ORBITAL-FREE DENSITY FUNCTIONAL THEORY
PREDICTION OF THE STRUCTURE OF Mg, Al AND Si CRYSTALS

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ABSTRACT

In this paper, we perform Orbital Free-Density Functional Theory (OF-DFT) to study the properties of metals (Mg and Al) and a semiconductor (Si), we calculate the total energy for various Mg, Al and Si structures and volumes employing the Wang-Teter (WT) Kinetic Energy Density Functional (KEDF) and the Wang–Govind–Carter (WGC) KEDF. We use the local density approximation (LDA) and the generalized gradient approximations (GGAs) for the exchange correlation functional.

Key words: Density functional theory, orbital-free, local density approximation, generalized gradient approximations

1 INTRODUCTION

Modern quantum theories based on determining electronic orbitals and wave functions have led to significant progress in understanding the electronic structure of atoms, molecules and solids. In order to find the electronic structure and the properties of a matter, the time-independent Schrödinger equation must be solved:

\[
\hat{H}\Psi = E\Psi
\]

where \(\hat{H}\) is the Hamiltonian operator, \(E\) is the total energy and \(\Psi\) is the many-body electronic wave function under the Born–Oppenheimer approximation (BO). The \(\Psi\) that corresponds to the lowest \(E\) then contains all information about the ground state of the system. However, \(\Psi\) contains \(3N\) degrees of freedom (\(N\) is the number of electrons), the time consuming in the calculation of \(\Psi\) is long, and needs a large space to store.

Equation (1) cannot be solved analytically except for the special case of the hydrogen atom. The solution of the hydrogen atom provides useful insights regarding the nature of the atom, but difficulties arise when many electron atoms are considered. This is mainly because the strength of the electron-electron interactions is comparable to the nucleus-electron interaction. Hence, approximate methods have to be used.

Different methods are used to obtain the properties of many-electron systems such as the Hartree (H) [1], the Hartree-Fock (HF) [2,3] and many other methods. They are base on the complicated many-electron wave function, which depends on several variables for each electron. An alternative scheme to solve for the ground state properties without making any explicit reference to the wave function was formulated by Hohenberg, Kohn and Sham. This method is the called Density Functional Theory (DFT), which has the electron density as a fundamental quantity. In (1964) Hohenberg and Kohn (HK) [4, cf. Gregory, Ligneres and Carter 5] established two crucial theorems.

The first theorem of Hohenberg and Kohn provides the fundamentals of DFT, by stating that the ground-state energy of a system is uniquely determined by the corresponding electron density, that is the energy is a functional of the density, and the ground state electron density \(\rho\) contains everything necessary to recover all information about the electronic ground state, including, for example the electronic wave function, the total energy, the associated forces on the nuclei and the stress in the unit cell. In the theory, using the density entirely obviates the need to compute or store a full \(N\)-body electronic wave function. Since the electron density only has three coordinates associated with it, this theorem formally reduces the number of degrees of freedom from \(3N\) to 3, an enormous simplification. The second theorem is a variational principle that provides a way to find this ground state electron density by minimizing the electronic total energy with respect to variations in the electron density.

Kohn and Sham [6,7] provided the first practical computational scheme, by postulating a reference system of non-interacting electrons, moving in an effective potential. This effective potential includes the external potential (of the nuclei) but also the Coulomb interaction of the electron density with in itself and corrections to this averaged treatment of the electron-electron repulsion. These corrections are the exchange correlation, which originates from the fact that electrons are fermions, thus described by an antisymmetric wave function, and the Coulomb correlation, which is caused by the fact that electrons avoid each other due to their mutual electrostatic repulsion. The non-interacting reference system is then represented by a one-determinant wave function, yielding the exact density of the interacting system and the corresponding exact energy. This is computationally highly efficient, since one is not
challenged by a multi-determinantal wave function. However, modeling the functional dependence of the exchange correlation energy on the electronic density is the problematic part of Kohn-Sham DFT.

In Kohn-Sham DFT (KS-DFT), the interacting kinetic energy is approximated by the kinetic energy of a non-interacting system with the same electron density, and is then represented by a one-determinantal wave function yielding an exact solution. The density of the non-interacting system is

\[ \rho(r) = \sum_i |\psi_i(r)|^2 \]  

(2)

The total energy \( E[\rho] \) in (KS-DFT) is evaluated as [6,8]:

\[ E[\rho] = \int \rho(r) \psi^*(r) \psi(r) \, dr + T[\rho] + E_n[\rho] + E_x[\rho] \]  

(3)

where \( \psi \) is the external potential, the second term is the kinetic energy of the non-interacting system of electrons, the third term is the Hartree electron-electron repulsion energy and \( E_x \) is the exchange-correlation energy.

Although KS-DFT exhibits much better scaling than traditional correlated \( ab \) initio methods while retaining reasonable accuracy, typical implementations still scale roughly as \( O(N^2) \) where \( N \) is a measure of the system size, due to necessary manipulations related to the reintroduced wavefunction (for example orbital orthonormalization). The scaling can vary from quadratic to quartic, depending on the implementation, and of course each algorithm and numerical implementation is subject to a different prefactor.

For condensed matter systems, the KS method has another bottleneck: the need to sample the Brillouin zone for the wave function (also called 'K-point sampling') can add several orders of magnitude in cost to the computation.

The computational cost scales to \( O(N^\prime N) \) by the traditional self-consistent matrix diagonalization techniques, and is due to the diagonalization process. Currently, this is not viable for large systems with thousands of atoms. To reduce the computational cost, another group of linear scaling method is then proposed, which is the so-called Orbital-Free Density Functional Theory (OF-DFT). The OF-DFT works directly with density, without introducing the orbital. The calculations scale as \( O(N' \ln N') \) because the orthogonalization and k-point sampling steps are eliminated.

Then OF-DFT is a first principle quantum mechanical method primarily for condensed matter that can be made to scale linearly with system size [5]. Among all the first-principles methods based on the density functional theory (DFT) [4,9], the linear scaling Orbital-Free (OF) DFT scheme may be the most capable of treating large systems (>1000 atoms) at lowest cost [10,11,12,13]. Unlike traditional orbital-based first-principles techniques, such as Hartree-Fock [2,3] and Kohn-Sham (KS)-DFT[6], the OF-DFT method avoids solving self-consistency for one-electron orbitals and instead only utilizes the electron density, a function of three coordinates, as its sole variational parameter[14]. Consequently, the costs associated with manipulating orbitals (for example orthonormalization) are completely eliminated. That means, in an Orbital-Free (OF) DFT scheme, the calculation of a wave function of the noninteracting reference system is completely avoided [15]. This leads to a scheme that is much more efficient, since only the density itself has to be determined and no orbitals have to be calculated.

2 THEORETICAL CONSIDERATIONS

2.1 ORBITAL-FREE ENERGY FUNCTIONAL

Due to the expensive scaling of the KS orbital methods, an accurate treatment of the kinetic energy as well as the potential energy contributions in terms of the electron density only could have a major impact in practical calculations [16,17,18]. To that end, considerable efforts have been invested in developing the "Orbital-Free Density Functional Theory" (OF-DFT) by making direct approximations for \( T[\rho] \) [9,19-31].

The KS-DFT total energy is given by Eq.(3). The KS total energy functional based on the density functional theory, for a system consisting of \( N \) atoms and \( N \) interacting electrons, where each electron moves in an effective field due to the rest of the electrons can be written as:

\[ E[\rho] = T[\rho] + E_n[\rho] + E_x[\rho] + E_o[\rho] \]  

(4)

The first term in Eq.(4) resembles the kinetic energy of the non-interacting electron gas. As mentioned above, an attractive alternative is to seek an accurate kinetic energy functional in terms of the charge density \( \rho(r) \) directly. Obviously, this will simplify the problem enormously since the total energy then can be minimized directly as a function of the charge density. We begin with the standard expression for the total energy of a system consisting of \( N \) atoms and \( N \) interacting electrons, under the influence of an external field [5]:

\[ E[\rho] = T[\rho] + E_n[\rho] + E_x[\rho] + E_o[\rho] \]  

(5)

where \( T[\rho] \) is the electronic kinetic energy, \( E_n[\rho] \) is the ion-electron potential energy, \( E_x[\rho] \) is the Coulomb repulsion energy between electrons, \( E_o[\rho] \) is the exchange-correlation energy and \( E_o[\rho] \) is the ion-ion repulsion energy. Except for the first term representing the kinetic energy of non-interacting electrons, all other energy contributions are functionals of \( \rho(r) \). Several attempts have been made to obtain the kinetic energy as a functional of the electronic charge density. The most accurate functional available to date for condensed matter was developed by Wang, Go- 

vind and Carter (WGC) [24]. It consists of the Thomas-Fermi (TF) functional plus the von Weizsacker (vW) functional plus a term that accounts for the linear response of a uniform electron gas. The WGC functional builds a nonloc-
al density dependence into the kernel of an earlier functional proposed by Wang and Teter (WT) [19], which also consists of the TF and vW KEDFs, plus a linear response term.

The Thomas-Fermi kinetic energy density functional TF KEDF [32, 33, 34], the simplest one available, is completely local and depends only on the density. It is the Local Density Approximation (LDA) for the kinetic energy that is exact for a uniform electron gas. The Thomas–Fermi functional [15,32,33] is:

\[ T_{\text{TF}}[\rho] = C_{\text{TF}} \int \rho(r)^{3/2} d\mathbf{r} \]

where \( C_{\text{TF}} = \frac{3}{10} (3\pi^2)^{3/5} \approx 2.871 \). However, this functional by itself predicts no shell structure for atoms and no molecular binding [35,36], and therefore is clearly inadequate on its own for describing atoms, molecules and real materials. While the TF functional describes the limiting case of a uniform electron gas, the von Weizsacker energy density functional vW KEDF [37] is exact for any single orbital system, that is for up to two singlet-coupled fermions or any number of bosons. The vW functional by itself is a lower bound to the true kinetic energy, since it neglects spin and the Pauli Exclusion Principle. Imposition of the Pauli Principle on the TF kinetic energy functional gives the Thomas–Fermi kinetic energy density functional TF KEDF [37] is exact for any single orbital system, but also on the nonlocal two-body Fermi wave vector [24]

\[ \eta = \frac{k_r}{\pi^2} \]

where \( k_r = [3\pi^2 \rho \phi(r)]^{1/3} \) is the local one-body Fermi wave vector and \( \gamma \) is a parameter. An overview of these kinds of different linear-response based kinetic-energy functionals such as, WT and WGC are discussed in the below.

An improve of the KEDF for nearly-free-electron materials was first developed by Wang and Teter [19] and later extended by others [21,23]. The full Wang–Teter (WT) KEDF enforcing linear response has the form [19]:

\[ T_{\text{WT}}[\rho] = T_{\text{TF}}[\rho] + T_{\text{vW}}[\rho] + T_{\text{e}}[\rho] \]

Here, \( \alpha \) and \( \beta \) are parameters. For instance, the choice \( \alpha = \beta = \frac{5}{6} \) corresponds to the original WT functional [19]. Eq. (13) can be solved in reciprocal space using the convolution theorem:

\[ T_{\text{WT}}[\rho] = C_{\text{TF}} \int [\rho(r) \widehat{F}_{\alpha \beta}(\mathbf{q}) \rho(\mathbf{q})] d\mathbf{q} \]

requiring only knowledge of the kernel \( w_{\alpha \beta}(\mathbf{q}) \) in reciprocal space, \( \widehat{F} \) denotes the reverse fast Fourier transform \( \widehat{F}(f(\mathbf{q})) = f(\mathbf{q}) = \sum f(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}} \) and \( \rho(\mathbf{q}) \) are the Fourier components of the electron density. In order to enforce the correct linear response behavior for the entire KEDF, the linear response kernel must have the form [22]:

\[ \widehat{F}_{\alpha \beta}(\mathbf{q}) = \frac{X_{\alpha \beta} - X_{\alpha} - X_{\beta}}{2\alpha \beta C_{\text{TF}} \rho_0^{\alpha \beta - 2}} \]

where \( \widehat{F} \) denotes a forward Fast Fourier Transform (FFT), defined as [5]

\[ \hat{F}(f(\mathbf{r})) = f(\mathbf{q}) = \frac{1}{N_{\text{r}}} \sum f(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{r}} \]

\[ X_{\alpha \beta} = \frac{k_r}{\pi^2} \]

\[ X_{\alpha \beta} = \frac{1}{2} \ln \left( 1 + \left| \mathbf{q} \right| \right) \]

It is more convenient to express \( \widehat{w}_{\alpha \beta} \) in terms of \( \tilde{\mathbf{q}} \) where \( \tilde{\mathbf{q}} = |\mathbf{q}|/(2k_r) \) is a dimensionless momentum [20]:
\[
\hat{u}_{e,i}(\rho) = \frac{5}{9\alpha\beta\rho^{a+\beta-3}} \left( \left( \frac{1 + |\rho|^2}{4|\rho|^2} - \ln \left( \frac{1 + |\rho|^2}{|\rho|^2} \right) \right)^{\beta/2} - 3|\rho|^2 - 1 \right)
\] (16)

One weakness of the WT KEDF is that the electron density of the entire system is expected to obey the linear response calculated for only one value of the density, \( \rho_c \). A way to systematically improve the WT KEDF is to introduce a density dependence into the linear response kernel. WGC devised a way to do this within periodic boundary conditions (PBCs), while preserving \( O(N^3\ln N) \) scaling [24]. The KEDF takes the form:

\[
T_{\text{WT}}^{\alpha,\beta}[\rho] = T_{\text{C}}[\rho] + T_{\text{ad}}[\rho] + T_{\text{WGC}}^{\alpha,\beta}[\rho]
\] (17)

where

\[
T_{\text{WGC}}^{\alpha,\beta}[\rho] = C_{\text{WGC}} \left( \rho^{\alpha}(\bar{r}) \rho^{\beta}(\bar{r}) \right)\rho^{\alpha}(\bar{r}) \rho^{\beta}(\bar{r}) \right)
\] (18)

and

\[
\xi_{\gamma}(\bar{r}, \bar{r}) = \left( k'_{\gamma}(\bar{r}) + k'_{\gamma}(\bar{r}) \right)^{1/2} \left( k'_{\gamma}(\bar{r}) + k'_{\gamma}(\bar{r}) \right) / 2
\] (19)

is the nonlocal two-body Fermi wavevector from which the density dependence arises. Although universal values of \( \alpha \) and \( \beta \) were derived from asymptotic analysis [24]:

\[
\alpha = 5 + \sqrt{5} / 6, \quad \beta = 5 - \sqrt{5} / 6
\]

is the first WGC functional [23], the optimal value for \( \gamma \) varies depending on whether a metallic \((\gamma_{\text{opt}} = 2.7)\) or a semiconducting \((\gamma_{\text{opt}} = 4.2)\) material is studied [9]. (Note that although Ref. [9] refers to \( \gamma_{\text{opt}} = 4.2 \) as the optimal value for semiconductors, there is recent evidence that \( \gamma_{\text{opt}} = 4.2 \) is superior [5].)

The expressions for other terms of Eq.(5) that is, potential energy functionals, are given in the following:

\[
E_{\text{ie}}[\bar{r}] = \text{the ion-ion energy, where the interaction energy between ions (nuclei fully screened by their associated core electrons) is given in atomic units by [5]:}
\]

\[
E_{\text{ie}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{Z_i Z_j}{R_{ij}}
\] (20)

where \( N \) is the number of ions, \( Z_i \) is the net charge on ion \( i \), and \( R_{ij} = |\bar{R}_i - \bar{R}_j| \) is the distance between ion \( i \) and \( j \).

Under periodic boundary conditions (PBCs), Eq.(20) becomes a conditionally (and notoriously slowly) convergent sum for a neutral system (which means that the result depends on the order of the summation) [39,40], and diverges for a charged system. However, by introducing an artificial distribution of charge system to screen the charges in real space, which then can be subtracted out in reciprocal space, it is possible to transform the summation into a sum of two rapidly converging series plus a constant (It is extremely difficult to compute the Coulomb energy of the ionic system using a direct real-space summation because the Coulomb interaction is long ranged). The Coulomb interaction is also long ranged in reciprocal space, so the problem is not solved by performing the summation in reciprocal space [41]. Ewald first originated this technique in 1921 [42], and the method has since been extended by many others [43,44].

The Ewald energy is given by [40,42,45]:

\[
E_e = E_{\text{recip}} + E_{\text{nec}} + E_{\text{self}} + E_{\text{background}}
\] (21)

where \( E_{\text{recip}} \) and \( E_{\text{nec}} \) are quickly converging summations in real and reciprocal space, \( E_{\text{self}} \) is a correction term to eliminate interactions between each artificial counter charge with itself and \( E_{\text{background}} \) is a uniform compensating background charge that adds a correction to the energy for a system that is not charge neutral. The individual terms are found in [40,48].

\[
E_{\text{recip}}[\rho] \text{ is the ion-electron energy. The interaction of the ions with the electrons in principle is a simple electrostatic interaction between the positively charged nucleus and the electrons. Although it is possible to describe the interaction of the nucleus with all the electrons in a system (both valence and core electrons), this is expensive and generally not necessary. Often, the properties of interest involve only the valence electrons, in which case the core electrons can be lumped together with the positively charged nucleus, and their combined effect on the valence electrons approximated by an effective potential, a so called pseudopotential (PS).}

The OF-DFT uses local pseudopotentials that depend only on the distance of the electron from the nucleus. Local pseudopotentials tend to work best for main group metals, which exhibit a more isotropic electron distribution, and less well for transition metals and semiconductors, where the electron density naturally has an angular dependence. However, recent advances in pseudopotential construction have greatly improved the quality of these local pseudopotentials for transition metals and semiconductors [46,47]. Although an error in the KEDF is usually the main source of error within OF-DFT calculations, the constraint of using local pseudopotentials accounts for the majority of the error in OF-DFT in cases where the KEDF is very accurate [48]. Once a pseudopotential is constructed, the ion-electron terms are simple to compute. Under PBCs, the pseudopotential is often expressed in reciprocal space. Then the ion-electron energy is computed as [41]

\[
E_{\text{recip}}[\rho] = \Omega \sum_{g \in \mathbb{Z}} \rho(g) \mathcal{W}_v(-g) + N V_{\text{iec}}(\hat{g} = 0) = 0
\] (22)

where \( \Omega \) is the volume of the periodic cell, \( N \) (i.e., \( \rho(g = 0) \)) is the number of electrons and \( V_{\text{iec}}(-\hat{g}) \) is the total ion-electron potential in reciprocal space. The pure Coulomb contribution to the pseudopotential gives rise to a singularity at \( \hat{g} = 0 \). This contribution is subtracted out, leaving only the average non-Coulombic contribution in the pseudopotential at \( \hat{g} = 0, V_{\text{iec}}(\hat{g} = 0) \). Pseudopotentials can either be ab initio, derived from an all electron quantum calculation, or empirical, based on fits to
experiment. In the present work, we use the first principles derived by Hung and Carter for bulk local pseudopotentials (BLPS-HC) [47] for aluminum Al, magnesium Mg and silicon Si.

\[ E_{\text{H}}[\rho] \] in Eq. (5) is the Hartree electron-electron repulsion energy. The Hartree energy for the electron density at a point \( \vec{r} \) interacting with the electron density at another point \( \vec{r}' \) is expressed as [5]

\[ E_{\text{H}}[\rho] = \frac{1}{2N} \sum_{\vec{r}, \vec{r}'} \rho(\vec{r})\rho(\vec{r}') \frac{2\pi}{|\vec{r} - \vec{r}'|} \Omega \vec{r} d\vec{r}' d\vec{r}' \tag{23} \]

Under PBCs, it is possible to perform this convolution in reciprocal space with \( O(N'\ln N') \) scaling to obtain the Hartree energy as

\[ E_{\text{H}}[\rho] = \frac{\Omega}{2} \sum_{\vec{r}, \vec{r}'} \rho(\vec{r})\rho(-\vec{r}) \tag{24} \]

where \( \rho(\vec{r}) \) is obtained as \( \rho(\vec{r}) = \hat{F}(\rho(\vec{r})) \), where \( \hat{F} \) denotes a forward Fast Fourier Transform (FFT).

\[ E_{\text{xc}}[\rho] \] is the Exchange-correlation energy. The OF-DFT uses the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) for the exchange-correlation (xc) energy. The LDA assumes that the exchange-correlation energy density at every position in space for the non-uniform electron gas is the same as it would be for the uniform electron gas having the same density as found at that position [49,50]. The LDA-xc energy is [50]:

\[ E_{\text{LDA-xc}} = \int \left( \epsilon_x(\rho) + \epsilon_c(\rho) \right) \rho(\vec{r}) d\vec{r} \tag{25} \]

where the functions \( \epsilon_x(\rho) \) and \( \epsilon_c(\rho) \), for the homogenous electron gas, represent the exchange and correlation energies per electron, respectively, and are numerically known, and the density \( \rho(\vec{r}) \), represents as usual the number of electrons per unit volume.

Although beautifully simple, the LDA-xc functional typically overestimates the binding energies of molecules and solids, sometimes even leading to wrong phase ordering [13,14,51]. The Generalized Gradient Approximation (GGA) for xc was designed to solve this problem [52,53]. The GGA functionals depend on the gradient of the density as well as the value of the density.

There are many flavors of GGA-xc functionals. We have chosen to implement the functional developed by Perdew, Burke and Ernzerhof (PBE) (the most recent GGA) described in Ref.[53]. The PBE energy can be split into two parts:

\[ E_{\text{GGA-xc}} = E_{\text{xc-GGA}} + E_{\text{c-GGA-xc}} \tag{26} \]

The OF-DFT total energy is given by Eq.(5).

\[ E_{\text{OF-DFT}} = \int \rho(\vec{r}) \hat{V} d\vec{r} \tag{27} \]

while the correlation energy is:

\[ E_{\text{c-GGA-xc}} = \int \rho(\vec{r}) \hat{V} d\vec{r} \tag{28} \]

where the functions \( \hat{V} \) and \( \hat{V} \) for the homogenous electron gas has been found in Refs. [54,5], and are numerically known [54]. \( \hat{V} \) and \( \hat{V} \) are enhancement factors depending on the density and its gradient and are numerically known [54].

### 3 Results and Discussion

#### 3.1 The Total Energy

All calculations were performed with the PRinceton Orbital-Free Electronic Structure Software (PROFESS) code [5]. The three elements under study, Mg, Al and Si, are found in groups IIA, IIIA and IVA of the periodic table, respectively. The structure of Mg is the hexagonal-close-packed (hcp) with two atoms in the primitive cell. The primitive cell has \( a=b=3.16 \) \( A^\circ \) with an included angle of 120° and the axis \( c=5.17 \) \( A^\circ \) is normal to the plane of a and b [55]. The Al structure is face-center-cubic (fcc) of four atoms. The cell lattice vector has \( a=b=c=4.0322 \) \( A^\circ \) with included angle of 90° [5]. The Si structure is diamond (dia). The space lattice of diamond is fcc with \( a=b=c=5.43 \) \( A^\circ \) and included angle of 90° [9]. Since the lattice points of fcc is 4 it follows that the diamond structure have eight lattice points (24*8) atoms.

The OF-DFT total energies for Al (fcc), Mg (hcp) and Si (dia) using BLPS-HC were calculated, and the results are compared with other reported results that used KEDFs and KS-DFT as listed in table (1),(2) and (3). For the exchange-correlation functional, we used the LDA and GGA developed by Perdew, Burke and Ernzerhof (GGA-PBE). For the Kinetic energy density functionals (KEDFs), we employed the Wang Govind Carter (WGC) and Wang Teter (WT). The OF-DFT total energy is given by Eq.(5).

The total energy of Al (fcc) BLPS-HC using WGC-LDA, WGC-GGA, WT-LDA and WT-GGA is (-231.7268 eV), (-231.7448 eV), (-231.7171 eV) and (-231.7342 eV) respectively, the results are compared with the WGC-LDA KEDFs and KS-DFT [47] using the same BLPS in table (1), where good agreement can be observed. Since Al has a nearly-free-electron-like density, then we see from table (1) that the linear-response kinetic energy density functionals (LR KEDFs) do well and agree well with other results.

For Mg (hcp) BLPS-HC, the total energy using WGC-LDA, WGC-GGA, WT-LDA and WT-GGA are (-48.2303 eV), (-48.2465 eV), (-48.1758 eV) and (-48.1888 eV), respectively. Then our results were compared with the WGC-LDA[47] KEDFs, and KS-DFT [47] using the same BLPS, and compared with WGC-LDA, WT-LDA, Perdew and SM [55] KEDFs, and KS-DFT [55] using different PS as in table (2), where good agreement is observed. The electron density of Mg is less free-electron-like than that of Al, which implies a...
more difficult task to the kinetic energy density functionals. From table (2), we see that LR KEDFs agree less well with other results.

For Si (dia) BLPS-HC the total energy using WGC-LDA, WGC-GGA, WT-LDA and WT-GGA were (-874.4919eV), (-875.6063eV), (-870.8041eV) and (-871.6276eV), respectively we compared our results with the KS-DFT [47] using the same BLPS, and with WGC-LDA [9,25]. Low wave vectors (LQ) and High wave vectors (HQ) [56] KEDFs, and KS-DFT [9] using the BLPS developed by Zhou et al. [25], see table (3). There is fair agreement except for a small difference which can be attributed to the fact that Si is no free-electron-like (covalent).

3.2 Energies of Various Crystal Structures

In order to understand how the electron density is distributed in the crystal and how the solid is stabilized, and in order to understand why aluminum dose exists in the fcc structure or Mg has (hcp) and Si has dia structure’s, we will vary the lattice geometry in order to find the most stable geometry, that is the lowest energy structure and analyze \( \rho(r) \) for that structure. Different arrays of ion positions lead to different phases, such as fcc, dia, body-centered-cubic (bcc), simple cubic (sc), hcp and so on. In the present work, we calculated the total energies of Al and Si using BLPS-HC at the first four different phases, and the total energy of Mg BLPS-HC for the five different phases. We used periodic boundary conditions with a cubic cell containing 4 atoms for (fcc), 8 atoms for (dia), 2 atoms for (bcc), 8 atoms for (sc) and 2 atoms for (hcp). In all calculations, we used the LDA and GGA-PBE for the \( E_{xc} \) and employed WT and WGC for kinetic energy density functionals. Our results compared with other reported results are in table (4)-(6). We see from the first line in tables (4), (5) and (6) for Al, Mg and Si BLPS-HC, respectively, that the orbital-free functional gives the minimum value for the energy of (fcc), (hcp) and (dia) structure’s for Al, Mg and Si, respectively. The results show clearly that the lowest energy of all considered structures was indeed found to be (fcc) for Al, (hcp) for Mg and (dia) for Si. It is clear from table (4)-(6) that the energy of other crystal lattices and the differences from the (fcc), (hcp) and (dia) structure’s are designed in this way: 

\[
E_{\text{fcc}} < E_{\text{sc}} < E_{\text{bcc}} < E_{\text{dia}}
\]

for Mg and 
\[
E_{\text{fcc}} < E_{\text{sc}} < E_{\text{bcc}} < E_{\text{dia}}
\]

for Si. Then while the (fcc), (hcp) and (dia), in the present work, our results were compared with the WT-LDA[23,24,55], WGC-LDA [9,23,24,25,47,55], LQ-LDA and HQ-LDA[56] KEDFs, and KS-DFT [23,24,25,29,47,55], which were previously computed using the same BLPS and different BLPS as can be seen in tables (4)-(6).

For Al BLPS-HC, see table (4), all LR-based models perform similarly, and agree well with KS DFT. From table (4) and (5), it is clear that all OF-DFT approximations work better for Mg’s and Al’s (fcc) and (bcc) structures than for their diamond and (sc) structures, since the former are more close-packed, which makes the electron density distributed

<table>
<thead>
<tr>
<th>TABLE 1</th>
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<tbody>
<tr>
<td><strong>Total energy (eV) for Al fcc BLPS-HC with other reported results that used the same pseudopotential.</strong></td>
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<tr>
<td><strong>a-KS from [47].</strong></td>
</tr>
<tr>
<td><strong>b-WGC(LDA) from [47].</strong></td>
</tr>
</tbody>
</table>

| WT(LDA) | -231.717 |
| WT(GGA) | -231.734 |
| WGC(LDA) | -231.726 |
| WGC(GGA) | -231.744 |

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total energy (eV) for Mg hcp BLPS-HC with other reported results that used the same and different pseudopotential.</strong></td>
</tr>
<tr>
<td><strong>a- WT(LDA) from [55].</strong></td>
</tr>
<tr>
<td><strong>b,c,d- parrot(LDA), SM(LDA) and KS respectively using LPS-GNH from [55].</strong></td>
</tr>
<tr>
<td><strong>e,f- KS using NLPS-GNH and BLPS-HC from [55,47] respectively.</strong></td>
</tr>
<tr>
<td><strong>g,h- WGC(LDA) from [47,55] respectively.</strong></td>
</tr>
</tbody>
</table>

| WT(LDA) | -48.175 |
| WT(GGA) | -48.188 |
| WGC(LDA) | -48.250 |
| WGC(GGA) | -48.246 |

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total energy (eV) for Si dia BLPS-HC with other reported results that used the same and different pseudopotentials.</strong></td>
</tr>
<tr>
<td><strong>a,b- LQ(LDA), HQ(LDA) using BLPS-Z from [56] respectively.</strong></td>
</tr>
<tr>
<td><strong>c,d,e- KS using BLPS-Z, NLPS and BLPS-HC from [9,47] respectively.</strong></td>
</tr>
<tr>
<td><strong>f,g- WGC(LDA) from [25,9] respectively.</strong></td>
</tr>
</tbody>
</table>

| WT(LDA) | -870.804 |
| WT(GGA) | -874.491 |
| WGC(LDA) | -874.606 |
| WGC(GGA) | -877.032 |
more evenly, closer to a nearly-free-electron gas. Since the WGC KEDF and WT KEDF are based on the nearly-free-electron gas, it makes sense that the close-packed structures are described more accurately.

It can be seen in table (6), that both LR based models perform worse than for Al, especially when compared with KS-DFT [25] using different PS, and we see that both LR based models agree with each other when compared with KS [47] using the same PS. From table (6) Si the result from [56] using density pathways LQ and HQ compared with the KS results and with other are incorrect and the errors increase when the densities of the systems are more rapidly varying. Since Si is a covalent material, the density inside the covalent bond regions is quite different from that out side and this error is due to this. We see from table (6) that the result of Ref.[9] for WGC-LDA are in very good agreement with KS-DFT of Ref.[25] and different from our result, that is because Ref.[9] and [25] used the new parameter set ($\gamma = 3.6$), while we used a new set parameter ($\gamma = 4.2$) our results are in good agreement with KS [47] that used the same BLPS. For Mg in table (5), we see that all our results agree well with each others, and also well with other reported results [47] that used the same BLPS and lattice parameters.

### TABLE 4

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>WTC (LDA)</th>
<th>WTC (GGA)</th>
<th>WGC (LDA)</th>
<th>WGC (GGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LDA</td>
<td>GGA</td>
<td>LDA</td>
<td>GGA</td>
</tr>
<tr>
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<td>0.59812</td>
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<td>0.59678</td>
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<tr>
<td>N</td>
<td>0.3134</td>
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<td>0.31336</td>
<td>0.31336</td>
<td>0.31336</td>
</tr>
<tr>
<td>L</td>
<td>0.6966</td>
<td>0.6966</td>
<td>0.6966</td>
<td>0.6966</td>
<td>0.6966</td>
</tr>
</tbody>
</table>

Energy per atom (eV) for Si BLPS-HC various structure with other reported results that used the same and different pseudopotentials.

### 3.3 ENERGIES OF VARIOUS VOLUMES

Fig. 1 shows the relation between the total energy and the atomic volume for Mg (hcp) using BLPS-HC. Four different sets of data are plotted corresponding to the formulation WGC KEDF-LDA (A), WGC-GGA (B), WT-LDA (C) and the WT-GGA (D). The lowest energy is obtained in WGC-GGA formula and the improvement of the WGC KEDF over the WT KEDF is evident and lowest energy value was obtained for the (22.355 Å³) volume. Also we investigate here the relation between the total energy and the volume for Al and Si respectively, therefore for Al we show the four formulations agree well with each other when volume increases. The improvement of the WGC KEDF over the WT KEDF and GGA over LDA is evident and lowest energy value is obtained by WGC-GGA. we see that when volume decreases the energy decreases as well. The WT-GGA and WGC-LDA matches very well for (15.84 Å³) volume. The improvement of WGC-GGA over all other formulation is evident, the total energy from WGC-GGA has a distinct minimum, unlike all in (15.5 Å³). But for Si show we that the four formulation are almost parallel to each other. It is evident that the total energy obtained using WGC KEDF is much better than those obtained using the other KEDF. Both cases of approximation with WGC are better than with WT and that both manifest the superiority of the WGC KEDF to WT KEDF, since both total energies have clear minima unlike the WT total energy. The improvement of the WGC KEDF over the WT KEDF and GGA over LDA is evident, the minimum energy is for the (21.601 Å³) atomic volume.
4 CONCLUSIONS

The Orbital-Free Density Functional Theory (OF-DFT) is a first principles quantum mechanical method that can be formulated to scale linearly with the system size. OF-DFT can be used to study samples consisting of tens of thousands of atoms on a single processor.

The present study concludes that for near-free-electron-like solids, the Linear Response-based OF-DFT works quite well, when compared with the KS-DFT, while it performs less well in covalent materials such as Si. The best $\gamma$ parameter in the WGC KEFD for Al ($\gamma = 2.7$) is not the optimal one for Si ($\gamma = 4.2$). The results obtained in the present work are in good agreement with other reported results. In Al, Mg and Si, the improvement of WGC over WT is evident. The results obtained using both kinds of KEFD and $E_p$ approximations agree well with other reported results. In general, there is no reason to believe that any LR-based OF-DFT should work well for arbitrary systems. In this work, we know why aluminum does exist in the face-center-cubic structure, Mg has (hcp) and Si has (dia) structures.

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REFERENCES