019524	0.019437	0.08

Bulk Properties	BCC		DIA	
	a_0 (Bohr)	B (GPa)	a_0 (Bohr)	B (GPa)
Local	6.34	18.62	6.15	11.54
Nonlocal	6.34	13.92	5.78	10.79

Surface Energies

	Local (mRy/Bohr^2)	Nonlocal (mRy/Bohr^2)	Kokko et al.[1] (mRy/Bohr^2)
BCC (100)	0.704	0.684	0.64
BCC (110)	0.674	0.721	0.69

1. K. Kokko, P.T. Salo, R.L.Laihia, and K.Mansikka, Phys. Rev. B, 52, 3, (1995)

Conclusion

- Lithium LPS was not accurate
  - Surface energy decrease from bcc(100) to bcc(110)
- Possible Reason for inaccuracy
  - Need to take into account the $1s^2$ electrons

Future Work

- Use Core Correction for Local Pseudopotential
- Calculate Bulk Properties for more structures

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