



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Lehtomäki, Jouko; Lopez-Acevedo, Olga

## Large-Z limit in atoms and solids from first principles

Published in: Journal of Chemical Physics

DOI: 10.1063/1.5129397

Published: 28/12/2019

Document Version Publisher's PDF, also known as Version of record

Please cite the original version: Lehtomäki, J., & Lopez-Acevedo, O. (2019). Large-Z limit in atoms and solids from first principles. *Journal of Chemical Physics*, 151(24), 1-8. Article 244101. https://doi.org/10.1063/1.5129397

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

# Large-Z limit in atoms and solids from first principles

Cite as: J. Chem. Phys. **151**, 244101 (2019); https://doi.org/10.1063/1.5129397 Submitted: 30 September 2019 . Accepted: 03 December 2019 . Published Online: 23 December 2019

Jouko Lehtomäki, and Olga Lopez-Acevedo ២



## ARTICLES YOU MAY BE INTERESTED IN

### Wigner numbers

The Journal of Chemical Physics 151, 244122 (2019); https://doi.org/10.1063/1.5135721

Curing basis set overcompleteness with pivoted Cholesky decompositions The Journal of Chemical Physics **151**, 241102 (2019); https://doi.org/10.1063/1.5139948

Energy decomposition analysis based on broken symmetry unrestricted density functional theory

The Journal of Chemical Physics 151, 244106 (2019); https://doi.org/10.1063/1.5114611





J. Chem. Phys. **151**, 244101 (2019); https://doi.org/10.1063/1.5129397 © 2019 Author(s).

## Large-Z limit in atoms and solids from first principles

Cite as: J. Chem. Phys. 151, 244101 (2019); doi: 10.1063/1.5129397 Submitted: 30 September 2019 • Accepted: 3 December 2019 • Published Online: 23 December 2019



Jouko Lehtomäki<sup>1,a)</sup> and Olga Lopez-Acevedo<sup>2,b)</sup> 🕩

#### AFFILIATIONS

 <sup>1</sup> Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Finland
 <sup>2</sup> Grupo de Física Atómica y Molecular, Instituto de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia UdeA, Calle 70 No. 52-21, 050010 Medellín, Colombia

<sup>a)</sup>Electronic mail: jouko.lehtomaki@aalto.fi

<sup>b)</sup>Electronic mail: olga.lopeza@udea.edu.co

#### ABSTRACT

We present density functional theory (DFT) calculations of atomic ionization potentials and lattice constants of simple solids from low atomic numbers *Z* to the large-*Z* limit. We compare different kinetic energy functional approximations [Kohn-Sham (KS) vs simple orbital-free functionals] and, in the case of orbital free, also different methods for including the nuclear potential (all-electron with the projector augmented wave method vs local pseudopotentials). For both ionization potentials and lattice constants, all-electron orbital-free DFT does yield the general trend of KS DFT for moderate values of the atomic number *Z*. For large values of *Z*, all-electron orbital-free DFT deviates from the KS DFT results. Local pseudopotentials give a better qualitative description by adding shell oscillations to the orbital-free DFT model. We show that both all-electron orbital-free DFT and KS DFT have a finite value for nonrelativistic lattice constants in the large-*Z* limit.

Published under license by AIP Publishing. https://doi.org/10.1063/1.5129397

#### I. INTRODUCTION

Orbital-free density functional theory (OFDFT) is at the intersection of much celebrated density functional theory<sup>1</sup> and semiclassical physics.<sup>2–4</sup> In contrast to more popular Kohn-Sham (KS) DFT,<sup>5</sup> where each noninteracting orbital is solved explicitly, OFDFT requires solving only for one quasiorbital (square-root of the electronic density<sup>6</sup>). In OFDFT, in addition to the exchange-correlation functional, the kinetic energy functional must be written as an explicit functional of density. In principle, OFDFT is exact due to Hohenberg-Kohn theorems, but for realistic approximations of the kinetic energy functional, there is a trade-off between speed and accuracy. The nature of the trade-off is semiclassical:<sup>3,4</sup> Many quantum effects present in KS-DFT are not present in OFDFT.

Underlying the density functional theory is the Thomas-Fermi theory.<sup>7</sup> The implications of the Thomas-Fermi theory have been investigated in numerous contexts over multiple decades. Especially the Thomas-Fermi theory of atoms (and its extensions) has yielded a

plethora of interesting results.<sup>3,4</sup> Our interest here is the limit of large atomic numbers,  $Z \rightarrow \infty$ , where some semiclassical results become exact.<sup>4,7</sup> The large-*Z* limit has yielded multiple results of remarkable simplicity for atoms, of which we mention the total energy of neutral atoms and ionization potential.<sup>4,8</sup>

Our purpose is to connect theoretical and computational results to *ab initio* OFDFT calculations and, for the first time, extend them to solids. In modern OFDFT, use of Kohn-Sham derived local pseudopotentials is required to get quantitatively correct results. We will study pseudopotentials by comparing them to OFDFT results obtained with the projector augmented wave (PAW) method<sup>9</sup> which provides access to all-electron values.

We will explicitly investigate the large-Z limit of ionization potentials for atoms and lattice constants of simple solids. The original work for ionization potentials is by Constantin *et al.*,<sup>8</sup> where Hartree-Fock and Kohn-Sham models are considered, while we present OFDFT results. We also discuss the ionization potentials for bulk derived local pseudopotentials (BLPS)<sup>10</sup> which are derived from Kohn-Sham calculations. We extend the large-Z limit results from atoms to simple solids and explore the large-*Z* limit of both OFDFT and Kohn-Sham models. We also discuss how the BLPS improves all-electron results qualitatively.

The paper is organized as follows: First, we introduce the computational methods used throughout this work and then introduce the concept of semiclassical average. Then, we explore the ionization potential of the OFDFT models in atomic systems. We discuss the differences and similarities for bulk results between all-electron and BLPS. Finally, we uncover large-*Z* limits in simple solids present in both OFDFT and Kohn-Sham models.

#### A. Computational methods

We consider a standard DFT framework where we start from the total energy density functional  $^{\rm 6}$ 

$$E_{\text{tot}}[n] = T_s[n] + E_{\text{Ha}}[n] + E_{\text{xc}}[n] + \int d\mathbf{r} \ v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \mu \Big(N - \int d\mathbf{r} \ n(\mathbf{r})\Big),$$
(1)

where the particle number restriction *N* has been included through the Lagrangian multiplier  $\mu$ ,  $T_s[n]$  is the noninteracting kinetic energy functional,  $E_{\text{Ha}}$  is the electrostatic Hartree energy, and  $E_{\text{xc}}[n]$  is the exchange-correlation functional. By finding the stationary point of the functional  $\frac{\delta E_{\text{tot}}[n]}{\delta n} = 0$ , we arrive at the Euler equation

$$\frac{\delta T_s[n]}{\delta n} + v(\mathbf{r}) - \mu = 0, \qquad (2)$$

which we need to solve self-consistently to find the ground-state density  $n(\mathbf{r})$  and chemical potential  $\mu$ . The potential  $v(\mathbf{r})$  is the usual DFT potential,  $v(\mathbf{r}) = v_{\text{Ha}} + v_{\text{xc}} + v_{\text{ext}}$ , where  $v_{\text{Ha}}$  is the Hartree potential,  $v_{\text{xc}}$  is the exchange-correlation potential, and  $v_{\text{ext}}$  is the external potential. For the Kohn-Sham method,  $T_s$  is approximated with the noninteracting orbitals  $\{\phi_i\}$  which are obtained by solving the Kohn-Sham equations. For OFDFT, the Euler equation is usually reformulated into an eigenvalue equation by incorporating the von Weizsäcker term  $T_{\text{vW}}[n] = \frac{1}{8} \frac{|\nabla n|^2}{n}$  into the kinetic energy functional T[n] which results in

$$\left(-\frac{1}{2}\nabla^2 + \frac{\delta T_{\theta}[n]}{\delta n} + v(\mathbf{r})\right)n^{1/2} = -\mu n^{1/2},\tag{3}$$

where the Pauli term is  $T_{\theta}[n] = T_s[n] - T_{vW}[n]$ .<sup>6</sup> The corresponding potential is called the Pauli potential,  $v_{\theta} = \frac{\delta T_{\theta}[n]}{\delta n}$ , which has been studied extensively.<sup>11–14</sup>

Atomic calculations are done with the all-electron atomic calculator with spherical symmetry. OFDFT calculations of solids are done with the PAW OFDFT solver implemented within the GPAW DFT software.<sup>15,16</sup> The OFDFT PAW setups do not have frozencore; thus, OFDFT PAW implementation allows us to access the OFDFT all-electron values. Kohn-Sham PAW calculations of solids do use frozen core approximation. We use a plane wave basis to expand the square root of the density, and an energy cutoff of 1000 eV is used throughout this work. All the OFDFT pseudopotential calculations are done with PROFESS<sup>17</sup> with a plane wave cutoff of 1600 eV. Additional details on PAW setups can be found in Appendix B.

#### **B.** Kinetic energy functionals

In this paper, we investigate a few distinct kinetic energy functionals. The simplest and most typical functional is the TF-vW functional,

$$T_{\rm TF-vW} = T_{\rm TF} + \lambda T_{\rm vW} = \int d\mathbf{r} \ \tau_{\rm TF} \left(1 + \lambda \frac{5}{3} s^2\right), \tag{4}$$

where  $\tau_{\rm TF} = \frac{3}{10} (3\pi^2)^{2/3} n^{5/3}$  is the Thomas-Fermi kinetic energy density and  $s = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$  is the reduced gradient of the density. A few values of  $\lambda$  are noteworthy. The value  $\lambda = \frac{1}{9}$  corresponds to second order gradient expansion of the kinetic energy,<sup>18</sup> and the value  $\lambda = \frac{1}{5}$  has been found to be the most accurate for atoms.<sup>19</sup> We will study mostly  $\lambda = \frac{1}{5}$  which provides reasonable atomic reference and is qualitatively similar to  $\lambda = \frac{1}{9}$ .

Another functional<sup>20</sup> which we will explore is named RATIONAL<sup>p</sup> which is a bit more sophisticated GGA (Generalized Gradient Approximation) level kinetic energy functional. The functional has the following form:

RATIONAL<sup>*p*</sup> = 
$$T_{\rm vW} + \int d\mathbf{r} \ \tau_{\rm TF} \left(1 + \frac{C_2}{p} s^2\right)^{-p}$$
, (5)

where *p* and  $C_2$  are free parameters. The functional form is designed with (3) in mind. We fix  $p = \frac{3}{2}$  and  $C_2 = 0.845$  in this paper as the parameter values. From earlier study,<sup>20</sup> we obtained that a valid parameter for  $C_2$  is 0.812 and minor parameter changes do not affect our results qualitatively. We could study other functionals which are very similar to RATIONAL such as LKT<sup>21</sup> or Pauli-Gaussian (PG),<sup>22</sup> but they are qualitatively the same as RATIONAL<sup>*p*</sup>.<sup>20</sup> Recently, there have been advances for OFDFT functionals by incorporating Laplacian of density to the functionals,<sup>23</sup> but here we only consider functionals with reduced gradient of density due to their simplicity.

#### C. Semiclassical average

The central concept which we study is the *semiclassical average* which we will define to be the smooth part of a quantity as a function of particle number *N* or atomic number *Z*. Formally, this reads as

$$E(N) = \tilde{E}(N) + \delta E(N), \tag{6}$$

where  $\tilde{E}$  is the smooth part and  $\delta E$  is the oscillating part. In general, the smooth part gives the trend of the quantity and is a relatively simple function. The oscillating term depends on the exact quantum effects. For some quantities, it is possible to extract the smooth part  $\tilde{E}$  by completely semiclassical methods and, in some cases, it can be extracted from oscillating data. A good example is the total energy of neutral atoms as a function of atomic number *Z*,

$$\tilde{E}^{\text{atomic}}(Z) = -0.7687745Z^{7/3} + 0.5Z^2 - 0.2699Z^{5/3}.$$
 (7)

In short, semiclassical refers to the fact that the smooth part is, in many cases, attainable with semiclassical methods. In many cases, the oscillations  $\delta E(N)$  are called shell oscillations as they are due to filling of quantum mechanical shells.

The orbital-free method is semiclassical in the sense that the kinetic energy functionals are based on semiclassical approximations (Thomas-Fermi theory and corrections). Thus, all-electron OFDFT quantities will vary smoothly as a function of atomic number Z, which allows us to probe the large-Z limit with relative ease. The large-Z limit is interesting in itself, but it also has relevance for the development of density functionals.<sup>24,25</sup> Note that OFDFT usually has only one semiclassical average or limit while Kohn-Sham usually has multiple possible averages and limits,<sup>8</sup> as the latter has shell oscillations and the former does not. This notion will be made clear in following sections.

The simple TF-vW model is a really simple OFDFT model and has theoretical flaws which we will discuss later, but it still produces results that do resemble semiclassical averages. In the following sections, we will discuss the semiclassical averages of ionization potentials and lattice constants of solids produced by the TF-vW model.

#### **D.** Ionization potential

All-electron OFDFT calculations require acknowledging the fact that the atomic reference systems do have some fundamental flaws. The fundamental flaws can described in (at least) two different ways: Flaws in Pauli potential<sup>26</sup> and problems in describing strongly bound electrons<sup>4</sup> in the atomic inner core where  $V(\mathbf{r}) \sim -\frac{Z}{r}$ . Both methods of analysis expose the same problem: Near the nucleus of the atom where  $V(\mathbf{r}) \sim -\frac{Z}{r}$ , the kinetic energy functionals fail (to be exact, single point functionals fail).

For self-consistent functionals, the problem near the nucleus has been analyzed to some extent. It is known that many forms of GGA exhibit singular Pauli potentials near the nucleus,<sup>13</sup> and even when there is no singularity, the potential is qualitatively wrong.<sup>27</sup> For Kohn-Sham atoms, it has been analyzed that the kinetic energy density from the von Weizsäcker term significantly differs from the Kohn-Sham kinetic energy density<sup>28,29</sup> even though the simplistic analysis with almost noninteracting 1s electrons and nuclear cusp condition suggests the von Weizsäcker term should be accurate near the nucleus. It is quite hard to analyze to which extent the problematic nucleus affects the self-consistent ionization potentials or results for solids.

The potential functionals<sup>30-32</sup> which correspond to the TF-vW density functional model do require explicit corrections for the atomic inner core region, and it is possible to augment potential functionals with an improved description of strongly bound electrons.

We note that Pauli potential constraints, like positivity of the Pauli potential, are relevant constraints also for pseudopotentials and pseudodensities even though they do not contain strongly bound electrons.<sup>21</sup> As the atomic inner core is removed for local pseudopotentials, they do not suffer from insufficient description of strongly bound electrons.

This leads us to look at ionization potential which is obtained from a total energy difference and thus suffers less from poor approximations near the nucleus than the total energy.

#### **II. RESULTS AND DISCUSSION**

#### A. Ionization potential of atoms

The ionization potential is calculated as

$$IP_{Z} = E(Z, Z - 1) - E(Z, Z),$$
(8)

where E(Z, N) is the total energy of self-consistent DFT calculations, where Z is the atomic number and N is the number of electrons. For Kohn-Sham DFT, it has been computationally found that each column of the periodic table has a well-defined ionization potential limit IP<sub> $\infty$ </sub> in the large-Z limit  $Z \rightarrow \infty$ .<sup>8</sup> As OFDFT does not have shell effects, each OFDFT model has one limit value IP<sub> $\infty$ </sub>.

Ionization potential is an interesting test case for self-consistent OFDFT models and for functional development where semiclassical results can be applied to find better functionals.<sup>20,24</sup> All the calculations for ionization potential are nonrelativistic and spin-unpolarized, and only Dirac exchange is used.

#### 1. All-electron ionization potentials

We assess the all-electron ionization potentials of OFDFT models in the large-Z limit. The ionization potential has an analytically calculated value of 3.15 eV for the extended Thomas-Fermi (ETF) model, which contains quantum corrections to Thomas-Fermi and the leading term of exchange<sup>4</sup> (Dirac exchange). While the prediction is for all Z, the statistical nature of the ETF approximation makes it a better prediction for the large-Z limit than for low-Zatoms.

It was found<sup>8</sup> for Kohn-Sham model with local-density approximation (LDA) that, depending on the column of the periodic table, the ionization potential limit IP<sub> $\infty$ </sub> is in the range 1.56–4.29 eV and the average over columns 1–8 in the large-*Z* limit produces a value of 3.07 eV which corresponds well to the result of 3.15 eV found in the ETF model.

The ionization potential for low to moderate values of Z is shown in Fig. 1, where we can see the shell oscillations of the KS model and the averaging effect of the TF-vW model. From the



**FIG. 1**. Ionization potential as a function of Z for multiple models. TF-vW model results are with  $\lambda = \frac{1}{5}$ . The noble atoms are the upper limit of the ionization potential, and the alkali atoms are the lower limit.

ionization potential of relatively low-Z atoms, it would be tempting to conclude that the TF-vW model produces a semiclassical average of the Kohn-Sham results.

We calculate the ionization potential IP<sub>∞</sub> for the TF-vW model by calculating ionization potentials up to Z = 700 and then doing a parabolic least-squares fit to the results in  $Z^{-1/3}$ . The ionization potential limit IP<sub>∞</sub> is then the constant coefficient in the fit. The IP<sub>∞</sub> results for multiple  $\lambda$  values of the TF-vW model are shown in Fig. 2. We also do a parabolic fit to the ionization potential limits IP<sub>∞</sub><sup>TF-vW</sup>( $\lambda$ ). In the extrapolated limit  $\lambda \rightarrow 0$ , we find an ionization potential IP<sub>∞</sub><sup>TF-vW</sup>(0) of 3.98 eV. The trend is simple: When  $\lambda$  grows, so does the ionization potential because of added binding of the von Weizsäcker term.

While TF-vW generates an average of the ionization potential for moderate values of *Z* in Fig. 1, it is not a semiclassical average as the predictions are not valid in the large-*Z* limit. The trend of ionization potential for the noble atoms with Kohn-Sham LDA produces an upper limit of 4.29 eV, and the alkali atoms produce a lower limit of 1.56 eV,<sup>8</sup> while even  $\lambda = \frac{1}{9}$  yields an IP<sub>∞</sub> value of 4.58 eV.

We can compare this to the self-consistent prediction of the Englert-Schwinger (ES) model.<sup>4,27</sup> We do not go into detail here, but the ES model is the potential functional version of the TF- $\frac{1}{9}$ vW model which includes explicit corrections for the atomic core. For the self-consistent ES model, we obtain an ionization potential limit of 2.83 eV which is much closer to the value obtained analytically from the ETF model, and it produces the semiclassical average in the large-Z limit. For lower atomic number values, the ES result is slightly below the Kohn-Sham prediction for the alkali atoms.

It is not trivial to analyze why the TF-vW model does not produce the semiclassical average. One possible reason is the incorrect distribution of electrons near the nucleus affects the ionization potential.

More sophisticated GGA kinetic energy functionals do not fare any better: Constantin<sup>33</sup> found that Pauli-Gaussians, which are qualitatively similar to LKT and RATIONAL, yield ionization potentials  $IP_{\infty}$  of size ~11 eV. We must remember that the more sophisticated GGA kinetic energy functionals are designed for pseudopotentials and not for all-electron calculations. The successful predictions of ionization potential in the large-*Z* limit attracts interest to the ES model, and consequently for potential functionals, as a potential alternative to kinetic energy density functionals for OFDFT calculations. New and more sophisticated potential functionals have been developed which predict the electronic density from the effective potential with nonlocal expression.<sup>34</sup> Further development to this direction is required to assess which energy functionals would be appropriate to use with the density expression.

#### 2. Local pseudopotential ionization potentials

The use of local pseudopotentials reintroduces shell effects into the OFDFT model as shown in Fig. 1. For BLPS, more systematic study of ionization potentials is not possible due to the limited amount of BLPS pseudopotentials. We can, however, study columns of the periodic table to test if *ordering* of ionization potentials is correct. The ionization potentials of group 3 and 4 pseudopotentials are shown in Table I.

The Kohn-Sham ordering for column 3 is IP(Ga) > IP(AI) > IP(In). The simple TF-vW model fails to produce the correct ordering; in fact, it reverses it. Here, the RATIONAL functional is able to reproduce the correct ordering. For column 4, Kohn-Sham predicts ordering IP(P) > IP(As) > IP(Sb), which is the easier case as the ordering is roughly reproduced by both TF-vW and RATIONAL.

We note that varying the functional parameter does not change the results qualitatively in any of the cases. More quantitatively, the differences between ionization potentials stay roughly constant with different functional parameters.

Thus, for BLPS ionization potentials, one can see that RATIO-NAL is qualitatively better than TF-vW, and we expect similar results for other Pauli functionals. The improvement is quite visible in Fig. 1.

#### B. Lattice constants of simple solids

For ionization potentials, it is rather easy to see the averaging nature of the all-electron OFDFT models (with the PAW method)



FIG. 2. Left: lonization potential for the chosen TF-vW models and ES model. Right: lonization potential IP<sub>∞</sub> as a function of  $\lambda$  for the TF-vW mode, where  $\lambda$  is the fraction of the von Weizsäcker term included.

J. Chem. Phys. **151**, 244101 (2019); doi: 10.1063/1.5129397 Published under license by AIP Publishing

**TABLE I**. Ionization potentials for group 3 and 4 BLPS with KS and a few chosen OFDFT models. TF-vW model results are with parameter value  $\lambda = \frac{1}{\epsilon}$ .

		Group 3		Group 4			
Model	Ga	Al	In	Р	As	Sb	
KS	0.15	0.18	0.24	0.28	0.27	0.26	
TF-vW	0.23	0.23	0.22	0.24	0.23	0.21	
RATIONAL	0.23	0.25	0.27	0.31	0.30	0.26	

even though the TF-vW is unable to produce a true semiclassical average due to failure in the large-Z limit. Now, we focus on simple solids. Our primary focus is on the qualitative difference between allelectron and BLPS and on finding if the TF-vW model can produce a good semiclassical average in solids. We first study the crystal structures of simple solids. In order to access all-electron OFDFT values, we use the PAW method with no frozen core.

#### 1. Low to moderate atomic numbers

In order to evaluate the qualitative difference, we calculate the equilibrium energy  $E_0$  for lithium, magnesium, and aluminum in sc, fcc, bcc, and hcp structures in order to evaluate the preferred structure. The results are calculated with the Perdew-Zunger LDA exchange-correlation functional. We compare all-electron and local pseudopotential (BLPS) results for equilibrium energy  $E_0$  which are in Table II. For the TF-vW model, we chose  $\lambda = \frac{1}{5}$ , but the choice of  $\lambda$  does not affect the results qualitatively.

**TABLE II.** Equilibrium energy  $E_0$  results for various DFT models for Li, Mg, and Al in sc, fcc, bcc, and hcp crystal structures. The minimum energy for each model (row) is given in bold. If multiple structures have the same minima, then both are given in bold. The Kohn-Sham results are from Ref. 35.

	SC	fcc	Bcc	Hcn		
		100	200	m		
	Li					
TF-vW (AE)	-1.530	-1.620	-1.617	-1.620		
KS (BLPS)	-7.414	-7.551	-7.550	-7.550		
TF-vW (BLPS)	-7.623	-7.752	-7.748	-7.752		
RATIONAL (BLPS)	-7.481	-7.617	-7.615	-7.617		
		Ν	ſg			
TF-vW (AE)	-2.152	-2.362	-2.352	-2.362		
KS (BLPS)	-23.838	-24.233	-24.217	-24.246		
TF-vW (BLPS)	-24.820	-25.070	-25.059	-25.069		
RATIONAL (BLPS)	-24.364	-24.674	-24.668	-24.674		
	Al					
TF-vW (AE)	-2.189	-2.407	-2.396	-2.407		
KS (BLPS)	-56.868	-57.202	-57.121	-57.178		
TF-vW (BLPS)	-58.786	-59.036	-59.021	-59.035		
RATIONAL (BLPS)	-57.465	-58.048	-58.025	-58.048		

The all-electron PAW and BLPS results are naturally not directly comparable in absolute values. For the all-electron PAW case, we always see a similar result: fcc and hcp are the preferred phase. This is a general feature over all Z: the energetic ordering of structures is constant as fcc ~ hcp > bcc > sc, which demonstrates that the pure orbital-free model can not describe differences between structures. With pseudopotentials, OFDFT GGAs fare a bit better but discerning between fcc and hcp is quite hard for RATIO-NAL, although it is slightly better than TF-vW which predicts fcc for magnesium.

Even though the TF-vW model is quite crude, it already exhibits similar trends to the more refined GGA models with pseudopotentials. Two-point kinetic energy density functionals such as Wang-Govind-Carter (WGC) improve the OFDFT prediction power qualitatively with BLPS (not shown here).<sup>35</sup> The two-point functionals, such as WGC, are very accurate for one type of system, e.g., metals in the case of WGC, while GGAs are easily applied for any type of system.

Now, we focus on all-electron values obtained with PAW calculations for low to moderate Z to see the trends. In Fig. 3, we show TF-vW and KS values for  $V_0^{1/3}$  (proportional to the lattice constant), where  $V_0$  is the equilibrium volume. The results are calculated for the fcc structure (the preferred structure for TF-vW) and up to the atomic number Z = 54. The TF-vW model averages over the shell effects of Kohn-Sham results. It is quite similar to the case of ionization potentials. Note that, again, the BLPS introduces the shell effects to the OFDFT model.

One obvious fact is that Kohn-Shame derived local pseudopotentials are critical for the success of kinetic energy functionals. The lattice constants of the TF-vW model are just an average over Kohn-Sham results, while the BLPS results are much closer to the Kohn-Sham values. With better functionals, the results are considerably better, but we use the TF-vW model for consistency. The result is not surprising as all the fine details of the electronic structure are lost in the fully orbital-free model, while the pseudopotential contains a lot of information about the electronic structure as it is constructed from Kohn-Sham calculations. In the orbital-free scheme, pseudopotentials are not just a technical tool as in the Kohn-Sham



**FIG. 3.** Lattice constants for the fcc lattice for Kohn-Sham and TF-vW models for the fcc crystal structure. The TF-vW model volumes are calculated with parameter value  $\lambda = \frac{1}{\epsilon}$ .



FIG. 4. Lattice constants of TF-vW models and Kohn-Sham LDA lattice constants for groups 7 and 8 of the periodic table.

scheme, but they are an essential part of its success. In contrast, the TF-vW model does yield an average of the Kohn-Sham values with respect to *Z*, and it would be again tempting to point out that TF-vW produces a semiclassical average.

#### 2. Large-Z limit

We evaluate the large-Z limit for lattice constants as we did for the ionization potentials. We calculate fcc bulk systems up to Z = 500. Note that for OFDFT calculations, the exact Z values are of no concern as every quantity is a smooth function of Z. The results are shown in Fig. 4. It is immediate that the inverse of  $V_0^{1/3}$  is almost linear in  $Z^{-1/3}$  for large-Z. We do a parabolic least-squares fit in  $Z^{-1/3}$ to obtain a limit value in  $Z \rightarrow \infty$ , which depends on  $\lambda$  (and on the crystal structure).

Due to oscillations, such a limit does not exist for Kohn-Sham systems, at least in the strict sense. For ionization potentials,<sup>8</sup> the case is similar. Hypothetically for each *column* of the periodic table, there exists well-defined  $IP_{\infty}$ . In the figure, we plot periodic table columns 7 and 8 with the fcc crystal structure. We fit a linear function in  $Z^{-1/3}$  to the values instead of parabolic fit due to more oscillatory data.

The PAW potentials used in the calculation are based on the electronic structure from the aufbau rule, and for both column 7 and 8 elements, only the highest s- and p-states are included in the valence and the rest of the electrons are dealt with in the frozen core approximation. The largest elements included in the results are Z = 459 and Z = 460 for columns 7 and 8. For OFDFT calculations, the largest element is Z = 450.

Only the last two columns are included because the s- and pstates are enough for the valence. Already for column 6, the semicore d states start to be relevant for higher Z values, complicating the PAW setup generation considerably. All the PAW setups are nonrelativistic. Additional details on the PAW setups can be found in Appendix B.

Figure 4 presents the first time that the large-Z limit has been explored for solids with *ab initio* methods. As the data are not complete with all the columns of the periodic table, it is not obvious if the TF-vW model produces a real semiclassical average of the Kohn-Sham results with respect to Z in the large-Z limit. From Fig. 4

**TABLE III.** Values for  $V^{-1/3}$  and V in the large-Z limit. The units are in Å<sup>-1</sup> and Å<sup>3</sup>, respectively.

Туре	$V^{-1/3}$	V
Kohn-Sham column 7	0.167	214.461
Kohn-Sham column 8	0.161	241.818
TF-vW $\lambda = \frac{1}{5}$	0.265	53.849
TF-vW $\lambda = \frac{1}{9}$	0.244	69.254

and comparing to the ionization potential results, there is a suggestion that while in the low-Z regime TF-vW is a good average, it is not a proper semiclassical average due to failure in the large-Z limit. We do not show results for RATIONAL as it does not produce a good average even for low-Z.

The limiting values for  $V^{-1/3}$  and V are shown in Table III. Similar analysis can be done for any crystal structure. We have provided values for the bulk modulus in Appendix A. We note that binding of elements in column 8 is due to well-known overbinding of LDA functionals as they are van der Waals crystals, which bind due to dispersion effects, not through exchange-correlation effects. The results for column 8 are thus the proof-of-concept for the KS + LDA model.

#### **III. CONCLUSION**

We have explored the difference between all-electron and pseudopotential OFDFT results where the solid all-electron values are obtained with PAW. The all-electron values have less resolving power, which clearly shows that in the orbital-free scheme, pseudopotentials derived from Kohn-Sham calculations are not just a technical tool to make the quantities smoother for numerics as in the Kohn-Sham scheme, but they are an essential part of the success of OFDFT.

Perhaps, the most surprising result is that the primitive TF-vW does not produce a semiclassical average for the ionization potential, although it does produce an average of the moderate Z values. Ionization potential does produce consistency check for kinetic energy functionals and pseudopotentials. If more local pseudopotentials are developed to fill the columns of the periodic table, then ionization potential ordering provides a qualitative measure for the kinetic energy functionals.

The semiclassical average of all-electron OFDFT uncovered the semiclassical limit for the lattice constants of bulk systems which is, in our knowledge, the first *ab initio* large-*Z* limit prediction for solids. Systematic study of the large-*Z* regime could provide important information for exchange-correlation functional development. As the "correct" limit is not known, the limit would have to be investigated with "beyond-DFT" methods such as GW.

#### ACKNOWLEDGMENTS

This work was supported by the Academy of Finland, Project Nos. 279240, 284621, and 312556, and by Vicerrectoría de Investigación UdeA (Estrategia de Sostenibilidad 2018–2019). The authors are also grateful to CSC, the Finnish IT Center for Science Espoo, and the Applied Physics Department of Aalto for computations.

#### APPENDIX A: BULK MODULUS OF HEAVY ELEMENTS

Here, we briefly show results for bulk moduli of heavy elements. We show the results for a large range of Z in Fig. 5. The bulk modulus of each element is calculated by calculating 16 points near the equilibrium, which are then fitted to the Birch-Murnaghan equation of state.<sup>36</sup> It is quite probable that also the bulk modulus has a finite large-Z limit, but we do not analyze it further here.

#### APPENDIX B: PAW SETUPS

We detail here the construction of OFDFT PAW setups used in this manuscript and KS PAW setups used to obtain results in Fig. 4.

Most of the OFDFT PAW setup generation is identical to the setup generation in GPAW<sup>15,16</sup> with the difference that instead of orbitals  $\phi_i$  from the spherically symmetrical Kohn-Sham atom, we use the quasiorbital  $n(\mathbf{r})^{1/2}$  to generate the appropriate partial waves, pseudopartial waves, and projectors. We emphasize that we do not use frozen core approximation in OFDFT PAW setups. The GPAW software package, including the orbital-free calculator/setup generator, is open-source.



FIG. 5. Bulk modulus of column 7 and column 8 elements with the Kohn-Sham scheme.



**FIG. 6**. Energy volume curves for elements Z = 459 and Z = 460 which are the heaviest elements in columns 7 and 8.

TABLE IV.	The PAW setu	p cutoffs fo	or large-Z Ko	ohn-Sham	elements
			~		

Column 7	Z	17	35	53	85	117	167	217	289	361	459
	r <sub>c</sub>	1.5	2.1	2.2	2.3	2.6	2.8	3.1	3.3	3.5	3.6
Column 8	Z	18	36	54	86	118	168	218	290	362	460
	r <sub>c</sub>	1.6	2.2	2.2	2.3	2.6	2.7	3	3.2	3.4	3.6

Each OFDFT PAW setup consists of three radially distinct partial waves: one constructed from nodeless radial quantity  $n(r)^{1/2}$ and two unbound states with s- and p-like symmetry from the Schrödinger-like equation (3). Each partial wave has its associated pseudopartial wave, which is generated from the partial wave by choosing a cutoff  $r_c$ , and then the part of the partial wave closer to the nucleus is replaced with 6th degree polynomial of even powers such that the result is smooth at the cutoff  $r_c$ . Smooth projector functions are constructed by applying pseudo-Hamiltonian in the Schrödinder-like equation (3) to the pseudopartial waves. In addition, we have standard Gaussian charge compensation functions, which have the same cutoff as the partial waves  $r_c$ .

The scheme has been shown to yield same results as fully all-electron OFDFT calculations with unmodified nuclear potential.<sup>9</sup> The most critical quantity which has to be decided depending on the atomic size is the radial cutoff  $r_c$ . For OFDFT elements in Fig. 4, we used  $r_c$  of 1.6 bohr for atomic numbers smaller than Z = 200 and  $r_c$  of 2.0 bohrs for atomic numbers larger than Z = 200.

The Kohn-Sham PAW setups are generated with the same generator. For both column 7 and column 8, the setups are quite similar. Only the highest s-state and p-state are used as valence electrons, and the rest of the electrons are treated with frozen core approximation. The PAW setups have partial waves, pseudopartial waves, and projector sets generated from the valence electrons. In addition, unbound waves with s, p, and d symmetry are used. All the radial functions use the same cutoff  $r_c$ . The cutoffs for elements used in Fig. 6 are tabulated in Table IV.

#### REFERENCES

- <sup>1</sup> P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
- <sup>2</sup> P. Elliott, D. Lee, A. Cangi, and K. Burke, Phys. Rev. Lett. **100**, 256406 (2008).
- <sup>3</sup>M. Brack and R. Bhaduri, *Semiclassical Physics*, Frontiers in Physics (Addison-Wesley, Advanced Book Program, 1997).
- <sup>4</sup>B.-G. Englert, Semiclassical Theory of Atoms, 3rd ed., Lecture Notes in Physics Vol. 300 (Springer, 1988).
- <sup>5</sup>W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- <sup>6</sup>M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A 30, 2745 (1984).
- <sup>7</sup>E. H. Lieb and B. Simon, Adv. Math. 23, 22 (1977).

<sup>8</sup>L. A. Constantin, J. C. Snyder, J. P. Perdew, and K. Burke, J. Chem. Phys. 133, 241103 (2010).

<sup>9</sup>J. Lehtomäki, I. Makkonen, M. A. Caro, A. Harju, and O. Lopez-Acevedo, J. Chem. Phys. **141**, 234102 (2014).

- <sup>10</sup>B. Zhou, Y. A. Wang, and E. A. Carter, Phys. Rev. B **69**, 125109 (2004).
- <sup>11</sup>K. Finzel, Int. J. Quantum Chem. **116**, 1261–1266 (2016).
- <sup>12</sup>M. Levy and H. Ou-Yang, Phys. Rev. A 38, 625 (1988).

<sup>13</sup> V. V. Karasiev, R. S. Jones, S. B. Trickey, and F. E. Harris, Phys. Rev. B 80, 245120 (2009). <sup>14</sup>H. Levämäki, A. Nagy, K. Kokko, and L. Vitos, Phys. Rev. A **92**, 062502 (2015).

<sup>15</sup>J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B 71, 035109 (2005).

<sup>16</sup>J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dułak, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. A. Hansen, H. H. Kristoffersen, M. Kuisma, A. H. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. G. Moses, J. Ojanen, T. Olsen, V. Petzold, N. A. Romero, J. Stausholm-Møller, M. Strange, G. A. Tritsaris, M. Vanin, M. Walter, B. Hammer, H. Häkkinen, G. K. H. Madsen, R. M. Nieminen, J. K. Nørskov, M. Puska, T. T. Rantala, J. Schiøtz, K. S. Thygesen, and K. W. Jacobsen, J. Phys.: Condens. Matter 22, 253202 (2010).

<sup>17</sup>M. Chen, J. Xia, C. Huang, J. M. Dieterich, L. Hung, I. Shin, and E. A. Carter, Comput. Phys. Commun. **190**, 228 (2015).

<sup>18</sup>D. Kirzhnits, Sov. Phys. JETP 5, 64 (1957).

(2018).

<sup>19</sup>K. Yonei and Y. Tomishima, J. Phys. Soc. Jpn. **20**, 1051 (1965).

<sup>20</sup> J. Lehtomäki and O. Lopez-Acevedo, "Semilocal kinetic energy functionals with parameters from neutral atoms," Phys. Rev. B 100, 165111 (2019).
 <sup>21</sup> K. Luo, V. V. Karasiev, and S. B. Trickey, Phys. Rev. B 98, 041111

- <sup>22</sup>L. A. Constantin, E. Fabiano, and F. Della Sala, J. Phys. Chem. Lett. 9, 4385 (2018).
- <sup>23</sup>L. A. Constantin, E. Fabiano, and F. Della Sala, J. Chem. Theory Comput. 15, 3044 (2019).
- <sup>24</sup> P. Elliott and K. Burke, Can. J. Chem. **87**, 1485 (2009).
- <sup>25</sup>L. A. Constantin, E. Fabiano, S. Laricchia, and F. Della Sala, Phys. Rev. Lett. 106, 186406 (2011).
- <sup>26</sup>V. Karasiev and S. Trickey, Comput. Phys. Commun. 183, 2519 (2012).
- <sup>27</sup>J. Lehtomäki and O. Lopez-Acevedo, J. Chem. Phys. 147, 234102 (2017).
- <sup>28</sup>F. Della Sala, E. Fabiano, and L. A. Constantin, Phys. Rev. B **91**, 035126 (2015).
- <sup>29</sup>L. A. Constantin, E. Fabiano, and F. D. Sala, Computation 4, 19 (2016).
- <sup>30</sup>B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2331 (1984).
- <sup>31</sup>B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2339 (1984).
- <sup>32</sup>B.-G. Englert and J. Schwinger, Phys. Rev. A 29, 2353 (1984).
- <sup>33</sup>L. A. Constantin, Phys. Rev. B **99**, 155137 (2019).
- <sup>34</sup>T. T. Chau, J. H. Hue, M.-I. Trappe, and B.-G. Englert, New J. Phys. **20**, 073003 (2018).
- <sup>35</sup>J. Xia and E. A. Carter, Phys. Rev. B **91**, 045124 (2015).
- <sup>36</sup>M. Hebbache and M. Zemzemi, Phys. Rev. B **70**, 224107 (2004).