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A lithium projector augmented wave potential suitable for use in VASP at high compression and temperature

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Abstract

Density Functional Theory (DFT) based Equation of State (EOS) construction is a prominent part of Sandia's capabilities to support engineering sciences. This capability is based on augmenting experimental data with information gained from computational investigations, especially in those parts of the phase space where experimental data is hard, dangerous, or expensive to obtain. A key part of the success of the Sandia approach is the fundamental science work supporting the computational capability. Not only does this work enhance the capability to perform highly accurate calculations but it also provides crucial insight into the limitations of the computational tools, providing high confidence in the results even where results cannot be, or have not yet been, validated by experimental data. This report concerns the key ingredient of projector augmented-wave potentials for use in pseudo-potential computational codes. While the insights are general for all materials and codes, I specifically address calculations of highly compressed, high temperature, lithium using the Vienna *Ab-initio* Simulation Package.

Acknowledgment

I am grateful for invaluable help from Dr. John Wills, Los Alamos National Laboratory, who provided all-electron density of states. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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Nomenclature

Dirac The Dirac Equation: The relativistic quantum mechanical wave equation describing electrons in relativistic matter, such as heavy materials like actinides.

SE The Schrödinger Equation: The non-relativistic limit of the Dirac Equation, sufficiently accurate to describe electrons in lighter materials.

DFT Density Functional Theory: The formally exact reformulation of the wave-function based Shrödinger and Dirac Equations in terms of density and currents.

KS The Kohn-Sham Equations: A calculational approach derived from the Dirac/SE using DFT. These are the equations implemented in DFT codes.

Functional A short name for an approximation for the Exchange-Correlation functional which is the only part of DFT that needs to be approximated. The functional sets the possible accuracy of DFT calculations.

LMTO Linear Muffin Tin Orbital: A calculational method used in the RSPt code.

LAPW Linear Augmented Plane Wave: Another calculational method. It is considered the implementation method that gives the most accurate DFT results. Other methods are usually verified against this method.

plane-wave code A code using plane waves as a basis set. This is the computationally most effective approach because Fourier Transforms can be used. Calculations can also be systematically improved by increasing the number of basis functions used, usually specified by the so called 'cut-off'. However, describing core electrons accurately requires a very large cut-off, leading to expensive calculations. The plane-wave approach thus is mostly used together with pseudo-potentials (see below).

all-electron code A code treating all electrons explicitly. LMTO and LAPW codes are all-electron.

pseudo-potential code The chemically inert core electrons are treated in a collective way via pseudo potentials, which increases the computational efficiency considerably. A number of different approaches exist; all are verified by comparing to all-electron, usually LAPW, results.

PAW Projected Augmented Wave: The pseudo potential technique currently considered the most accurate.

RSPt Relativistic Spin-Polarised test: The name of an all-electron, full potential, LMTO code developed by Dr. John M. Wills at Los Alamos National Laboratory.

VASP Vienna *Ab-initio* Simulation Package: A plane wave, pseudo potential (PAW), DFT code extensively used at Sandia.

core electron An electron close to the nucleus. In an LMTO or LAPW treatment these electrons are considered inert and their properties only depend on the closest nuclei. In a pseudo-potential code the effect of the core electrons on the valence electrons is included via pseudo potentials.

semi-core electron An electron that is intermediate between a core and a valence electron. It has the same angular momentum quantum number as some of the valence electrons but has a lower principal quantum number (it is in a lower shell). For the heavier nuclei (or for lighter nuclei at high pressure) these electrons need to be treated as valence electrons.

valence electron The outermost electrons are valence electrons and their properties are dependent on many nuclei. These electrons are forming bonds that hold a solid or molecule together.

Chapter 1

Introduction and Motivation

Density functional theory (DFT) is the preferred computational method for exploring materials properties, and Sandia scientists are at the forefront of DFT-based equation of state (EOS) construction, where information from both experiments and computational investigations are used (See Figure 1.1).

DFT[6,9] is a formally exact reformulation of the Schrödinger Equation (SE) for the ground state of an electron system. Since the DFT equations are far easier to solve than the many-body SE, DFT has become the preferred computational method for exploring properties of materials. One example of a Sandia effort in this area is the recent use of DFT results combined with Z experiments to construct a new Quartz standard leading to resolution of an important discrepancy between flyer plate and laser driven shock data for deuterium.[8] Another example is similar work for Xenon,[19] a material of importance for DOE. Here DFT results helped both in showing that the available Equation of State (EOS) tables were inaccurate at high pressures and in the construction of a new, more accurate, EOS.

For elemental bulk materials with simple structures, such as face-centered cubic (fcc) or body-centered cubic (bcc) atomic arrangements, a computational cell with only one atom can be used. For such simple materials, DFT codes that treats all electrons very precisely can be used, at least at low temperatures. However, for more complicated structures and for calculations at higher temperatures, larger computational cells with more atoms are needed for a good description of the material. For these applications pseudo-potential codes, such as the Vienna *ab-initio* simulation program (VASP),[10,11] have become the workhorse computational tool. In such a code the inert core electrons are replaced by a pseudo-potential (pp) and only the valence electrons are treated explicitly, allowing for more efficient use of computer resources. High quality pseudo-potentials are available for VASP and other codes, the quality usually being determined by comparing zero temperature lattice constants and bulk moduli with results from equivalent calculations with an all-electron code. It is important to note that the quality of a pseudo-potential can only be determined by comparison to all-electron calculations, never by comparison to experiment.

The key issue with pseudo-potentials are their transferability. A pp is usually constructed from the all-electron results of a single, free, spherically symmetric atom. For this atom the pp is generally producing the same results as an all-electron cal-

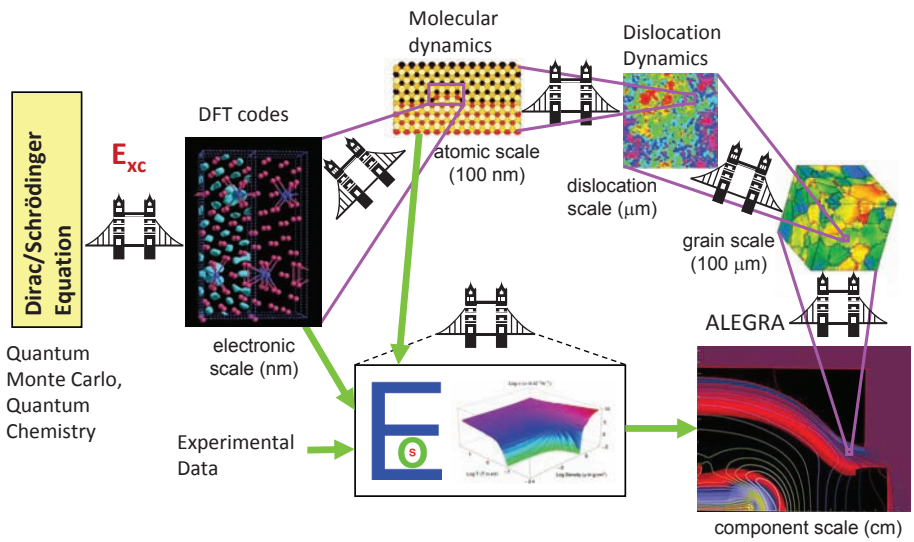


Figure 1.1. The foundation of Science Based Engineering is to build bridges from the fundamental Laws of Nature up to the Engineering codes, bridging several length and time scales. In this figure two different paths are depicted. The upper one is quite complicated and illustrates the general problem of bridging several different scales. The lower path is already in use at Sandia. For Equation of State construction, data provided by Density Functional Theory (DFT) based calculations are used in addition to experimental data. The DFT calculations are used in two ways, either directly or as a provider of forces in a Molecular Dynamics scheme.

culation. However, the success of transferring a pp to a different environment, such as to an atom in a bulk lattice, is dependent on a number of factors. Until recently most pps have been constructed for bulk matter at equilibrium and at fairly low temperatures. While these pps usually produce very good zero temperature equilibrium lattice constants and bulk moduli, their use in other environments can produce less reliable results. At Sandia we are using the projector augmented-wave (PAW) pseudo-potentials in VASP for shock physics applications. It is well known that both the dense matter and the elevated temperatures in this regime can make these pp results less accurate. The aim of my work on PAW potentials for VASP is to understand and remedy the limitations of standard VASP potentials.

Chapter 2

Density Functional Theory

Density Functional Theory (DFT) is an exact reformulation of the fundamental law of nature governing the behavior of electrons. If electrons are in materials with heavy ions, the fundamental law is the Dirac equation. For materials composed of lighter ions, such as Li, the non-relativistic limit of the Dirac equation, the Schrödinger equation, might be used.

Density Functional Theory was first developed using the Schrödinger equation. Using the Hohenberg-Kohn theorem,[6] the Shrödinger equation, which decides the electronic properties of a material via many-body electronic wave-functions, can be cast in the form of the Kohn-Sham (KS) equations, which instead decide the behavior of ground state electrons via auxiliary non-interacting single particle Kohn-Sham orbitals forming the true electron density of the material. The key point is that solving for non-interacting single particles is a much less demanding task than solving for many-body wave-functions.

Despite the theory in itself being exact, approximations for the *Exchange-Correlation functional* still need to be done since the form of this object is unknown. The accuracy of the approximation for the Exchange-Correlation functional is the factor that decides the ultimately attainable accuracy of the calculations. No calculations based on DFT can ever give better results than this approximation allows. If the 'divine'[13] functional were known, however, the KS equations would yield the exact same results as the fundamental law of nature, the Schrödinger Equation.

The KS equations are often interpreted as the equations of electrons moving in a field formed by all the other electrons, so called mean-field theory. From a mean-field theory perspective the KS orbitals can be interpreted as approximations for the true many-body electron wave-functions. This alternative interpretation of the KS equations can be very fruitful if handled correctly, but it also has created, and is creating, a lot of confusion in the field. In Figure 2.1 we try to compare the two views. In addition to the 'pure' KS equations, several mean-field theory based schemes are also implemented in VASP.

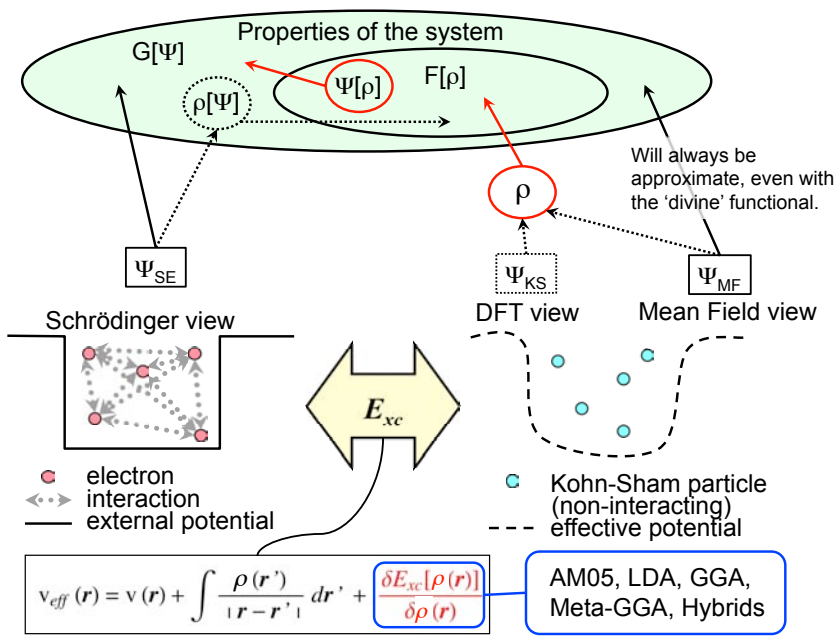


Figure 2.1. The exact functional would give the exact density, ρ, and thus the exact properties via density functionals, $F[\rho]$. The unknown wave function density functional, $\Psi[\rho]$, would in this case give all properties that can be calculated from the Schrödinger equation exactly. However, the mean field view of using the KS orbitals as approximate electron wave functions would be approximate. Only the density and properties calculated via density functionals are guaranteed to be exact. The quality of a functional can thus not be judged by how well it reproduces wave function derived properties. From Reference 12.

Chapter 3

The Projector Augmented Wave method

The computational advantages of the DFT method are further advanced by combining it with a pseudo-potential method. In contrast to the approximate exchange-correlation functionals, a pseudo-potential approximation is a numerical one. The results obtained with a pseudo-potential should give the exact same results as an all-electron calculation, *provided the same exchange-correlation functional is used*.

The projector augmented-wave (PAW) method was developed by Blöchl in 1994.[2] The version of the PAW method implemented in VASP is thoroughly described in Reference 11 and the PAW potentials produced for this method are now the only recommended ones for use in VASP. A library of functional-specific PAW potentials is distributed together with the source code. The distribution deployed in April 2012 contains many 'GW PAWs' which are of special interest to the Sandia shock physics community.

Pseudo-potentials can also be used in many-body schemes based on the mean-field view of the KS equations (see Fig. 2.1). One such method of relevance for this work is the GW method. This method uses the unoccupied states (which have no real meaning in DFT since they do not contribute to the density) and it has been noted that PAWs that give very accurate ground state properties still can produce highly deficient unoccupied states. Since the Fermi-Dirac distribution of electrons at high temperatures distributes electrons also to states that are unoccupied at zero temperature, where pseudo-potentials are constructed, we have noted that using the GW PAWs improves the quality of calculations for high-temperature shock physics applications.

The many components of a PAW potential for VASP are contained in a file named POTCAR. The individual components are well described in section "IV. PAW DATASETS" in Reference 11. A computer program generating POTCAR files have been provided to me by the main VASP developer, Dr. George Kresse, who has also produced all the standard PAW potentials distributed with VASP. The generator program takes a minimum of two input files, V_RHFIN and PSCTR, and there are at least 30 parameters that can be set in those files. This report will not concern all of them. However, for the understanding of the results and insights presented below, a

few of these parameters need to be discussed. At the beginning of each POTCAR file is an information section stating the values of relevant parameters. Note that, although the VASP default units are Ångström (Å) and electron Volt (eV), lengths in this section are in bohr, if not otherwise specified.

The all-electron calculation

A pseudo-potential is constructed from an all-electron calculation on a single, free, atom. The aim is to obtain a pseudo-potential that in a pseudo-potential calculation would reproduce selected all-electron results for this atom.

Atom configuration

Contained in the PAW generator program is thus an all-electron DFT code that produces wave-functions and eigenvalues for a spherically symmetric atom. However, in many cases we need to have higher angular momentum components available in a VASP calculation, even though these states are not occupied in an atom. One example is the higher angular momentum state often used to produce the local potential (see below). Sometimes, we also want to use an excited atom as the bases for the PAW construction; this is the case for most of the Li PAWs discussed in more detail below. The input to the all-electron calculation in the PAW generation is contained in the V_RHFIN file. In POTCAR files produced with the newer versions of the PAW generator code, such as the version I have used in this work, the atomic configuration is printed in the information section at the beginning of the file.

The exchange-correlation functional

The all-electron calculation performed in the process of generating the pseudo-potential is using a specific exchange-correlation functional. This is also specified in the V_RHFIN file. In general a pseudo-potential is functional specific and should not be used with another functional. However, the PAW implementation used in VASP is very insensitive to the functional used in producing the PAW, and from version 5 of VASP accurate results can be obtained with any implemented functional used on the standard LDA or PBE[18] PAW potentials. In Reference 14 we show that both LDA and PBE[18] PAWs can be used together with AM05[1] in VASP 5, giving nearly identical results. This allows the use of new functionals in VASP 5 without the substantial work of generating functional specific pps. Many of the calculations at Sandia are made using both LDA and AM05, and we have thus been focusing on making LDA PAWs for use in shock physics applications. The functional used in the production of the PAW is written in the information section as the value of the tag LEXCH. Note

that the value CA ('Ceperly and Alder parameterized by J.Perdew and Zunger') denotes LDA with the Perdew-Zunger correlation,[17] which is fitted to the Ceperly and Alder Quantum Monte-Carlo results for the uniform electron gas.[4]

The number of valence electrons

A crucial decision to make in the PAW construction is how many of the electrons should be classified as core or valence. The core electrons in a PAW potential are represented as core charge densities based on the atomic calculation. As long as the core electrons in a VASP calculation are still atomic like and inert, that is, they do not participate in the binding, this is a good approximation. However, as matter is compressed, core electrons that at equilibrium are inert, can start to participate in the binding of the material, thus becoming valence electrons. Another problematic case is at very high temperatures, when core electrons might need to be promoted to higher energy states according to the Fermi-Dirac distribution. This is a very strong limitation of a pseudo-potential and no calculation can be trusted in the regime where electrons assumed to be inert in a PAW potential actually are not. The solution to this problem is to design PAW potentials that promote some of the atomic core electrons to valence electrons. In the case of compressed Li we need to have all three electrons as valence electrons. So the PAW potentials I discuss here all have no core charges. The number of core vs valence electrons are also set in the V_RHFIN file. The very first number after the name of the PAW potential in the POTCAR file is the number of valence electrons.

The PAW generation

The first and most important criteria for a good PAW potential is that it reproduces the most important results of the all-electron calculation on the single, free, atom. There is no hope to be able to mimic all-electron results for more complicated systems if the PAW potential cannot at least reproduce the atomic properties. Theoretically, the PAW method is able to exactly reproduce the all-electron wave-functions of the *valence electrons*, but in practice this is never attainable. By evaluating the logarithmic derivatives of the atomic pseudo wave-functions and compare them to the logarithmic derivatives of the exact atomic wave-functions produced in an all-electron calculation, the quality of the scattering properties can be assessed. The PAW generator code is printing out logarithmic derivatives of the atomic wave-functions from the all-electron, the bare pseudo-potential, and the full PAW calculations in a file named DDE. In the previous distribution of PAW potentials, this DDE file was given together with the POTCAR, the V_RHFIN, the PSCTR, and a file with the all-electron atomic potential, named V_TABIN (used to speed up the all-electron atomic calculations by giving a good input potential for the self-consistent loop).

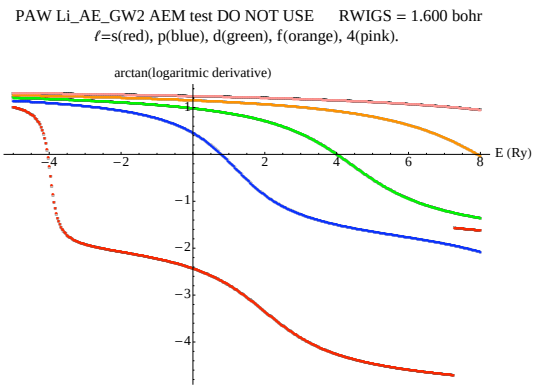
The DDE file is the main tool for tuning the parameters in the PSCTR file for obtaining an accurate PAW potential. A good correspondence between the all-electron and the PAW logarithmic derivatives is a necessary but not sufficient criteria for a good PAW potential.

The logarithmic derivatives are calculated at a specified distance from the atom center. This radius is given in the POTCAR information section as RWIGS. In newer versions of the generator code the value of RWIGS can be set to any value without influencing any other setting, thus, the rest of the POTCAR file is independent of this value. However, this value is still a good indicator as to the smallest nearest neighbor distance at which the PAW potential can be trusted. More stringent restrictions of the maximum compression at which the PAW potential can be trusted are set by the various cutoff radii used in the PAW construction. The RWIGS value is usually set slightly larger than the largest of these radii. Examples of logarithmic derivative plots are shown in Figure 3.1 and they will be discussed further below.

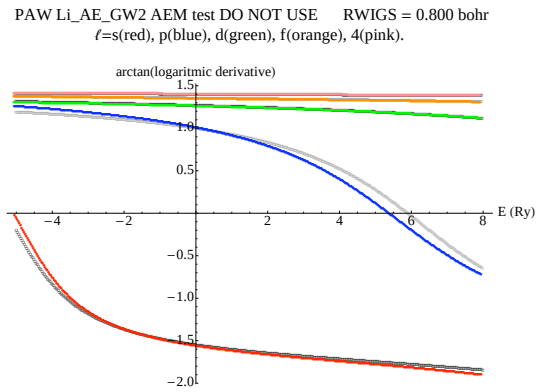
The basic idea with a pseudo-potential is to smoothen out the rapidly varying wavefunctions near the atomic center, permitting the use of a smaller basis to resolve the variations of the pseudo-wave functions compared to the all-electron wave functions. The basis size in a plane-wave code is determined by the kinetic energy cutoff (ENMAX in the POTCAR file, but ENCUT in the calculation input file, INCAR). The computational cost of a calculation is highly dependent on this cutoff energy. Standard PAW potentials are constructed with both accuracy and speed in mind, and while accuracy demands smaller radii, speed requires larger, and the final choice of radii will always be a compromise. However, for the applications we are interested in for this work, the primary focus is on accuracy, not the speed of the calculations.

The local potential

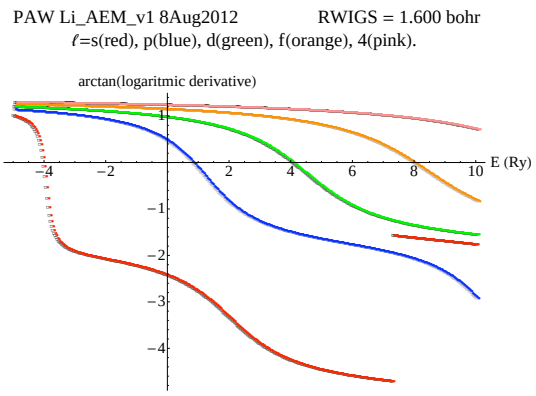
The local potential is used for all angular momentum channels that do not have their own projectors or pseudo-potentials. It can be constructed from either 1) a higher angular momentum pseudo-potential or 2) an independent pseudized construction based on the all-electron potential. In both cases the local potential outside of a certain radius is equal to the self-consistent, all-electron potential while it is modified inside this radius. The first case is used if the tag ICORE is set. The value of ICORE is the angular momentum channel that is used as the local potential and its radius can be found in the last line of the "Description" part of the information section in POTCAR (which should, of course, have the same angular momentum, l, as the ICORE value). In the second case the cutoff radius is shown by the RCLOC tag. The harder (having smaller radius) this local potential is the better description of the scattering properties we get. After all, if the radius is 0 we recover the all-electron potential. However, the harder we make the local potential, the easier it is to have unphysical "ghost" states appearing. Signs of ghost states sometimes can be seen already in the DDE plots, but sometimes only further testing, such as the Density



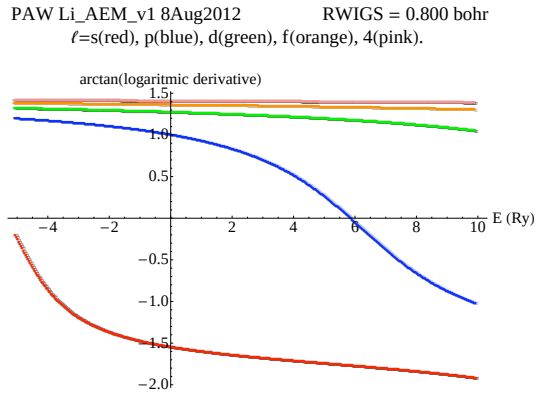
(a) Li_AE_GW2 logarithmic derivatives at radius 1.600 bohr.



(b) Li_AE_GW2 logarithmic derivatives at radius 0.800 bohr.



(c) Li_AEM_v1 logarithmic derivatives at radius 1.600 bohr.



(d) Li_AEM_v1 logarithmic derivatives at radius 0.800 bohr.

Figure 3.1. The arctan of the logarithmic derivatives of pseudo wave-functions (colored) compared to those of all-electron wave-functions (black and grey, not seen if the colored points are exactly on top). In order to generate the DDE files plotted in (a) and (b), I have had to regenerate the full POTCAR file. In order to not accidentally use these in real calculations I have marked them with "DO NOT USE".

of States (DOS) calculations discussed below, reveals them.

Partial wave cutoffs

A PAW potential contains partial waves and projectors. These are constructed from all-electron wave-functions obtained in the all-electron calculation. There are two types of wave-functions used: wave-functions calculated at the atomic eigenenergies, and wave-functions calculated at non-eigenenergies. In both cases pseudo-wave func-

tions are constructed by pseudizing inside a specified radius, as is shown in Figure 3.2.

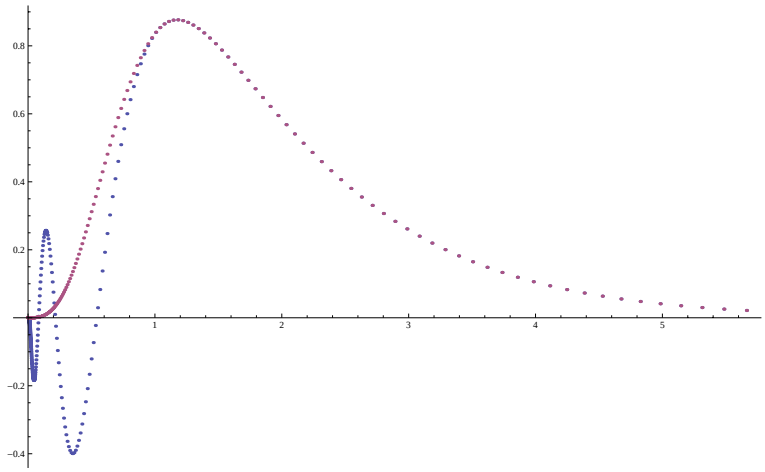


Figure 3.2. A pseudized radial wave-function (red) compared to an all-electron radial wave-function (blue). Since the match at the cutoff radius (1.058 Ångström) is to second order, the two wave-functions agree fairly well also some distance inside this cutoff. The horizontal axis in the plot is the distance from the nucleus in units of Ångström.

The values of the energies and the cutoff radii for the partial waves are listed in the "Description" part of the information section in the POTCAR file. The largest of the cutoff radii is also listed in the RCORE tag. This value is a good indicator of the limit at which further compression would cause accuracy concerns.

Number of projectors

The energies and radii of the partial waves and the number of projectors are determined by examining the DDE plots. The simple rule is that you add a projector if the desired accuracy can not be obtained with the current set. However, determining the energy of this added projector is a highly non-linear process, and some amount of trial-and-error is usually needed. Since harder potentials generally are more accurate, fewer projectors are usually needed for those PAW potentials. However, for improving the scattering properties in the higher energy range required for high temperature calculations, more projectors are needed. Having more than 3 projectors with the same angular momentum is very hard to achieve, this problem is similar to the problem of over-complete basis sets in all-electron codes. A general observation is that constructing PAW potential encompasses many of the same problems and questions as constructing accurate basis sets for all-electron codes.

The valence compensation charge

Claims have been made that the introduction of valence compensation charges into the VASP PAW scheme is problematic (see Reference 7 and references therein). It seems this problem, if present, is small in LDA PAWs and in fact I see no sign of any problems that might be attributed to the presence of compensation charges. However, I have also taken great care in using an appropriate setting for the dense augmentation grid. I routinely use an augmentation grid energy cutoff (ENAUG) double that of the plane-wave grid specified by ENCUT. I have also made sure the compensation charge radius, RDEPT, in my Li PAW is comparable to other cutoffradii.

Chapter 4

A Li PAW for hot dense matter

The library of standard PAW potential deployed in April 2012 contains 8 Li LDA PAWs. Two of them, Li and Li_GW, are one-electron potentials which are not adequate for our applications. Of the remaining 6 I have chosen 3 to examine more closely, together with my new Li PAW.

PAW potentials, three standard and one new

The three standard Li PAW potentials I have chosen to examine more closely are Li_sv_old, which is the three-electron one from the older distribution, Li_sv_GW, and Li_AE_GW2. The new Li PAW designed for use in highly compressed and hot Li is named Li_AEM_v1, and the information section of the POTCAR file is reproduced below. All 4 PAWs are produced from an atom with 2 electrons in the $1s$ state. However, the remaining electron is in the $2s$ state for Li_sv_old but in the $2p$ state for the other ones (see the Atomic configuration part of the information section below). As mentioned, all are LDA PAWs.

The pertinent details of the standard potentials are given in Table 4.2 together with the same details of Li_AEM_v1.

From Table 4.2 it is clear that of the standard potentials Li_AE_GW2 should give best scattering properties at smaller radii. I thus chose to compare my new Li PAW with this one. In Figure 3.1 I compare the DDE plots for this potential and the new Li_AEM_v1 at the RWIGS radius of both. It is clearly seen that while Li_AE_GW2 is excellent at its RWIGS of 1.600 bohr, outside of all cutoff radii, it is failing in reproducing the all-electron scattering properties at 0.800 bohr, a radius that is far inside of all cutoff radii. The interaction of two atoms positioned within each others cutoff radii can thus be completely corrupt. This severely limits the accuracy of calculations of compressed matter.

Note that the DDE files provided in the old distribution of PAW potentials usually only give data in the energy range -2 to 2 Rydberg (for PAWs with core electrons in the valence the range is usually extended to include the core state energy, in this case around -4 Ry). The much larger range I am using now is to make sure the

```
 PAW Li_AEM_v1 8Aug2012
  3.00000000000000
parameters from PSCTR are:
  VRHFIN =Li: 1s2p AEM
  LEXCH  = CA
  EATOM  =   197.8207 eV,   14.5394 Ry

  TITEL  = PAW Li_AEM_v1 8Aug2012
  LULTRA =        F    use ultrasoft PP ?
  IUNSCR =        0    unscreen: 0-lin 1-nonlin 2-no
  RPACOR =    0.000    partial core radius
  POMASS =    7.010; ZVAL   =    3.000    mass and valenz
  RCORE  =    0.800    outmost cutoff radius
  RWIGS  =    0.800; RWIGS  =    0.423    wigner-seitz radius (au A)
  ENMAX  = 1323.165; ENMIN  =  992.373 eV
  RCLOC  =    0.705    cutoff for local pot
  LCOR   =        T    correct aug charges
  LPAW   =        T    paw PP
  EAUG   = 3296.472
  RMAX   =    1.268    core radius for proj-oper
  RAUG   =    1.300    factor for augmentation sphere
  RDEP   =    0.802    radius for radial grids
  RDEPT  =    0.750    core radius for aug-charge
  QCUT   =   -9.862; QGAM   =   19.723    optimization parameters

  Atomic configuration
   5 entries
    n  l   j            E        occ.
    1  0  0.50       -52.5301   2.0000
    2  0  0.50        -2.8763   0.0000
    2  1  0.50        -1.5828   1.0000
    3  2  1.50        -1.3606   0.0000
    4  3  2.50        -1.3606   0.0000
  Description
    l       E           TYP  RCUT    TYP  RCUT
    0    -52.5300617     23  0.700
    0    -53.8913162     23  0.700
    0    217.6932160     23  0.770
    1     -1.5828088     23  0.800
    1    122.4524340     23  0.800
    2     54.4233040     23  0.800
```

Table 4.1. The information section of the Li_AEM_v1 POTCAR file.

Table 4.2. All lengths in bohr and all energies in eV.

	Li_sv_old	Li_sv_GW	Li_AE_GW2	Li_AEM_v1
RWIGS	2.050	1.800	1.600	0.800
ENMAX	270.990	433.253	509.283	1323.165
EAUG	428.394	806.423	1188.107	3296.472
RCLOC or ICORE/RCUT	2/1.550	1.003	1.206	0.705
RCORE	2.000	1.500	1.350	0.800
RDEPT	1.550	1.500	1.500	0.750
s projectors RCUT	1.550	1.200	1.100	0.700
	2.000	1.200	1.100	0.700
	—	1.300	1.300	0.770
p projectors RCUT	2.000	1.500	1.350	0.800
	2.000	1.500	1.350	0.800
	—	—	1.350	—
d projectors RCUT	—	1.500	1.350	0.800
	—	—	1.350	—
f projectors RCUT	—	1.500	1.350	—

scattering properties are good also at the large energies that will be populated at high temperatures due to the Fermi-Dirac distribution.

Calculations using the new Li PAW potential and comparison with other calculations

In order to further test the new PAW potential and also gain some insight into the limitations of the standard ones I have performed several sets of calculations. The calculations have been performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) developed at the Institut für Materialphysik of the Universität Wien.[10,11]

The Li_AEM_v1 calculations are performed with a plane-wave kinetic energy cutoff (ENCUT) of 4080 eV, while the augmentation grid cutoff (EAUG) is 8160 eV. The standard potentials are used with ENCUT = 2040 and ENAUG = 4080. All calculations are done with a Γ centered $32 \times 32 \times 32$ Monkhorst-Pack[15] $\boldsymbol{k}$-point mesh which resulted in 969 irreducible $\boldsymbol{k}$-points. All calculations are made with the tetrahedron scheme with Blöchl corrections[3] (ISMEAR = -5)

Equilibrium density

According to the LAPW results of Haas *et. al.*,[5] that are considered the most accurate calculations of lattice constants to date, the LDA, zero temperature equilibrium bcc lattice constant is 3.363 Ångström. As seen in Figure 4.1, all potentials give the same energy vs lattice constant curves.

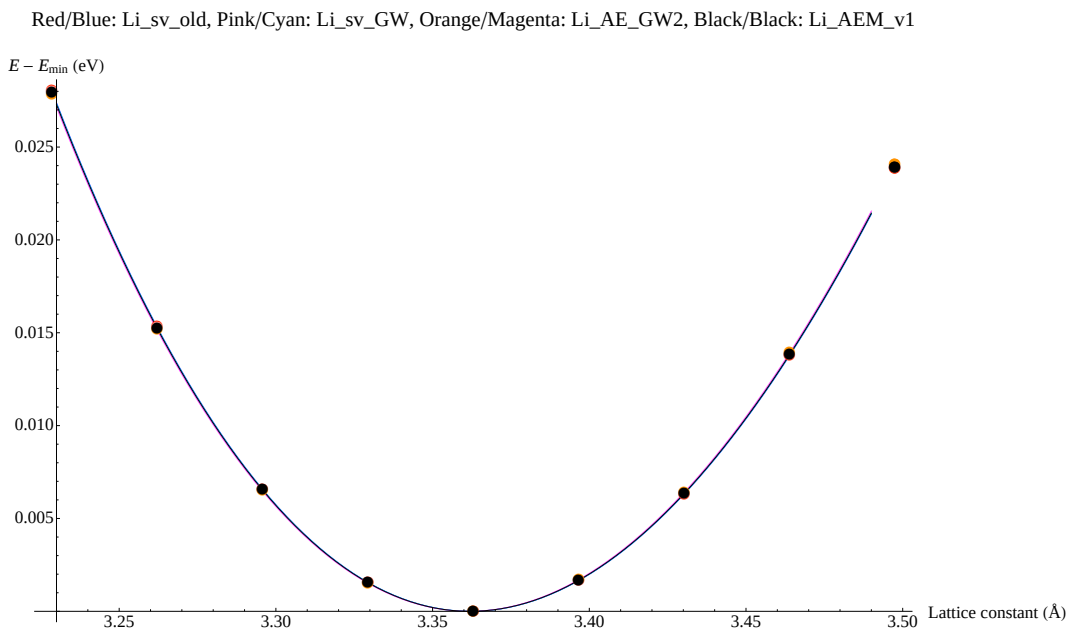


Figure 4.1. Energy versus volume near equilibrium calculated using different PAW potentials. As seen the different potentials give nearly identical curves, resulting in identical equilibrium volume and bulk modulus.

A fit to the Murnaghan Equation of State[16] gives equilibrium lattice constants of 3.362 Ångström for all potentials while the bulk modulus is 15.07 GPa.

Pressure

We can expect the differences between potentials to be more apparent at higher pressures, where the differences in cutoff radii start to influence the results. In Reference 7, calculations with various pseudo-potentials using various codes are made for compressed Li up to 25 g/cm^3. In Figures 4.2 and 4.3 I compare my results with those of Figures 4 and 5 of Reference 7. The PAW potential used in the Karasiev *et. al.* Abinit and Quantum Expresso (QE) calculations have a cutoff radius of 0.8

bohr, equivalently to the Li_AEM_v1 PAW. These three pressure curves are on top of each other in Figure 4.2, and only show minor differences in the differently scaled Figure 4.3. The blue and magenta curves in Figures 4.2 and 4.3, are calculated with the same PAW (Li_sv_old) in VASP, but, as is evident from Figure 4.3, they do not give exactly the same results. This possibly indicates that one or the other, or both, calculations are not converged. However, it should also be noted that the discrepancies are only seen when the Li_sv_old PAW potential is used outside of its range of validity.

On the top of both Figures 4.2 and 4.3, I have added a scale expressing the density in half the nearest neighbor (nn2) distance. If the density is such that this distance is smaller than the cutoff radii in the PAW potential we can suspect that the PAW potential might not be accurately describing the system. While it is clear that accurate pressures are obtained for densities with smaller nn2 distances than the RWIGS and RCORE values, the accuracy does eventually deteriorate as the nn2 distance becomes smaller. Unfortunately the calculations can still be performed: they do not break until the nn2 distance is far smaller than the smallest projector RCUT. In this case this means that the calculations do not break until the 1s electron wave-functions on different atoms have a substantial overlap. However, the pressure is in large error at this point.

It is well known that since the matching of the pseudo-wavefunctions and the all-electron wavefunctions at the RCUT radius is both for the value and the derivative, the pseudo and all-electron wavefunctions usually agree to some smaller radius than RCUT (see Figure 3.2). I have verified that this radius is at least RCUT/1.2 for all the Li partial waves studied in this project. I empirically find that a maximum density corresponding to an nn2 distance of RCORE/1.2 is a good indicator for accurate pressure (as long as RDEPT is smaller than RCORE). This translates to a Li bcc maximum density of 2.7, 6.5, 8.9, and 42.6 g/cm^3 for Li_sv_old, Li_sv_GW, Li_AE_GW2, and Li_AEM_v1, respectively. The Li_AE_GW2 pressure starts to deviate before this compression: I attribute this to the RDEPT value being larger than the RCORE value, and taking this into account, the maximum density for this potential is 6.5 g/cm^3.

Density of States

To address the issue of ghost states I have calculated the density of states (DOS) at different compressions. Ghost states give a DOS that has peaks that should not be there and in order to address this we thus need to know the true DOS for Li. Dr. John Wills, Los Alamos National Laboratory, used his RSPt[20,21] all-electron, full potential, LMTO code to provide me with reference DOS at three different compressions: these are show in Figure 4.4(a). The RSPt code has been shown to give the same results as VASP PAWs for equilibrium lattice constants and bulk moduli.[14]

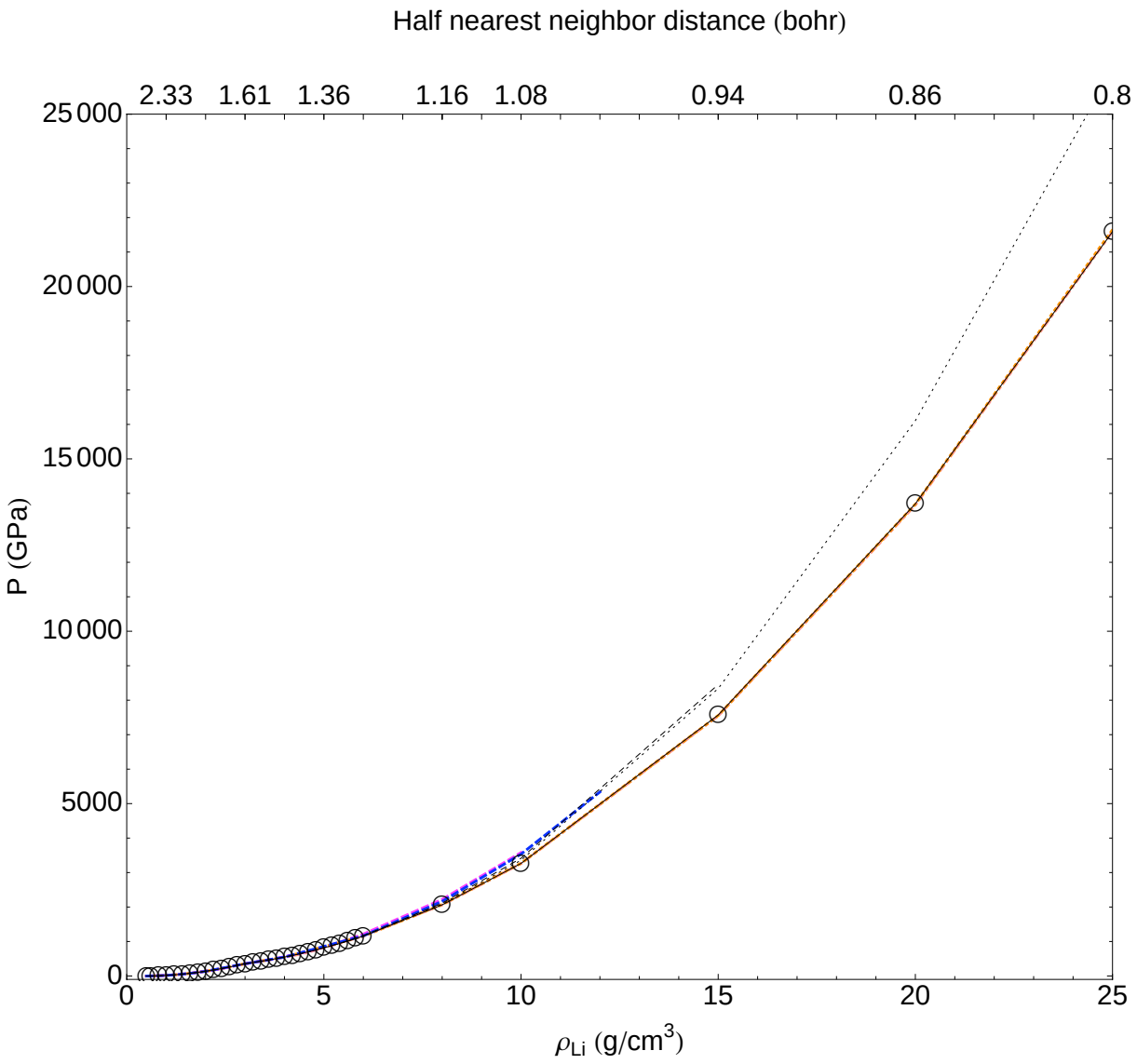


Figure 4.2. Comparison with results from Reference 7 (Figure 4).

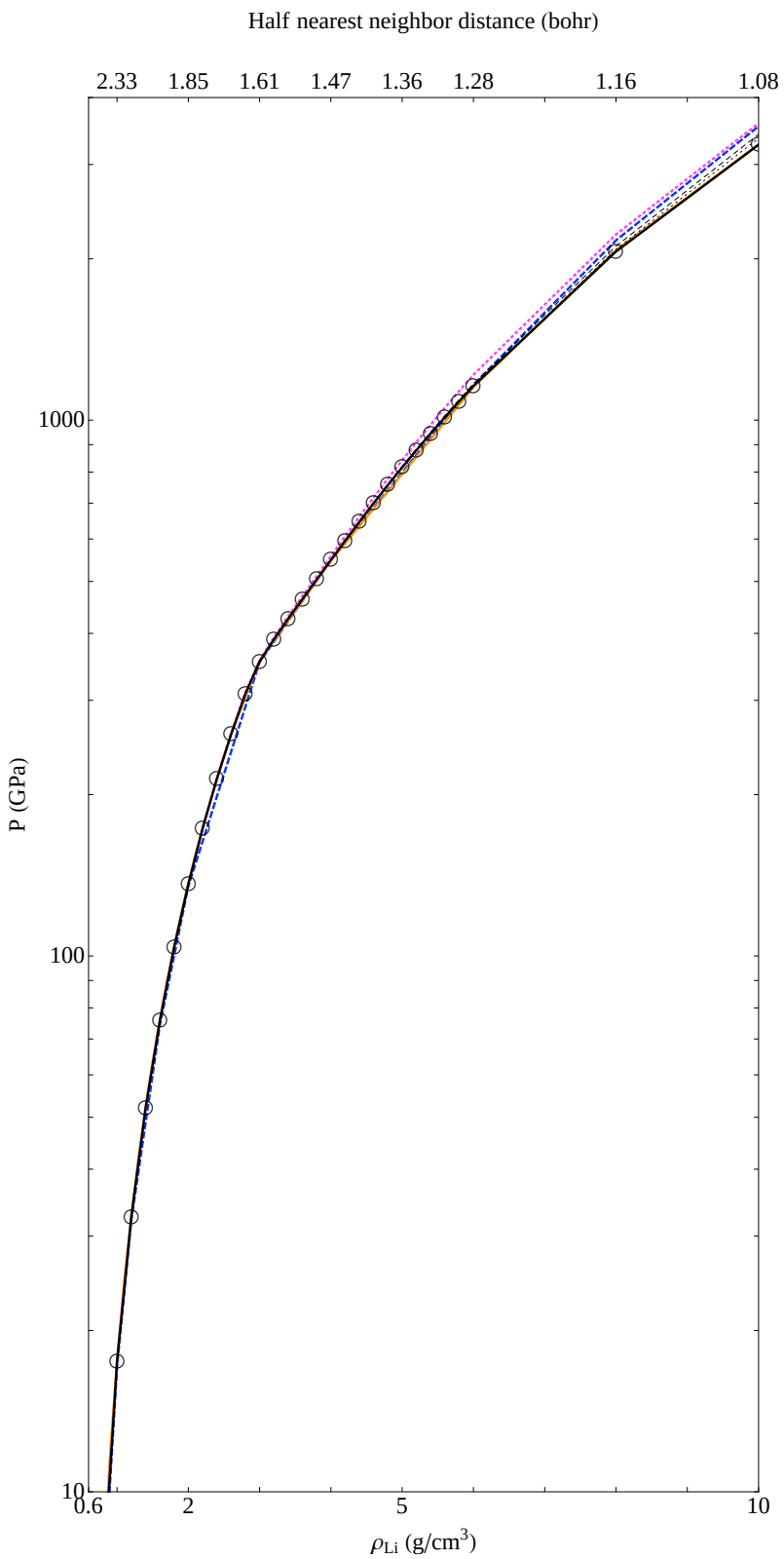
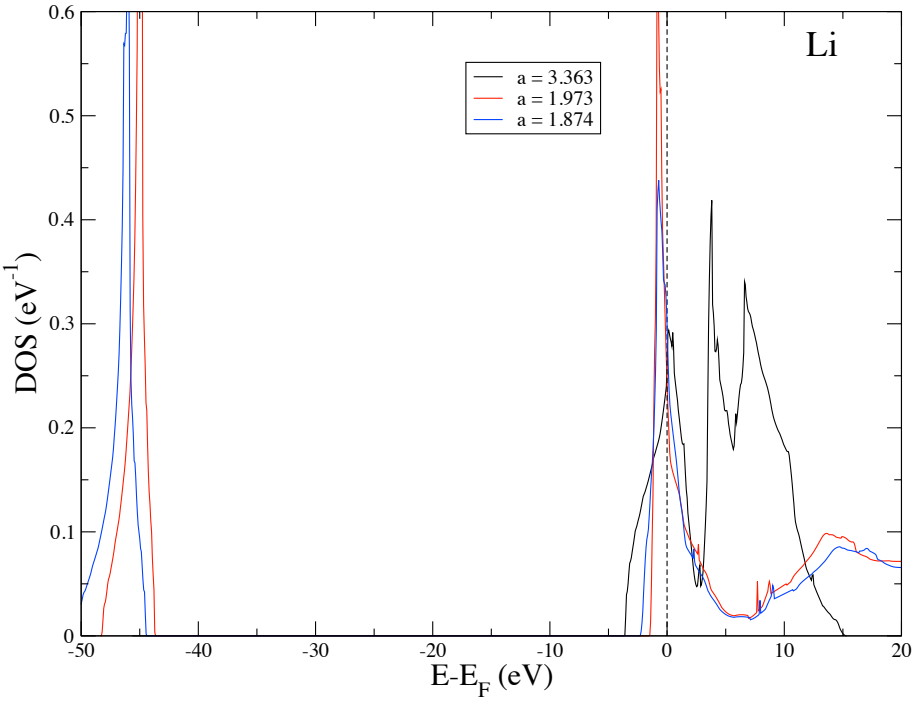
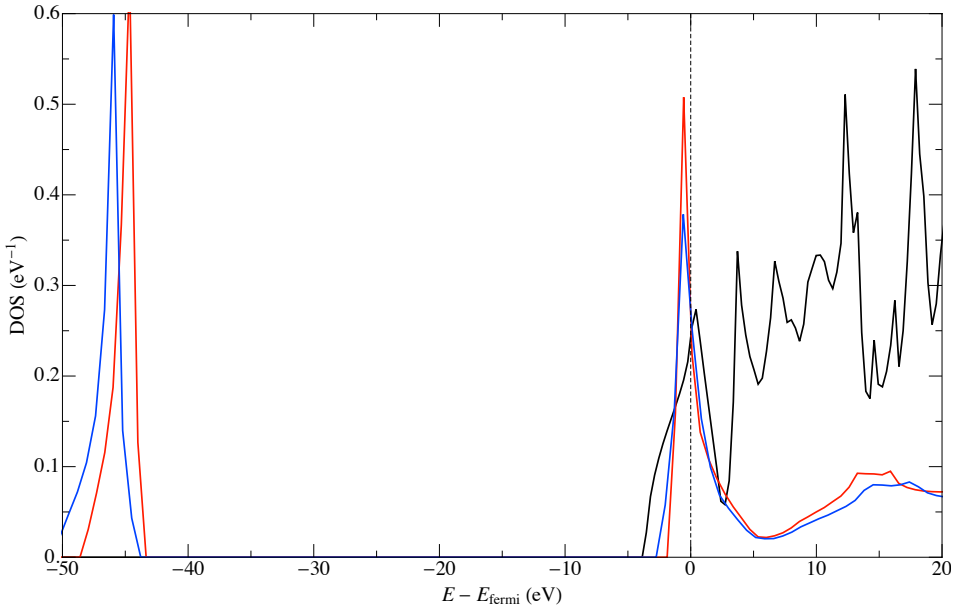


Figure 4.3. Comparison with results from Reference 7 (Figure 5).That the blue dashed line sometimes is lower than the rest up to around 3 g/cm^3 is an artifact of fewer points.



(a) Reference DOSs calculated with the all-electron, full-potential, LMTO code, RSPt.[20,21] The legend gives the lattice constants used in Ångström, corresponding to 0.6, 3.0, and 3.5 g/cm^3.



(b) DOSs calculated with Li_AEM_v1 using VASP. Legend as in (a).

Figure 4.4. Verification of DOS. Considering the vast difference in methods, these DOSs can be considered equivalent. In particular there is no sign of significant extra peaks introduced by ghost states in the VASP DOS. The differences above ~ 10 eV are numerical artifacts (number of bands taken into account).

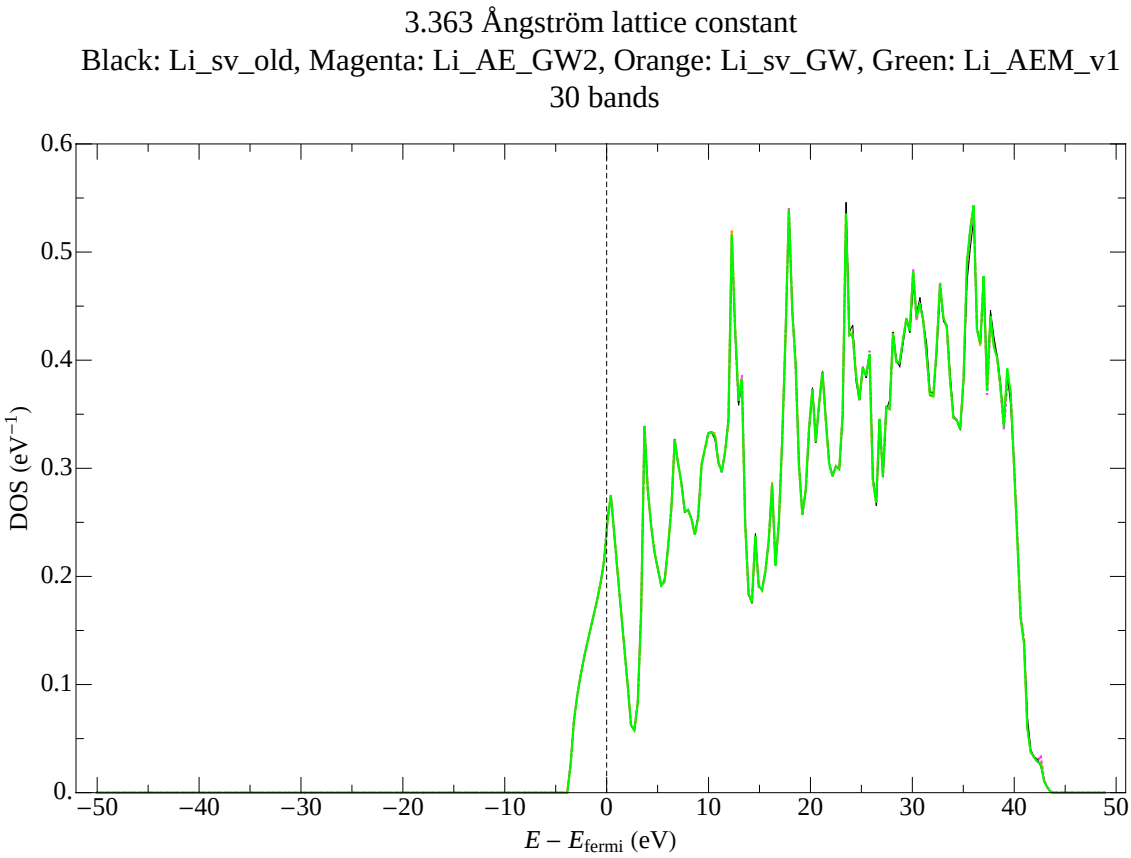


Figure 4.5. DOS at the LDA equilibrium density (0.6 g/cm^3) calculated using different PAW potentials in VASP.

Finally we compare the DOS of all 4 potentials considered in this work. As seen all potentials give the same DOS at equilibrium density. At higher densities, in particular the Li_sv_old DOS starts to differ from the Li_AEM_v1 DOS. It is however evident from Figure 4.7 that quite similar DOS still can give rise to substantial differences in pressure, see Figure 4.3.

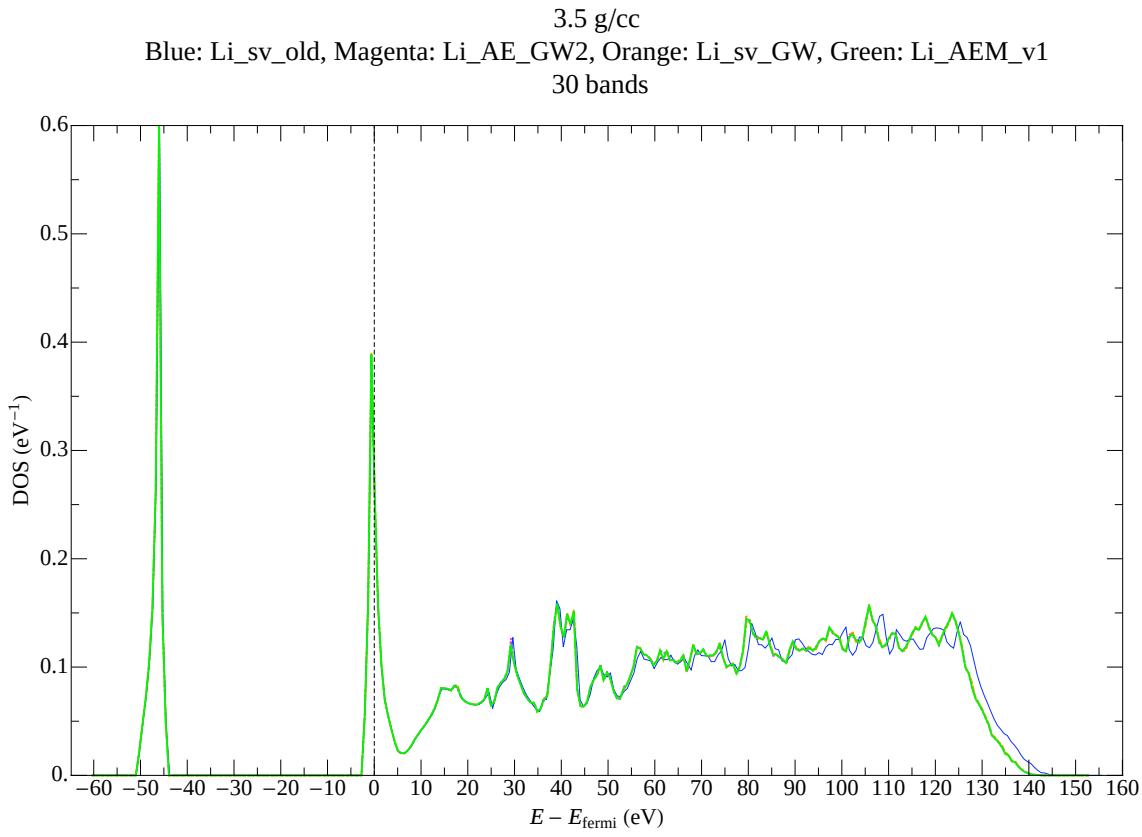


Figure 4.6. DOS at 3.5 g/cm^3 calculated using different PAW potentials in VASP.

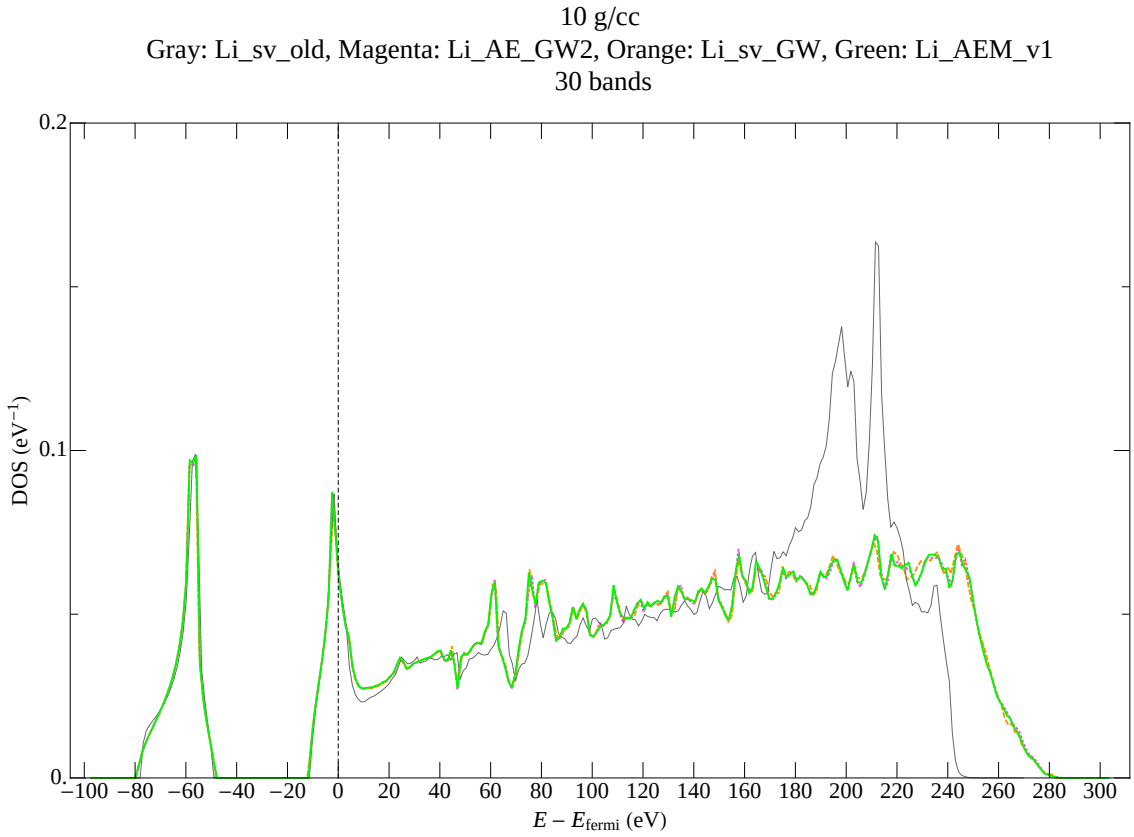


Figure 4.7. DOS at 10 g/cm^3 calculated using different PAW potentials in VASP.

Chapter 5

Summary and Conclusion

As the codes available for use in Engineering Sciences become more and more sophisticated, materials models used in these codes need to be increasingly accurate. Sandia scientists are at the forefront of DFT-based EOS construction, where experimental information is augmented with information obtained in computational investigations, in order to achieve improved accuracy. The success of the Sandia effort is based on insights and development obtained via studies such as this.

In a pseudo-potential code, such as the Vienna *ab-initio* simulation package (VASP), every atom needs to be described by a pseudo-potential. While other calculational settings, such as $\boldsymbol{k}$-point sampling and planewave basis size, can be tuned at will, these pseudo-potentials are constructed outside of the computational code and need to be provided as input to the calculation. If the accuracy of a provided pseudo-potential is not enough for the application at hand, another one needs to be constructed.

In this study three lithium projector augmented wave (PAW) potentials distributed together with VASP have been investigated and their range of applicability determined. In addition a new Li PAW potential has been constructed and investigated in the same manner. In Table 5.1, the estimated limitations of the Li PAW potentials studied are given.

Table 5.1. Estimated limits for accurate use of certain PAW potentials

		Li_sv_old	Li_sv_GW	Li_AE_GW2	Li_AEM_v1
minimum nearest	(Å)	0.882	0.661	0.661	0.353
neighbor distance	(bohr)	1.667	1.250	1.250	0.667
maximum bcc Li density	(g/cm^3)	2.7	6.5	6.5	42.6
Highest substantially	(eV)	34.0	> 109	> 109	> 136
populated energy	(Ry)	2.5	> 8	> 8	> 10

As a general rule, PAW potentials should not be used for compressions resulting in a nearest neighbor distance of less than 2× MAX(RCORE,RDEPT)/1.2. Note also that a PAW potential should not be used for temperatures that substantially depopulates the lowest energy valence state. In such cases a PAW potential with more valence

electrons should be used. Unfortunately there is no general rule for determining the highest substantially populated energy, as this is determined from the accuracy of the logarithmic derivatives.

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