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## RESEARCH ARTICLE

### A New Look at Thomas-Fermi Theory

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*Dedicated to Andreas Savin*

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In this short note we argue that Thomas-Fermi Theory the simplest of all density functional theories, although failing to explain features such as **molecular** binding or stability of positive ions, is surprisingly accurate in estimating sizes of atoms. We give both numerical, experimental and rigorous mathematical evidence for this claim. Motivated by this we formulate two new mathematical conjectures on the exactness of Thomas-Fermi Theory.

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## 1. Introduction

With the enormous success of density functional theories in computational chemistry and the refinement they have undergone in the past half century (see [1] for a recent review of successes and challenges in DFT) it may be surprising if there should still be anything to be learned from as old and basic a model as Thomas-Fermi (TF) Theory (Thomas 1927 [2] and Fermi 1927 [3]). TF Theory goes back to the early days of quantum mechanics and is, indeed, the oldest density functional theory.

Thomas-Fermi Theory completely ignores exchange correlation effects and is unable to predict many basic properties of atoms and molecules. Atoms do not bind in Thomas-Fermi Theory and negatively charged ions are unstable (Teller's No-Binding Theorem [4]).

It is nevertheless the purpose of this short note to show that TF Theory, surprisingly enough, is quite adequate at describing certain specific and at the same time important properties of atoms and molecules. As an example we shall see that the size of alkali atoms is not just qualitatively, but even from a quantitative point of view rather accurately described by TF Theory. We shall also briefly discuss evidence that TF theory accurately describes the short distance behavior of the Born-Oppenheimer energy curves of diatomic molecules. As a consequence of the No-Binding Theorem there is no equilibrium point in the TF approximation to the Born-Oppenheimer curve, but at much shorter distances the TF curve may as we shall discuss give a surprisingly good approximation.

We will discuss the new point of view on the validity of TF theory both in a stringent mathematical formulation but also based on experimental and numerical evidence. The paper is organized as follows. In Section 2 we briefly review Thomas-Fermi Theory and give its mathematical justification based on the large  $Z$  asymptotics of the ground state energy. In Section 3 we discuss new asymptotic limits which may be accurately described by TF theory and which we believe are closer at capturing real and important chemical aspects of atoms and molecules than the ground state energy asymptotics. Finally, in Section 4 we discuss simple numerical calculations of the radii of atoms in TF Theory which, at least for the larger alkali atoms give extraordinarily good agreement with the empirical data of Bragg [5] and Slater [6] (see Table 1 below).

## 2. Thomas-Fermi Theory and the large $Z$ limit

Thomas-Fermi Theory for a molecule or atom is defined from the energy functional (in atomic units)

$$\mathcal{E}^{\text{TF}}(\rho) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(r)^{5/3} - V(r)\rho(r)d^3r + \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r' + U,$$

where  $V$  is the electron-nuclear attraction and  $U$  is the internuclear repulsion, i.e.,

$$V(r) = \sum_{k=1}^M \frac{Z_k}{|r - R_k|}, \quad U = \sum_{1 \leq k < \ell \leq M} \frac{Z_k Z_\ell}{|R_k - R_\ell|}.$$

Here we have  $M$  nuclei at positions  $R_k$ ,  $k = 1, 2, \dots, M$ . In particular, for an atom

$$U = 0 \quad \text{and} \quad V(r) = \frac{Z}{|r|}.$$

It is not difficult to see that for an atom the minimizing energy satisfies

$$E^{\text{TF}}(Z) = \min_{\rho} \mathcal{E}^{\text{TF}}(\rho) = -C_{\text{TF}} Z^{7/3}$$

for some constant  $C_{\text{TF}} > 0$  whose numerical value does not play a role to our discussion. The minimizing density  $\rho^{\text{TF}}$  satisfies  $\int \rho^{\text{TF}} = Z$ , i.e., the atom is neutral and solves the TF-equation

$$\frac{1}{2}(3\pi^2)^{2/3} \rho^{\text{TF}}(r)^{2/3} = V(r) - \int \frac{\rho^{\text{TF}}(r')}{|r - r'|} d^3 r'.$$

If we minimize with the restriction that  $\int \rho(r') d^3 r' = N < Z$  we arrive at the Thomas-Fermi energy  $E^{\text{TF}}(N, Z)$  of a positive ion. As already pointed out negative ions are unstable.

The mathematical justification of Thomas-Fermi Theory was given in [7, 8] (see also [9]). In these works TF Theory is justified as giving the correct leading order ground state energy asymptotics of atoms for large atomic number  $Z$ . The limit  $Z$  tending to infinity is of course in some sense purely academic. It is, however, necessary, in order to state mathematically that an approximation becomes exact, to consider a precise limiting situation, even if that takes us out of the physically interesting regime. The large  $Z$  limit is in general also a good test for approximating schemes, see e.g. [10].

It is known that the large  $Z$  asymptotics of the exact total ground state energy of an atom is given by

$$E(Z) = -C_{\text{TF}} Z^{7/3} + C_{\text{S}} Z^2 + C_{\text{DS}} Z^{5/3} + o(Z^{5/3}),$$

where the leading term is, indeed, the Thomas-Fermi energy as established in [7]. We are using the convention that a quantity, such as the total ground state energy  $E(Z)$ , without a superscript, denotes the exact value whereas the approximation in, say, Thomas-Fermi Theory is denoted with a superscript  $E^{\text{TF}}(Z)$ .

In atomic units  $C_{\text{S}} = 1/2$  and this  $Z^2$  correction was predicted by Scott in [11] and proved in [12, 13]. Finally, the last term of order  $Z^{5/3}$  was derived by Schwinger [14] based partly on Dirac's exchange estimate [15] and established mathematically in a series of papers by Fefferman and Seco (see [16]).

To the order  $Z^{5/3}$  the asymptotics above agrees [17, 18] with the ground state energy in Hartree-Fock Theory as well as with the ground state energy in Kohn-Sham theory with the exchange-correlation energy given by the Dirac exchange term

$$-C_{\text{D}} \int \rho(r)^{4/3} d^3 r.$$

Establishing the ground state energy to order  $Z^{5/3}$  is a mathematical tour de force and has led to a wealth of beautiful mathematics. Unfortunately, this order is far from what is needed in order to control quantities of interest to chemistry such as ionization energies, atomic radii, molecular bond lengths, or Born-Oppenheimer

energy curves. These quantities are all expected to be of order  $O(1)$  in the large  $Z$  limit. This claim is known in the mathematical physics literature as the *ionization conjecture* [19–21]. Establishing the accuracy of any approximating scheme for the total ground state energy to the order  $O(1)$  is beyond reach of any known method. In particular, improving the expansion above does not seem to be a promising route to prove the ionization conjecture and the conjecture is, indeed, still one of the outstanding problems in mathematical physics [19].

This does not rule out, however, that we may be able to establish the adequate accuracy of approximating schemes in estimating ionization energies, bond lengths, etc. To illustrate this very simple point recall that the first ionization energy is

$$I_1(Z) = E(N = Z - 1, Z) - E(Z),$$

i.e., a difference of two quantities of order  $Z^{7/3}$ . Estimating the total energies independently is of course a bad idea, when we are interested in their difference. In the next section we will propose an asymptotic formula directly for the ionization energies and atomic radii.

### 3. New Asymptotic Limits

Our first observation is that the ionization conjecture, in fact, holds in Thomas-Fermi Theory. Much more is actually true. If we define the  $m$ -th ionization energy of an atom by

$$I_m(Z) = E(N = Z - m, Z) - E(Z)$$

then in Thomas-Fermi Theory we have that

$$\lim_{Z \rightarrow \infty} I_m^{\text{TF}}(Z) = a^{\text{TF}} m^{7/3}$$

for some positive explicit constant  $a^{\text{TF}} \geq 0$  which is not the same as  $C^{\text{TF}}$  above.

Likewise, if we define the radius  $R_m(Z)$  to the last  $m$  electrons in an atom by

$$\int_{|r| > R_m(Z)} \rho(r) d^3r = m$$

we have in Thomas-Fermi Theory

$$\lim_{Z \rightarrow \infty} R_m^{\text{TF}}(Z) = b^{\text{TF}} m^{-3}$$

for an explicit constant  $b^{\text{TF}} > 0$  (in fact,  $b^{\text{TF}} = (81\pi^2/2)^{1/3}$ ).

In analogy to the the energy expansion we conjecture that the exact values of  $\lim_{Z \rightarrow \infty} I_m(Z)$  and  $\lim_{Z \rightarrow \infty} R_m(Z)$  have leading order asymptotic expansions given by the TF expressions above when  $m \rightarrow \infty$ . To be a little more precise we, in fact, do not believe that the limits of  $I_m(Z)$  and  $R_m(Z)$  necessarily exist as  $Z \rightarrow \infty$ . They may oscillate between upper and lower limits (liminf and limsup). I.e., for the ionization energy we have the upper and lower limits  $\underline{\lim}_{Z \rightarrow \infty} I_m(Z) \leq \overline{\lim}_{Z \rightarrow \infty} I_m(Z)$  and likewise for the radius  $\underline{\lim}_{Z \rightarrow \infty} R_m(Z) \leq \overline{\lim}_{Z \rightarrow \infty} R_m(Z)$ . We conjecture that for both the ionization energy and the radius the upper and lower limits have the same asymptotics for large  $m$  and that they are given by the Thomas-Fermi expressions. We are hence led to the following conjecture.

**Generalized Ionization Conjecture for Atoms:** *The large  $Z$  (upper and lower) limits of the ionization energies and the radii of atoms satisfy the asymptotic formulas*

$$\overline{\lim}_{Z \rightarrow \infty} I_m(Z) = a^{\text{TF}} m^{7/3} + o(m^{7/3}) \quad (1)$$

$$\overline{\lim}_{Z \rightarrow \infty} R_m(Z) = b^{\text{TF}} m^{-1/3} + o(m^{-1/3}) \quad (2)$$

as  $m \rightarrow \infty$ .

A strong theoretical argument in favor of this conjecture is that it was proved to hold in Hartree-Fock Theory in [22]. It should be emphasized that when we talk about Hartree-Fock Theory we mean the totally unrestricted theory where the minimization is over all Slater determinants, i.e., not restricted to any particular basis set. Whereas the proof in the case of Hartree-Fock Theory does not generalize to the full many-body quantum context it should apply to a variety of models, e.g., some restricted Hartree-Fock models or Kohn-Sham density functional theories with local exchange correlation terms.<sup>1</sup> In Section 4 below we present some experimental evidence that the approximation in (2) may not only be asymptotically good, but even remarkably accurate for real atoms.

We turn next to the generalized ionization conjecture for molecules, which is concerned with the asymptotics of the Born-Oppenheimer curves for diatomic molecules. For simplicity let us consider neutral homonuclear diatomic molecules with two nuclei of charge  $Z$  situated a distance  $R$  from each other. We denote the ground state energy by  $E_{\text{mol}}(Z, R)$  and subtract the dissociation energy  $2E(Z)$ . As a consequence of the No-Binding Theorem we have in Thomas-Fermi Theory that

$$E^{\text{TF}}(Z, R) - 2E^{\text{TF}}(Z) > 0.$$

Moreover, this expression has a universal behavior [23]

$$\lim_{Z \rightarrow \infty} (E^{\text{TF}}(Z, R) - 2E^{\text{TF}}(Z)) = D^{\text{TF}} R^{-7}.$$

This leads to the following molecular version of the ionization conjecture.

**Generalized Ionization Conjecture for Molecules:** *The large  $Z$  (upper and lower) limits of the homonuclear diatomic Born-Oppenheimer curve satisfies the asymptotic formula*

$$\overline{\lim}_{Z \rightarrow \infty} (E(Z, R) - 2E(Z)) = D^{\text{TF}} R^{-7} + o(R^{-7}). \quad (3)$$

as  $R \rightarrow 0$ .

This conjecture is still open even in Hartree-Fock Theory, but I strongly believe that it can be settled in that case. Strong numerical evidence that the TF Born-Oppenheimer curve is a good approximation at short internuclear distances was presented in [24].

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<sup>1</sup>I would like to thank Andreas Savin for pointing out that there could be an interest in generalizing the result beyond Hartree-Fock Theory

Table 1. Radii of alkali atoms in pm. Empirical values of Bragg [5] and Slater [6] compared to the values of the Thomas-Fermi Radius  $R_1$

Element	Bragg 1920	Slater 1964	TF radius $R_1$
Li	150	145	101
Na	177	180	181
Rb	225	235	235
K	207	220	207
Cs	237	260	250
Fr	?	?	266

Table 2. Group 2 atomic radii in pm. Empirical values of Bragg [5] and Slater [6] compared to the the Thomas-Fermi Radius  $R_{1.4}$

Element	Bragg 1920	Slater 1964	TF radius $R_{1.4}$
Be	115	105	87
Mg	150	142	149
Ca	170	180	173
Sr	195	200	199
Ba	210	215	213

#### 4. Comparison of $R_m^{\text{TF}}(Z)$ with empirical radii

Here we finally present the results of comparing numerical calculations of the Thomas-Fermi radii  $R_m^{\text{TF}}(Z)$  with the empirical radii found in [5] and [6]. It is natural to assume that the approximation is best for the case of alkali atoms with one electron outside a closed shell atom, i.e., that the radius  $R_1(Z)$  is a good measure for the empirical radius. Table 1 shows the remarkably good comparison of the calculated values of  $R_1^{\text{TF}}(Z)$  and the empirical values of Bragg and Slater. We have also considered the case of group 2 atoms. Here it is not clear for which  $m$ ,  $R_m(Z)$  would be a good measure of the empirical radius. It is natural to believe that it should be the same  $m$  through the group and that  $1 < m < 2$ . Table 2 shows the comparison of the empirical radii with the calculated values for  $R^{\text{TF}}(Z)$  for  $m = 1.4$ . Figure 1 Shows the graph of the radius function  $R_1^{\text{TF}}(Z)$  again with empirical values of Bragg and Slater.

To emphasize the simplicity in finding  $R_m^{\text{TF}}(Z)$  we briefly comment on the calculation. If we introduce the Thomas-Fermi potential for a neutral atom

$$\phi^{\text{TF}}(r) = \frac{Z}{|r|} - \int \frac{\rho^{\text{TF}}(r')}{|r-r'|} d^3 r'$$

we have that

$$\int_{|r|>R} \rho^{\text{TF}}(r) d^3 r = -R^2 \frac{d}{dr} \phi^{\text{TF}}(R).$$

Thus the defining equation for  $R_m^{\text{TF}}(Z)$  is  $-R_m^{\text{TF}}(Z)^2 \frac{d}{dr} \phi^{\text{TF}}(R_m^{\text{TF}}(Z)) = m$ . To determine  $\phi^{\text{TF}}$  we note that from the scaling property of Thomas-Fermi Theory

$$\phi^{\text{TF}}(r) = 2^{7/3} (3\pi)^{-2/3} Z^{4/3} \phi_0(Z^{1/3} 2^{7/3} (3\pi)^{-2/3} r)$$

for a positive function  $\phi_0$  independent of  $Z$  satisfying the differential equation

$$-\Delta \phi_0(r) = \phi_0(r)^{3/2}, \quad r \neq 0$$

with  $\lim_{r \rightarrow 0} r \phi_0(r) = 1$  and vanishing at infinity. Since  $\phi_0$  is spherical it is straightforward to solve this as an ODE. We find that  $\phi_0(r) = r^{-1} - 1.588 + o(1)$  for small  $r$

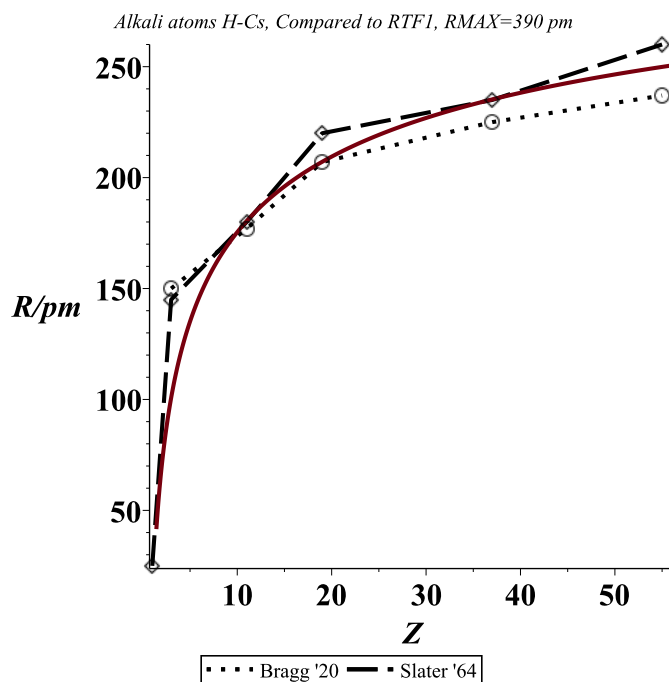


Figure 1. The Thomas-Fermi radius  $R_1$  plotted against the Bragg and Slater empirical radii for alkali elements

and that  $\phi_0(r) = 144r^{-4}(1 - 13.26r^{-\zeta}) + o(r^{-4-\zeta})$  for large  $r$ , where  $\zeta = \frac{1}{2}(\sqrt{73} - 7)$ .

Having found  $\phi_0$  we have  $R^{\text{TF}}(Z) = 2^{7/3}(3\pi)^{-2/3}Z^{-1/3}r$  where  $r$  is determined from  $-r^2\phi_0'(r) = m/Z$ .

## 5. Conclusion

We have proposed a new way to view the validity of the Thomas-Fermi approximation which is more directly linked to properties of chemical interest than the traditional point of view based on the total binding energy. We have given arguments for this new approach based both on exact mathematical results for the Hartree-Fock model and comparisons with experimental and numerical evidence. In particular, we have found surprisingly good (and probably better than expected) agreement between the Thomas-Fermi calculated radii of atoms and empirical values.

In analogy the ground state energy, where the correction terms to the TF asymptotics are known, it would be very interesting if it would be possible to find the next corrections to the proposed formulas (1), (2), and (3).

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