

Thomas-Fermi model: The second correction

Julian Schwinger

Department of Physics, University of California, Los Angeles, California 90024

(Received 8 December 1980)

A simple derivation is given for the first quantum correction to the Thomas-Fermi kinetic energy. Its application to the total binding energy of neutral atoms exploits the technique for handling strongly bound electrons that was developed in a preceding paper, and justifies the numerical value of the second correction adopted there. A proposal is made for extrapolating this improved description to the outer regions of the atom.

INTRODUCTION

In a previous paper<sup>1</sup> the leading correction to the Thomas-Fermi (TF) calculation of the total binding energy of a neutral atom, the correction of relative order  $Z^{-1/3}$ , was produced by a method that justified an earlier conjecture.<sup>2</sup> In the comparison with experiment for low- $Z$  atoms, however, use was also made of a correction at the next level, of relative order  $Z^{-2/3}$ . The latter is dominated by the exchange effect that, in contrast with the Dirac modification,<sup>3</sup> is omitted in the simple TF model. But there is also a smaller contribution, in the nature of a kinetic energy correction. This had already been computed numerically, using WKB approximations to energy values,<sup>4</sup> and that result was simply accepted in Ref. 1. This naturally posed the problem of whether the TF treatment could be made more self-contained by extending the method of Ref. 1 to the second correction. That can indeed be done. And then it turned out, once again, that I had supplied a derivation that justified an already published statement. In the hope that my method is of some interest, nevertheless, it is described here; a brief comparison with the earlier work is provided at the end. And new ground is broken in a tentative attempt to extend the statistical description toward the outer regions of the atom.

EXCHANGE

It will emerge that the kinetic energy effect in which we are interested is simply related to the exchange term. Accordingly, we begin with a short elementary review of the latter, which also serves to supply some of the needed background. In the TF model the energy of Coulomb repulsion among the electrons is

$$\frac{1}{2} \int (d\vec{r})(d\vec{r}') n(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}'|} n(\vec{r}'), \tag{1}$$

where the electron density  $n(\vec{r})$  is evaluated as the momentum integral (2 is the spin factor)

$$n(\vec{r}) = 2 \int \frac{(d\vec{p})}{(2\pi\hbar)^3} \exp\left[-\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right] \exp\left[\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right]. \tag{2}$$

The domain of integration is the interior of the sphere of radius  $p_F(\vec{r})$ , defined by

$$\frac{1}{2m} [p_F(\vec{r})]^2 + V(\vec{r}) = 0, \tag{3}$$

which introduces the electron potential energy

$$V(\vec{r}) = -\frac{Ze^2}{r} + \int (d\vec{r}') \frac{e^2}{|\vec{r}-\vec{r}'|} n(\vec{r}'). \tag{4}$$

In writing (2) we have made explicit the underlying wave functions; this also emphasizes that the evaluation of the interaction energy (1) involves products of two-particle wave functions:

$$\left[ \exp\left[-\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right] \exp\left[-\frac{i}{\hbar} \vec{p}' \cdot \vec{r}'\right] \right] \times \left[ \exp\left[\frac{i}{\hbar} \vec{p}' \cdot \vec{r}'\right] \exp\left[\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right] \right]. \tag{5}$$

But Fermi-Dirac statistics requires antisymmetry of the two-particle wave functions for otherwise indistinguishable electrons, those of common spin component. That is effectively introduced by supplementing (5) with

$$- \left[ \exp\left[-\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right] \exp\left[-\frac{i}{\hbar} \vec{p}' \cdot \vec{r}'\right] \right] \times \left[ \exp\left[\frac{i}{\hbar} \vec{p}' \cdot \vec{r}'\right] \exp\left[\frac{i}{\hbar} \vec{p} \cdot \vec{r}\right] \right], \tag{6}$$

which then yields the exchange-energy correction term

$$\delta E_{\text{ex}} = -\frac{1}{2} \int (d\vec{r})(d\vec{r}') 2 \left[ \int \frac{(d\vec{p})}{(2\pi\hbar)^3} \exp \left[ -\frac{i}{\hbar} \vec{p} \cdot (\vec{r} - \vec{r}') \right] \right] \frac{e^2}{|\vec{r} - \vec{r}'|} \left[ \int \frac{(d\vec{p}')}{(2\pi\hbar)^3} \exp \left[ \frac{i}{\hbar} \vec{p}' \cdot (\vec{r} - \vec{r}') \right] \right]. \quad (7)$$

The upper limits of these two momentum integrals,  $p_F(\vec{r})$  and  $p_F(\vec{r}')$ , respectively, are not the same. However, for  $|\vec{r} - \vec{r}'| \gg \hbar/p_F$ , which is a small distance in the TF domain of validity, these integrals become negligible. Accordingly, once integration is performed over the explicit relative coordinate  $\vec{r} - \vec{r}'$ , the integrand is effectively local. And so, beginning with the integral ( $\vec{r} - \vec{r}'$  is here denoted by  $\vec{r}$ )

$$\int \frac{(d\vec{p})}{(2\pi\hbar)^3} \exp \left[ -\frac{i}{\hbar} \vec{p} \cdot \vec{r} \right] = \frac{p_F^3}{2\pi^2\hbar^3} \frac{1}{y^3} (\sin y - y \cos y), \quad y = p_F r / \hbar, \quad (8)$$

we then encounter

$$\int_0^\infty dy y^2 \frac{1}{y} \left[ \frac{\sin y - y \cos y}{y^3} \right]^2 = \frac{1}{4} \quad (9)$$

and arrive at the result

$$\delta E_{\text{ex}} = -\frac{e^2}{4\pi^3} \int (d\vec{r}) \left[ \frac{p_F}{\hbar} \right]^4. \quad (10)$$

This can be rewritten, in terms of the density

$$n = \frac{1}{3\pi^2\hbar^3} p_F^3, \quad (11)$$

as

$$\delta E_{\text{ex}} = -\frac{e^2}{4\pi^3} (3\pi^2)^{4/3} \int (d\vec{r}) n^{4/3}. \quad (12)$$

It is more immediately useful, however, to introduce the potential energy in the form

$$V(\vec{r}) = -\frac{Ze^2}{r} f(x), \quad x = r/a \quad (13)$$

where

$$a = \left[ \frac{1}{2} (3\pi/4)^{2/3} = 0.8853 \right] a_0 Z^{-1/3}, \quad a_0 = \hbar^2 / me^2, \quad (14)$$

and  $f(x)$  obeys the TF differential equation

$$\frac{d^2 f(x)}{dx^2} = \frac{1}{x^{1/2}} [f(x)]^{3/2}, \quad f(0) = 1, \quad f(\infty) = 0. \quad (15)$$

This version of the exchange energy is ( $e^2/a_0$  units)

$$\delta E_{\text{ex}} = -\frac{4}{\pi^2} (0.8853) \left[ \int_0^\infty dx [f(x)]^2 \right] Z^{5/3}. \quad (16)$$

The known integral

$$\int_0^\infty dx f^2 = 0.6154 \quad (17)$$

then gives

$$\delta E_{\text{ex}} = -0.2208 Z^{5/3}. \quad (18)$$

#### QUANTUM CORRECTION

The leading correction discussed in Ref. 1 is associated with the strongly bound electrons. The correction we now consider is a property of the bulk of the electrons. It expresses the inadequacy of the semiclassical approximation that relates the particle density at a point to just the potential energy at that point [Eqs. (3) and (11)]. There is a particularly simple way of looking at this effect. It begins in one spatial dimension.

With a suitable choice of origin along the  $x$  axis, the potential function in a small interval can be represented as

$$V(x) = V_0 + \frac{1}{2} m\omega^2 x^2, \quad (19)$$

which has the appearance of the oscillator potential (although  $\omega^2$  need not be positive). The exact dynamical solution of the oscillator is presented in the time transformation function

$$\langle xt | x'0 \rangle = \left[ \frac{m\omega}{2\pi i \hbar \sin \omega t} \right]^{1/2} \exp \left[ \frac{i}{\hbar} \right], \quad (20)$$

$$w = -V_0 t + \frac{m\omega}{2 \sin \omega t} [(x^2 + x'^2) \cos \omega t - 2xx'],$$

which is easily produced by a variety of techniques,<sup>5</sup> or, at worst, can be verified to obey the Schrödinger equation and the initial condition

$$\lim_{t \rightarrow 0} \langle xt | x'0 \rangle = \delta(x - x'). \quad (21)$$

Anticipating the application to particle density, we

place  $x' = x$  and get

$$\langle xt | x0 \rangle = \left[ \frac{m\omega}{2\pi i \hbar \sin \omega t} \right]^{1/2} \exp \left[ -\frac{i}{\hbar} V_0 t \right] \\ \times \exp \left[ -\frac{i}{\hbar} m \omega x^2 \tan \left( \frac{1}{2} \omega t \right) \right]. \quad (22)$$

As one verifies through its consequences, the semi-classical limit is produced by the restriction

$$|\omega t| \ll 1, \quad (23)$$

for then

$$\langle xt | x0 \rangle \rightarrow \left[ \frac{m}{2\pi i \hbar t} \right]^{1/2} \exp \left[ -\frac{i}{\hbar} \left( V_0 + \frac{1}{2} m \omega^2 x^2 \right) t \right] = \int_{-\infty}^{\infty} \frac{dp}{2\pi \hbar} \exp \left[ -\frac{i}{\hbar} \left[ \frac{1}{2m} p^2 + V(x) \right] t \right], \quad (24)$$

which exhibits the classical specification of the energy.

We now proceed to the next stage, in which the cubic terms are retained in expanding the trigonometric functions of (22). With the identifications

$$\omega^2 = \frac{1}{m} \frac{d^2 V(x)}{dx^2}, \quad m \omega^4 x^2 = \frac{1}{m} \left[ \frac{dV(x)}{dx} \right]^2, \quad (25)$$

this yields

$$\langle xt | x0 \rangle \cong \left[ \frac{m}{2\pi i \hbar t} \right]^{1/2} \exp \left[ -\frac{i}{\hbar} V(x) t \right] \left[ 1 + \frac{t^2}{12m} \frac{d^2 V(x)}{dx^2} - \frac{i}{\hbar} \frac{t^3}{24m} \left[ \frac{dV(x)}{dx} \right]^2 \right]. \quad (26)$$

It is then an immediate step to three dimensions, particularly if one adopts a local coordinate system that diagonalizes the dyadic  $\vec{\nabla} \vec{\nabla} V(\vec{r})$ , so that the three oscillator motions are independent:

$$\langle \vec{r}t | \vec{r}0 \rangle = \left\langle \vec{r} \left| \exp \left[ -\frac{i}{\hbar} Ht \right] \right| \vec{r} \right\rangle \\ \cong \left[ \frac{m}{2\pi i \hbar t} \right]^{3/2} \exp \left[ -\frac{i}{\hbar} V(\vec{r}) t \right] \left[ 1 + \frac{t^2}{12m} \nabla^2 V(\vec{r}) - \frac{i}{\hbar} \frac{t^3}{24m} [\vec{\nabla} V(\vec{r})]^2 \right]. \quad (27)$$

The electron density is computed as the additive contribution of all bound electrons, those for which the single-particle energy  $H$  is negative. They are selected by the operator

$$\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{dt}{t} \exp \left[ -\frac{i}{\hbar} Ht \right], \quad (28)$$

where the integration path runs under the origin in the complex plane. The resulting particle density is

$$n(\vec{r}) = 2 \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{dt}{t} \left\langle \vec{r} \left| \exp \left[ -\frac{i}{\hbar} Ht \right] \right| \vec{r} \right\rangle, \quad (29)$$

and the initial term of (27) does indeed produce the TF density:

$$n_{\text{TF}}(\vec{r}) = 2 \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{dt}{t} \left[ \frac{m}{2\pi i \hbar t} \right]^{3/2} \\ \times \exp \left[ -\frac{i}{\hbar} V(\vec{r}) t \right] \\ = \frac{1}{3\pi^2 \hbar^3} [-2mV(\vec{r})]^{3/2}. \quad (30)$$

And then the additional terms of (27) correct this density to

$$n = n_{\text{TF}} - \frac{\hbar^2}{12m} \nabla^2 V \frac{d^2}{dV^2} n_{\text{TF}} - \frac{\hbar^2}{24m} (\vec{\nabla} V)^2 \frac{d^3}{dV^3} n_{\text{TF}} \quad (31)$$

or

$$3\pi^2\hbar^3n = (-2mV)^{3/2} - \frac{\hbar^2}{4}m\nabla^2V(-2mV)^{-1/2} - \frac{\hbar^2}{8}m^2(\vec{\nabla}V)^2(-2mV)^{-3/2}. \quad (32)$$

Another way of presenting this quantum correction to the density is

$$(3\pi^2\hbar^3n)^{2/3} = -2mV + \frac{\hbar^2}{12} \left[ \frac{\nabla^2V}{V} - \frac{1}{4} \frac{(\vec{\nabla}V)^2}{V^2} \right], \quad (33)$$

where the latter bracket is also given by

$$\vec{\nabla} \cdot \left[ \frac{\vec{\nabla}V}{V} \right] + \frac{3}{4} \left[ \frac{\vec{\nabla}V}{V} \right]^2 \cong \frac{1}{3} \left[ 2\vec{\nabla} \cdot \left[ \frac{\vec{\nabla}n}{n} \right] + \left[ \frac{\vec{\nabla}n}{n} \right]^2 \right], \quad (34)$$

the last form being consistent for small corrections. The equivalent variational statement

$$\delta(E) = \int (d\vec{r}) \delta n \left\{ \frac{1}{2m} (3\pi^2\hbar^3n)^{2/3} + V - \frac{\hbar^2}{72m} \left[ 2\vec{\nabla} \cdot \left[ \frac{\vec{\nabla}n}{n} \right] + \left[ \frac{\vec{\nabla}n}{n} \right]^2 \right] \right\} = 0, \quad (35)$$

with  $V$  given by (4), makes clear the modified form of the total energy (apart from the exchange term), namely,

$$E = \int (d\vec{r}) \left\{ \frac{3}{5} \frac{1}{2m} (3\pi^2\hbar^3)^{2/3} n^{5/3} + \frac{\hbar^2}{36} \frac{1}{2m} \frac{(\vec{\nabla}n)^2}{n} - \frac{Ze^2}{r} n \right\} + \frac{1}{2} \int (d\vec{r})(d\vec{r}') n(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}'|} n(\vec{r}'). \quad (36)$$

It displays the first quantum correction to the kinetic energy. The stationary property of the energy functional implies that the energy shift produced by this correction is just

$$\delta E = \frac{\hbar^2}{36} \frac{1}{2m} \int (d\vec{r}) \frac{(\vec{\nabla}n)^2}{n}, \quad (37)$$

where  $n$  is the density in the absence of the correction. We therefore write

$$n \left[ \frac{\vec{\nabla}n}{n} \right]^2 = \frac{1}{3\pi^2\hbar^3} (-2mV)^{3/2} \frac{9}{4} \left[ \frac{\vec{\nabla}V}{V} \right]^2 = -\frac{3}{\pi^2} \frac{m}{\hbar^3} \vec{\nabla}V \cdot \vec{\nabla}(-2mV)^{1/2}, \quad (38)$$

and rearrange the latter form to get

$$\delta E = \frac{1}{24\pi^2} \frac{1}{\hbar} \int (d\vec{r}) \left[ (-2mV)^{1/2} \nabla^2V + \frac{1}{3m} \nabla^2(-2mV)^{3/2} \right]. \quad (39)$$

It is time to recognize that this correction should not be applied in the region of strongly bound electrons where it is seriously in error (the introduction of the Coulomb potential gives a divergent result). We follow the procedure used in Ref. 1; the incorrect TF contribution of strongly bound electrons is deleted and the correct quantum contribution is set in its place. Strongly bound electrons are characterized by the single-particle energy requirement  $(p^2/2m) + V < -\epsilon$ , where

$$\frac{Ze^2}{a_0Z^{-1/3}} \ll \epsilon \ll \frac{Ze^2}{a_0Z^{-1}}. \quad (40)$$

This shift in the upper limit of single-particle energies, from zero to  $-\epsilon$ , is effectively produced by the substitution  $V \rightarrow V_c + \epsilon$ , where the subscript  $c$  is merely a reminder that the potential energy of a strongly bound electron is essentially the Coulombic function

$$V_c(r) = -(Ze^2/r) + \epsilon_0, \quad \epsilon_0 = B(Ze^2/a). \quad (41)$$

Thus, we subtract from (39) the analogous expression with  $V$  replaced by  $V_c + \epsilon$ . But nothing need then be added to represent specifically the quantum correction to the kinetic energy of the strongly bound electrons; the complete quantum energy of those electrons has already been found in Ref. 1. The volume integral of the difference,

$$\nabla^2[(-V)^{3/2} - (-V_c - \epsilon)^{3/2}], \quad (42)$$

is equal to zero, for the equivalent surface integrals vanish, both at the outer limits, and at the origin. Then, the multiple of  $\delta(\vec{r})$  that evaluates  $\nabla^2V_c$  cancels against the analogous term in  $\nabla^2V$ , inasmuch as  $(-V)^{1/2} - (-V_c - \epsilon)^{1/2}$  vanishes at the origin. That leaves only the contributions to  $\nabla^2V$  produced by the electron charge density. Accordingly, the desired quantum energy correction is

$$\delta E_{\text{qu}} = \frac{1}{24\pi^2} \frac{1}{\hbar} \int (d\vec{r}) (-2mV)^{1/2} (-4\pi e^2 n) = -\frac{e^2}{18\pi^3} \int (d\vec{r}) \left[ \frac{-2mV}{\hbar^2} \right]^2 = \frac{2}{9} \delta E_{\text{ex}}. \quad (43)$$

The total correction of relative order  $Z^{-2/3}$  is

( $e^2/a_0$  units)

$$\delta E = \delta E_{\text{ex}} + \delta E_{\text{qu}} = \frac{11}{9} \delta E_{\text{ex}} \quad (44)$$

or

$$\begin{aligned} \delta E &= -\frac{44}{9\pi^2} (0.8853) \left[ \int dx [f(x)]^2 \right] Z^{5/3} \\ &= -0.2699 Z^{5/3}. \end{aligned} \quad (45)$$

This numerical coefficient differs insignificantly from that adopted in Ref. 1, 0.266.

### DISCUSSION

There is another way of looking at the quantum correction. It begins with the stationary energy expression (36), in which  $Z$  is now regarded as a parameter:

$$-\frac{\partial E}{\partial Z} = \int (d\vec{r}) \frac{e^2}{r} n(\vec{r}). \quad (46)$$

$$-\frac{\partial \delta E}{\partial Z} \Big|_{\text{expl}} = \int (d\vec{r}) \frac{e^2}{r} \frac{1}{3\pi^2 \hbar^3} \left( -\frac{1}{8} \hbar^2 m \right) (-2mV)^{-1/2} (-4\pi e^2 n) = \frac{4}{9\pi^3} (0.8853) \frac{e^2}{a_0} Z^{2/3} \int_0^\infty dx f(x) \quad (49)$$

and ( $e^2/a_0$  units)

$$\delta E_{\text{expl}} = -\frac{2}{9} \frac{4}{\pi^2} (0.8853) Z^{5/3} \frac{3}{10} \int_0^\infty dx f(x), \quad (50)$$

which is the following multiple of  $\delta E_{\text{qu}}$  [Eqs. (43) and (16)]:

$$\frac{3}{10} \left[ \int_0^\infty dx f(x) \right] \Big/ \left[ \int_0^\infty dx [f(x)]^2 \right]. \quad (51)$$

I am indebted to L. DeRaad for the numerical evaluation

$$\int_0^\infty dx f(x) = 1.80, \quad (52)$$

which says that 88% of  $\delta E_{\text{qu}}$  is supplied by  $\delta E_{\text{expl}}$ . What gives the remaining 12%? Looking back at the density expression (47) we see that this relatively small piece comes from the TF density through its dependence on  $V$ , which is also changed by the quantum correction to the density. We shall not trouble now (but see later) to verify that the needed amount is supplied by this implicit part. Instead we take up this indication that the structure of the TF theory has been altered by the quantum correction.

Let me review the domain in which the quantum correction is small, for which we return to Eq. (32). The last term on the right side (which is more gen-

The particle density  $n$  is given by (32) or, equivalently,

$$\begin{aligned} 3\pi^2 \hbar^3 n &= (-2mV)^{3/2} - \frac{1}{8} \hbar^2 m (-2mV)^{-1/2} \nabla^2 V \\ &\quad + \frac{1}{8} \hbar^2 \nabla^2 (-2mV)^{1/2}. \end{aligned} \quad (47)$$

We first work out the quantum correction associated with the explicit structure of the last two terms in (47), keeping in mind the necessity of removing the contribution of the strongly bound electrons. In the integral

$$\int (d\vec{r}) \frac{1}{r} \nabla^2 [(-V)^{1/2} - (-V_c - \epsilon)^{1/2}] \quad (48)$$

the function  $\delta(\vec{r})$  that is produced by the transference of  $\nabla^2$  has a vanishing coefficient at the origin and this integral is zero. The  $\delta$  function that evaluates  $\nabla^2 V_c$ , and also occurs in  $\nabla^2 V$ , similarly has a vanishing coefficient. We are left with

erally representative) implies the restriction

$$\frac{\hbar^2 (\nabla V)^2}{m (-V)^3} < < 1 \quad (53)$$

or

$$\frac{1}{Z^{2/3}} \frac{[(d/dx)(f/x)]^2}{(f/x)^3} < < 1. \quad (54)$$

For the bulk of the electrons, those with  $x \sim 1$ , this is satisfied through the large value of  $Z^{2/3}$ . For small  $x$  the restriction becomes

$$x \gg Z^{-2/3}, \quad r \gg a_0/Z, \quad (55)$$

which is the already stressed exclusion of strongly bound electrons. Now to large  $x$ . The known asymptotic form of the TF function is

$$x \gg 1: f(x) \sim (12)^2/x^3, \quad (56)$$

and therefore, with numerical factors set aside, the restriction (54) reads

$$x \ll Z^{1/3}, \quad r \ll a_0. \quad (57)$$

It is clear that when  $r$  becomes  $\sim a_0$  the first quantum correction is no longer small and higher corrections will also be significant. In short we would be entering the low density region that is the domain of chemistry, where a full quantum treatment is required.<sup>6</sup> The question we now pose is

this: Can one suggest a simple but physically plausible generalization of TF that might serve as an extrapolation to cover the domain between (57) and  $r \sim a_0$ ?

It is with the hope of doing this that we return to the energy functional, this time including the exchange term, and present an alternative form in which  $n(\vec{r})$  and  $V(\vec{r})$  are independent variables.

$$\int (d\vec{r}) \left[ -\frac{Ze^2}{r} \right] n(\vec{r}) + \frac{1}{2} \int (d\vec{r})(d\vec{r}') n(\vec{r}) \frac{e^2}{|\vec{r}-\vec{r}'|} n(\vec{r}') \\ = \int (d\vec{r}) V(\vec{r}) n(\vec{r}) - \frac{1}{8\pi e^2} \int (d\vec{r}) \left[ \vec{\nabla} \left[ V(\vec{r}) + \frac{Ze^2}{r} \right] \right]^2. \quad (59)$$

The latter form is stationary for variations of  $V$  about the solution of (58). The correct treatment of strongly bound electrons is still left implicit in the new version of the energy functional:

$$E = \int (d\vec{r}) \left\{ \frac{3}{5} \frac{(3\pi^2 \hbar^3)^{2/3}}{2m} n^{5/3} - \frac{e^2}{4\pi^3} (3\pi^2 n)^{4/3} + \frac{\hbar^2}{36} \frac{1}{2m} \frac{(\vec{\nabla} n)^2}{n} + nV - \frac{1}{8\pi e^2} \left[ \vec{\nabla} \left[ V + \frac{Ze^2}{r} \right] \right]^2 \right\}. \quad (60)$$

The  $n$ -dependent exchange and quantum kinetic energy corrections are of relative order  $Z^{-2/3}$ . To that level of accuracy, it suffices to exploit the stationary property with respect to  $n$  variations and insert the form of  $n$  produced by the initial TF energy, namely the  $n_{TF}$  of Eq. (30), which involves no restriction on  $V$ . That produces, as an intermediate stage,

$$-E = \int (d\vec{r}) \left\{ \frac{1}{5m} \frac{(-2mV)^{5/2}}{3\pi^2 \hbar^3} + \frac{e^2}{4\pi^3 \hbar^4} (-2mV)^2 + \frac{1}{8\pi e^2} (\vec{\nabla} V)^2 \left[ 1 - \frac{e^2}{3\pi} \frac{m}{\hbar} (-2mV)^{-1/2} \right] \right. \\ \left. + \frac{1}{8\pi e^2} \left[ 2\vec{\nabla} V \cdot \vec{\nabla} \frac{Ze^2}{r} + \left[ \vec{\nabla} \frac{Ze^2}{r} \right]^2 \right] \right\}.$$

Then, the introduction of the new variable

$$\bar{V} = V + (e^2/6\pi\hbar)(-2mV)^{1/2}, \quad (61)$$

which is a small change under the TF circumstance,  $|V| \gg e^2/a_0$ , gives

$$-E = \int (d\vec{r}) \left\{ \frac{1}{5m} \frac{(-2m\bar{V})^{5/2}}{3\pi^2 \hbar^3} + \frac{11}{9} \frac{e^2}{4\pi^3 \hbar^4} (-2m\bar{V})^2 \right. \\ \left. + \frac{1}{8\pi e^2} \left[ \vec{\nabla} \left[ \bar{V} + \frac{Ze^2}{r} \right] \right]^2 \right\}. \quad (62)$$

In writing the final form we have omitted the term

$$- \int (d\vec{r}) \frac{1}{4\pi e^2} \vec{\nabla} \left[ \frac{e^2}{6\pi\hbar} (-2mV)^{1/2} \right] \cdot \vec{\nabla} \frac{Ze^2}{r} \quad (63) \\ = - \frac{Ze^2}{6\pi\hbar} (-2mV)^{1/2} \Big|_{\vec{r} \rightarrow 0},$$

which will be canceled on deleting the TF contribution of strongly bound electrons. Indeed one can recognize here the  $\delta$ -function part of  $\nabla^2 V$  in the

Using the definition of  $V(\vec{r})$  in Eq. (4) and the related Poisson equation

$$\nabla^2 \left[ V(\vec{r}) + \frac{Ze^2}{r} \right] = -4\pi e^2 n(\vec{r}), \quad (58)$$

we can verify the electrostatic energy identity

first right-hand term of (39); the second term has been absorbed in the definition of the variable  $\bar{V}$ .

In retrospect, it is clear that replacing  $V$  by  $\bar{V}$  provides an approximate local description for the nonlocality introduced by the quantum correction to the particle density. A more convenient energy expression emerges on writing

$$\bar{V} = -\frac{Ze^2}{r} \bar{f}(x), \quad \bar{f}(0) = 1, \quad (64)$$

which uses the TF dimensionless coordinate  $x = r/a$ . We find that

$$-E = \frac{Z^2 e^2}{a} \int_0^\infty dx \left[ \frac{1}{2} \left( \frac{d\bar{f}}{dx} \right)^2 + \frac{2}{5} \frac{\bar{f}^{5/2}}{x^{1/2}} + \frac{1}{2} \lambda^2 \bar{f}^2 \right], \quad (65)$$

provided

$$\lim_{x \rightarrow 0} \left[ \frac{\bar{f}(x) - 1}{x^{1/2}} \right]^2 = 0. \quad (66)$$

The parameter  $\lambda$  is

$$\lambda = \frac{(88)^{1/2}}{3\pi} (0.8853)Z^{-1/3}, \quad \frac{(88)^{1/2}}{3\pi} = 0.9953 \quad (67)$$

The stationary condition (65) supplies the differential equation

$$\frac{d^2\bar{f}}{dx^2} = \frac{\bar{f}^{3/2}}{x^{1/2}} + \lambda^2\bar{f} \quad (68)$$

The initial behavior of its solution

$$x \ll 1: f(x) = 1 - \bar{B}x + \frac{4}{3}x^{3/2} + \frac{1}{2}\lambda^2x^2 + \dots \quad (69)$$

is compatible with (66). If the last term of (65) is considered small, and  $\bar{f}$  replaced by  $f$ , the implied energy shift is just that of Eq. (45). But suppose this energy functional, and the implied differential equation (68), is taken seriously as it stands? The obvious new consequence is at very large distances, such that the last term of (68) dominates over the preceding TF structure:

$$\bar{f}^{1/2}/x^{1/2} \ll Z^{-2/3}, \quad (70)$$

where

$$x \gg 1: \frac{d^2\bar{f}}{dx^2} \cong \lambda^2\bar{f} \quad (71)$$

That gives the asymptotic form

$$\bar{f}(x) \sim e^{-\lambda x} = e^{-0.9953r/a_0}, \quad (72)$$

which is qualitatively reasonable.

This suggests a program of reexamining those physical properties, involving the outer reaches of the atom, for which TF has not been very successful; immediate examples are diamagnetic susceptibility and electric polarizability. The necessary numerical integration of the differential equation (68) might be awkward, in view of the explicit appearance of  $Z$  in

$$\lambda = 0.8812Z^{-1/3} \quad (73)$$

But that can be somewhat avoided through the redefinitions

$$y = \lambda x, \quad \phi(y) = \lambda^{-3}\bar{f}(x) \quad (74)$$

They produce the universal differential equation

$$\frac{d^2\phi}{dy^2} = \frac{\phi^{3/2}}{y^{1/2}} + \phi \quad (75)$$

although at the expense of altering the boundary condition at the origin to

$$\phi(0) = 1.461Z \quad (76)$$

One would then begin with the asymptotic form, some multiple of  $e^{-y}$ , and integrate the equation in to the origin, which would disclose the corresponding value of  $Z$ .

When one adopts this new scale of length,

$$a/\lambda = 1.005a_0, \quad (77)$$

the appropriate energy expression is ( $e^2/a_0$  units)

$$-E = 0.4661 \left\{ \int_0^\infty dy \left[ \frac{1}{2} \left( \frac{d\phi}{dy} \right)^2 + \frac{2}{5} \frac{\phi^{5/2}}{y^{1/2}} + \frac{1}{2} \phi^2 \right] + \frac{d\phi}{dy}(0)[\phi(0) - 1.461Z] \right\}, \quad (78)$$

which is so written that (76) emerges as a derived property. Accordingly, we can now regard  $Z$  as a variable parameter and infer that

$$-\frac{\partial E}{\partial Z} = 0.6811 \left[ -\frac{d\phi}{dy}(0) \right] = \frac{\bar{B}}{0.8853} Z^{4/3}, \quad (79)$$

which generalizes the relation between energy and the initial slope of the potential function. A similar procedure applied to the energy functional (65), with its leading  $Z^{7/3}$  factor, yields

$$Z \frac{\partial E}{\partial Z} - \frac{7}{3}E = \frac{44}{9\pi^2} (0.8853) \frac{2}{3} \left[ \int_0^\infty dx \bar{f}^2 \right] Z^{5/3} \quad (80)$$

The combination of this with (79) then gives the binding energy

$$-E = \frac{3}{7} \frac{\bar{B}}{0.8853} Z^{7/3} + \frac{44}{9\pi^2} (0.8853) \frac{2}{7} \left[ \int_0^\infty dx \bar{f}^2 \right] Z^{5/3}, \quad (81)$$

and a reapplication of (79) supplies the information

$$-\frac{\partial \bar{B}}{\partial Z} = \frac{44}{9\pi^2} (0.8853)^2 \frac{2}{3} Z^{-7/3} \frac{\partial}{\partial Z} \left[ Z^{5/3} \int_0^\infty dx \bar{f}^2 \right] \quad (82)$$

As a check of these results we apply the latter to the situation of a small quantum correction,  $\bar{f} \cong f$ , so that

$$-\frac{\partial \bar{B}}{\partial Z} \cong \frac{44}{9\pi^2} (0.8853)^2 \frac{10}{9} \left[ \int_0^\infty dx f^2 \right] Z^{-5/3} \quad (83)$$

and

$$\begin{aligned}\bar{B} &\cong B + \frac{44}{9\pi^2} (0.8853)^2 \frac{5}{3} \left[ \int_0^\infty dx f^2 \right] Z^{-2/3} \\ &= B + \frac{5}{6} \lambda^2 \int_0^\infty dx f^2.\end{aligned}\quad (84)$$

This is indeed the result of differentiating

$$-E \cong \frac{Z^{7/3}}{0.8853} \left[ \frac{3}{7} B + \frac{1}{2} \lambda^2 \int_0^\infty dx f^2 \right], \quad (85)$$

or of directly using (81).

For an independent derivation of (84) we consider the differential equation (68) under the assumption

$$\delta f = \bar{f} - f \ll f, \quad \delta f(0) = 0. \quad (86)$$

We are led to solve

$$\left[ \frac{d^2}{dx^2} - \frac{3}{2} \frac{f^{1/2}}{x^{1/2}} \right] \delta f = \lambda^2 f. \quad (87)$$

An essential remark here follows from the observation [implicit in the transformation (74)] that  $\beta^3 f(\beta x)$  also obeys the TF equation for arbitrary constant  $\beta$ , a statement that sharpens into an invariance of the asymptotic form (56). Accordingly, the function

$$\chi(x) = \frac{1}{3} \frac{\partial}{\partial \beta} \beta^3 f(\beta x) \Big|_{\beta=1} = f(x) + \frac{1}{3} x \frac{d}{dx} f(x) \quad (88)$$

is a solution of the differential equation

$$\left[ \frac{d^2}{dx^2} - \frac{3}{2} \frac{f^{1/2}}{x^{1/2}} \right] \chi(x) = 0, \quad (89)$$

the one that obeys the boundary conditions

$$\chi(0) = 1, \quad -\frac{d}{dx} \chi(0) = \frac{4}{3} B. \quad (90)$$

Now let us multiply (87) by  $\chi(x)$  and (89) with  $\delta f(x)$ , followed by subtraction of the two equations. This gives

$$\begin{aligned}\frac{d}{dx} \left[ \chi \frac{d}{dx} \delta f - \delta f \frac{d}{dx} \chi \right] &= \lambda^2 \chi f \\ &= \lambda^2 \left[ f^2 + \frac{1}{6} x \frac{d}{dx} f^2 \right],\end{aligned}\quad (91)$$

and a subsequent integration from 0 to  $\infty$  produces

$$-\frac{d}{dx} \delta f(0) = \frac{5}{6} \lambda^2 \int_0^\infty dx f^2, \quad (92)$$

in agreement with (84).

With all this before us, we can profitably return to the question that, at the beginning of this section, was left in limbo. For a quick review and re-statement we begin with (46),

$$-\frac{\partial E}{\partial Z} = \int (d\vec{r}) \frac{e^2}{r} n = - \int (d\vec{r}) \frac{1}{4\pi r} \nabla^2 \left[ V + \frac{Ze^2}{r} \right], \quad (93)$$

and the expression of (47) in terms of the change in the interaction  $V$  produced by the quantum correction:

$$\begin{aligned}-\nabla^2 \delta V &= \frac{4\pi e^2}{3\pi^2 \hbar^3} \left[ \frac{3}{2} (-2mV)^{1/2} (-2m\delta V) \right. \\ &\quad \left. + \frac{\hbar^2 m}{8} \frac{4\pi e^2}{3\pi^2 \hbar^3} (-2mV) \right. \\ &\quad \left. + \frac{1}{8} \hbar^2 \nabla^2 (-2mV)^{1/2} \right].\end{aligned}\quad (94)$$

The discussion of (48) shows that the last, Laplacian, term is effectively removed, on excising the contribution of strongly bound electrons from the quantum energy shift. Accordingly, that energy shift is determined by

$$-\frac{\partial}{\partial Z} \delta E_{\text{qu}} = - \int (d\vec{r}) \frac{1}{4\pi r} \nabla^2 \delta \bar{V}, \quad (95)$$

where

$$\delta \bar{V} = \delta V + \frac{e^2}{6\pi \hbar} (-2mV)^{1/2} \quad (96)$$

obeys

$$-\nabla^2 \delta \bar{V} = -\frac{3}{2} \frac{8}{3\pi a_0} \left[ \frac{-2mV}{\hbar^2} \right]^{1/2} \delta \bar{V} - \frac{4}{9\pi^2 a_0^2} V. \quad (97)$$

The last term of (97) produces the explicit effect given in (49). What precedes it in (97) is the object of this inquiry. But it is simpler to work out the total effect, the combination of explicit and implicit contributions. To that end we rewrite (97) as

$$-\nabla^2 \delta \bar{V} = -\frac{3}{2} \frac{8}{3\pi a_0} \left[ \frac{-2mV}{\hbar^2} \right]^{1/2} \delta \bar{V} - \frac{16}{9\pi^2 a_0^2} V. \quad (98)$$

Then the introduction of the TF dimensionless variable



$$\delta\bar{V} = -\frac{Ze^2}{r}\delta f(x) \quad (99)$$

[note that, in contrast with (86), the exchange effect is not considered here] converts (95) and (98) into

$$-\frac{\partial}{\partial Z}\delta E_{\text{qu}} \equiv -\frac{Ze^2}{a}\frac{d}{dx}\delta f(0) \quad (100)$$

and

$$\left[\frac{d^2}{dx^2} - \frac{3}{2}\frac{f^{1/2}}{x^{1/2}}\right]\delta f = \frac{16}{9\pi^2}(0.8853)^2 Z^{-2/3}f. \quad (101)$$

The application of (87) and (72) then gives ( $e^2/a_0$  units)

$$-\frac{\partial}{\partial Z}\delta E_{\text{qu}} = \frac{5}{3}Z^{2/3}\frac{8}{9\pi^2}(0.8853)\int_0^\infty dx f^2 \quad (102)$$

and

$$\delta E_{\text{qu}} = -\frac{8}{9\pi^2}(0.8853)\left[\int_0^\infty dx f^2\right]Z^{5/3}, \quad (103)$$

in agreement with (43) and (16).

The first attempt at the quantum kinetic energy correction was that of von Weizsäcker.<sup>7</sup> I am indebted to D. Clark for a number of references<sup>8</sup> in which it is shown that this proposal is too large by a factor of 9. The correct quantum kinetic energy correction [as in our Eq. (36)] was applied to the neutral atom binding energy calculation,<sup>9</sup> where the failure of this limited improvement at small and large distances was handled by arbitrarily cutting off the particle density and imposing boundary conditions. According to the authors, "It can be said that an electron cloud of a normal atom in the considered model reminds one of an apricot without a stone." This approach produces a correction of relative order  $Z^{-1/3}$ , but with the wrong coefficient; it does, however, give, for the correction of relative order  $Z^{-2/3}$ , what we now know to be the right answer.

Finally, it is worth mentioning that total binding energies, with their relativistic modifications, may soon be directly measurable through the development of mass spectroscopy on completely stripped heavy ions.

<sup>1</sup>J. Schwinger, Phys. Rev. A **22**, 1827 (1980).

<sup>2</sup>J. Scott, Philos. Mag. **43**, 859 (1952).

<sup>3</sup>P. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930).

<sup>4</sup>N. March, Adv. Phys. **6**, 1 (1957).

<sup>5</sup>See, for example, R. Finkelstein, *Nonrelativistic Mechanics* (Benjamin, Reading, Mass., 1973), Chap. 3.

<sup>6</sup>There is a related discussion in E. Lieb and B. Simon, Adv. Math. **23**, 22 (1977).

<sup>7</sup>C. von Weizsäcker, Z. Phys. **96**, 431 (1935).

<sup>8</sup>A. Kompaneets and E. Pavlovskii, Zh. Eksp. Teor. Fiz. **31**, 427 (1956) [Sov. Phys.—JETP **4**, 328 (1957)]; D. Kirzhnits, *ibid.* **32**, 115 (1957) [*ibid.* **5**, 64 (1957)]; C. Hodges, Can. J. Phys. **51**, 1428 (1973). Other references are given in the last paper.

<sup>9</sup>G. Plindov and I. Dmitrieva, Phys. Lett. **64A**, 348 (1978).