MEASURING THE PERFORMANCE OF RECENT GENERALIZED GRADIENT APPROXIMATIONS TO DENSITY FUNCTIONAL THEORY IN MOLECULES AND SOLIDS

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Abstract

MEASURING THE PERFORMANCE OF RECENT GENERALIZED GRADIENT APPROXIMATIONS TO DENSITY FUNCTIONAL THEORY IN MOLECULES AND SOLIDS.

Density functional theory is a successful theory used in physics, chemistry and nanoscience to describe the ground state properties of solids and molecules. It calculates ground state energies and related properties by using the density of the valence electrons as a fundamental variable. In a system of interacting electrons, the electrons will correlate due to the Pauli exclusion principle, as well as their coulomb repulsion. This interaction energy is known as the exchange-correlation energy and is approximated in density functional theory because it is the only unknown in the energy as a functional of density. The simplest model to approximate this exchangecorrelation energy is the local density approximation, which only relies on the local density of the valence electrons at every point. Generalized gradient approximations are approximations which build upon the local density approximation by also using the gradient of the local density. Recently, many new versions of the generalized gradient approximation have been developed to attempt to obtain better energetic and structural properties either at the same time, or at the expense of the other. In this study, we examine the performance of these models by calculating the atomization energy of the AE6 test set. The cohesive energy, lattice constant and bulk modulus of a four solid test set was also calculated. These calculations were done using ABINIT, a density functional theory code that uses a pseudopotential model with plane waves to examine molecules and solids. One of the more recently developed generalized gradient approximation models, the SOGGA, is tested to compare with the standard models. The accuracy of using a pseudopotential model is also tested. It was found that by using a generalized gradient approximation that was better for energy calculations, the structural property calculations would not be as accurate. The SOGGA is a functional that approximates structural properties of solids accurately but does not calculate energies as well. It was also found that using a pseudopotential model resulted in a 1% difference from the all electron calculations.

Contents

Acknowledgments

1	Intr	Introduction					
	1.1	Density Functional Theory	1				
	1.2 Exchange-Correlation Energy						
	1.3	The Thesis Work	3				
	1.4	Preview	3				
2	Der	nsity Functional Theory	5				
	2.1	Overview	5				
	Density Functional Theory	6					
		2.2.1 Local Density Approximation	9				
		2.2.2 Generalized Gradient Approximation	12				
	2.3 Pseudopotentials						
	2.4	Basic Methodology	21				
3	Mo	lecular Data	25				
	3.1	Molecular data	25				
		3.1.1 The AE6 test set	25				
		3.1.2 Convergence calculations	28				

	3.2	Test Set Measurements	29		
4	Soli	ids	33		
		4.0.1 Introduction	33		
		4.0.2 Silicon and Sodium Chloride	33		
		4.0.3 Na and Cu	35		
		4.0.4 Murnaghan Equation of State	36		
		4.0.5 Results	38		
5	Sec	ond Order GGA	41		
	5.1	Testing the Functional	42		
6	Dis	cussion and conclusions	46		
	6.1	Introduction	46		
	6.2	The pseudopotential model	47		
	6.3	Performance of GGA's	49		
	6.4	SOGGA	49		
	6.5	Summary	50		
A	List	t of acronyms	52		
в	Diff	ference files from xcpbe.F90 file in ABINIT-5.8.3 and edited ABINI	[T-		
	5.8.	3	53		
\mathbf{C}	C Difference files from drivexc.F90 from ABINIT-5.8.3 to edited ABINIT-				
	5.8.	3	61		
Bi	Bibliography 66				

List of Figures

2.1	The LDA exchange energy as a function of \mathbf{r}_s is in red and the correla-	
	tion energy as a function of \mathbf{r}_s is green. The units of energy is measured	
	in hartrees.	11
2.2	Exchange enhancement factors versus the inhomogeneity parameter s	
	for various functionals.	17
2.3	The exchange-correlation enhancement factor vs. the inhomogeneity	
	for selected Wigner-Seitz radius using PBE, PBEsol and SOGGA	20
2.4	Flowchart of a self consistent calculation	24
3.1	The molecules of the AE6 test set.	27
3.2	The changing of the total energy of a molecule as the plane wave energy	
	cutoff is changed for a $16 \times 16 \times 16$ cell. The final energy cutoff used was	
	35 Ha	29
3.3	The total energy of a molecule changes when the cell size is varied.	
	The optimal cell size was a cube of side 16	31
4.1	The total energy measurements as the lattice constant is shifted $\pm 5\%$	
	in 1% increments for Si. The plane wave energy is varied to show a	
	convergence. Atomic units are used	34
5.1	The calculated exchange enhancement factor for the SOGGA functional.	42

5.2 The calculated XC enhancement factor of the SiH₄ in dark blue, the solid Si in light blue and the theoretical XC enhancement factor in red. The inhomogeneity is plotted on the x-axis, the Wigner-Seitz radius is plotted on the y-axis and the XC enhancement factor is plotted on the z-axis.
43

List of Tables

2.1	The various exchange functionals that were studied and their input	
	parameters	16
2.2	The recent performance data for two sets of molecules listed in various	
	papers. The citation for the paper is inside the number in brackets.	18
2.3	The performance of various functionals when measuring the cohesive	
	energy, and lattice constant.	19
2.4	The mean average error for bulk modulus calculations for two sets of	
	metals	19
3.1	The atom involved in the bonding, the type of bond, the bond length	
	and the percent difference of our measurements. Experimental data	
	taken from the computational chemistry comparison and benchmark	
	database	26
3.2	The optimal value of the parameters for each molecule using an LDA	
	model	30
3.3	The calculated and experimental values for the atomization energy of	
	each molecule using an LDA model and the PBE model. Experimental	
	data is from AE6 [32] study. \ldots \ldots \ldots \ldots \ldots \ldots \ldots	32
4.1	The various input parameters used to test the solids	38

4.2	The calculated cohesive energy for 3 different DFT models and their	
	respective errors. Experimental data taken from JANAF Thermochem-	
	ical Tables using the zero temperature data	39
4.3	The calculated lattice constants and experimental results from two	
	sources, Kittel and Staroverov	39
4.4	The calculated percent errors in lattice constant for LDA, PBE and	
	PBEsol	40
4.5	The calculated bulk modulus of the tested solids.	40
4.6	The errors in bulk modulus compared to the two sources	40
5.1	The calculated and experimental cohesive energy for the four solids	
	tested. Percent error, mean signed error and mean unsigned error are	
	also listed	44
5.2	The calculated and experimental lattice constants for the four solids	
	tested. Percent error, mean signed error and mean unsigned error are	
	also listed.	45
5.3	The calculated and experimental bulk modulus for the four solids	
	tested. Percent error, mean signed error and mean unsigned error	
	are also listed	45
6.1	LDA calculations for lattice constant compared with calculated and	
	experimental results from Staroverov. MSD is the mean signed percent	
	difference	47
6.2	PBE calculations for lattice constant compared with calculated and	
	experimental results from Staroverov. MSD is the mean signed percent	
	difference	47

6.3 LDA calculations for bulk modulus compared with calculated and e				
	perimental results from Staroverov. MSD is the mean signed percent			
	difference	48		
6.4	PBE calculations for bulk modulus compared with calculated and ex-			
	perimental results from Staroverov. MSD is the mean signed percent			
	difference	48		

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Chapter 1

Introduction

1.1 Density Functional Theory

Density functional theory is a popular theory used in condensed matter physics, chemistry, nanosciences and biophysics. In 1998, Walter Kohn was awarded the Nobel prize in chemistry for the development of this theory. The theory is used to study systems with interacting electrons in an external potential. The basic idea for density functional theory is that you do not need to know the motion of every interacting particle in a system. Only the density of valence electrons as a function of position is needed [1]. The density can be found by examining an auxiliary system of independent particles [2]. By knowing only the density, you can calculate total energy, bulk modulus, lattice constant, thermal and electrical conductivity [3]. Some uses in chemistry include the calculation of bonding, spectroscopy, structure and reactivity. This theory is useful because it is much simpler than solving the many body Hamiltonian. Due to the simplicity of density functional theory compared to solving the many body Hamiltonian, the computational time is much faster. With a faster computational method, density functional theory has the capability to solve larger problems. In 2001 Shimojo, Kalia, Nakano and Vashishta were able to study a system of 110,592 atoms using density functional theory [4]. Other applications of DFT include the study of biological molecules such as DNA [5] or the study of carbon nano tubes [6].

1.2 Exchange-Correlation Energy

In a system of interacting electrons, the electrons will correlate due to the Pauli exclusion principle, as well as their coulomb repulsion. This interaction energy is known as the exchange-correlation energy. This is a very important quantity because it is the only unknown in the many body Hamiltonian. Local density approximation (LDA) has long been used to approximate the exchange-correlation energy [2]. The LDA is the simplest model and it only depends on the local density at a point in space. To improve in this approximation, functionals have been developed which use the electron density and the gradient of the density [7–16]. The Perdew-Burke-Ernzerhof functional [7] has been the standard generalized gradient approximation (GGA) having over 11000 citations. Many new models [8–15] have been developed to improve certain measurements for either molecules or solids. The most common measurements to be improved over the PBE are the energy or the structure. Current research suggests that looking at the Laplacian might be helpful to improve calculations beyond the generalized gradient approximation. It has been observed that the error in the energy density in the LDA matches the Laplacian of the density [17].

1.3 The Thesis Work

There were three main goals for this thesis. The first goal was to collect data on the performance of many GGA functionals as well as LDA and experiment. To do this, results of standard test sets were examined. There are well known test sets of molecules used to test these functionals, but there is no standard test set for solids yet. To compare these functionals, plots of their behavior were produced. By examining the behavior of the plots, it may be possible to predict if a model is better for testing molecules or solids.

The second goal of this study was to test a new GGA model, the second order generalized gradient approximation (SOGGA) [11] and compare results with experiment, LDA, and two well known GGA models. To test a functional, we first had to implement this functional into a DFT code, ABINIT [18]. Then properties such as cohesive energy, lattice constant and bulk modulus are calculated. The measuring of the bulk modulus using the SOGGA functional has not previously been done.

The third goal was to test if using a pseudopotential model was as accurate as using an all electron model. A pseudopotential model keeps the effective potential of the valence electrons but treats the core electrons as if they were frozen. Most publicly available open source DFT codes use pseudopotentials.

1.4 Preview

Chapter 2 contains the mathematical background and a description of the fundamental theorems of density functional theory. Also included in chapter 2 is a detailed description of local density approximation and generalized gradient approximation. The basic methodology is also described in this chapter. Chapter 3 contains a description of the molecules tested and how to optimize the parameters in ABINIT. This chapter also contains the theoretical data we obtained and the experimental data we are comparing our work to.

In Chapter 4, the solids tested are listed, also a description on how to optimize the input parameters is listed. In this chapter, the Murnaghan equation of state is discussed. The calculated and experimental data is placed in tables in the last section with a discussion on these results.

Chapter 5 is dedicated to the second order generalized gradient approximation functional. Included in this chapter is a description on what the functional is and why it was developed. The changes to ABINIT required to add this functional are briefly listed as well as the calculated results. These results are compared against two simpler functionals.

Chapter 6 contains the conclusions which discuss the final results of this study.

Chapter 2

Density Functional Theory

2.1 Overview

Density functional theory (DFT) is a theory used in chemistry and physics to find a description of ground state properties of solids and molecules using energy functionals which depend on the electron density. One of the main goals of DFT is to approximate the exchange-correlation (XC) energy with high accuracy. There are two popular methods in DFT to approximate the XC energy, Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). LDA is an approximation that only depends on the electronic density at each point in space [2]. The XC energy in the LDA model can be expressed as

$$E_{xc}^{LDA}[n] = \int n\epsilon_{xc}(n)d^3r \qquad (2.1)$$

where n is the density and ϵ_{xc} is the XC energy per electron at position r. GGA is an approximation that depends on the electronic density at each point in space and the gradient of the density [7]. The XC energy in GGA can be expressed as

$$E_{xc}^{GGA}[n] = \int n\epsilon_x^{unif}(n) F_{xc} d^3r.$$
(2.2)

Here F_{xc} is the XC enhancement factor. LDA models are generally better for finding the structure of a molecule, where GGA models are better for finding atomization/cohesive energy.

2.2 Density Functional Theory

To understand what the exchange-correlation energy is, it is beneficial to first examine the Hamiltonian of an atom with multiple electrons. For an atom with multiple electrons, the Hamiltonian in atomic units ($\hbar = m_e = e^2 = 1$) looks like,

$$\hat{H} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} - \sum_{i}^{N_{a}} \frac{1}{2M_{a}} \nabla_{a}^{2} + \sum_{i} \sum_{j \neq i} \frac{1}{r_{i} - r_{j}} - \sum_{i} \sum_{a} \frac{Z_{a}}{r_{i} - R_{a}} + \sum_{a}^{N_{a}} \sum_{b \neq a} \frac{Z_{a}Z_{b}}{R_{a} - R_{b}}.$$
 (2.3)

 M_a and R_a are the mass and position of the *a*-th nucleon, r_i and r_j are the position of the *i*-th and *j*-th electrons, and Z_a is the charge of the *a*-th nucleon. The first term in the equation is the kinetic energy of the electrons. The next term is the kinetic energy of the nucleons. The third term is the interaction between the electrons. The fourth term is the interaction between the electrons and the nucleons, and the last term is the interaction between the nucleons. Using the Born-Oppenheimer approximation [19], the kinetic energy of the nucleons can be set to zero because the mass difference between the nucleus and the electrons is large. This equation can be rewritten as [1]

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{ext} + \hat{V}_{II}.$$
(2.4)

 \hat{V}_{II} is the interaction between nuclei, \hat{V}_{ee} is the electron-electron interaction, \hat{V}_{ext} is the electron-nuclei interaction and \hat{T} is the kinetic energy of the electrons.

In order to look at the Hamiltonian, we can use the Hohenberg-Kohn theorems [1]. The first theorem of Hohenberg and Kohn states that for any system of interacting particles in an external potential, the potential, V_{ext} , can be uniquely determined by the ground state density. This is because the external potential is the only term in the Hamiltonian that will change for different systems. Normally in quantum mechanics, the ground state wavefunction, ψ_0 , depends on the external potential. The second theorem of Hohenberg and Kohn states that there exists a universal functional for the ground state energy of the electrons, E[n], in terms of the ground state electron density. So,

$$E[n] = \langle \psi_0[n] | \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} | \psi_0[n] \rangle, \qquad (2.5)$$

where ψ_0 is the ground state wavefunction. In terms of density, this becomes

$$E[n] = T[n] + E_{ext}[n] + E_{ee}[n], \qquad (2.6)$$

where T[n] is the expectation value of the kinetic energy, $E_{ext}[n]$ is the expectation value of the external potential and E_{ee} is the expectation value of the electron-electron interactions. This functional can be valid for any external potential. The exact ground state energy of the system is the global minimum of this functional and the density which minimizes this is the ground state density. Now we can use the variational principle, which states that the energy computed from a guessed wavefunction is an upper bound of the true ground state. To get the true ground state, we must minimize this.

To solve this problem, we can now use the Kohn-Sham approximation. We can

now replace the many-body problem with an auxiliary independent particle problem. The goal of this approximation is to find the ground state density of this auxiliary system. The ground state density of this auxiliary system is not always equal to the original interacting system. Let

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{KS}(r)$$
(2.7)

be the auxiliary Hamiltonian. We can solve this Hamiltonian to obtain the orbitals.

$$\hat{H}_{KS}\psi_i = E_i\psi_i. \tag{2.8}$$

After obtaining the orbitals, the density can be obtained by

$$n(r) = \sum_{i} |\psi_i(r)|^2.$$
 (2.9)

For this system the energy is

$$E_{KS} = T_s[n] + \int dr V_{ext}(r)n(r) + E_H + E_{xc}$$
(2.10)

where T_s is the kinetic energy for the auxiliary system which does not equal the kinetic energy of the real system. Here T_s , V_{ext} and E_H are known and E_{xc} is the only unknown. Now we can write E_{xc} as

$$E_{xc}[n] = E_{ee} - E_H + T[n] - T_s[n].$$
(2.11)

 $E_H[n]$ is the Hartree energy and this takes the form of

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3r.$$
(2.12)

The Hartree energy can be defined as the static charge density energy [20].

The exchange-correlation terms are very important to study because they are the only unknowns in the equations above. From the Hohenberg-Kohn theorem,

$$E_{xc} = F[n] \tag{2.13}$$

where F[n] is a functional of the density of the ground state of the system. So, by knowing only the ground state density, it is possible to determine all other properties about the system. The exchange energy can be defined as the energy reduction caused by the spatial separation of two electrons with the same spin. The correlation energy is the interaction energy between electrons due to Coulomb repulsion [3] and the change of the kinetic energy due to this interaction. The exchange-correlation energy can be expressed as

$$E_{xc} = E_x + E_c. (2.14)$$

To calculate these quantities in density functional theory, there is a hierarchy of approximations that can be done. The simplest of these approximations is LDA. The next approximation in this hierarchy is GGA, which builds on the LDA.

2.2.1 Local Density Approximation

The basic idea of LDA is to assume that the density of the system is weakly varying. There are two types of weakly varying systems. One weakly varying system can be defined as a system where the density gradually changes with respect to position. The second type of weakly varying system can be described as a system where the density may change rapidly, but the amount of change is small compared to the average density. If the density is slowly varying, then the local density at each point should be roughly constant. With the density roughly the same at each point locally, the system can be viewed as a homogeneous electron gas (HEG). A HEG is a system of interacting electrons on constant density, with a uniform positive background charge to neutralize the system. A HEG is described by the Fermi energy (ϵ_f), Fermi wave vector (k_f) and the Wigner-Seitz radius (r_s). The Fermi energy is the energy of the highest occupied state. The Fermi wave vector is a vector from the origin to the Fermi surface in k-space. The Wigner-Seitz radius the radius of a volume that an electron occupies in the HEG. The Wigner-Seitz radius can be written as

$$r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}} \tag{2.15}$$

In the HEG the Fermi energy is

$$\epsilon_f = \frac{\hbar k_{k_f}^2}{2m},\tag{2.16}$$

where

$$k_f = (3\pi^2 n)^{\frac{1}{3}}.$$
(2.17)

The advantage of using the HEG is that the exchange energy is known analytically for this system and the correlation energy is known numerically. Let $\epsilon_x[n]$ be the exchange energy per particle of a HEG system with a density of n. The exchange energy is written as [3]

$$\epsilon_x^{unif}(r_s) = -\frac{3}{4\pi} \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{e^2}{r_s a_0},\tag{2.18}$$



Figure 2.1: The LDA exchange energy as a function of r_s is in red and the correlation energy as a function of r_s is green. The units of energy is measured in hartrees.

where a_0 is the Bohr radius. The exchange energy in LDA is

$$E_x[n] = \int \epsilon_x^{unif}(n(\vec{r}))n(\vec{r})d^3r \qquad (2.19)$$

[2] shown in Figure 2.1. The correlation used in this study was derived from the numerical calculation of Ceperley-Alder [21] and has the form [22]

$$\epsilon_c^{unif} = \begin{cases} 0.0311ln(r_s) - 0.048 + 0.0020r_sln(r_s) - 0.0116r_s, & r_s < 1\\ -0.1423 & r_s > 1 \end{cases}$$
(2.20)

plotted in Figure 2.1.

In the LDA model

$$E_c = \int \epsilon_c^{unif} [n(\vec{r})] n(\vec{r}) d^3r. \qquad (2.21)$$

The XC energy is a combination of the exchange energy and the correlation energy

$$E_{xc} = E_x + E_c. \tag{2.22}$$

2.2.2 Generalized Gradient Approximation

GGA is built upon LDA but it tries to better model the effects of the inhomogeneity of a system by including the local gradient of the density. The main goal of most GGA functionals has been to calculate accurate energies and structural parameters at the same time. So far there has not been a functional that can calculate both of these accurately. By calculating energies better there seems to be a loss in the accuracy of the structure.

In GGA, the exchange energy can be written as

$$\epsilon_x^{GGA} = F_x(s^2)\epsilon_x^{LDA}.$$
(2.23)

In this equation, $F_x(s^2)$ is known as the exchange enhancement factor and s is the measure of the inhomogeneity of the system. Here

$$s = \frac{|\nabla n|}{2k_f n} \tag{2.24}$$

is a logarithmic derivative of the density. This is a measure of how rapidly the density is changing as compared to the Fermi wave vector. There have been several exchange functionals developed over the years. One of the most used GGA functionals has been the Perdew-Burke-Ernzerhof functional [7]. The PBE exchange functional can be expressed as

$$F_x(s) = 1 + \kappa - \left(\frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}\right).$$
(2.25)

In the small s^2 limit

$$F_x \sim 1 + \mu s^2 \tag{2.26}$$

and in the large s^2 limit

$$F_x \sim 1 + \kappa. \tag{2.27}$$

The value of μ was chosen to be

$$\mu = \beta(\frac{\pi^2}{3}),\tag{2.28}$$

where β is a parameter discussed later in correlation. The value of μ was chosen to ensure that the XC enhancement is flat at small *s* like the LDA. Here κ is determined by the Lieb-Oxford bound [23]. The Lieb-Oxford bound is

$$E_x[n] \ge -1.679e^2 \int n^{\frac{4}{3}} d^3r.$$
(2.29)

and used to ensure that the energy can not get too deep. The values of κ and μ in the PBE are 0.804 and 0.21951 respectively.

The PBE functional uses the Ceperley-Alder model for correlation [21] plus a gradient correction [7].

$$E_c^{GGA} = \int n[\epsilon_c^{unif}(r_s,\zeta) + H(r_s,\zeta,t)] d^3r \qquad (2.30)$$

Here

$$H = \left(\frac{e^2}{a_0}\right)\gamma\phi^3 ln\left(1 + \frac{\beta}{\gamma}t^2\left[\frac{1 + At^2}{1 + At^2 + A^2t^4}\right]\right)$$
(2.31)

and

$$A = \frac{\beta}{\gamma} \left[e^{-\epsilon_c^{unif}/\gamma \phi^3 e^2/a_0} - 1 \right]^{-1}$$
(2.32)

Here t is a measure of inhomogeneity similar to s in the exchange term,

$$t = \frac{|\nabla|n}{2\phi k_s n},\tag{2.33}$$

 ζ is the relative spin polarization, ϕ is the spin-scaling factor and k_s is the Thomas-Fermi screening length. The Thomas-Fermi screening length is the distance in a HEG where the positive hole around the electron screens the electron from the others. Now in the slowly varying limit taking the second order gradient expansion as $t \to 0$

$$H \to \left(\frac{e^2}{a_0}\beta\phi^3 t^2\right). \tag{2.34}$$

[3] The value of β is 0.0066725. At high $t \ (t \rightarrow \infty)$

$$H \to -\epsilon_c^{unif}$$
. (2.35)

This causes the correlation energy to die off at large s shown in Figure 2.3. This can be explained by examining a system with large changes in density. The changes in density must be caused by potential wells. An electron will not interact with electrons in different potential wells when they become very deep because the electrons act as if frozen in place. This can be seen in Figure 2.3 as each curve starts to converge on the large s value for the exchange enhancement factor.

Since the PBE functional, there have been several functionals that attempt to give more accurate calculations using modified exchange or correlation functionals. Most GGA's share the large and small s^2 limit but differ by changing the functional form or by changing the μ value. Researchers have been generating new functionals trying to obtain correct values for energies and structures of molecules and solids. So far one functional that can calculate both measurements well has not been found. One functional that uses the same form as the PBE exchange functional is the revPBE [10]. This functional uses the same correlation as PBE but changes the κ value to 1.245. This functional increases the accuracy of atomization energy calculations over the standard PBE. Another functional studied is the rPBE functional [13]. This functional uses the same μ and κ values as revPBE, but they use a new form as their functional. Their exchange functional is

$$F_x = 1 + \kappa - \left(1 - e^{\frac{\mu s^2}{\kappa}}\right). \tag{2.36}$$

This functional has the same large and small s^2 behavior as the PBE. Some functionals have been developed to improve calculations on solids. One of these functionals is the PBEsol [8]. In this functional, they use the same correlation enhancement factor as the PBE but they use a different β value. This new beta value is 0.046. The exchange enhancement factor has the same form as the PBE but they change the value of μ to 10/81 and is obtained by gradient expansion. This functional is able to measure structures of solids with high accuracy. The RGE2 [9] functional is similar to the PBEsol functional, but there is another term in the fraction of the exchange. The exchange functional has the form

$$F_x = 1 + \kappa - \left(\frac{\kappa}{1 + \frac{\mu s^2}{\kappa} + \left(\frac{\mu s^2}{\kappa}\right)^2}\right).$$
(2.37)

The RGE2 uses the same μ as PBEsol and the κ from the PBE. Another functional that differs from the PBE is named the VMT1 [12]. The VMT1 has an exchange

Functional	Functional Form	μ	κ	β
PBE	$1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}$	0.21951	0.804	0.0066725
PBEsol	$1 + \kappa - \left(\frac{\kappa}{1 + \frac{\mu s^2}{\kappa}}\right)$	10/81	0.804	0.046
revPBE	$1+\kappa-\left(\frac{\kappa}{1+\frac{\mu s^2}{\kappa}}\right)$	0.21951	1.245	0.0066725
RGE2	$1 + \kappa - \kappa / \left[1 + \frac{\mu s^2}{\kappa} + \left(\frac{\mu s^2}{\kappa} \right)^2 \right]$	10/81	0.804	0.046
rPBE	$1 + \kappa (1 - e^{\frac{-\mu s^2}{\kappa}})$	0.21951	1.245	0.0066725
SOGGA	$1 + \kappa \left(1 - \frac{1}{2} \frac{1}{1 + \frac{\mu s^2}{\kappa}} - \frac{1}{2} e^{\frac{-\mu s^2}{\kappa}} \right)$	10/81	0.552	0.006725
VMT1	$1 + \left(\frac{\mu s^2 e^{(-\alpha s^2)}}{1 + \mu s^2}\right)$	0.21951	0	0.006725
		10/81		

Table 2.1: The various exchange functionals that were studied and their input parameters.

functional of the form

$$F_x = 1 + \left(\frac{\mu s^2 e^{(-\alpha s^2)}}{1 + \mu s^2}\right).$$
 (2.38)

Here α is chosen to satisfy the Lieb-Oxford bound and is 0.001553. The last exchange functional studied was the second order GGA or SOGGA [11]. This functional uses the PBE correlation functional with the PBEsol β , but mixes the PBE and the RPBE exchange functionals to get

$$F_x = 1 + \kappa \left(1 - \frac{1}{2} \frac{1}{1 + \frac{\mu s^2}{\kappa}} - \frac{1}{2} e^{\frac{-\mu s^2}{\kappa}} \right).$$
(2.39)

The κ value used in the exchange enhancement factor is lower than the PBE and PBEsol. Table 2.1 shows the difference in the choices of the functionals, μ values and κ values.

The following Figure 2.2 shows how the various exchange enhancement factors behave as the inhomogeneity is varied. The exchange enhancement factor is shown on the y-axis and the inhomogeneity is shown on the x-axis. There are three colors



Figure 2.2: Exchange enhancement factors versus the inhomogeneity parameter \boldsymbol{s} for various functionals.

Functional	AE6	AE (20 Molecules)
	kcal/mol	kcal/mol
LDA	15.91/bond [11]	
PBE	3.00/bond [11]	8.1 [10]
	15.5 [9]	6.95 [12]
revPBE		4.9 [10]
rPBE	2.08/bond [11]	
PBEsol	7.149/bond [11]	14.94 [12]
	35.9 [9]	
RGE2	20.0 [9]	
SOGGA	7.379/bond [11]	
VMT1 (PBE)		4.67 [12]
VMT1 (PBEsol)		11.74 [12]

Table 2.2: The recent performance data for two sets of molecules listed in various papers. The citation for the paper is inside the number in brackets.

in this figure. The red curves are exchange enhancement factors that use the PBE μ . The blue curves use the PBEsol μ and the green curve uses a different form than the previous two. From the AE6 test set, the rPBE has the best energy calculations per bond as shown in Table ??. The VMT1 using the PBE μ performed the best on the 20 molecule test set. PBE seems to do the best with energy calculations for Table 2.3. SOGGA was developed to improve lattice constant calculations, which is verified in Table 2.3. The bulk modulus performance was only reported for s-type metals and d-type metals using LDA, PBE and PBEsol functionals. From Table 2.4, you can see that LDA is by far the least accurate in calculating the bulk modulus. PBE has the best performance for both sets of metals. The functionals with the same μ as PBE do better with molecular and solid energy calculations. The functionals with the μ as PBEsol do better at calculating the structure of solids.

Now, by adding the correlation to the exchange enhancement factors we can obtain

Functional	Lattice Constant	Cohesive Energy	
	Mean Average Error 18 Solids	Mean Average Error 8 Solids	
	a ₀	На	
LDA	0.50 [9]	17.76 [11]	
	0.056 [11]		
PBE	0.074 [9]	9.224 [11]	
	0.067 [11]		
revPBE			
rPBE			
PBEsol	0.030 [9]	12.683 [11]	
	0.025		
RGE2	0.067 [9]		
SOGGA	0.020 [11]	13.144 [11]	
VMT1			

Table 2.3: The performance of various functionals when measuring the cohesive energy, and lattice constant.

Functional	Bulk Modulus Mean Average Error (GPa)			
	10 s-type Metals	5 d-type Metals		
LDA	3.24	72.8		
PBE	1.01	35.2		
PBEsol	2.49	56.0		

Table 2.4: The mean average error for bulk modulus calculations for two sets of metals.

the exchange-correlation enhancement factor. This factor can be shown as

$$F_{xc} = \frac{\epsilon_{xc}^{GGA}}{\epsilon_x^{LDA}}.$$
(2.40)

This is shown in Figure 2.3 using only the PBE, PBEsol and SOGGA functionals. There were four different values of r_s chosen. It is clear that all three have different slopes. This is due to either their choice in μ in the exchange or their choice in β in the correlation enhancement factor. From Figure 2.3, it is possible to see that the PBE chooses μ so that the F_{xc} is constant at small s. The PBEsol dips down slightly at small s, and the SOGGA has a much larger dip. All of these functionals converge



Figure 2.3: The exchange-correlation enhancement factor vs. the inhomogeneity for selected Wigner-Seitz radius using PBE, PBEsol and SOGGA.

towards their exchange value of large s. This is because at large s, the correlation effects go to zero.

2.3 Pseudopotentials

In density functional theory, we examine systems with slowly varying valence electron density. To construct a slowly varying system, we replace the electron potential with a pseudopotential, an effective potential that keeps the charge density of the valence electrons unchanged, but treats the core electrons as frozen with the nucleus. This is important for plane wave codes as discussed below. In this study, Troullier-Martins pseudopotentials [24] were used. As a data check, we compared results obtained by N. Troullier and José Martins for copper with our results using their psuedopotentials supplied by ABINIT. Our results listed in Chapter 4 are in agreement with their semi-relativistic calculations for lattice constant.

2.4 Basic Methodology

In this section I will discuss the method of solving problems in density functional theory as well as the calculations ABINIT [18,25–27] performs. The basic method to solve problems in density functional theory is performing self-consistent calculations. There are five steps to performing this self consistent calculation. The first step is to make an initial guess on what the density is as a function of position. Next, calculate the effective potential this density would cause from the condition that the Kohn-Sham energy is minimized with respect to the density

$$V_{eff} = V_{ext} + V_H + V_{xc}.$$
 (2.41)

Then, place this effective potential into the Kohn-Sham equation

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}\right]\psi_i = E_i\psi_i.$$
(2.42)

Calculate the density as a function of position and compare to the initial guess

$$n = \sum_{i} |\psi_i|^2.$$
 (2.43)

If this new density is within the desired tolerance then you can stop the calculation. If the two densities differ by more than the tolerance, you place the new density into the second step and continue to loop through the steps until the new and old densities are within your tolerance. This process is shown in Figure 2.4. ABINIT uses this self consistent method for fixed atoms as well as other calculations to approximate the XC energy. One of these other calculations is the Broyden-Fletcher-Goldfarb-Shanno minimization method [28] used to find the optimum geometry of the molecule or solid. This method involves moving the atoms and calculating the forces between them and second derivatives of the energy to speed up calculations. When the forces are minimized, the atoms are at their optimum positions.

ABINIT constructs periodic cells of the atoms, molecules or solids. By using a periodic array of cells we can apply the Bloch theorem. The eigenfunctions of the wave equation in a periodic potential are the product of plane waves. Using plane waves has benefits on the computation time needed. The fast fourier transform is a very efficient algorithm and can be used using this plane wave method [29]. We can now write the eigenfunction of a periodic system

$$\psi_{ik}(r) = \mu_{ik}(r)e^{ik \cdot r}, \qquad (2.44)$$

where *i* is the band and *k* is the wave vector. μ has the periodicity of the system. Because μ_k is periodic, it can be expanded as a set of plane waves

$$\psi_i(r) = \sum_G c_G^k e^{i(k+G)r}.$$
(2.45)

Here G is a vector that obeys the periodic boundary conditions of the system:

$$G \cdot T = 2\pi M, \tag{2.46}$$

where T is the lattice vector and M is an integer. An infinite number of G's cannot be used so a G_{max} needs to be chosen.

$$\frac{\hbar^2}{2m}G_{max}^2 = E_{max} \tag{2.47}$$

To keep G_{max} small, psueodpotentials must be used. This energy is the energy cutoff parameter discussed in Chapter 3. The density must be summed over a finite kpoint grid. Not all k's are needed, you just need to sum over the k's in the brillouin zone [30]. Different grids of k-points can be chosen to get the density within a desired accuracy. There are also different grids of k-points for different brillouin zones [31]. Now we can plug these wavefunctions into the Kohn-Sham equation and calculate the resulting density for a given potential.



Figure 2.4: Flowchart of a self consistent calculation.

Chapter 3

Molecular Data

3.1 Molecular data

3.1.1 The AE6 test set

The atomization energy can be defined as the energy difference between a molecule and its individual atoms. In this study, we examined a set of molecules with known atomization energies and compared them with our calculated values. This set of molecules is known as the AE6 benchmark [32] and contains SiH₄, SiO, S₂, C₃H₄ and C₂H₂O₂ and C₄H₈. These were chosen because it was found that these 6 molecules are good representatives of a larger test set containing 109 molecules for predicting atomization energy. The chemical name for SiH₄ is silane. This molecule is tetrahedral in shape and consists of a silicon atom bonded by single bonds to the hydrogen atoms (Figure 3.1a)). The large gray atom in the center is the silicon while the lighter, smaller atoms are the hydrogens. SiO is known as silicon monoxide and consists of a silicon atom bonded by a double bond to the oxygen atom (Figure 3.1 b)). The silicon is the larger red atom and oxygen is the smaller gray atom. S₂ is sulfur is bonded by a double bond (Figure 3.1 c)). $C_2H_2O_2$ is known as glyoxal or ethanedial and consists of a double bond between the oxygen and carbon, single bonds between the carbons and single bonds between the hydrogen and the carbon (Figure 3.1 d)). Here the oxygen atoms are red, the carbon atoms are the large gray ones and the hydrogen are the smallest ones. C_3H_4 is propyne and consists of a triple bond between two of the carbons and single bonds between the hydrogen and the other carbon atoms. In Figure 3.1 e) the carbon atoms are the larger darker circles and the hydrogens are the lighter ones. C_4H_8 is named cyclobutane. This molecule is a ring of four carbons with two hydrogen atoms bonded to each carbon (Figure 3.1 f)).

This test set has a variety of bond types and molecule sizes. The set ranges in size from a diatomic molecule of S_2 to a chain of $C_2H_2O_2$. It also contains a tetrahedral molecule, SiH_4 , and a ring, C_4H_8 . Listed in Table 3.1 are the types of bonds and the bond lengths of the molecules that were tested. The calculated values and reported errors will be discussed in following section.

Molecule	Bond	Type	Exp. (\mathring{A})	LDA % Diff.	GGA % Diff.
SiH_4	Si-H	Single	1.48	0.34	0.18
SiO	Si-O	Double	1.51	0.67	0.91
S_2	S-S	Double	1.89	0.32	0.71
$C_2H_2O_2$	C-C	Single	1.53	1.04	1.04
	C-H	Single	1.13	1.14	1.14
	C-O	Double	1.12	1.14	1.14
C_3H_4	C-C	Single	1.46	1.42	1.42
	C-C	Triple	1.20	0.63	0.63
	C-H	Single	1.10	0.42	0.42
	C-H	Single	1.06	0.76	0.63
C_4H_8	C-C	Single	1.55	0.8	0.18
	C-H	Single	1.1	0.59	0.04
	C-H	Single	1.1	0.44	0.16

Table 3.1: The atom involved in the bonding, the type of bond, the bond length and the percent difference of our measurements. Experimental data taken from the computational chemistry comparison and benchmark database [33].


Figure 3.1: The molecules of the AE6 test set.

3.1.2 Convergence calculations

The first molecule tested was silane (SiH₄). We first used an LDA model with LDA pseudopotentials. In order to find the atomization energy of this molecule, first we had to find the optimum energy cutoff value of the plane waves used to probe this system. The energy cutoff is used to control the number of plane waves at a given k point. If the energy cutoff value is too low, the total energy calculation will not be accurate. After the energy cutoff becomes high enough, the total energy calculation takes more computing time without changing the answer. The optimal energy cutoff was chosen so that the total energy differed by no more than one millihartree between calculations. This was done by changing the value of the energy cutoff of the plane waves while keeping the size of the simulation cell constant. Each run would finish when the atoms would be moved into a position where the forces differed between the runs were within our tolerance. The tolerance used in our runs was 5×10^4 hartree/bohr. To find the optimum energy cutoff, I examined the final energy of the molecule after each run and waited for them to converge. This convergence test for SiH₄ is shown in Figure 3.2 and led to a choice of 35 hartrees.

The next task is to find the optimum simulation cell size. Finding this value is similar to finding the optimum energy cutoff. This was done by using the energy cutoff value found earlier and changing the cell size between runs. The optimum cell size would be found when the energies between the previous runs would converge. It is important that the cell is of the proper size because we want to make sure that the wavefunction of the molecule goes to zero at the boundaries. If the wavefunction did not go to zero, part of the valence electrons would be out of the test cell and overlapping with the neighbor molecule. Figure 3.3 shows how this optimized parameter was determined. The optimal parameters used to test each molecule is listed in Table 3.2.



Figure 3.2: The changing of the total energy of a molecule as the plane wave energy cutoff is changed for a 16x16x16 cell. The final energy cutoff used was 35 Ha.

These parameters were used in both LDA and PBE tests.

3.2 Test Set Measurements

Now, knowing the proper energy cutoff and simulation cell size values, it is possible to run the program with both of the optimum parameters in place to make accurate measurements of ground state properties. After the final run, it is possible to find the atomization energy by taking the difference of energies between the molecule and the individual particles used to build it. We are also able to find the bond length between the silicon atom and the hydrogen atoms by looking at the final geometry

Molecule	Energy Cut Off	Cell Size
	(Ha)	(a_0)
SiH ₄	35	16 16 16
SiO	35	$16\ 16\ 16$
S_2	20	$14 \ 14 \ 14$
C_3H_4	25	$12 \ 12 \ 12$
$C_2H_2O_2$	30	16 16 16
C_4H_8	40	18 18 18

Table 3.2: The optimal value of the parameters for each molecule using an LDA model.

of the molecule. After calculating the atomization energy, we compared our results with the experimental findings. After finding the values using LDA, we changed to the PBE functional while still using the LDA pseudopotentials. This was done by writing a script that would copy each molecule input file into another folder. The script would then change the exchange-correlation to the functional chosen. The last command the script would execute would be to run the new input files on the cluster. Once we changed the model, we optimized the parameters in the same fashion as before and calculated the atomization energy and bond length of silane.

Using the same steps as silane, the atomization energies and bond lengths were calculated for all of the molecules in the test set for both LDA and GGA models. Listed in Table 3.3 are the results of the atomization energy calculations using the LDA and PBE models. These were calculated using the optimized parameters described in Table 3.2. These results shown in Table 3.3 show the PBE with a lower error than the LDA for each molecule. The mean signed error (MSE) was calculated using the formula

$$MSE = \frac{1}{n} \sum e_i, \tag{3.1}$$

here n is the number of measurements and e_i the error in the *i*th measurement. The MSE is helpful to know because it will show if the model is over-binding or



Figure 3.3: The total energy of a molecule changes when the cell size is varied. The optimal cell size was a cube of side 16.

under-binding. The under-binding would agree with most literature in Table 2.2 as PBE is known to improve energy calculations over LDA but under-bind the system. Examining the bond types and their associated error, LDA seems to do worse when the molecule contains a double or triple bond. S_2 , SiO and $C_2H_2O_2$ are all double bond molecules and the errors associated with LDA are much larger than the errors associated with PBE. The GGA greatly improves on these calculations. This could be due to the fact that valence electron density varies greatly in a molecule with a double or triple bond. This is caused by multiple electrons being contained between the atoms with these bonds. The GGA fixes some of the error in these molecules

Molecule	LDA AE	PBE AE	Experiment	% Error	% Error
	(Kcal/mol)	(Kcal/mol)	(Kcal/mol)	LDA	PBE
SiH ₄	345	316	322.4	7.11	-1.99
SiO	223	204	192.1	16.0	6.47
S_2	131.7	110.1	101.7	29.5	8.27
C_3H_4	781	714	704.8	10.8	1.3
$C_2H_2O_2$	735.3	670	633.4	16.1	5.8
C_4H_8	1279.4	1167.4	1149.0	11.35	1.6
MSE	_	_	_	15.15	3.58

Table 3.3: The calculated and experimental values for the atomization energy of each molecule using an LDA model and the PBE model. Experimental data is from AE6 [32] study.

because it takes the gradient of the electron density into account.

Chapter 4

Solids

4.0.1 Introduction

We chose four solids as a test set: NaCl, Si, Na and Cu. NaCl was chosen because it is a well known ionic insulator. Solid silicon is a semiconductor crystal containing covalent bonds. We chose an alkali metal and a d-type metal to study because they differ in electronic structure. The alkali metals generally have low binding energy. In d-type metals there is additional cohesion from the electrons in the inner shells. This causes the d-type metals to have a higher cohesive energy. The solids listed were tested using LDA and three GGA functionals.

4.0.2 Silicon and Sodium Chloride

Silicon was the first solid tested. The first step to test this solid was to optimize the convergence parameters. The first parameter optimized was the number of k points. This was done by running the program with a set plane wave energy cutoff and changing the number of k points between each run. The next parameter that needed tuning was the plane wave energy cutoff. This was done by fixing the number of k points and

changing the energy of the plane wave between each run. To find the optimum values for both of these parameters, the total energy of the solid was examined after each run and once the energy converged to the millihartree, the parameter was optimized. Once the energy was converged, the solid was tested with both optimum parameters. Next, the calculation was repeated but the lattice constant was shifted $\pm 5\%$ in 1% increments. This allowed for the properties such as the lattice constant and bulk modulus to be calculated, shown in Figure 4.1. The bulk modulus was found using



Figure 4.1: The total energy measurements as the lattice constant is shifted $\pm 5\%$ in 1% increments for Si. The plane wave energy is varied to show a convergence. Atomic units are used.

the Murnaghan equation of state, which is discussed below. The cohesive energy was calculated by finding the energy difference between one primitive cell of crystalline silicon and 2 individual silicon atoms. To add a correction to compare this value to experiment, the zero point energy is subtracted off this cohesive energy. Our cohesive energy is shown below as

$$E_{cohesive} = E_{atom} - E_{solid} - E_{zpe} \tag{4.1}$$

. To find the E_{zpe} , the formula

$$E_{zpe} = \frac{9}{8} k_B \theta_D \tag{4.2}$$

is used where θ_D is the Debye temperature. The Debye temperature for silicon is $\theta_D = 640K$, for sodium chloride is $\theta_D = 321K$, for sodium is $\theta_D = 158K$ and for copper $\theta_D = 343K$.

The next solid that was tested was sodium chloride. The same convergence tests were performed as in silicon.

4.0.3 Na and Cu

Next the two metals were tested, sodium and copper. With sodium, the normal convergences, energy cutoff, lattice constant and k-points had to be done. Next a new input variable, tsmear, had to be converged. This tsmear stands for the temperature of smearing. In metals, temperature can cause a broadening of the occupation numbers on the Fermi surface. This will cause the number of k-points needed to be less. When tsmear was 0.01 the amount of k-points needed was much larger. This caused the computation time to increase. The higher the value for tsmear, the lower the number of k-points were needed to make the calculation. A higher temperature means that the metal is no longer in the ground state, so there was a balancing act between the tsmear and k-point parameters. After finding the best setup of input variables, the solid was tested and the total energy, lattice constant and bulk modulus were calculated by the same method for Si and NaCl. Copper was tested in a similar manner.

4.0.4 Murnaghan Equation of State

An equation of state is a relationship between state variables such as, temperature, pressure, volume, energy and entropy. An example of an equation of state would be the ideal gas law. Here we are looking at a system made of solids so we will need a different equation of state. In our solid system we can look at pressure, volume, energy and bulk modulus as our state variables. The bulk modulus can be defined as

$$B = -V\left(\frac{dP}{dV}\right).\tag{4.3}$$

The physical interpretation of the bulk modulus is the resistance to the change of volume under a uniform pressure. From the Murnaghan equation of state [34], we can define our bulk modulus as:

$$B(P) = B_0 + B'P (4.4)$$

where

$$B_0 = B(0). (4.5)$$

Now combining the previous equations above, we can get:

$$-V\left(\frac{dP}{dV}\right) = B_0 + B'P. \tag{4.6}$$

From this equation we can solve for P vs. V by using separation of variables and integrating from P = 0 to P and from our initial V to the final V. Solving this equation for P gives us:

$$P = \frac{B_0}{B'} \left[\left(\frac{V_0}{V} \right)^{B'} - 1 \right].$$
(4.7)

At constant entropy

$$dU = -PdV \tag{4.8}$$

and

$$P = -\frac{dU}{dV} \tag{4.9}$$

 \mathbf{SO}

$$dU = -\frac{B_0}{B'} \left(\frac{V_0}{V}^{B'} - 1\right) dV.$$
 (4.10)

Here V_0 is the volume at the minimum energy. Now by integrating we get

$$U(V) = U_0 - \frac{B_0}{B'} \left[\int \left(\frac{V_0}{V} \right)^{B'} dV - \int (dV) \right].$$
 (4.11)

By definition,

$$\frac{dU}{dV} = 0 \tag{4.12}$$

is expected to be the minimum of U(V). By using some substitutions we can get

$$U(V) = U_0 - \left(\frac{B_0}{B'}V_0\right) \left(\frac{\frac{V_0}{V}B'^{-1} - 1}{1 - B'} - \frac{V_0}{V} + 1\right)$$
(4.13)

where U_0 is the minimum energy. Now that we have energy as a function of volume we can fit a curve to it by putting constraints on the maximum and minimum total energy, volume, bulk modulus and pressure derivative of the bulk modulus. By using a least squares fit to the curve we can see these optimum values for U_0 , B_0 , B' and V_0 . Also by knowing the volume it is possible to get the lattice constant

$$V_0 = a_0^3. (4.14)$$

4.0.5 Results

After finding the optimum input variables, it was possible to find the cohesive energy, lattice constant and bulk modulus. Table 4.1 lists the optimum input parameters for the solids tested. From these parameters it can be seen that using a higher

Solid	Plane Wave Cutoff	k Point Grid	No. of k points	Tsmear
	Ha			
Si (FCC)	18.0	4 4 4	10	_
NaCl (FCC)	38.0	$2 \ 2 \ 2$	2	—
Na (BCC)	15.0	$6\ 6\ 6$	14	0.02
		888	26	0.01
Cu (FCC)	45.0	$6\ 6\ 6$	28	0.02
		888	60	0.01

Table 4.1: The various input parameters used to test the solids.

temperature smearing results in needing less k points for data convergence. This is good for reducing computation time while still obtaining accurate results . Table 4.2 shows the calculated and experimental cohesive energies for the tested solids. The mean signed error and mean unsigned error is also calculated. From this table the PBE functional has the lowest MSE and MUE. The MUE is calculated in a similar fashion as the MSE,

$$MUE = \frac{1}{n} \sum |e_i|. \tag{4.15}$$

The MUE is a helpful tool to show the absolute deviation from the accepted value. The PBEsol functional is close to the PBE in the MSE but the MUE is much larger. The LDA is by far the lowest in accuracy of the models tested. The LDA has the tendency to over bind the system, where PBE tends to under-bind. The PBEsol functional is an improvement over the LDA but it still isn't as accurate as the PBE when comparing the MUE. Table 4.3 shows the calculated lattice constants for the

Solid	Cohe	Cohesive Energy in Hartree					or
	LDA	PBE	PBEsol	Exp.	LDA	PBE	PBEsol
Si	0.3879	0.3388	0.3668	0.3403	13.99	-0.44	7.79
NaCl	0.2573	0.2253	0.2252	0.2352	9.38	-4.23	-2.27
Na	0.0459	0.0395	0.0366	0.0409	12.31	-3.33	-10.42
Cu	0.1534	0.1190	0.1401	0.1283	19.79	-7.26	9.19
MSE	_	_	_	_	13.87	-3.72	1.07
MUE	_	_	_	_	13.87	3.72	7.42

Table 4.2: The calculated cohesive energy for 3 different DFT models and their respective errors. Experimental data taken from JANAF Thermochemical Tables [35] using the zero temperature data.

tested solids. The over binding of LDA as well as the under binding of the PBE can be seen in Tables 4.3-4.4. The MSE of the LDA has the lowest error of the three with respect to both experimental sources. Depending on the data set, PBE or PBEsol has the highest MSE. The PBE has the highest MUE, meaning that this functional has the highest average deviation from the correct value. The PBEsol seems to correct some of the under-binding that PBE does. From looking at these two experimental measurements, NaCl seems to be the only solid that differs much between the two sources. Tables 4.5-4.6 show the calculated bulk modulus of the tested solids. For

Solid		Lattice Constant in a_0					
	LDA	PBE	PBEsol	Exp. (Kittel)	Exp. (Staroverov)		
Si	10.20	10.25	10.20	10.26	10.26		
NaCl	10.47	10.70	10.87	10.64	10.57		
Na	7.81	8.16	8.20	7.98	7.98		
Cu	6.74	6.97	6.85	6.82	6.81		

Table 4.3: The calculated lattice constants and experimental results from two sources, Kittel [30] and Staroverov [36].

this calculation the error in the LDA is much larger than the GGA tests. The PBEsol

Solid	% I	% Error (Kittel)			or (Sta	roverov)
	LDA	PBE	PBEsol	LDA	PBE	PBEsol
Si	-0.59	-0.10	-0.59	-0.59	-0.10	-0.59
NaCl	-1.60	0.56	2.16	-0.95	1.23	2.84
Na	-2.13	2.26	2.76	-2.13	2.26	2.76
Cu	-1.17	2.20	0.44	-1.03	2.35	0.59
MSE	-1.37	1.23	1.19	-0.96	1.44	1.40
MUE	1.37	1.28	1.49	0.96	1.49	1.70

Table 4.4: The calculated percent errors in lattice constant for LDA, PBE and PBEsol.

has the lowest errors for this calculation. There is some difficulty in judging how well a functional does in measuring the bulk modulus. These two experimental results differ noticeably, so it is a difficult physical property to test.

Solid		Bulk Modulus in (10^{11}N/m^2)					
	LDA	PBE	PBEsol	Exp. (Kittel)	EXP. (Staroverov)		
Si	0.955	0.907	0.969	0.988	0.992		
NaCl	0.349	0.239	0.261	0.240	0.266		
Na	0.091	0.081	0.074	0.068	0.075		
Cu	1.791	1.297	1.540	1.370	1.42		

Table 4.5: The calculated bulk modulus of the tested solids.

Solid	% Error (Kittel)			% Er	ror (Star	roverov)
	LDA	PBE	PBEsol	LDA	PBE	PBEsol
Si	-3.34	-8.20	-1.92	-3.73	-8.57	-2.32
NaCl	45.54	-0.42	8.75	31.20	-10.15	-1.88
Na	33.82	19.12	8.82	21.33	8.00	-1.33
Cu	30.79	-5.33	12.41	26.13	-8.66	8.45
MSE	26.73	1.30	7.02	18.73	-4.85	0.73
MUE	28.40	8.27	7.98	20.60	8.85	3.50

Table 4.6: The errors in bulk modulus compared to the two sources.

Chapter 5

Second Order GGA

After testing two well known GGA functionals, the SOGGA [11] was tested. SOGGA stands for second order generalized gradient approximation. This functional was briefly described in Chapter 2. It is called this because a second order density gradient expansion on the exchange enhancement factor is performed,

$$F_x = 1 + \mu s^2 + \dots (s \to 0).$$
 (5.1)

The exchange enhancement factor is a mixture of the PBE and the rPBE. The gradient expansion is also respected in the correlation enhancement factor. The correlation is the same as the PBE correlation. The SOGGA enforces a tighter Lieb-Oxford bound than the PBE making $\kappa = 0.552$. This functional was developed to improve the lattice constants in solids. This is done by using the β value of the PBE correlation enhancement factor and by using the μ value from the PBEsol exchange enhancement factor. The choices of parameters are exact for the first type of slowly varying system described in Chapter 2. Solids have much smaller *s* values than molecules do.

The SOGGA was not included in the ABINIT package, so it had to be added. To



Figure 5.1: The calculated exchange enhancement factor for the SOGGA functional.

do this, there were two files that needed to be modified. These changes have been listed in the appendix.

5.1 Testing the Functional

To test our version of SOGGA on ABINIT, we printed out the exchange energy divided by the LDA exchange energy against the inhomogeneity parameter shown in Figure 5.1. By comparing this plot against the the theoretical plots (Figure 2.2), we could see if there were any errors in our program. Another way to check for errors was to plot the calculated XC energy on the z-axis, s on the x-axis and r_s on the y-axis shown in Figure 5.2. Here the calculated values of F_{xc} , s and r_s land on the



Figure 5.2: The calculated XC enhancement factor of the SiH_4 in dark blue, the solid Si in light blue and the theoretical XC enhancement factor in red. The inhomogeneity is plotted on the x-axis, the Wigner-Seitz radius is plotted on the y-axis and the XC enhancement factor is plotted on the z-axis.

theoretical model. The theoretical model is

$$F_{xc} = \frac{\epsilon_{xc}^{SOGGA}}{\epsilon_x^{LDA}}.$$
(5.2)

The difference between solids and molecules can be seen in Figure 5.2. The solid has a small s compared to the molecule. As the r_s goes up the density is going down. This means, for the solid, the maximum r_s value plotted is either at the ion core or in the center of the primitive cell. The molecule would have a maximum where the density goes to zero. Another check we used was to compare the total energy of the PBE against the SOGGA. The SOGGA XC energy should always be lower than the PBE. This is shown in Figure 2.3. This will ensure that the total energy will always be lower in the SOGGA. This does not mean that the cohesive energy will always be lower because cohesive energy is the difference of energy between a primitive cell in a solid and the individual atoms that make up that cell.

Tables 5.1-5.3 show the results of our measurements using the SOGGA. Listed in Table 5.1 are the results of our cohesive energy calculations for the SOGGA functional as well as the results from Chapter 4. The error in the energy calculations was higher

Solid	Cohesive Energy in Hartree		% Error		
	SOGGA	LDA	PBE	PBEsol	SOGGA
Si	0.3758	13.99	-0.44	7.79	10.43
NaCl	0.2198	9.38	-4.23	-2.27	-6.55
Na	0.0466	12.31	-2.22	-7.26	13.94
Cu	0.1445	19.79	-7.26	9.19	12.63
MSE	_	13.87	-3.72	1.07	7.61
MUE	_	13.87	3.72	7.42	10.89

Table 5.1: The calculated and experimental cohesive energy for the four solids tested. Percent error, mean signed error and mean unsigned error are also listed.

then the other GGA's. The SOGGA performed better then the LDA, but the best functional tested for energy calculations was the PBE.

Solid	Lattice Constant in a_0	Experiment		%	Error
	SOGGA	Kittel	Staroverov	Kittel	Staroverov
Si	10.17	10.26	10.26	-0.88	-0.88
NaCl	10.52	10.64	10.57	-1.13	-0.47
Na	8.19	7.98	7.98	2.63	2.63
Cu	6.83	6.82	6.81	0.15	0.29
MSE	—	_	_	0.14	0.39
MUE	_	_	_	1.20	1.07

Table 5.2: The calculated and experimental lattice constants for the four solids tested. Percent error, mean signed error and mean unsigned error are also listed.

For the lattice constant in Table 5.2, the SOGGA performs the best. This functional has the lowest MSE and MUE. The SOGGA was developed to improve lattice constant calculations in solids. These results agree with the thought that the functionals cannot obtain accurate lattice parameters and energies at the same time.

Solid	Bulk Modulus in 10^{11} N/m^2	Experiment		% Error	
	SOGGA	Kittel	Staroverov	Kittel	Staroverov
Si	1.01	0.988	0.992	2.23	1.18
NaCl	0.272	0.240	0.266	13.33	2.26
Na	0.079	0.068	0.075	16.18	5.33
Cu	1.60	1.370	1.420	16.79	12.68
MSE	_	—	_	12.13	5.52
MUE	_	_	_	12.13	5.52

Table 5.3: The calculated and experimental bulk modulus for the four solids tested. Percent error, mean signed error and mean unsigned error are also listed.

As seen in Chapter 4, the experimental bulk moduli differ enough to give mixed results. Using Kittel's experimental data, the PBE-sol is the best functional for determining the bulk modulus. The Staroverov data shows that the SOGGA is the best at calculating this property.

Chapter 6

Discussion and conclusions

6.1 Introduction

In this chapter the results of this study will be displayed and discussed. The first discussion will compare our results using a pseudopotential model with Staroverov's results using an all electron model [36]. The second discussion will be on the performance of the various GGA's examined. The next discussion will cover the testing and results of the SOGGA functional [11]. The errors in this study will also be discussed.

There were some controlled and uncontrolled errors in this study. Some of the controlled errors include the converging of the plane wave energy cutoff, the cell size, the k-point grid and the smearing temperature. These errors were minimized by converging the energy change between runs of increasing accuracy to the milihartree. Some of the errors that were uncontrolled would be the pseudopotential model. The pseudopotential model replaces the actual core and the valence electron orbitals with a smooth potential. There are also some errors due to computer rounding in the results of Chapters 3-5.

Solid	Lattice Co	onstant a ₀	Experiment (Staroverov)
	Calculated	Staroverov	
Si	10.20	10.25	10.26
NaCl	10.47	10.34	10.57
Na	7.81	7.65	7.98
Cu	6.74	6.67	6.81
MSD	0.98	_	_

Table 6.1: LDA calculations for lattice constant compared with calculated and experimental results from Staroverov. MSD is the mean signed percent difference.

Solid	Lattice Constant a_0		Experiment (Staroverov)
	Calculated	Staroverov	
Si	10.25	10.37	10.26
NaCl	10.70	10.77	10.57
Na	8.16	7.93	7.98
Cu	6.97	6.87	6.81
MSD	1.54	_	_

Table 6.2: PBE calculations for lattice constant compared with calculated and experimental results from Staroverov. MSD is the mean signed percent difference.

6.2 The pseudopotential model

In this study, we used Troullier-Martin pseudopotentials [24]. The cohesive energy, lattice constant and bulk modulus was calculated for Si, NaCl, Na and Cu. We can now compare the results for our LDA and PBE calculations to Staroverov's [36], who used an all electron model. Table 6.1 lists our lattice constant for our LDA calculations against Staroverov's and the mean signed difference (MSD) between the two. In three of our solids, our psuedopotential model under-binds our lattice constant for LDA. This gives more accurate results compared to experiment values listed in Staroverov's paper. Also listed in these tables is the mean signed difference between our calculations and Staroverov's. In the LDA calculations, our model on average under-bound the atoms by 0.98% compared to Staroverov's. The PBE results are listed in Table 6.2. Here three of our calculations show an under-binding as well. The

Solid	Bulk Modulus 100 GPa		Experiment (Staroverov)
	Calculated	Staroverov	
Si	0.955	0.951	0.992
NaCl	0.349	0.322	0.266
Na	0.091	0.091	0.075
Cu	1.79	1.88	1.42
MSD	1.01		_

Table 6.3: LDA calculations for bulk modulus compared with calculated and experimental results from Staroverov. MSD is the mean signed percent difference.

Solid	Bulk Modulus 100 GPa		Experiment (Staroverov)
	Calculated	Staroverov	
Si	0.907	0.886	0.992
NaCl	0.239	0.237	0.266
Na	0.081	0.077	0.075
Cu	1.54	1.50	1.42
MSD	2.77	_	_

Table 6.4: PBE calculations for bulk modulus compared with calculated and experimental results from Staroverov. MSD is the mean signed percent difference.

MSD for the PBE calculations is 1.54 % Next, the bulk modulus can be compared. For the bulk modulus, both models are relatively close in calculations except for the NaCl measurement. The MSD is low for this calculation, 1.01%, but this is due to a high error being partially canceled out with a negative error. Looking at the PBE measurements in Table 6.4, both models are close again being 2.77%. By examining the results in Tables 6.1-6.4, using a pseudopotential model is more accurate in measuring the lattice constant in the LDA model. The PBE loses some accuracy in the measuring of the lattice constant. The bulk modulus did not differ by much in either LDA or PBE calculations. Looking back to Table 2.2, the PBE had a 15.5 kcal/mol error in the cohesive energy calculations. Our calculations resulted in a 16.5 kcal/mol error. These results show that using a pseudopotential model will not cause a significant loss in accuracy in measurements.

6.3 Performance of GGA's

From the data collected in Tables 2.2-2.4, it is possible to assess which functional best measures a certain property. The rPBE [13] was a functional developed to improve atomization energies over the PBE functional [7]. By changing the functional form and the κ value, this functional obtained the lowest error in the AE6 test set [32]. The revPBE [10] had the lowest error in atomization energy for the 20 molecule test set. The revPBE functional is the same as the PBE except the κ value in the exchange enhancement factor is changed from 0.804 to 1.245. By examining Figure 2.2, the exchange enhancement factors with the fastest slopes, $\mu = 0.21951$, generally were the best at measuring atomization energies in molecules. The functional that was the best for measuring the structure of a test set of 18 solids was the SOGGA functional. For cohesive energy the PBE functional performed the best for an eight solid test set. For measuring the bulk modulus of ten s-type and five d-type metals, the PBE outperformed the other functionals. The bulk modulus is a difficult calculation to compare to experiment. The experimental value for the bulk modulus is not a well known measurement in most cases. Our mean unsigned error results for the four solids tested in Chapter 4 agree with this. The functionals with the blue enhancement factors, $\mu = 10/81$, are better for measuring structure. The data collected in Table 4.4 agrees with this.

6.4 SOGGA

In this study, the SOGGA functional was compared against experimental data as well as the LDA, the PBE functional and the PBEsol functional [8]. To test this functional, it is helpful to examine the behavior of this functional. The XC energy is in the SOGGA always lower than the XC energy of the PBE. This will cause the total energy to always be lower in the SOGGA. While testing the cohesive energy of the four solids the SOGGA performed worse than the other GGA functionals tested. The SOGGA however did improve over the LDA on this calculation. The SOGGA did improve the measured lattice constants over the other GGA's having a 1.2% or 1.07% MUE depending on the experimental data. This would agree with the performance data from Table 2.3. For the bulk modulus, which has not before been measured, the SOGGA had a 12.13% or 5.52% error. Compared to our results for the LDA, PBE and PBEsol, the SOGGA improved the measurements over the LDA and PBE models. The PBEsol was the best functional to measure the bulk modulus for our four solid data set.

6.5 Summary

By comparing the results for our LDA and PBE calculations using a pseudopotential model with Staroverov's all electron model, we can check if a pseudopotential model is accurate. Our results show that using a pseudopotential model will not lead to any significant errors. After analyzing several GGA functionals, a trend can be observed. The functionals that use the PBE μ value are generally better at measuring energies. The functionals with the PBEsol μ value are better at calculating the structure of solids. The data from Chapters 3 and 4 agree with this trend in the literature. After testing a relatively new GGA from the literature, the SOGGA functional, we found this functional to improve structural calculations over the PBEsol. This functional also improves the bulk modulus measurements over the LDA and PBE.

There are some well known test sets for molecules such as the AE6 test set. Solids do not have a standard test set. Our study only used four solids, with the largest core being copper. For further study we could test multiple solids of each type as well as solids with larger cores.

After examining the models that rely on the local density and models that rely on the local density and the gradient of the density, the next logical choice of study would be examining a model that would rely on the Laplacian of the density.

Appendix A

List of acronyms

- 1. **ABINIT** Density functional theory code
- 2. AE6 6 molecule test set for atomization energy
- 3. **DFT** Density functional theory
- 4. LDA Local density approximation
- 5. **GGA** Generalized gradient approximation
- 6. **PBE** Perdew-Burke-Ernzerhof functional
- 7. **PBEsol** Perdew-Burke-Ernzerhof functional for solids
- 8. revPBE Variation of the Perdew-Burke-Ernzerhof functional
- 9. RGE2 Variation of the PBEsol functional
- 10. **rPBE** Variation of the Perdew-Burke-Ernzerhof functional
- 11. SOGGA Second order generalized gradient approximation
- 12. VMT1 Exchange functional different from the PBE form
- 13. XC Energy Exchange-correlation energy

Appendix B

Difference files from xcpbe.F90 file in ABINIT-5.8.3 and edited ABINIT-5.8.3

23a24

< if (option <=-3 .or. option==0 .or. option==4 .or. option >=8) then

```
> !write(6,*)' xcpbe : break 1', option
```

```
> if (option <=-3 .or. option ==0 .or. option ==4 .or. option >=10) then
```

211, 212c217, 218

< ! call wrtout(06,message,'COLL')

```
< ! call leave_new('COLL')
```

```
_____
```

```
> call wrtout(06,message,'COLL')
```

```
> call leave_new('COLL')
```

213a220

> !write(6,*) ' xcpbe : break 2', option

248a256

```
>! write(6,*) "xcpbe break 3", 2*nspden-1, ngr2
```

277 c285

```
<
```

```
> !write(6,*) "break 4 ", initialized
```

311,312c319,320

<

```
< if(option/=5)then
```

```
_____
```

```
> !write(6,*) "break 5"
```

> if(option/=5 .and. option/=9)then

```
316, 319c324, 328
```

< kappa=kappa_revpbe

< mu_divkappa=mu_divkappa_revpbe

```
< end if
<
> if(option==5)then
> kappa=kappa\_revpbe
> mu_divkappa=mu_divkappa_revpbe
> endif
> endif
413c422
<
> !write(6,*) "break 6"
627,628c636,637
< else if((option==6) .or. (option==7)) then
<
> else if((option==6) .or. (option==9) .or. (option==7)) then
> !write(6,*) "break 7", npts
630c639,641
<
> !write(6,*) ipts, rhoarr(ipts)
> !write(6,*) ipts, rhom1_3(ipts)
> !write(6,*) dvxcdgr(ipts,:)
668c679
< else
```

```
> else if(option==7) then
```

```
686a698,741
```

>

```
> else
```

```
> !write(6,*) "break 8"
```

>! This is SOGGA modification (option==9)

- > ! Convert to PBE for debug
- > !kappa = kappa_pbe
- > !mu_divkappa = mu_divkappa_pbe

>

```
> kappa = kappa_sogga
```

- >mu_divkappa = mu_sogga_divkappa_sogga
- > divss=one/(one+(mu_divkappa*ss))
- $> divexp = exp(-mu_divkappa^*ss)$
- >
- >! Convert to PBE for debug
- >!divss=2*divss
- > !divexp=0*divexp
- > !ddivss=0.5*ddivss
- >
- > !ddivss is the derivative of divss wrt ss
- > ddivss=(-mu_divkappa)*divss*divss

```
>
```

- > !d
divexp is the derivative of divexp wrt ss
- $> ddivexp = (-mu_divkappa)^* divexp$

>

> dfxdss = -0.5 * kappa * (ddivss + ddivexp)

- >
- > !d2divss os the second derivative of divss wrt ss
- $> d2divss = (2*mu_divkappa**2)/((1+mu_divkappa*ss)**3)$
- > !d2divexp is the second derivative of divexp wrt ss

```
> d2divexp=(mu_divkappa**2)*divexp
```

```
>
```

```
> d2fxdss2 = -0.5*kappa*(d2divss + d2divexp)
```

>

```
> fx = 1 + kappa^{*}(1 - 0.5 * divss - 0.5 * divexp)
```

```
> ex_gga = ex_lsd*fx
```

```
> dssdn = -eight*third*ss*rho_inv
```

```
> dfxdn = dfxdss^*dssdn
```

```
> vxci(ipts,ispden)=ex_lsd*(four_thirds*fx+rho*dfxdn)
```

>

```
> dssdg = two*coeffss
```

```
> dfxdg=dfxdss*dssdg
```

```
> dvxcdgr(ipts,ispden)=ex_lsd*rho*dfxdg
```

```
> exc=exc+ex_ga*rho
```

```
>! write(6,*)'zzzzzzz s', sqrt(ss)
```

702a758

```
>! write(6,*)' xxxxxx rs', rs, sqrt(ss)
```

799c855,857

```
<
```

- >! if (rs<10 .and. ss<100)then
- >! write(6,*) 'zzzzzzzrs, s, Exc/Exlda', rs, sqrt(ss), exci(ipts)/ex_lsd

>! end if

3767,3770c3825,3864

- < if(option/=6)then
- < divss=one/(one+mu_divkappa*ss)
- < dfxdss= mu*divss*divss
- < d2fxdss2=-mu*two*mu_divkappa*divss*divss
- >! if(option/=6)then
- > if((option/=6) .and. (option/=9))then
- > divss=one/(one+mu_divkappa*ss)
- $> dfxdss = mu^*divss^*divss$
- $> d2 fx dss 2 = -mu^* two^* mu_divkappa^* divss^* divss$
- $> fx = one+kappa^*(one-divss)$
- > else if(option==9)then
- >! This is SOGGA modification (option==9)
- >! Convert to PBE for debug
- >!kappa = kappa_pbe
- > !mu_divkappa = mu_divkappa_pbe
- > kappa = kappa_sogga
- > mu_divkappa = mu_sogga_divkappa_sogga
- $> divss=one/(one+(mu_divkappa^*ss))$
- $> divexp = exp(-mu_divkappa^*ss)$
- >
- > ! Convert to PBE for debug
- >!divss=2*divss
- > !divexp=0*divexp
- > !ddivss=0.5*ddivss

> !

```
> !ddivss is the derivative of divss wrt ss
> ddivss=(-mu_divkappa)*divss*divss
>!
> !ddivexp is the derivative of divexp wrt ss
> ddivexp=(-mu_divkappa)*divexp
>!
> dfxdss = -0.5 * kappa * (ddivss + ddivexp)
> !
> !d2divss is the second derivative of divss wrt ss
> d2divss = (2*mu_divkappa**2)/((1+mu_divkappa*ss)**3)
> !d2divexp is the second derivative of divexp wrt ss
> d2divexp = (mu_divkappa^{**}2)^*divexp
>!
> d2fxdss2=-0.5*kappa*(d2divss + d2divexp)
>!
> fx = 1 + kappa^{*}(1 - 0.5 * divss - 0.5 * divexp)
> ! if((rs<10) and. (ss<100)) then
>! write(6,*) "zzzzzzz s, fx", sqrt(ss), fx
>! end if
3774a3869
> fx = one+kappa^*(one-divss)
3776d3870
< fx = one+kappa^*(one-divss)
3874c3968
< if(option==2 .or. option==5 .or. option==6 .or. option==7)then
```

> if(option==2 .or. option==5 .or. option==6 .or. option==7 .or. option==9)then

3947c4041,4045

<

- $> coeffss = quarter*sixpi2m1_3*sixpi2m1_3*rhotot_inv*rhotot_inv*rhotmot*rhotmot$
- $> ss = ((sqrt(grho2_updn(ipts,1)) + sqrt(grho2_updn(ipts,2)))^{**}2)^{*}coeffss$
- >! if (rs<10 .and. ss<100)then
- > ! write(6,*)'zzzzzz rs, s, fxc', rs, sqrt(ss), exci(ipts)/ex_lsd
- > ! end if

Appendix C

Difference files from drivexc.F90 from ABINIT-5.8.3 to edited ABINIT-5.8.3

169c169

< if((11<=ixc .and. ixc<=19).or.(23<=ixc .and. ixc<=29))xclevel=2 ! GGA

> if ($(11 \le ixc .and. ixc \le 19).or.(23 \le ixc .and. ixc \le 39)$)xclevel==2 ! GGA 219c219 < if ((ixc /¿ 17 .and. ixc / = 23 .and. ixc / =26 .and. ixc / =27) .or. (ixc >= 0 .and. ixc < 11))then

> if ((ixc >17 .and. ixc <23) .or. (ixc >=0 .and. ixc <11))then 367c367

< else if (((ixc>=7 .and. ixc<=15) .or. (ixc==23)) .and. ixc/ =10 .and. ixc/ =13) then

> else if (((ixc>=7 .and. ixc<=15) .or. (ixc==23 .or. ixc==25)) .and. ixc/ =10 .and.

```
\begin{split} & \operatorname{ixc}/=&13 \ ) \ \text{then} \\ & 384a385,387 \\ & > ! \ \text{SOGGA} \\ & > \operatorname{if}(\operatorname{ixc}=&25) \operatorname{optpbe}=&9 \\ & > ! \ \operatorname{write}(6,*) \ "optpbe \ is ", \ optpbe \\ & 410c413 \\ & < \operatorname{else} \ \operatorname{if} \ ((\operatorname{ixc} >=& 11 \ .\operatorname{and.} \ \operatorname{ixc} <=& 15) \ .\operatorname{or.} \ (\operatorname{ixc}=& 23)) \ \operatorname{then} \\ & -- \\ & > \ \operatorname{else} \ \operatorname{if} \ ((\operatorname{ixc} >=& 11 \ .\operatorname{and.} \ \operatorname{ixc} <=& 15) \ .\operatorname{or.} \ (\operatorname{ixc}=& 23) \ .\operatorname{or.} \ (\operatorname{ixc}=& 25) \ ) \ \operatorname{then} \\ & 412c415,416 \\ & < \ \operatorname{call} \ \operatorname{xcpbe}(\operatorname{exc,npts,nspden,optpbe,order,rho\_updn,vxc,ndvxc, \\ & \ \operatorname{ngr2,nd2vxc,dvxcdgr}=& \operatorname{vxcgr,exexch}=& \operatorname{exexch}, \& \end{split}
```

> ! write(6,*) "entering xcpbe, optpbe, order = ", optpbe, order > call xcpbe(exc,npts,nspden,optpbe,order,rho_updn,vxc,ndvxc, ngr2,nd2vxc,dvxcdgr=vxcgr,exexch=exexch,&
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