Chapter Two

THOMAS - FERMI MODEL

The crude models of the preceding Chapter taught us that it may be useful to treat the electrons in an atom (or ion) as if they were moving independently in an effective potential. We shall now take this idea very seriously, without, however, making explicit assumptions about the effective potential, V. It is clear that V possesses the general structure[1,2]

$$V = -\frac{Z}{r} + [\text{electron-electron part}] \quad , \qquad (2\text{-}1)$$

and the challenge consists in finding the electron-electron part in a consistent way. The fundamental tool for achieving this aim is the electrostatic Poisson equation

$$-\frac{1}{4\pi}\nabla^2 V_{es} = n \quad , \qquad (2\text{-}2)$$

which relates the electron density, n, to the electrostatic potential, V_{es}, due to the electrons. As soon as we shall have managed to express both V_{es} and n in terms of V, Eq.(2) will determine the effective potential.

General formalism. The dynamics of the electrons is controlled by the independent-particle Hamilton operator

$$H = \tfrac{1}{2}p^2 + V(\vec{r}) \quad . \qquad (2\text{-}3)$$

The electrons fill the eigenstates of H successively in such a way that all states with binding energy larger than a certain value, ζ, are occupied, whereas those with less binding energy are not. The parameter ζ is thus determined by the requirement that the count of occupied states equals the number of electrons N. Just as in Eq.(1-27) this is expressed as

$$N = \operatorname{tr} \eta(-H-\zeta) \quad , \qquad (2\text{-}4)$$

where we remember that the spin mulitplicity of two is included in the trace.

The sum of independent-particle energies is, analogously,

$$E_{IP} = \mathrm{tr}\, H\eta(-H-\zeta) \quad . \tag{2-5}$$

The combination $H+\zeta$, that appears in the argument of Heaviside's step function η, invites rewriting E_{IP} as

$$E_{IP} = \mathrm{tr}(H+\zeta)\eta(-H-\zeta) - \zeta \mathrm{tr}\, \eta(-H-\zeta) \quad , \tag{2-6}$$

which, with the aid of (4) and the definition

$$E_1 \equiv \mathrm{tr}(H+\zeta)\eta(-H-\zeta) \quad , \tag{2-7}$$

reads

$$E_{IP} = E_1 - \zeta N \quad . \tag{2-8}$$

In this equation, N is the given number of electrons, and both E_{IP} and E_1 are function(al)s of the effective potential V and the minimum binding energy ζ.

Let us make contact with Eqs.(1-27) and (1-32), in that we write

$$E_1(\zeta) = - \int_{\zeta}^{\infty} d\zeta' \, N(\zeta') \quad , \tag{2-9}$$

where

$$N(\zeta') = \mathrm{tr}\, \eta(-H-\zeta') \tag{2-10}$$

is the count of states with binding energy exceeding ζ'. Equation (4) appears now as

$$N = N(\zeta) \quad . \tag{2-11}$$

Equation (9) can be equivalently presented as a differential statement. If ζ deviates from its correct value [which is determined by Eq.(11)] by the amount $\delta\zeta$, then E_1 is off by

$$\delta_{\zeta} E_1 = \frac{\partial E_1}{\partial \zeta} \delta\zeta = N(\zeta)\delta\zeta = N\delta\zeta \quad . \tag{2-12}$$

This has the important implication that E_{IP} of Eq.(8) is stationary under variations of ζ (around its correct value, of course):

$$\delta_\zeta E_{IP} = \delta_\zeta E_1 - N\delta\zeta = o \quad . \tag{2-13}$$

In addition to ζ, E_1 and E_{IP} also depend on V. The local response of both energies to variations of the potential exhibits the electron density n:

$$\delta_V E_{IP} = \delta_V E_1 = \int(d\vec{r}\,')\delta V(\vec{r}\,')\; n(\vec{r}\,') \quad . \tag{2-14}$$

Although this is intuitively obvious, let us supply a formal proof. The first equality follows immediately from (8), because N is the given number of electrons and ζ is a parameter that we regard as independent of V. For the second equality, we need the following identity:

$$\delta_H \operatorname{tr} f(H) = \operatorname{tr} \delta H\, f'(H) \quad , \tag{2-15}$$

which expresses the change in the trace of a function of an operator H as the trace of the product of the change in the operator, δH, and the derivative of that function. [Note that (15) is not true without the trace operation, unless δH commutes with H:

$$\delta_H f(H) = \delta H\, f'(H) \quad \text{only if} \quad [\delta H, H] = o. \tag{2-16}$$

Under the trace the possible noncommutativity does not matter.] In our application,

$$\begin{aligned} f(H) &= (H+\zeta)\eta(-H-\zeta) \quad , \\ f'(H) &= \eta(-H-\zeta) \end{aligned} \tag{2-17}$$

[compare with Eq.(1-29)], and $\delta H = \delta V$. Accordingly,

$$\begin{aligned} \delta_V E_1 &= \operatorname{tr} \delta V\, \eta(-H-\zeta) \\ &= 2 \int(d\vec{r}\,')\; \langle \vec{r}\,' | \delta V(\vec{r})\eta(-H(\vec{p},\vec{r}) - \zeta) | \vec{r}\,' \rangle \quad . \end{aligned} \tag{2-18}$$

We use, again, primes to distinguish numbers from operators; the factor of two is, once more, the spin multiplicity. Now, since

$$\langle \vec{r}\,' | \delta V(\vec{r}) = \delta V(\vec{r}\,')\; \langle \vec{r}\,' | \quad , \tag{2-19}$$

and, anticipating that

$$2\langle\vec{r}'|\eta(-H-\zeta)|\vec{r}'\rangle = n(\vec{r}') \quad , \tag{2-20}$$

Eq.(18) implies Eq.(14). Indeed, equation (20) is nothing but the representation of the density as the sum of squared wavefunctions over all occupied states. Upon labelling these wavefunctions by their energies E' and additional quantum numbers, α, the left-hand side of (20) is

$$\begin{aligned} &2\sum_{E',\alpha} \psi^*_{E',\alpha}(\vec{r}')\ \eta(-E'-\zeta)\psi_{E',\alpha}(\vec{r}') \\ &= 2\sum_{E',\alpha}|\psi_{E',\alpha}(\vec{r}')|^2\eta(-E'-\zeta) \quad , \end{aligned} \tag{2-21}$$

which is recognized as the usual definition of the density.

For consistency, the integrated density must equal the number of electrons,

$$N = \int(d\vec{r}')n(\vec{r}') \quad . \tag{2-22}$$

This follows immediately from Eq.(20):

$$\begin{aligned} \int(d\vec{r}')n(\vec{r}') &= 2\int(d\vec{r}')\langle\vec{r}'|\eta(-H-\zeta)|\vec{r}'\rangle \\ &= \mathrm{tr}\ \eta(-H-\zeta) = N(\zeta) = N \quad . \end{aligned} \tag{2-23}$$

Another, and more instructive, proof makes use of (i) the definition of n in Eq.(14); (ii) the circumstance that E_1 does not depend on V and ζ individually, but only on the sum V+ζ; (iii) Equation (12). Consider infinitesimal changes in ζ and V such that $\delta V(\vec{r}) = -\delta\zeta$.[3] Then $\delta(V+\zeta)=0$, implying $\delta E_1=0$. In view of Eqs.(12) and (14) this means

$$\begin{aligned} 0 &= \delta_\zeta E_1 + \delta_V E_1 = N\delta\zeta + \int(d\vec{r}')(-\delta\zeta)n(\vec{r}') \\ &= \delta\zeta(N-\int(d\vec{r})n(\vec{r})) \quad , \end{aligned} \tag{2-24}$$

which is equivalent to (22). This second proof has the advantage of remaining valid when the trace in E_1 is evaluated approximately. There is no assurance that the densities derived from (14) and (20) are identical in a certain approximation. If they are not, Eq.(14) is the preferable definition. (We shall, indeed, be confronted with this possibility later, in Chapter Four.)

Equation (14) relates the density to the effective potential, so that we have taken care of the right-hand side of Eq.(2). We are left with the problem of expressing the electrostatic potential of the electrons, V_{es}, in terms of V.

We proceed from noting that E_{IP} is not the energy of the system. Just as in the preceding Chapter [recall the remark after Eq.(1-65)], the use of the effective potential causes a double counting of the electron-electron interaction energy, E_{ee}. The interaction potential V_{ee} which is the electron-electron part of V in Eq. (1), is naturally given as the response of E_{ee} to variations of the density,

$$\delta E_{ee} = \int (d\vec{r}\,')\ \delta n(\vec{r}\,')\ V_{ee}(\vec{r}\,') \quad . \tag{2-25}$$

[Please do not miss the analogy to Eq.(14).] Since V and ζ are the fundamental quantities in our "potential-functional formalism," $\delta n(\vec{r})$ must be regarded as the change in the density induced by variations of V and ζ.

Some evidence in favor of (25) is supplied by considering the electrostatic interaction energy

$$E_{es} = \frac{1}{2} \int (d\vec{r}\,')(d\vec{r}\,'')\ \frac{n(\vec{r}\,')n(\vec{r}\,'')}{|\vec{r}\,'-\vec{r}\,''|} \quad , \tag{2-26}$$

for which

$$\delta E_{es} = \int (d\vec{r}\,')\delta n(\vec{r}\,')\ \int (d\vec{r}\,'')\ \frac{n(\vec{r}\,'')}{|\vec{r}\,'-\vec{r}\,''|} \quad . \tag{2-27}$$

Thus, Eq.(25) implies the familiar expression

$$V_{es}(\vec{r}\,') = \int (d\vec{r}\,'')\ \frac{n(\vec{r}\,'')}{|\vec{r}\,'-\vec{r}\,''|} \quad , \tag{2-28}$$

which is equivalent to the Poisson equation (2).

The electron-electron interaction energy, as it is incorrectly contained in E_{IP} ("double counting of pairs"), is

$$\begin{aligned} &\mathrm{tr}\ V_{ee}\ \eta(-H-\zeta) \\ &\quad = 2 \int (d\vec{r}\,')\ V_{ee}(\vec{r}\,')\langle\vec{r}\,'|\eta(-H-\zeta)|\vec{r}\,'\rangle \\ &\quad = \int (d\vec{r}\,')V_{ee}(\vec{r}\,')n(\vec{r}\,') \quad ; \end{aligned} \tag{2-29}$$

the last step uses Eq. (20). Consequently, the correct energy expression is

$$E = E_{IP} - \int (d\vec{r}) V_{ee} n + E_{ee} \quad . \tag{2-30}$$

The second term removes the incorrect account for the electron-electron interaction contained in E_{IP}, and the last term adds the correct amount.

The energy of Eq. (30) is endowed with the important property of being stationary under variations of both V and ζ,

$$\delta_\zeta E = \delta_V E = o. \tag{2-31}$$

In order to see this, first appreciate

$$\begin{aligned} &\delta (- \int (d\vec{r}) V_{ee} n + E_{ee}) \\ &= - \int (d\vec{r}) (\delta V_{ee} n + V_{ee} \delta n) + \int (d\vec{r}) \delta n \, V_{ee} \\ &= - \int (d\vec{r}) n \delta V_{ee} \quad , \end{aligned} \tag{2-32}$$

which is an implication of Eq. (25). Further, a consequence of Eqs. (13) and (14) is

$$\begin{aligned} \delta E_{IP} &= \delta_\zeta E_{IP} + \delta_V E_{IP} \\ &= \int (d\vec{r}) n \delta V \quad . \end{aligned} \tag{2-33}$$

Then, the change in E is

$$\delta E = \int (d\vec{r}) n (\delta V - \delta V_{ee}) = \int (d\vec{r}) n \delta (V - V_{ee}) \tag{2-34}$$

In view of [Eq. (1)]

$$V = - \frac{Z}{r} + V_{ee} \quad , \tag{2-35}$$

the variation $\delta(V-V_{ee})$ vanishes, and Eq. (34) implies Eq. (31), indeed.

It is useful to separate E_{ee} into the classical electrostatic part, E_{es}, of Eq. (26), and the remainder E'_{ee}, which consists of the exchange interaction and possibly other effects. Accordingly, we write

$$E_{ee} = E_{es} + E'_{ee} \quad , \tag{2-36}$$

and likewise

$$V_{ee} = V_{es} + V'_{ee} \quad . \tag{2-37}$$

The electrostatic contribution to the energy (30) can be rewritten, with the aid of the Poisson equation (2), in terms of the electrostatic field $-\vec{\nabla}V_{es}$:

$$\begin{aligned} - \int (d\vec{r})\, n\, V_{es} + E_{es} &= - \frac{1}{2} \int (d\vec{r})\, n\, V_{es} \\ &= \frac{1}{8\pi} \int (d\vec{r})\, (\nabla^2 V_{es}) V_{es} = - \frac{1}{8\pi} \int (d\vec{r})\, (\vec{\nabla} V_{es})^2 \quad . \end{aligned} \tag{2-38}$$

[The surface term of the partial integration is zero, because $V_{es} \cong N/r$ for large r.] Further, we combine Eqs. (35) and (37) into

$$V_{es} = V + \frac{Z}{r} - V'_{ee} \quad , \tag{2-39}$$

thereby expressing V_{es} in terms of V, as needed in (2). The energy now reads

$$\begin{aligned} E = E_{IP} &- \frac{1}{8\pi} \int (d\vec{r})\, [\vec{\nabla}(V + \frac{Z}{r} - V'_{ee})]^2 \\ &- \int (d\vec{r})\, n\, V'_{ee} + E'_{ee} \quad . \end{aligned} \tag{2-40}$$

This expression for the energy is our basis for approximations. Various models emerge depending upon the accuracy to which the trace in E_{IP} [Eqs. (7) and (8)] is evaluated, and upon the extent to which E'_{ee} is taken into account. Of course, a consistent description requires a balanced treatment of both.

The TF model. The simplest model based upon Eq. (40) is the TF model. It neglects E'_{ee} entirely [then V'_{ee} also disappears from (40)], and evaluates the trace of Eq. (7) in the highly semiclassical approximation of Eq. (1-43). The TF energy expression is therefore

$$\begin{aligned} E_{TF} = 2 \int \frac{(d\vec{r})\,(d\vec{p})}{(2\pi)^3} &(\tfrac{1}{2}p^2 + V + \zeta)\, \eta(-\tfrac{1}{2}p^2 - V - \zeta) - \zeta N \\ &- \frac{1}{8\pi} \int (d\vec{r})\, [\vec{\nabla}(V + \frac{Z}{r})]^2 \quad . \end{aligned} \tag{2-41}$$

We recognize the last term as the quantity E_2 of Eq. (1-67), which was there introduced to remove the doubly counted (electrostatic) interaction energy; the term plays the same role here. The phase-space integral is the TF version of E_1, properly denoted by $(E_1)_{TF}$. We shall, however, suppress the subscript TF until it will become a necessary distinction from other models.

The step function cuts off the momentum integral at the (r-dependent) maximal momentum (the so-called "Fermi momentum")

$$P = \sqrt{-2(V+\zeta)} \quad , \tag{2-42}$$

so that

$$\begin{aligned} E_1 &= \int (d\vec{r})\ \frac{2}{(2\pi)^3}\ 4\pi \int_0^P dp\ p^2 \left(\tfrac{1}{2}p^2 - \tfrac{1}{2}P^2\right) \\ &= \int (d\vec{r})\ \frac{1}{\pi^2}\left(\frac{1}{10} - \frac{1}{6}\right) P^5 \quad , \end{aligned} \tag{2-43}$$

or, square roots of negative arguments being zero,

$$E_1 = \int (d\vec{r}) \left(-\frac{1}{15\pi^2}\right) [-2(V+\zeta)]^{5/2} \quad . \tag{2-44}$$

This is the <u>Thomas-Fermi result for E_1</u>. The entire <u>energy functional in the TF model</u> is then

$$\begin{aligned} E_{TF} &= E_1 + E_2 - \zeta N \\ &= \int (d\vec{r}) \left(-\frac{1}{15\pi^2}\right) [-2(V+\zeta)]^{5/2} - \frac{1}{8\pi}\int (d\vec{r})\,[\vec{\nabla}(V+\tfrac{Z}{r})]^2 - \zeta N \quad . \end{aligned} \tag{2-45}$$

Is there any reality to it? Yes. Look back to Chapter One, where (45) has been used unconsciously for the Coulomb potential $V=-Z/r$. In this situation, E_2 equals zero, and E_{TF} gives the leading term of Eq.(1-22) [see Eqs.(1-26) through (1-37)]. Since V is essentially equal to the Coulomb potential in a highly ionized atom, we conclude

$$E_{TF} \cong - Z^2 \left(\tfrac{3}{2}N\right)^{1/3} \quad \text{for} \quad N \ll Z \quad . \tag{2-46}$$

We shall return to highly ionized systems in a while and find the modification of (46) when accounting for the electron-electron repulsion. Before doing so, we have to study some implications of Eq.(45).

The stationary property of E_{TF} with respect to variations of V and ζ reads

$$
\begin{aligned}
o = \delta E_{TF} = &\int (d\vec{r})\,\delta V\{\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} + \frac{1}{4\pi}\nabla^2(V+\frac{Z}{r})\} \\
&+ \delta\zeta\{\int (d\vec{r})\,\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} - N\} \\
&- \frac{1}{4\pi}\int (d\vec{r})\,\vec{\nabla}\cdot(\delta V\,\vec{\nabla}(V+\frac{Z}{r})) \quad .
\end{aligned}
\tag{2-47}
$$

The value of the last integral is zero, because the equivalent integration over a remote surface vanishes in view of $\delta V=o$ for $r\to\infty$. The variations of V and ζ are independent, so that the two curly brackets equal zero individually. Accordingly,

$$
-\frac{1}{4\pi}\nabla^2(V+\frac{Z}{r}) = \frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}
\tag{2-48}
$$

and

$$
\int (d\vec{r})\,\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} = N \quad ,
\tag{2-49}
$$

of which the first is the Poisson equation, and the second the normalization of the density to N. Obviously, Eq.(49) is the TF version of (11), as we notice that Eq.(10) is realized as

$$
N(\zeta') = 2\int\frac{(d\vec{r})\,(d\vec{p})}{(2\pi)^3}\,\eta(-\frac{1}{2}p^2-V-\zeta') = \int (d\vec{r})\frac{1}{3\pi^2}[-2(V+\zeta')]^{3/2} .
\tag{2-50}
$$

This, inserted into Eq.(9), reproduces (44), as it should.

On the right-hand side of (48) as well as under the integral of (49) we have the TF density

$$
n = \frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} \quad .
\tag{2-51}
$$

In the classically forbidden domain, characterized by $V>-\zeta$, this density vanishes. There is a sharp boundary assigned to atoms in the TF model. In contrast, in an exact quantum mechanical description the transition from the classically allowed to the classically forbidden region is smooth. We have just learned about one of the deficiencies of the TF model. It is going to be removed later when we shall incorporate quantum corrections of the sort discussed briefly after Eq.(1-43).

The differential equation (48) for V, known as the TF equation for V, is supplemented by the constraint (49) and the short distance behavior of V,

$$r\,V \to -Z \quad \text{for} \quad r \to o \quad . \tag{2-52}$$

It signifies the physical requirement that for $r\to o$, the effective potential is mainly given by the electrostatic potential energy of an electron with the nucleus; formally, (52) is necessary to ensure the finiteness of E_2. Consequently, we have the following situation: for small r, the potential is large negative, and the density is large; as r increases the potential becomes less and less negative; finally, at the edge of the classically allowed region, it equals $-\zeta$, and the argument of the square root in (51) turns negative; beyond this distance, r_o, the density is zero, so that (48) is the homogeneous Poisson equation. Gauss's law, combined with Eqs.(49) and (52), then implies

$$V = -\frac{Z-N}{r} \quad \text{for} \quad r \geqq r_o \quad , \tag{2-53}$$

and the radius r_o of the atom is determined by

$$V(r=r_o) = -\zeta \quad , \tag{2-54}$$

or,

$$\zeta = \frac{Z-N}{r_o} \quad . \tag{2-55}$$

The electric field $-\vec{\nabla}V$ is continuous (there are no charged surfaces in an atom); in particular, at the edge we have

$$\frac{d}{dr}V(r)\Big|_{r_o} = \frac{Z-N}{r_o^2} = \frac{\zeta}{r_o} \quad . \tag{2-56}$$

Neutral systems, N=Z, have $\zeta=o$, so that both V and dV/dr vanish at $r=r_o$. Consequently, the TF equation for V, Eq.(48), requires $r_o=\infty$, since for a finite r_o it cannot have a solution satisfying these boundary conditions. We have just learned that neutral TF atoms are infinitely large, they do not have an "outside", only an "inside".

It is useful to measure $V+\zeta$ as as multiple of the potential of the nucleus by introducing a function f(x),

$$V + \zeta = -\frac{Z}{r}\,f(x) \quad , \tag{2-57}$$

the argument of which is related to the physical distance r by

$$x = Z^{1/3}r/a \quad , \quad a = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3} = 0.8853\ldots \tag{2-58}$$

The constant a is chosen such that the differential equation for f(x),

$$\frac{d^2}{dx^2} f(x) = \frac{[f(x)]^{3/2}}{x^{1/2}} \quad , \tag{2-59}$$

called the TF equation for f(x), is free of numerical factors. The boundary conditions (52),(54), and (56) translate into

$$f(o) = 1 \ , \quad f(x_o) = o \ , \quad -x_o \frac{d}{dx_o} f(x_o) = 1 - \frac{N}{Z} \equiv q \quad , \tag{2-60}$$

which introduces q, the degree of ionization. Of course, x_o is related to r_o through (58). Equation (53) now appears as

$$f(x) = q(1-x/x_o) \quad \text{for} \quad x \geq x_o \quad . \tag{2-61}$$

Please notice that Z and N do not appear individually in Eqs.(59) and (60). Consequently, f(x) is solely determined by the degree of ionization, q, so that all ions with the same q possess a common shape of the potential and of the density. The potential V itself does, of course, depend on Z; first through the factor Z/r, but then also because of the Z dependence of the TF variable x of Eq. (58). The factor $Z^{1/3}$ there implies the same shrinking of heavier atoms that we have already observed in Chapter One, when considering Bohr atoms with shielding, see Eq.(1-93).

For illustration, Fig.1 shows a sketch of f(x) for q = 1/2, for which $x_o \cong 3$. The geometrical significance of the third equation in (60) is indicated.

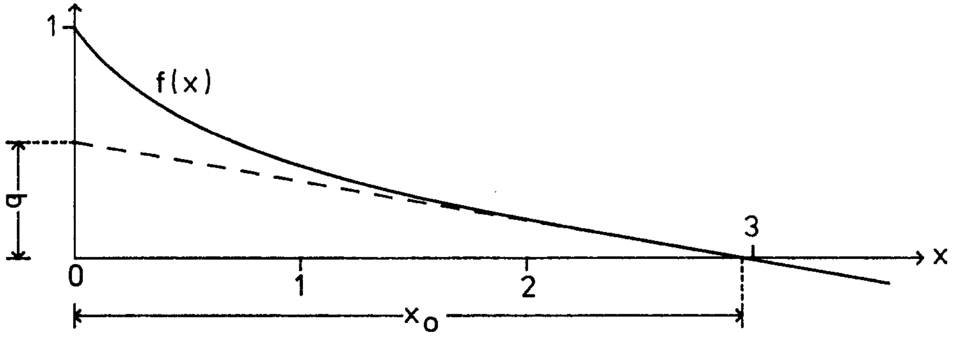

Fig. 2-1. Sketch of f(x) *for* q = 1/2.

Neutral TF atoms. For the solution of Eqs.(59) and (60) that belongs to q=o, we write F(x) and call it the TF function. It obeys

$$\frac{d^2}{dx^2} F(x) = \frac{[F(x)]^{3/2}}{x^{1/2}} \quad , \qquad (2\text{-}62)$$

and is subject to

$$F(o) = 1 \quad , \quad F(\infty) = o \quad . \qquad (2\text{-}63)$$

Its initial slope B,

$$F(x) = 1 - Bx + \ldots \qquad \text{for} \quad x \ll 1 \quad , \qquad (2\text{-}64)$$

has an important physical significance. We insert (64) into (57), use (58), and arrive at

$$V(r) \cong -\frac{Z}{r} + \frac{B}{a} Z^{4/3} \qquad \text{for} \quad r \to o \quad . \qquad (2\text{-}65)$$

The additive constant is the interaction energy of an electron, near the nucleus, with the main body of electrons. We can use it to immediately write down the change in energy caused by an infinitesimal change of the nuclear charge Z to Z + δZ. It is the analogous electrostatic energy of that additional charge, where a minus sign is needed to connect with the known energy, which is that of an electron:

$$\delta E_{TF} = -\frac{B}{a} Z^{4/3} \delta Z \quad . \qquad (2\text{-}66)$$

The simultaneous increase of the number of electrons from N=Z to N=Z+δZ has no effect on the energy since $\partial E/\partial N = -\zeta = o$ for N=Z, see Eq.(55). Consequently,

$$-E_{TF} = \frac{3}{7}\frac{B}{a} Z^{7/3} \qquad \text{for} \quad N = Z \quad . \qquad (2\text{-}67)$$

This is the TF formula for the total binding energy of neutral atoms.

The constant B is well known numerically. But before quoting the results of a numerical integration of Eqs.(62) and (63), let us use our insight to find an estimate for B. Indeed, in view of the physical approximations that led to the TF model, there is no need, at this stage of the development, of knowing B better than within a few percent. A first crude estimate is given by the comparison of (67) with (1-51), the result obtained in the model of Bohr atoms with shielding:

$$B \cong \frac{7a}{3}\,\frac{9}{14}\left(\frac{3}{2}\right)^{1/3} = \frac{9}{8}\left(\frac{\pi}{2}\right)^{2/3} = 1.52 \quad . \tag{2-68}$$

We have no way of judging, how accurate this number may be, but shall see later that it deviates by less than 5% from the correct value.

The stationary property of the energy functional (45) provides a tool for obtaining good estimates for B. If we evaluate $E_{TF}(V,\zeta)$ for a trial potential V and $\zeta = o$ (this much we know for sure when N=Z), the deviation of $E_{TF}(V,\zeta=o)$ from $-\frac{3}{7}\frac{B}{a}Z^{7/3}$ will be of second order in the error of V. As we shall see in the following section, the energy functional has a maximum for the correct potential. Consequently, any trial V gives an upper bound for the constant B:

$$B \leqq -\frac{7}{3}a\,Z^{-7/3}\,E_{TF}(V,\zeta) \quad , \quad (\text{for } N = Z) \quad , \tag{2-69}$$

where the equal sign holds only for ζ=o and $V = -(Z/r)F(x)$.

<u>Maximum property of the TF potential functional.</u> Let us consider finite deviations from the correct potential V and the correct value for ζ, denoted by ΔV and $\Delta\zeta$, respectively, as distinguished from the infinitesimal variations δV and $\delta\zeta$. Whereas $\Delta\zeta$ is quite arbitrary, ΔV is subject to

$$\begin{aligned} r\,\Delta V &\to o \quad \text{for} \quad r \to o \quad , \\ \Delta V &\to o \quad \text{for} \quad r \to \infty \quad , \end{aligned} \tag{2-70}$$

which are consequences of (52) and the normalization $V(r\to\infty)=o$. The deviations of the three terms of E_{TF} in (45) are then

$$\Delta E_1 = \int(d\vec{r})\left(-\frac{1}{15\pi^2}\right)\left([-2(V+\Delta V+\zeta+\Delta\zeta)]^{5/2} - [-2(V+\zeta)]^{5/2}\right) \quad , \tag{2-71}$$

and

$$\begin{aligned} \Delta E_2 &= -\frac{1}{8\pi}\int(d\vec{r})\left([\vec{\nabla}(V+\Delta V+\frac{Z}{r})]^2 - [\vec{\nabla}(V+\frac{Z}{r})]^2\right) \\ &= -\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}(\Delta V)]^2 - \frac{1}{4\pi}\int(d\vec{r})\,\vec{\nabla}(\Delta V)\cdot\vec{\nabla}(V+\frac{Z}{r}) \quad , \end{aligned} \tag{2-72}$$

which after a partial integration and the use of Eq.(48) reads

$$\Delta E_2 = -\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}(\Delta V)]^2 - \int(d\vec{r})\,\Delta V\,\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} \quad , \qquad (2\text{-}73)$$

as well as

$$\Delta(-\zeta N) = -(\Delta\zeta)N = -\int(d\vec{r})\,\Delta\zeta\,\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} \quad , \qquad (2\text{-}74)$$

where Eq.(49) has been employed. Accordingly,

$$\begin{aligned}\Delta E_{TF} &= \Delta E_1 + \Delta E_2 + \Delta(-\zeta N)\\ &= \int(d\vec{r})\,\left(-\frac{1}{15\pi^2}\right)\{[-2(V+\zeta)-2(\Delta V+\Delta\zeta)]^{5/2}-[-2(V+\zeta)]^{5/2}\\ &\qquad + 5(\Delta V+\Delta\zeta)[-2(V+\zeta)]^{3/2}\}\\ &\quad -\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}(\Delta V)]^2 \quad .\end{aligned} \qquad (2\text{-}75)$$

The contents of the curly brackets is of the structure

$$\begin{aligned}&[u+v]^{5/2} - u^{5/2} - \frac{5}{2}\,v\,u^{3/2}\\ &\quad = \frac{15}{4}\int_o^v dv'\,(v-v')\,[u+v']^{1/2} \geqq o \quad ,\end{aligned} \qquad (2\text{-}76)$$

where $u = -2(V+\zeta)$ and $v = -2(\Delta V+\Delta\zeta)$. The equal sign in (76) holds only if $v = o$, or, if $u+v' \leqq o$ over the whole range of integration (under which circumstance the square root vanishes). This implies

$$\Delta E_{TF} \leqq o \quad ; \quad = o \text{ only for } \Delta V = o \text{ and } \Delta\zeta = o \quad . \qquad (2\text{-}77)$$

In words: the TF potential functional of Eq.(45) has an absolute maximum at the correct V and ζ.

This maximum property might come as a surprise, as one naively expects the electrons to arrange themselves such that the energy achieves a minimum. True, but it is not different electron distributions that we compare; the competition is among different potentials. In the same sense, in which it is natural for the right density to minimize the energy, it is common for the right potential to maximize it. Let us illustrate this point by the analogous (and closely related) situation in electrostatics.

An electrostatic analogy. Consider the problem of finding the electrostatic potential, Φ, to a given charge density, ρ, in the vacuum.[4] They are related to each other by the Poisson equation

$$-\frac{1}{4\pi}\nabla^2\Phi = \rho \quad . \tag{2-78}$$

The electrostatic energy can be expressed in various ways:

$$\begin{aligned} E &= \frac{1}{2}\int(d\vec{r})\,\rho\Phi = \frac{1}{8\pi}\int(d\vec{r})\,(\vec{\nabla}\Phi)^2 \\ &= \int(d\vec{r})\,[\rho\Phi - \frac{1}{8\pi}(\vec{\nabla}\Phi)^2] \quad . \end{aligned} \tag{2-79}$$

If we insert the Φ that obeys (78) into any of these expressions, they all give the same answer. Suppose, however, that we do not know the correct Φ and have to resort to using an approximate one. In this situation, it is advisable to employ the third version of (79) in calculating the energy, because, unlike the other ones, this expression is stationary at the correct Φ:

$$\delta\int(d\vec{r})\,[\rho\Phi - \frac{1}{8\pi}(\vec{\nabla}\Phi)^2] = \int(d\vec{r})\,\delta\Phi[\rho + \frac{1}{4\pi}\nabla^2\Phi] = 0 \quad . \tag{2-80}$$

A finite deviation $\Delta\Phi$ from the right electrostatic potential results in the second order error in E that is given by

$$\Delta E = -\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}(\Delta\Phi)]^2 < 0 \quad ; \tag{2-81}$$

the energy is maximal for the right Φ. The analogy to the TF functional is, indeed, close, since the same term occurs also in (75).

Here is a little application of the stationary property of the electrostatic "potential functional."[5] Instead of inserting $\Phi(\vec{r})$, we evaluate the energy for $\Phi(\lambda\vec{r})$:

$$\begin{aligned} E(\lambda) &= \int(d\vec{r})\ \rho\Phi(\lambda\vec{r}) - \frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}\Phi(\lambda\vec{r})]^2 \\ &= \int(d\vec{r})\ \rho\Phi(\lambda\vec{r}) - \frac{1}{\lambda}\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}\Phi(\vec{r})]^2 \quad . \end{aligned} \tag{2-82}$$

For $\lambda=1$, it is the correct energy. Consequently,

$$\frac{d}{d\lambda} E(\lambda) = o \quad \text{for} \quad \lambda=1 \quad , \tag{2-83}$$

which implies

$$\frac{1}{8\pi} \int (d\vec{r})\, (\vec{\nabla}\Phi)^2 = \int (d\vec{r})\ \rho\vec{r}\cdot(-\vec{\nabla}\Phi) \quad . \tag{2-84}$$

We have thus found an unusual expression for the electrostatic energy: the integral of the scalar product of the dipole density $\rho\vec{r}$ with the electric field $-\vec{\nabla}\Phi$. Note, in particular, that there is no factor of 1/2. Since a translated charge distribution $\rho(\vec{r}+\vec{R})$ has the same electrostatic energy,

$$\int (d\vec{r})\, \rho(\vec{r}+\vec{R})\vec{r} \cdot (-\vec{\nabla}\Phi(\vec{r}+\vec{R})) = \int (d\vec{r})\, \rho(\vec{r})\vec{r}\cdot [-\vec{\nabla}\Phi(\vec{r})] \quad , \tag{2-85}$$

we find, after substituting $\vec{r}\to\vec{r}-\vec{R}$ on the left hand side, that the self force of any charge density vanishes:

$$\int (d\vec{r})\, \rho(-\vec{\nabla}\Phi) = o \quad . \tag{2-86}$$

(The stresses, of course, do not.)

A different problem is that of finding the correct charge density on the surface, S, of a conductor carrying a given total charge, Q. In this situation, the relevant equations are

$$\int dS' \frac{\sigma(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} = \text{const. for } \vec{r} \text{ on } S \quad , \tag{2-87}$$

and

$$\int dS\, \sigma(\vec{r}) = Q \quad , \tag{2-88}$$

where σ denotes the surface charge density. Here the stationary energy expression is

$$E = \frac{1}{2}\int dS dS' \frac{\sigma(\vec{r})\sigma(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \Phi_o (Q - \int dS \sigma(\vec{r})) \quad . \tag{2-89}$$

The last term incorporates the constraint (88). Infinitesimal variations of both σ and Φ_o imply Eqs. (87) and (88), thereby identifying Φ_o as the (constant) electrostatic potential on S. This energy is a minimum if only σ's obeying (88) are allowed in the competition, i.e., if various distributions of the same, given, amount of charge are compared.

We get

$$\Delta E = \frac{1}{2}\int ds ds' \frac{\Delta\sigma(\vec{r})\ \Delta\sigma(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \quad , \tag{2-90}$$

where $\Delta\sigma$ is the deviation from the optimal density σ. Since this is the electrostatic energy of some charge distribution, it is, indeed, positive.

<u>TF density functional.</u> This digression into the realm of electrostatics raises the question if it is possible to write down a functional of the density, in addition to the potential functional of (45), thus getting upper bounds on the energy, lower ones on the constant B. This can be done, indeed. It requires appropriate rewriting of (45), whereby the potential is replaced in terms of the density. Both Eq.(51) and the electrostatic relation

$$V(\vec{r}) = -\frac{Z}{r} + \int(d\vec{r}\,')\ \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \tag{2-91}$$

can and must be used in this process.

We start by undoing the step from Eq.(43) to Eq.(44), so that E_1 is split into the kinetic energy, E_{kin}, and a potential energy part:

$$\begin{aligned} E_1 &= \int(d\vec{r})\ \frac{1}{10\pi^2}[-2(V+\zeta)]^{5/2} - \int(d\vec{r})\ \frac{1}{6\pi^2}[-2(V+\zeta)]^{1+3/2} \\ &= \int(d\vec{r})\ \frac{1}{10\pi^2}(3\pi^2 n)^{5/3} + \int(d\vec{r})\,(V+\zeta)n \\ &= E_{kin} + \int(d\vec{r})\,(V+\frac{Z}{r})n - \int(d\vec{r})\ \frac{Z}{r}n + \zeta\int(d\vec{r})n \quad . \end{aligned} \tag{2-92}$$

E_2 is rewritten by first performing a partial integration, then making use of the Poisson equation, followed by employing Eq. (91):

$$\begin{aligned} E_2 &= -\frac{1}{8\pi}\int(d\vec{r})\,[\vec{\nabla}(V+\frac{Z}{r})]^2 = \frac{1}{2}\int(d\vec{r})\,(V+\frac{Z}{r})\ \frac{1}{4\pi}\nabla^2(V+\frac{Z}{r}) \\ &= -\frac{1}{2}\int(d\vec{r})\,(V+\frac{Z}{r})n(\vec{r}) = -\frac{1}{2}\int(d\vec{r})\,(d\vec{r}\,')\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \end{aligned} \tag{2-93}$$

Combining the two last versions into

$$E_2 = \frac{1}{2}\int(d\vec{r})(d\vec{r}\,')\,\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} - \int(d\vec{r})(V+\zeta)n \qquad (2\text{-}94)$$

makes the potential disappear from the sum of E_1 and E_2. The resulting <u>TF density functional</u> is

$$\begin{aligned} E &= E_1 + E_2 - \zeta N \\ &= \int(d\vec{r})\,\frac{1}{10\pi^2}(3\pi^2 n)^{5/3} - \int(d\vec{r})\,\frac{Z}{r}n + \frac{1}{2}\int(d\vec{r})(d\vec{r}\,')\,\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \\ &\qquad - \zeta(N - \int(d\vec{r})n) \quad . \end{aligned} \qquad (2\text{-}95)$$

All we know at this stage is that Eq.(95) gives the correct value of the energy, provided we insert the correct density. To be useful this functional has to be stationary about the right density. Not surprisingly, it is:

$$\begin{aligned} \delta E &= \int(d\vec{r})\;\delta n(\vec{r})\,[\tfrac{1}{2}(3\pi^2 n(\vec{r}))^{2/3} - \frac{Z}{r} + \int(d\vec{r}\,')\,\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \zeta] \\ &\qquad - \delta\zeta\;(N - \int(d\vec{r})n) = o \quad , \end{aligned} \qquad (2\text{-}96)$$

which uses Eqs.(51) and (91) in the combination[6]

$$V(\vec{r}) = -\frac{1}{2}(3\pi^2 n(\vec{r}))^{2/3} - \zeta = -\frac{Z}{r} + \int(d\vec{r})\,\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \quad , \qquad (2\text{-}97)$$

and the constraint (49), now reading

$$\int(d\vec{r})n = N \quad . \qquad (2\text{-}98)$$

The successive terms in Eq.(95) have the physical significance of the kinetic energy, the potential energy between the nucleus and the electrons, and the electron-electron potential energy. The last term incorporates the constraint (98), thereby identifying ζ as the corresponding Lagrangian multiplier. In contrast, the potential functional of Eq.(45) consists of the sum of independent particle energies, $E_1-\zeta N$, plus the removal of the doubly counted electron-electron-interaction energy, E_2. It is important to appreciate this difference in structure.

Let us now check if the density functional does have the expected property of being minimal for the correct n and ζ.

Minimum property of the TF density functional. In analogy to the previous discussion of the maximum property of the TF potential functional, we consider finite deviations Δn and $\Delta\zeta$ from the correct n and ζ. Again, $\Delta\zeta$ is quite arbitrary, whereas Δn is restricted by the requirement that the density be non-negative,

$$n + \Delta n \geq o \quad \text{for all } r \quad . \tag{2-99}$$

The derivation of (95) made use of (51) so that negative densities had been implicitly excluded.

The various contributions to ΔE are then

$$\Delta E_{kin} = \int (d\vec{r})\, \frac{(3\pi^2)^{5/3}}{10\pi^2} [(n+\Delta n)^{5/3} - n^{5/3}] \quad , \tag{2-100}$$

and

$$\begin{aligned}
&\Delta\Big(- \int (d\vec{r})\, \frac{Z}{r} n + \frac{1}{2}\int (d\vec{r})\,(d\vec{r}\,')\, \frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\Big) \\
&\quad = \int (d\vec{r}) \Delta n(\vec{r}) \Big[- \frac{Z}{r} + \int (d\vec{r}\,')\, \frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\Big] \\
&\qquad + \frac{1}{2} \int (d\vec{r})\,(d\vec{r}\,')\, \frac{\Delta n(\vec{r})\; \Delta n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \\
&\quad = \int (d\vec{r})\, \frac{(3\pi^2)^{5/3}}{10\pi^2} \Big[- \frac{5}{3} n^{2/3} \Delta n\Big] - \zeta \int (d\vec{r}) \Delta n \\
&\qquad + \frac{1}{2} \int (d\vec{r})\,(d\vec{r}\,')\, \frac{\Delta n(\vec{r})\; \Delta n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \quad ,
\end{aligned} \tag{2-101}$$

which uses Eq. (97), as well as

$$\Delta[- \zeta(N - \int (d\vec{r}) n)] = (\zeta + \Delta\zeta) \int (d\vec{r}) \Delta n \quad . \tag{2-102}$$

Consequently,

$$\begin{aligned}
\Delta E = &\int (d\vec{r})\, \frac{(3\pi^2)^{5/3}}{10\pi^2} \Big[(n+\Delta n)^{5/3} - n^{5/3} - \frac{5}{3} n^{2/3} \Delta n\Big] \\
&+ \frac{1}{2} \int (d\vec{r})\,(d\vec{r}\,')\, \frac{\Delta n(\vec{r})\; \Delta n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \quad +
\end{aligned}$$

$$+ \Delta\zeta \int (d\vec{r})\, \Delta n \quad . \tag{2-103}$$

The first term here is positive definite, which becomes obvious when we write it [compare Eq.(76)] in the form

$$\int (d\vec{r})\, \frac{(3\pi^2)^{5/3}}{10\pi^2}\, \frac{10}{9} \int_o^{\Delta n} d\nu\, (\Delta n - \nu)\, (n+\nu)^{-1/3} \tag{2-104}$$

$$\geq o \quad ; \quad = o \quad \text{only if} \quad \Delta n(\vec{r}) = o \quad \text{for all} \quad \vec{r} \quad .$$

The second term in (103) is the electrostatic energy of the charge density $\Delta n(\vec{r})$, thus it is also positive, unless $\Delta n = o$ everywhere. The third term does not have a definite sign. Therefore we restrict the class of trial densities n and trial ζ's such that

$$\Delta\zeta \int (d\vec{r})\, \Delta n = o \quad . \tag{2-105}$$

Then

$$\Delta E \geq o \quad ; \quad = o \quad \text{only for} \quad \Delta n(\vec{r}) = o \quad \text{for all} \quad \vec{r} \quad ; \tag{2-106}$$

the TF density functional of Eq.(95) has an absolute minimum at the correct density, provided Eq.(105) holds.

In general, satisfying (105) will mean to consider only such trial densities that obey the constraint (98), since then

$$\int (d\vec{r})\, \Delta n = o \quad . \tag{2-107}$$

The main exception are neutral atoms, about which we know that $\zeta = o$. Consequently, trial values for ζ need not be chosen, so that $\Delta\zeta = o$. Then Eq.(105) is satisfied without restricting the density according to (107). This observation will prove useful, when seeking lower bounds on the constant B.

Upper bounds on B. We pick up the story at Eq.(69). The calculation is considerably simplified by employing the TF variables x, x_o, and f(x), which have been introduced in Eqs.(57) through (60). In these, the TF potential functional appears as $[f'(x) \equiv \frac{d}{dx} f(x)]$

$$E = - (Z^{7/3}/a) \{ \frac{2}{5} \int_o^\infty dx\, \frac{[f(x)]^{5/2}}{x^{1/2}} + \frac{1}{2} \int_o^\infty dx\, [f'(x) + \frac{q}{x_o}]^2 +$$

$$+ \frac{q(1-q)}{x_o}\} \quad , \tag{2-108}$$

where, replacing V and ζ, it is now f(x) and x_o that have to be found.[7] Whereas arbitrary variations of x_o may be considered, f(x) is subject to

$$f(o) = 1 \tag{2-109}$$

and

$$f'(x) = -\frac{q}{x_o} \quad \text{for} \quad x\to\infty \quad . \tag{2-110}$$

The first of these is Eq.(52), the second comes from the inclusion of ζ, in Eq.(57), into the definition of f(x). In (108) it is needed to ensure the finiteness of the second integral. Note, in particular, that the trial functions do not have to obey

$$f(x_o) = o \quad , \quad -x_o f'(x_o) = q \tag{2-111}$$

[see(60)]. This, and the differential equation

$$f''(x) = \frac{[f(x)]^{3/2}}{x^{1/2}} \tag{2-112}$$

[see (59)] are implications of the stationary property of (108). Here is how it works: infinitesimal variations of f(x) cause a change in E,

$$\begin{aligned} o &= \delta[-(a/Z^{7/3})E] \\ &= \int_o^\infty dx\ \delta f(x)\{\frac{[f(x)]^{3/2}}{x^{1/2}} - f''(x)\} + \int_o^\infty dx\ \frac{d}{dx}\{\delta f(x)\,[f'(x)+\frac{q}{x_o}]\} \\ &= \int_o^\infty dx\ \delta f(x)\{\frac{[f(x)]^{3/2}}{x^{1/2}} - f''(x)\} \quad . \end{aligned} \tag{2-113}$$

where the first equality is the stationary property and the last one uses (109) and (110) in finding the null value of the integrated total differential. Thus (112) is implied. We combine it with (110) to conclude that beyond a certain (yet unspecified) $\bar{x}$, f(x) is negative and linear:

$$f(x) = q\,\frac{\bar{x}-x}{x_o} \quad \text{for} \quad x \geqq \bar{x} \quad . \tag{2-114}$$

Next, we consider variations of x_o. They produce

$$o = \delta[-(a/Z^{7/3})E]$$

$$= \delta(\frac{1}{x_o})\ q\ \{\int_o^\infty dx[f'(x)+\frac{q}{x_o}] + (1-q)\} \quad , \qquad (2\text{-}115)$$

implying the vanishing of the contents of the curly brackets. In view of (114), the integration stops at $\bar{x}$:

$$\begin{aligned} o &= \int_o^{\bar{x}} dx[f'(x)+\frac{q}{x_o}] + (1-q) \\ &= f(\bar{x}) - f(o) + q\frac{\bar{x}}{x_o} + 1 - q = q(\frac{\bar{x}}{x_o} - 1) \quad ; \end{aligned} \qquad (2\text{-}116)$$

the last step makes use of (109) and (114). Now we see that $\bar{x}=x_o$, so that (114) becomes (61) and implies (111).

Let us now turn to neutral atoms, q=o. The maximum property of the functional (108), combined with the known form of the neutral atom binding energy , Eq.(67), reads

$$\frac{3}{7}\ B \leq \frac{2}{5}\int_o^\infty dx\ \frac{[f(x)]^{5/2}}{x^{1/2}} + \frac{1}{2}\int_o^\infty dx[f'(x)]^2 \quad , \qquad (2\text{-}117)$$

where the equal sign holds only for f(x)=F(x). Note that x_o disappeared together with q, so that we do not need to use explicitly our knowledge of $x_o=\infty$ for q=o. According to (109) and (110), the competition in (117) is among trial functions that are subject to

$$f(o) = 1 \quad , \quad f'(x \to \infty) = o. \qquad (2\text{-}118)$$

For any trial f(x), we can always change the scale,

$$f(x) \to f(\mu x) \quad , \ (\mu>o) \ , \qquad (2\text{-}119)$$

and obtain another trial function. The optimal choice for μ minimizes the right hand side of

$$\frac{3}{7}\ B \leq \frac{2}{5}\int_o^\infty dx\ \frac{[f(\mu x)]^{5/2}}{x^{1/2}} + \frac{1}{2}\int_o^\infty dx[\frac{d}{dx}f(\mu x)]^2 =$$

$$= \mu^{-1/2} \frac{2}{5} \int_0^\infty dx \frac{[f(x)]^{5/2}}{x^{1/2}} + \mu \frac{1}{2} \int_0^\infty dx [f'(x)]^2 \qquad (2\text{-}120)$$

It is given by

$$\mu^{3/2} = \frac{2}{5} \int_0^\infty dx \frac{[f(x)]^{5/2}}{x^{1/2}} \bigg/ \int_0^\infty dx [f'(x)]^2 \quad . \qquad (2\text{-}121)$$

We insert it into (210) and arrive at the scale invariant version of (117):

$$B \leqq \frac{7}{2} \left[\frac{2}{5} \int_0^\infty dx \frac{[f(x)]^{5/2}}{x^{1/2}} \right]^{2/3} \left[\int_0^\infty dx [f'(x)]^2 \right]^{1/3} \quad , \qquad (2\text{-}122)$$

where now the equal sign holds for $f(x)=F(\mu x)$ with arbitrary $\mu>o$.

We are now ready to invent trial functions and produce upper bounds on B. Before doing so, let us make a little observation. If f equals F, the optimal μ in (120) is unity, since the equal sign in (117) holds only for $f(x)=F(x)$. Consequently, the numerator and denominator in (121) are equal for $f=F$. In this situation the related sum in (117) is (3/7)B. We conclude

$$\frac{2}{5} \int_0^\infty dx \frac{[F(x)]^{5/2}}{x^{1/2}} = \frac{2}{7} B \quad , \qquad (2\text{-}123)$$

and

$$\frac{1}{2} \int_0^\infty dx [F'(x)]^2 = \frac{1}{7} B \quad . \qquad (2\text{-}124)$$

An independent (and rather clumsy) derivation of these equations uses the differential equation obeyed by F(x) [Eq.(62)], combined with some partial integrations. Equations (123) and (124) can be employed for an immediate check of the equality in (122) for $f(x)=F(\mu x)$:

$$B = \frac{7}{2} \left(\mu^{-1/2} \frac{2}{7} B\right)^{2/3} \left(\mu \frac{2}{7} B\right)^{1/3} \quad . \qquad (2\text{-}125)$$

More about relations like (123) and (124) will be said in the section on the scaling properties of the TF model.

A very simple trial function is

$$f(x) = \frac{1}{1+x} \quad , \qquad (2\text{-}126)$$

for which

$$\frac{2}{5}\int_0^\infty dx\,\frac{[f(x)]^{5/2}}{x^{1/2}} = \frac{2}{5}\int_0^\infty dx\; x^{-1/2}(1+x)^{-5/2} = \frac{8}{15} \tag{2-127}$$

[the integral, in terms of Euler's Beta function, is $B(\frac{1}{2},2) = \frac{4}{3}$], and

$$\int_0^\infty dx[f'(x)]^2 = \int_0^\infty \frac{dx}{(1+x)^4} = \frac{1}{3} \quad . \tag{2-128}$$

Accordingly,

$$B < \frac{14}{3}\, 5^{-2/3} = 1.596 \quad . \tag{2-129}$$

A better value is obtained for

$$f(x) = \left(\frac{1}{1+x}\right)^{4/3} \quad , \tag{2-130}$$

when

$$B < 2^{-19/9}\left(\frac{77}{3}\right)^{1/3}\left[\pi\left(\frac{2}{3}\right)!\right]^{2/3}\left[\left(\frac{1}{3}\right)!\right]^{-4/3} = 1.5909 \quad . \tag{2-131}$$

This number is, as we shall see, very close to the actual one; so there is no point in considering more complicated trial functions.

Lower bounds on B. In order to express the density functional of Eq.(95) in terms of TF variables, we write

$$\begin{aligned} n(\vec{r}) &= -\frac{1}{4\pi}\nabla^2\left(V+\frac{Z}{r}\right) \\ &= -\frac{1}{4\pi}\frac{1}{r}\frac{d^2}{dr^2}\left[r\left(V+\frac{Z}{r}\right)\right] \\ &= \frac{1}{4\pi}\frac{1}{r}\frac{d^2}{dr^2}(Zf(x)) \\ &= \frac{1}{4\pi}\frac{Z^2}{a^3}\frac{f''(x)}{x} \quad , \end{aligned} \tag{2-132}$$

or, more conveniently here,

$$n(\vec{r}) = \frac{1}{4\pi}\frac{Z^2}{a^3}\frac{g'(x)}{x} \quad . \tag{2-133}$$

The function $g(x)$, thus introduced, differs from $f'(x)$, at most, by a constant. We choose this constant to be q/x_o,

$$g(x) = f'(x) + \frac{q}{x_o} \quad , \quad . \tag{2-134}$$

which in view of (110) is equivalent to requiring

$$g(x \to \infty) = o \quad . \tag{2-135}$$

With (133) and (135) we have for the interaction energy between the nucleus and the electrons

$$-\int (d\vec{r})\, \frac{Z}{r}\, n = -\frac{Z^{7/3}}{a}\int_o^\infty dx\; g'(x) = \frac{Z^{7/3}}{a}\, g(o) \quad , \tag{2-136}$$

whereas the electron-electron energy is

$$\frac{1}{2}\int (d\vec{r})\,(d\vec{r}\,')\,\frac{n(\vec{r})\,n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} = \frac{Z^{7/3}}{a}\,\frac{1}{2}\int_o^\infty dx\,[g(x)]^2 \quad . \tag{2-137}$$

[This quantity equals $-E_2$, so that Eq. (134), used in the second integral of (108), gives this result.] The remaining contributions to the density functional can be expressed in terms of $g(x)$ immediately. We arrive at

$$E = \frac{Z^{7/3}}{a}\Big\{\frac{3}{5}\int_o^\infty dx\; x^{1/3}[g'(x)]^{5/3} + g(o) + \frac{1}{2}\int_o^\infty dx\,[g(x)]^2 - \frac{q}{x_o}\Big[1-q-\int_o^\infty dx\; x\, g'(x)\Big]\Big\} \quad . \tag{2-138}$$

Again arbitrary variations of x_o may be considered, whereas g is restricted by the requirement of non-negative densities,

$$g'(x) \geq o \quad , \tag{2-139}$$

and by Eq. (135). Together, they imply

$$g(x) \leqq o \tag{2-140}$$

According to the discussion of Eq.(103), Eq.(138) supplies upper bounds on the energy, provided that Eq.(105) is obeyed. Expressed in terms of x_o and g, it reads

$$\Delta(\frac{1}{x_o}) \int_o^\infty dx\ x\ \Delta g'(x) = o \quad . \tag{2-141}$$

We did notice already [see the remark following Eq.(107)], that in the situation of neutral atoms, our knowledge of $x_o = \infty$ results in $\Delta(\frac{1}{x_o}) = o$, so that (141) is satisfied without further ado. In particular, $g(x)$ need not be subject to

$$\int_o^\infty dx\ x\ \Delta g'(x) = o \quad , \tag{2-142}$$

or [this is Eq.(98)], more precisely,

$$\int_o^\infty dx\ x\ g'(x) = 1-q\ ;\ = 1 \quad \text{for} \quad q=o \quad . \tag{2-143}$$

The minimum property of the functional (138), together with the known form of the neutral atom (q=o) binding energy, Eq.(67), implies

$$\frac{3}{7}\,B \geqq -\ \{\frac{3}{5} \int_o^\infty dx\ x^{1/3}[g'(x)]^{5/3} + g(o) + \frac{1}{2} \int_o^\infty dx[g(x)]^2\} \ , \tag{2-144}$$

where the equal sign holds only for $g(x) = F'(x)$. For this $g(x)$, the value of the two integrals is $\frac{3}{7}B$ and $\frac{1}{7}B$, respectively, as follows from Eqs.(123) and (124), and the differential equation (62) obeyed by $F(x)$. Consequently,

$$F'(o) = -B \quad , \tag{2-145}$$

which is nothing more than the original definition of B in (64).

As in the preceding section, we can consider changes of the scale. Here the possible scalings are even more general,

$$g(x) \rightarrow \mu_1 g(\mu_2 x) \quad , \quad (\mu_1,\mu_2 > o) \quad , \tag{2-146}$$

because there is no analog to the restriction $f(0)=1$, that we had to watch before. The optimal choices for μ_1 and μ_2 maximize the right hand side of

$$\frac{3}{7}B \geqq -\left\{\frac{3}{5}\int_0^\infty dx\, x^{1/3}\left[\mu_1\frac{d}{dx}g(\mu_2 x)\right]^{5/3} + \mu_1 g(0) + \frac{1}{2}\int_0^\infty dx\left[\mu_1 g(\mu_2 x)\right]^2\right\}$$

$$= -\left\{\mu_1^{5/3}\,\mu_2^{1/3}\,\frac{3}{5}\int_0^\infty dx\, x^{1/3}[g'(x)]^{5/3} + \mu_1 g(0) + \frac{\mu_1^2}{\mu_2}\,\frac{1}{2}\int_0^\infty dx[g(x)]^2\right\}$$

(2-147)

They are

$$\mu_1 = \left(\frac{1}{7}\right)^{4/3}\frac{[-g(0)]^{4/3}}{\frac{1}{5}\int_0^\infty dx\, x^{1/3}[g'(x)]^{5/3}}\left(\frac{1}{2}\int_0^\infty dx[g(x)]^2\right)^{-1/3} \qquad (2\text{-}148)$$

and

$$\mu_2 = \left(\frac{1}{7}\right)^{4/3}\frac{[-g(0)]^{4/3}}{\frac{1}{5}\int_0^\infty dx\, x^{1/3}[g'(x)]^{5/3}}\left(\frac{1}{2}\int_0^\infty dx[g(x)]^2\right)^{2/3} . \qquad (2\text{-}149)$$

Inserted into (147) they produce the scale invariant version of (144):

$$B \geqq \left(\frac{1}{7}\right)^{4/3}\frac{[-g(0)]^{7/3}}{\left(\frac{1}{5}\int_0^\infty dx\, x^{1/3}[g'(x)]^{5/3}\right)\left(\frac{1}{2}\int_0^\infty dx[g(x)]^2\right)^{1/3}} , \qquad (2\text{-}150)$$

where the equal sign holds only for $g(x)=\mu_1 F'(\mu_2 x)$ with arbitrary $\mu_1,\mu_2>0$. Indeed, for such a $g(x)$, we get

$$B = \left(\frac{1}{7}\right)^{4/3}\frac{[\mu_1 B]^{7/3}}{\left(\mu_1^{5/3}\mu_2^{1/3}\,\frac{1}{7}B\right)\left(\frac{\mu_1^2}{\mu_2}\,\frac{1}{7}B\right)^{1/3}} . \qquad (2\text{-}151)$$

The main contribution to the energy of an atom comes from the vicinity of the nucleus. Now, Eqs. (62) and (63) imply,

$$F''(x) \cong \frac{1}{\sqrt{x}} \text{ for } x \to o \; . \qquad (2\text{-}152)$$

Consequently, a good trial g(x) has to be such that

$$g'(x) \sim \frac{1}{\sqrt{x}} \quad \text{for} \quad x \to o \quad . \qquad (2\text{-}153)$$

An example is

$$g(x) = -(1+\sqrt{x})^{-\alpha} \quad , \quad \alpha > o \quad . \qquad (2\text{-}154)$$

It turns out, that the right hand side of (150) increases with α, so that we may immediately consider the limit $\alpha \to \infty$. The scaling invariance helps in this limit, since it allows to evaluate $g(x/\alpha^2)$ for $\alpha \to \infty$, instead of $g(x)$ for $\alpha \to \infty$. The limiting trial function is a simple exponential:

$$g(x) = \lim_{\alpha \to \infty} [-(1+\frac{1}{\alpha}\sqrt{x})^{-\alpha}] = -e^{-\sqrt{x}} \quad . \qquad (2\text{-}155)$$

For this g(x), we have in (150)

$$B > (\frac{1}{7})^{4/3} \frac{[-(-1)]^{7/3}}{(\frac{3}{25}\, 2^{-2/3})(\frac{1}{4})^{1/3}} = \frac{25}{3}(\frac{2}{7})^{4/3} \qquad (2\text{-}156)$$

$$= 1.5682 \quad .$$

Binding energy of neutral TF atoms. We have found an upper bound on B in (131) and a lower one in (156). Now we combine the two and state

$$1.5682 < B < 1.5909 \quad , \qquad (2\text{-}157)$$

or

$$B = 1.580 \pm 0.012 \quad . \qquad (2\text{-}158)$$

The margin in (158) is about 1.5% of the average value, so that we know B with a precision of 0.75%. Please appreciate how little numerical effort was needed in obtaining this result. In view of the crude physical picture that we are still using, the value for B in (158) is entirely sufficient. A higher precision is not called for at this stage of the development.

Inserted into (67), this B value produces

$$-E_{TF} = 0.765\ Z^{7/3} \quad , \tag{2-159}$$

which is the TF prediction for the total binding energy of neutral

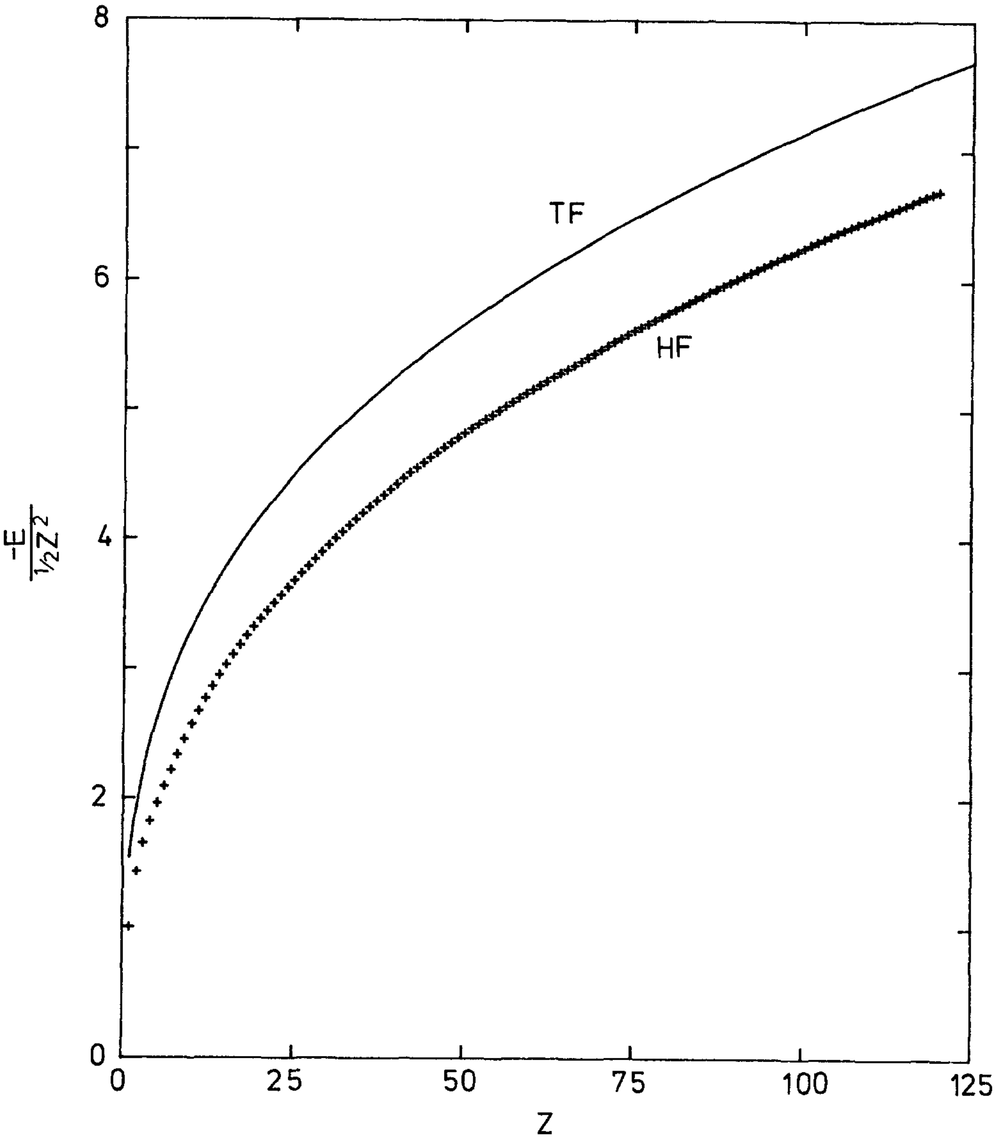

Fig. 2-2. Comparison of the TF prediction (160) with HF binding energies (crosses).

atoms. In Fig.2 the quantity

$$\frac{-E_{TF}}{\frac{1}{2}Z^2} = 1.53\ Z^{1/3} \tag{2-160}$$

is compared to the corresponding HF predictions[8] for integer values of Z. This plot shows that (160) does reproduce the general trend of the atomic binding energies. Altough the need for refinements is clear, it is nevertheless remarkable how well the TF model works despite the crudeness of the physical approximation that it represents. In Fig.2 the continuous TF curve is closer to the integer-Z HF crosses at small Z values than at large ones. This is, however, a deception since it is the fractional difference that counts. The amount of this relative deviation is 29, 24, 21, 17, 15, and 13 percent for Z=10, 20, 30, 60, 90, and 120, respectively. It decreases with increasing Z.

Why do we compare with HF predictions, and not with experimental binding energies? The reasons are the ones mentioned in the Introduction. Total binding energies are known experimentally only up to $Z \cong 20$ (in Fig.2 they are indistinguishable from the HF crosses). Even if they were available for large values of Z, the TF result should still be measured against different predictions based upon, e.g., the many-particle Hamilton operator of (1-7); this way we are sure to not be misled by relativistic effects, which are the more significant the larger Z.

TF function F(x). We have learned a lot about the initial slope B of the TF function. Naturally, there is much more to say about F(x). We shall do so in this section.

Let us proceed from recalling the defining properties of Eqs. (62) and (63). F(x) obeys the differential equation

$$\frac{d^2}{dx^2} F(x) = F''(x) = \frac{[F(x)]^{3/2}}{x^{1/2}} \tag{2-161}$$

and the boundary conditions

$$F(o) = 1 \quad , \quad F(\infty) = o \quad . \tag{2-162}$$

Upon using $\sqrt{x}$ as the main variable, the differential equation (161) appears as

$$\frac{d}{d\sqrt{x}} F(x) = 2\sqrt{x}\, F'(x) \quad ,$$

$$\frac{d}{d\sqrt{x}} F'(x) = 2[F(x)]^{3/2} \quad . \tag{2-163}$$

Whereas (161) is singular at x=o , this system of differential equations is well behaved at $\sqrt{x}=o$. We conclude that around x=o , F(x) can be expanded in powers of $\sqrt{x}$:

$$F(x) = \sum_{k=o}^{\infty} s_k\, x^{k/2} \quad , \tag{2-164}$$

which has become known as Baker's series.[9] The comparison with

$$F(x) = 1 - Bx + O(x^{3/2}) \tag{2-165}$$

[this is Eq.(64)] shows

$$s_o = 1 \quad , \quad s_1 = o \quad , \quad s_2 = -B \quad . \tag{2-166}$$

For the successive calculation of the s_k's for k>2, we need a recurrence relation. We gain it by inserting (164) into the differential equation (161). The left hand side is simple:

$$\begin{aligned} F''(x) &= \sum_{k=o}^{\infty} s_k \frac{k}{2}\left(\frac{k}{2} - 1\right) x^{k/2-2} \\ &= \frac{3}{4} s_3\, x^{-1/2} + \sum_{\ell=1}^{\infty} x^{(\ell-1)/2} \frac{(\ell+1)(\ell+3)}{4} s_{\ell+3} \quad , \end{aligned} \tag{2-167}$$

where s_1=o has been used, and the summation index shifted ($k=\ell+3$). The right hand side of Eq.(161) is nonlinear in F(x), so that the power series becomes more complicated. We have

$$\begin{aligned} [F(x)]^{3/2}/x^{1/2} &= x^{-1/2}[1 + \sum_{k=2}^{\infty} s_k\, x^{k/2}]^{3/2} \\ &= x^{-1/2}[1 + \sum_{j=1}^{\infty} \binom{3/2}{j} (\sum_{k=2}^{\infty} s_k\, x^{k/2})^j] \quad , \end{aligned} \tag{2-168}$$

where the binomial theorem is employed. Next, we make the j-th power of the sum over k explicit by writing it as the product of j sums over k_1 , k_2 , ... , k_j ; then the Kronecker Delta symbol ,

$$\delta_{\ell,k} = \begin{cases} 1 & \text{for } k = \ell \\ 0 & \text{for } k \neq \ell \end{cases} \quad , \tag{2-169}$$

is used to collect all terms of order $x^{-1/2}\, x^{\ell/2} = x^{(\ell-1)/2}$:

$$[F(x)]^{3/2}/x^{1/2} = x^{-1/2}[1+\sum_{j=1}^{\infty}\binom{3/2}{j}\sum_{k_1=2}^{\infty}\sum_{k_2=2}^{\infty}\cdots\sum_{k_j=2}^{\infty} s_{k_1}\, s_{k_2}\cdots$$

$$\times\cdots s_{k_j}\, x^{(k_1+k_2+\ldots+k_j)/2}]$$

$$= x^{-1/2} + \sum_{\ell=1}^{\infty} x^{(\ell-1)/2}\sum_{j=1}^{\infty}\binom{3/2}{j}\sum_{k_1=2}^{\infty}\cdots\sum_{k_j=2}^{\infty} s_{k_1}\cdots s_{k_j}$$

$$\times\ \delta_{\ell,k_1+k_2+\ldots+k_j} \ . \tag{2-170}$$

Since each k is at least two, we have

$$\ell = k_1 + k_2 + \ldots + k_j \geqq 2j \geqq 2 \quad , \tag{2-171}$$

so that the summation over ℓ starts really at $\ell=2$, and the largest j does not exceed $\ell/2$: $j \leqq [\ell/2]$, which makes use of the Gaussian notation for the largest integer contained in $\ell/2$. The individual k-summations stop, at the latest, at $\ell-2(j-1)$, since, again, the other k's, which are j-1 in number, are not less than two each. Accordingly,

$$[F(x)]^{3/2}/x^{1/2} = x^{-1/2} + \sum_{\ell=2}^{\infty} x^{(\ell-1)/2}\sum_{j=1}^{[\ell/2]}\binom{3/2}{j}\sum_{k_1=2}^{\ell-2j+2}\cdots$$

$$\times\cdots\sum_{k_j=2}^{\ell-2j+2} s_{k_1}\cdots s_{k_j}\,\delta_{\ell,k_1+\ldots+k_j} \ . \tag{2-172}$$

This must equal (167), implying

$$s_3 = 4/3 \quad , \quad s_4 = o \quad , \tag{2-173}$$

and

$$s_{\ell+3} = \frac{4}{(\ell+1)(\ell+3)} \sum_{j=1}^{[\ell/2]} \binom{3/2}{j} \sum_{k_1=2}^{\ell-2j+2} \cdots \sum_{k_j=2}^{\ell-2j+2} s_{k_1} \cdots s_{k_j} \delta_{\ell,k_1+\ldots+k_j} \tag{2-174}$$

$$\text{for} \quad \ell = 2,3,\ldots \quad .$$

The s_k with the largest index occurs on the right hand side for j=1; it is s_ℓ. Thus $s_{\ell+3}$ is here expressed in terms of s_k's with $k \leq \ell$, so that this is a recurrence relation, indeed. For illustration, consider ℓ=2,3,4, and 5. There is only the j=1 term for ℓ=2 and ℓ=3:

$$\begin{aligned} s_5 &= \frac{4}{15}\binom{3/2}{1} s_2 = \frac{4}{15}\,\frac{3}{2}(-B) = -\frac{2}{5}B \quad , \\ s_6 &= \frac{1}{6}\binom{3/2}{1} s_3 = \frac{1}{6}\,\frac{3}{2}\,\frac{4}{3} = \frac{1}{3} \quad . \end{aligned} \tag{2-175}$$

For ℓ=4 and ℓ=5 , there are both the j=1 and the j=2 contribution:

$$s_7 = \frac{4}{35}\left[\binom{3/2}{1} s_4 + \binom{3/2}{2} s_2^2\right] = \frac{4}{35}\left[\frac{3}{2}0 + \frac{3}{8}(-B)^2\right] = \frac{3}{70}B^2 \quad , \tag{2-176}$$

$$\begin{aligned} s_8 &= \frac{1}{12}\left[\binom{3/2}{1} s_5 + \binom{3/2}{2}(s_2 s_3 + s_3 s_2)\right] \\ &= \frac{1}{12}\left[\frac{3}{2}\left(-\frac{2}{5}B\right) + \frac{3}{8}2(-B)\frac{4}{3}\right] = -\frac{2}{15}B \quad . \end{aligned}$$

It is not difficult (only boring) to compute more s_k's. Let us be content with what we have so far:

$$F(x) = 1 - Bx + \frac{4}{3}x^{3/2} - \frac{2}{5}Bx^{5/2} + \frac{1}{3}x^3 + \frac{3}{70}B^2x^{7/2} - \frac{2}{15}Bx^4 + O(x^{9/2}) \tag{2-177}$$

The B dependence of the coefficients and their complicated recurrence relation (174) prohibit asking for the range of convergence of the expansion (164). We can, however, test the quality of the approximation to F(x) obtained by terminating the summation at, say, k=8. This is done by inserting the truncated series into the differential equation obeyed by F(x), and comparing both sides:

$$\sum_{k=3}^{8} \frac{k(k-2)}{4} s_k x^{(k-4)/2} \cong [\sum_{k=o}^{8} s_k x^{k/2}]^{3/2}/x^{1/2} \quad . \qquad (2-178)$$

For B=1.580 , our estimate in (158), the comparison is made in Table 1. It shows us, that this approximation to F(x) solves the differential equation with an accuracy of 1% for $\sqrt{x} \lesssim 0.4$; of $\frac{1}{10}$% for $\sqrt{x} \lesssim 0.25$; of $\frac{1}{100}$% for $\sqrt{x} \lesssim 0.20$. This kind of analysis can be repeated for sums truncated at a value of k much larger. One observes that a highly accurate solution to the differential equation (161) is given by these sums for $\sqrt{x} \lesssim 0.4$ only. This is, therefore, the (numerical) range of convergence of the series in Eq.(164); as a consequence, this expansion in powers of $\sqrt{x}$ is utterly useless.[10]

Table 2-1. Left hand side (LHS) and right hand side (RHS) of Eq.(178), and their relative deviation (DEV) for $\sqrt{x}$ = 0.05, ..., 0.50 . For B the value of Eq.(158) is used.

$\sqrt{x}$	LHS	RHS	DEV
0.05	19.8866012	19.8866017	2.3×10^{-8}
0.10	9.783683	9.783698	1.5×10^{-6}
0.15	6.35805	6.35816	1.7×10^{-5}
0.20	4.60944	4.60991	1.0×10^{-4}
0.25	3.5373	3.5387	4.0×10^{-4}
0.30	2.8071	2.8106	1.2×10^{-3}
0.35	2.275	2.282	3.3×10^{-3}
0.40	1.867	1.882	7.8×10^{-3}
0.45	1.542	1.568	1.7×10^{-2}
0.50	1.27	1.32	3.4×10^{-2}

For a precise knowledge of F(x), we cannot rely upon (164) because of its small range of convergence. The differential equation (161) itself has to be integrated numerically. It is not advisable to attempt doing this by starting from x=o with F(o)=1 and F'(o)=-B , using a suitable guess for B [as in Eq.(158)]. If the chosen value for B is too large, the numerical F(x) will turn negative eventually; if B is too small, it will start growing instead of decreasing steadily. One could imagine pinning down the correct value of B by an iteration based on this distinction between trial B's that are too large or too small. This is not going to work, unfortunately, because rounding-off errors cause a wrong large-x behaviour of the numerical F(x), even if one would start with the correct value of B. This difficulty can be circumvented, however, by integrating inwards from $x=\infty$ towards $x=o$ instead of outwards. Let us, therefore, turn our attention to the large-x properties of F(x).

We start by noting that $144/x^3$ is a particular solution of the differential equation (161).[11] Of the two boundary conditions in (162) it satisfies the one at $x=\infty$, whereas it is infinite at $x=o$. It is clear, that F(x) approaches $144/x^3$ for $x\to\infty$ from "below":

$$F(x) \lesssim \frac{144}{x^3} \qquad \text{for} \qquad x \to \infty \quad . \tag{2-179}$$

This invites the ansatz

$$F(x) = \frac{144}{x^3}\, G(y(x)) \tag{2-180}$$

with

$$y(x) \to o \qquad \text{for} \qquad x \to \infty \tag{2-181}$$

and

$$G(y) = 1 \qquad \text{for} \qquad y = o \quad . \tag{2-182}$$

The best choice for the function y(x) must be found from inserting (180) into the differential equation obeyed by F(x), Eq.(161). This leads to

$$\frac{1}{12}[xy'(x)]^2G''(y(x)) + \frac{1}{12}[x^2y''(x) - 6xy'(x)]G'(y(x))+G(y(x))$$
$$= [G(y(x))]^{3/2} \ , \tag{2-183}$$

which takes on a scale invariant form if we choose $xy'(x)$ to be proportional to $y(x)$:

$$xy'(x) = -\gamma y(x) \quad . \tag{2-184}$$

The optimal value for $\gamma>o$ has to be determined. Equation (184) and its immediate consequence

$$x^2y''(x) = (x\frac{d}{dx} - 1)\ xy'(x) = \gamma(\gamma+1)y(x) \quad , \tag{2-185}$$

used in (183), produce

$$\frac{\gamma^2}{12}\, y^2 G''(y) + \frac{\gamma(\gamma+7)}{12}\, y\, G'(y) + G(y) = [G(y)]^{3/2} \quad . \qquad (2\text{-}186)$$

The aforementioned scale invariance is obvious here: with $G(y)$ also $G(\mu y)$ is a solution to (186), for arbitrary μ. A unique value for γ is now implied by the requirement that $G(y)$ be regular at $y=o$,

$$G(y) = 1 - y + \mathcal{O}(y^2) \quad \text{for} \quad y \to o \quad . \qquad (2\text{-}187)$$

Note that because of the scale invariance of (186), the coefficient in front of the term linear in y can be chosen to be minus one [it has to be negative to not be in conflict with Eq.(179)]. With (187), Eq.(186) reads

$$1 - [1 + \frac{1}{12}\,\gamma(\gamma+7)]y + \mathcal{O}(y^2) = 1 - \frac{3}{2}\, y + \mathcal{O}(y^2) \quad , \qquad (2\text{-}188)$$

whence

$$\gamma(\gamma+7) = 6 \quad , \qquad (2\text{-}189)$$

or,

$$\gamma = \frac{1}{2}(-7+\sqrt{73}) = 0.77200\ldots \quad . \qquad (2\text{-}190)$$

The second solution to (189) is $-(\gamma+7) = -7.772\ldots$ and of no use to us in the present context.

The differential equation (186) is simplified a little bit by making use of (189):

$$\frac{\gamma^2}{12}\, y^2 G''(y) + \frac{1}{2}\, y\, G'(y) + G(y) = [G(y)]^{3/2} \quad . \qquad (2\text{-}191)$$

$G(y)$ is thereby subject to (187), which determines the solution to (191) entirely. This does not mean that we know $F(x)$ after finding $G(y)$, since the implication of Eq.(184)

$$y(x) = \beta\, x^{-\gamma} \qquad (2\text{-}192)$$

contains an undetermined constant, β. Its value is fixed by the requirement $F(x=o)=1$. This is, of course, analogous to the previous situation when $F'(o)=-B$ was determined by $F(x\to\infty)=o$.

Since $G(y)$ is, by construction, regular at $y=o$, we can expand it in powers of y:[12]

$$G(y) = \sum_{k=o}^{\infty} c_k \, y^k \quad , \tag{2-193}$$

where

$$c_o = 1 \quad , \quad c_1 = -1 \quad . \tag{2-194}$$

The steps that led us to (174) can be repeated here for (191) and (193) with the appropriate changes. Comparing powers of y^{ℓ} on both sides of Eq.(191) gives

$$\begin{aligned}&[\tfrac{\gamma^2}{12}\,\ell(\ell-1) + \tfrac{1}{2}\,\ell + 1]c_{\ell} \\ &\quad = \sum_{j=1}^{\ell}\binom{3/2}{j}\sum_{k_1=1}^{\ell-j+1}\cdots\sum_{k_j=1}^{\ell-j+1} c_{k_1}\cdots c_{k_j}\,\delta_{\ell,k_1+k_2+\ldots+k_j}\end{aligned} \tag{2-195}$$

for $\ell \geq 1$. The j=1 term equals $\frac{3}{2}c_{\ell}$ and has to be brought over to the left hand side. We then arrive at the recurrence relation

$$c_{\ell} = \frac{12}{(\gamma^2\ell+6)(\ell-1)}\sum_{j=2}^{\ell}\binom{3/2}{j}\sum_{k_1=1}^{\ell-j+1}\cdots\sum_{k_j=1}^{\ell-j+1} c_{k_1}\cdots c_{k_j}\,\delta_{\ell,k_1+\ldots+k_j}\,, \tag{2-196}$$

$$\text{for} \quad \ell = 2,\, 3,\, \ldots \quad .$$

For example,

$$\begin{aligned} c_2 &= \frac{12}{2\gamma^2+6}\binom{3/2}{2}c_1^2 = \frac{9}{4\gamma^2+12} = \frac{201+21\sqrt{73}}{608} \\ &= 0.625697\ldots \quad , \\ c_3 &= \frac{12}{(3\gamma^2+6)2}\left\{\binom{3/2}{2}(c_1c_2+c_2c_1)+\binom{3/2}{3}c_1^3\right\} \\ &= -\frac{3-\gamma^2/8}{(\gamma^2+2)(\gamma^2+3)} = -\frac{15377+1813\sqrt{73}}{98496} \\ &= -0.313386\ldots \quad . \end{aligned} \tag{2-197}$$

As we did before, in Eq.(178) and Table 1, we can again insert truncated versions of (193) into the differential equation (191) in order to find the numerical range of convergence of this series. The outcome is: the expansion (193) represents a highly accurate solution to (191) for $y \lesssim 1$, or, $x \gtrsim \beta^{1/\gamma}$. Anticipating that the actual value of β is about 13, this is $x \gtrsim 30$.[13] Does this mean that the expansion (193) is as useless as the one of Eq.(164)?

No. The power series of $G(y)$, for some $o<y<1$, is needed to get away from $x=\infty$, i.e., $y=o$, when integrating the differential equation for $F(x)$, Eq.(161), inwards. Here is a brief description of the essential ingredients of a computer program calculating $F(x)$ for the whole range of x, $o \leqq x < \infty$:(i) find $G(y)$ and $G'(y)$ for a suitably chosen y_1 ($\cong 0.3$ is a good choice) by employing (193), truncated at a sufficiently large k (depends on the chosen y_1 and the accuracy of the machine); (ii) integrate numerically the differential equation (191) up to a certain y_2 ($\cong 5$ is a good choice), so that we now know $G(y_2)$ and $G'(y_2)$ within the accuracy of the computer (the standard Runge-Kutta scheme is well suited for the numerical integration); (iii) choose a trial value, $\tilde\beta$ ($\cong 13$), for β, and use Eqs.(192) and (180) to find $\tilde x_2 = (\tilde\beta/y_2)^{1/\gamma}$ together with $\tilde F(\tilde x_2)$ and $\tilde F'(\tilde x_2)$; (iv) now integrate the differential equation for $F(x)$, in the form (163) with $\sqrt{x}$ as the relevant argument, down to $x=o$. At this stage, we have <u>a</u> solution to (161), the one corresponding to $\beta=\tilde\beta$. This $\tilde F(x)$ obeys $\tilde F(x=\infty)=o$, but not $\tilde F(x=o)=1$. Fortunately, one does not have to vary $\tilde\beta$ until $\tilde F(x=o)=1$ in order to find $F(x)$. Instead, the observation that, if $\tilde F(x)$ obeys (161), so does $\mu^3 \tilde F(\mu x)$ for arbitrary $\mu>o$, enables us to simply rescale $\tilde F(x)$. The last step in the procedure is therefore: (v) set

$$F(x) = \tilde F(\tilde x)/\tilde F(o) \quad , \tag{2-198}$$

where

$$\tilde x = x/[\tilde F(o)]^{1/3} \quad . \tag{2-199}$$

Accordingly, we have B given by

$$B = -F'(o) = -\tilde F'(o)/[\tilde F(o)]^{4/3} \quad , \tag{2-200}$$

and, as a consequence of

$$y_2 = \beta\, x_2^{-\gamma} = \tilde\beta\, \tilde x_2^{-\gamma} \quad , \tag{2-201}$$

β is related to $\tilde\beta$ through

$$\beta = \beta(x_2/\tilde{x}_2)^{\gamma} = \tilde{\beta}[\tilde{F}(o)]^{\gamma/3} \quad . \tag{2-202}$$

The sensitivity of the numerical results for B, β, and F(x), to the rounding-off errors of the computer can be tested by varying the parameters y_1, y_2, and $\tilde{\beta}$. Ideally, the outcome should be independent of them, numerically it is not. The little dependence that one observes shows how many decimals of the results can be trusted. For example, the realization of the procedure just described gave

$$B = 1.58807102261 \tag{2-203}$$

and

$$\beta = 13.270973848 \tag{2-204}$$

on a computer with a 15-decimal arithmetic.[14] For illustration, in Fig.3 we give a plot of F(x) for $o \leq x \leq 10$.

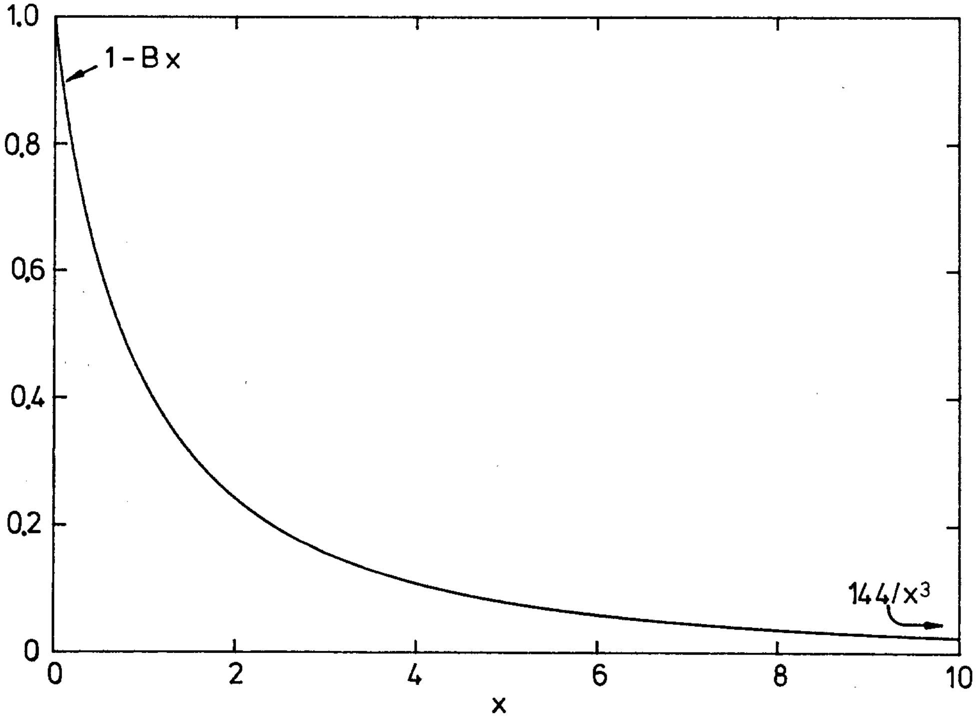

Fig.2-3. The TF function F(x).

Now that we know the actual value of B, let us look back at the bounds that we found earlier, Eq.(157). The upper bound is extremely good: it is too large by less than 0.18%. On the other hand, the lower bound is significantly worse: it is too small by 1.25%. This is a first sign of the superiority of the potential functional over the density functional.

With (203) we can give more significant decimals in the TF binding energy formula. Inserting B into Eq. (67) gives

$$-E_{TF} = 0.768745\, Z^{7/3} \quad . \tag{2-205}$$

There is no point in displaying more than six decimals.

Scaling properties of the TF model. In step (v) of our "computer program" for F(x) we made, in Eqs. (198) and (199), use of the invariance of the TF equation for f(x),

$$f''(x) = \frac{[f(x)]^{3/2}}{x^{1/2}} \tag{2-206}$$

[this is Eq. (59)], under the transformation

$$f(x) \rightarrow \mu^3 f(\mu x) \quad , \quad (\mu > o) \quad . \tag{2-207}$$

The TF model itself is not invariant under such a scaling, because the boundary condition f(o)=1 fixes the scale. Therefore, we have to be somewhat more careful when investigating the scaling properties of the TF model.

When we were looking for bounds on B, we found it advantageous to exploit certain scaling properties of the respective functionals. The scaling transformations that we considered then, were, Eq. (119):

$$f(x) \rightarrow f(\mu x) \tag{2-208}$$

and, Eq. (146) with $g(x)=f'(x)+q/x_o=f'(x)$ for $q=o$:

$$f(x) \rightarrow \frac{\mu_1}{\mu_2} f(\mu_2 x) \quad , \tag{2-209}$$

where μ, μ_1, and μ_2 were arbitrary (positive) numbers. Let us now examine the implications of transformations as general as (209) applied to the TF potential functional.

We return to Eq. (45),

$$E_{TF} = \int (d\vec{r}) \left(-\frac{1}{15\pi^2}\right) [-2(V+\zeta)]^{5/2} - \frac{1}{8\pi}\int (d\vec{r}) [\vec{\nabla}(V+\frac{Z}{r})]^2 - \zeta N$$

$$= E_1 + E_2 - \zeta N \quad , \tag{2-210}$$

and consider

$$V(r) \to \mu^{\nu}\, V(\mu r) \quad , \quad (\mu > o) \quad . \tag{2-211}$$

Since, for the existence of E_2, we need [Eq.(52)]

$$rV(r) \to -Z \qquad \text{for} \qquad r \to o \quad , \tag{2-212}$$

such a scaling transformation of V has to be accompanied by a scaling of Z,

$$Z \to \mu^{\nu-1}\, Z \quad . \tag{2-213}$$

For convenience, we also scale ζ by

$$\zeta \to \mu^{\nu}\, \zeta \quad , \tag{2-214}$$

so that the structure $V+\zeta$ is conserved.

In terms of $f(x)$, (211) and (214), <u>without</u> (213), read

$$f(x) \to \mu^{\nu-1}\, f(\mu x) \quad , \tag{2-215}$$

which identifies (207) and (208) as the special situations $\nu=4$ and $\nu=1$, whereas (209) is realized by $\mu_2=\mu$ and $\mu_1=\mu^{\nu}$. However, <u>with</u> (213), we just have (208), as we should have, since (212) is equivalent to requiring $f(o)=1$; and only (208) is consistent with this constraint.

Under (211), (213), and (214) the various contributions to E_{TF} scale according to

$$E_1 \to E_1(\mu) = \int (d\vec{r}) \left(-\frac{1}{15\pi^2}\right) [-2\mu^{\nu}(V(\mu r)+\zeta)]^{5/2}$$

$$= \mu^{5\nu/2-3}\, E_1 \quad , \tag{2-216}$$

and

$$E_2 \to E_2(\mu) = -\frac{1}{8\pi}\int (d\vec{r}) [\vec{\nabla}(\mu^{\nu}V(\mu r) + \frac{\mu^{\nu}Z}{\mu r})]^2 =$$

$$= \mu^{2\nu-1}\, E_2 \quad , \tag{2-217}$$

as well as

$$\zeta N \to \mu^{\nu}\, \zeta N \quad . \tag{2-218}$$

Consequently

$$E_{TF} \to E_{TF}(\mu) = \mu^{5\nu/2-3}\, E_1 + \mu^{2\nu-1}\, E_2 - \mu^{\nu}\zeta N \quad . \tag{2-219}$$

For $\mu=1$, this is just E_{TF}; for $\mu=1+\delta\mu$, we have $E_{TF}+\delta_\mu E_{TF}$. Now, since the energy is stationary under infinitesimal variations of V and ζ, all first order changes must originate in the scaling of Z. That is

$$\delta_\mu E_{TF} = \frac{\partial E_{TF}}{\partial Z}\, \delta_\mu(\mu^{\nu-1}\, Z) = (\nu-1)Z\frac{\partial E_{TF}}{\partial Z}\, \delta\mu \quad . \tag{2-220}$$

On the other hand, from (219) we get

$$\delta_\mu E_{TF} = [(\tfrac{5}{2}\nu-3)E_1 + (2\nu-1)E_2 - \nu\zeta N]\delta\mu \quad , \tag{2-221}$$

so that we conclude

$$(\tfrac{5}{2}\nu-3)E_1 + (2\nu-1)E_2 - \nu\zeta N = (\nu-1)Z\frac{\partial}{\partial Z}E_{TF} \quad . \tag{2-222}$$

This is a linear equation in ν. It has to hold for any ν. So we obtain two independent relations among the different energy quantities - two "virial theorems." Besides $\nu=1$, when

$$-\frac{1}{2}\, E_1 + E_2 - \zeta N = 0 \quad , \tag{2-223}$$

the other natural choice is the TF scaling $\nu=4$ [see the comment to Eq. (215)], for which

$$7E_1 + 7E_2 - 4\zeta N = 3Z\frac{\partial}{\partial Z}E_{TF} \quad . \tag{2-224}$$

The latter combines with $E_{TF}=E_1+E_2-\zeta N$ and

$$\frac{\partial}{\partial N}\, E_{TF} = -\zeta \tag{2-225}$$

to give

$$7E_{TF}(Z,N) = 3\left(Z\frac{\partial}{\partial Z}+N\frac{\partial}{\partial N}\right)E_{TF}(Z,N) \quad . \tag{2-226}$$

We have made explicit here, that the energy of an atom is a function of Z and N.

For N=Z, Eq.(226) has the simple implication

$$7E_{TF}(Z,Z) = 3Z\frac{d}{dZ}E_{TF}(Z,Z) \quad , \tag{2-227}$$

or

$$E_{TF}(Z,Z) = -\,C\,Z^{7/3} \quad , \tag{2-228}$$

where the constant C is yet undetermined. It is found by combining our knowledge of $\zeta = -\partial E_{TF}/\partial N = o$ for $N=Z$ with

$$\begin{aligned} Z\frac{\partial}{\partial Z}E_{TF} &= Z\frac{\partial}{\partial Z}E_2 = -\frac{1}{4\pi}\int(d\vec{r})\,\vec{\nabla}\left(V+\frac{Z}{r}\right)\cdot\vec{\nabla}\frac{Z}{r} \\ &= \int(d\vec{r})\,\left(V+\frac{Z}{r}\right)\frac{1}{4\pi}\nabla^2\frac{Z}{r} \\ &= -\,Z\left(V+\frac{Z}{r}\right)\Big|_{r=o} \;;= -\frac{B}{a}\,Z^{7/3} \quad \text{for} \quad N = Z \quad . \end{aligned} \tag{2-229}$$

The third step here is a partial integration; the fourth one recognizes $-Z\delta(\vec{r})$ as the source of the Coulomb potential Z/r; the last one, valid for N=Z only, uses Eq.(65). [The comment to that equation says that (229) identifies the interaction energy between the nuclear charge and the electrons:

$$E_{Ne} = Z\frac{\partial}{\partial Z}E_{TF} \quad , \tag{2-230}$$

which, according to (1-96), is a general statement, not limited to the TF model in its validity.] Now,

$$\begin{aligned} E_{TF}(Z,Z) &= \frac{3}{7}\left(Z\frac{\partial}{\partial Z}+N\frac{\partial}{\partial N}\right)E_{TF}(Z,N)\Big|_{N=Z} = \frac{3}{7}Z\frac{\partial}{\partial Z}E_{TF}(Z,N)\Big|_{N=Z} \\ &= -\,\frac{3}{7}\,\frac{B}{a}\,Z^{7/3} \quad , \end{aligned} \tag{2-231}$$

which identifies the constant C. This is, of course, the result that we had found earlier in Eq.(67).

The first of our "virial" theorems, Eq.(223), has the consequence

$$E_1 = 2(E_2-\zeta N) = 2(E_{TF} - E_1) \quad , \tag{2-232}$$

or,

$$E_1 = \frac{2}{3} E_{TF} \quad , \tag{2-233}$$

and

$$E_2 - \zeta N = \frac{1}{3} E_{TF} \quad . \tag{2-234}$$

For a Coulomb system, like the one we are considering, one expects the usual theorems about the kinetic and the potential energy:

$$E_{kin} = - E_{TF} \quad , \quad E_{pot} = 2E_{TF} \quad . \tag{2-235}$$

Indeed, they emerge from the relations that we have found so far. It is essential to remember how E_1 and E_2 are composed of E_{kin} and $E_{pot} = E_{Ne} + E_{ee}$:

$$\begin{aligned} E_1 &= E_{kin} + E_{Ne} + 2E_{ee} + \zeta N \quad , \\ E_2 &= - E_{ee} \quad . \end{aligned} \tag{2-236}$$

Note in particular the double counting of the electron-electron energy in E_1. With (230) we have

$$\begin{aligned} E_{pot} &= E_{Ne} + E_{ee} = Z\frac{\partial}{\partial Z}E_{TF} - E_2 \\ &= (Z\frac{\partial}{\partial Z} + N\frac{\partial}{\partial N})E_{TF} - (E_2-\zeta N) \quad , \end{aligned} \tag{2-237}$$

which makes use of (225). Now Eqs.(226) and (234) can be employed to produce the second statement of (235), which then implies the first one immediately.

The relative sizes are

$$\begin{aligned} E_{ee} : E_{kin} : (-E_{Ne}) &= (-\tfrac{1}{3}E_{TF}-\zeta N):(-E_{TF}):(-\tfrac{7}{3}E_{TF}+\zeta N) \quad ; \\ &= 1 : 3 : 7 \quad \text{for } N = Z, \text{ when } \zeta = 0 \ . \end{aligned} \tag{2-238}$$

In words: the electron-electron energy of a neutral TF atom is one third of the kinetic energy and one seventh of the (negative of the) nucleus-electron energy.

For ions, there is less specific information in Eq.(226). It merely implies that $E_{TF}(Z,N)$ can be written in the form

$$E_{TF}(Z,N) = Z^{7/3} \times [\text{function of } \frac{N}{Z}] \quad . \tag{2-239}$$

This invites introducing a reduced binding energy, e(q), that is a function of q=1-N/Z, the degree of ionization:

$$E_{TF}(Z,N) = -\frac{Z^{7/3}}{a}\, e(q) \quad . \tag{2-240}$$

We know e(q) for q=o, i.e., N=Z :

$$e(o) = \frac{3}{7}B \quad , \tag{2-241}$$

which is simply Eq.(231). The factor multiplying e(q) in (240) is the same as the one in Eqs.(108) and (138). The maximum (minimum) property of the TF potential (density) functional is, therefore, here expressed as

$$\begin{aligned} &\{\frac{2}{5}\int_o^\infty dx\,\frac{[f(x)]^{5/2}}{x^{1/2}} + \frac{1}{2}\int_o^\infty dx[f'(x)+\frac{q}{x_o}]^2 + \frac{q(1-q)}{x_o}\} \\ &\qquad \geqq e(q) \geqq \\ &\qquad -\{\frac{3}{5}\int_o^\infty dx\; x^{1/3}[g'(x)]^{5/3} + g(o) + \frac{1}{2}\int_o^\infty dx[g(x)]^2\} \quad . \end{aligned} \tag{2-242}$$

The competing g(x)'s are hereby restricted by [Eq.(98)]

$$\int_o^\infty dx\; xg'(x) = 1-q \quad , \tag{2-243}$$

whereas

$$f(x=o) = 1 \quad . \tag{2-244}$$

The equal signs in (242) hold only for $g(x)=f'(x)+q/x_o$, when f(x) obeys Eqs.(59) and (60), which also determine x_o.

We can relate e(q) to $x_o(q)$ by recognizing that Eq.(225) says

$$\frac{\partial}{\partial N}\left(-\frac{Z^{7/3}}{a}\,e(q)\right) = \frac{Z^{4/3}}{a}\frac{d}{dq}\,e(q) = -\zeta = -\frac{Z^{4/3}}{a}\frac{q}{x_o(q)} \quad , \tag{2-245}$$

thus,

$$\frac{d}{dq}\,e(q) = -\frac{q}{x_o(q)} \quad . \tag{2-246}$$

Consequently,

$$e(q) = \frac{3}{7}B - \int_o^q dq'\,\frac{q'}{x_o(q')} \quad , \tag{2-247}$$

and

$$e(q) = \int_q^1 dq'\,\frac{q'}{x_o(q')} \quad , \tag{2-248}$$

of which the first one should be applied to weakly ionized systems ($N \lesssim Z$, $q \gtrsim o$), whereas the second one is designed for highly ionized atoms ($N << Z$, $q \lesssim 1$). In Eq.(248) the obvious statement

$$e(q=1) = o \tag{2-249}$$

has been used; it says: no electrons - no binding energy.

For ions, Eq.(229) gives

$$Z\frac{\partial}{\partial Z}E_{TF} = -Z\left(V+\zeta+\frac{Z}{r}\right)\Big|_{r=o} + \zeta Z = \frac{Z^{7/3}}{a}\left[f_q'(o) + \frac{q}{x_o}\right] \quad , \tag{2-250}$$

so that Eq.(226) translates into

$$7e(q) = 3\left[-f'_q(o) - \frac{q^2}{x_o(q)}\right] \quad . \tag{2-251}$$

By writing a subscript q we emphasize the q dependence of $f_q(x)$ and its initial slope $f_q'(o)$. The comparison of (251) with (247) results in

$$
\begin{aligned}
-f_q'(o) &= B + \frac{q^2}{x_o(q)} - \frac{7}{3}\int_o^q dq'\, \frac{q'}{x_o(q')} \\
&= B + \int_o^q dq'\, q'^{7/3} \frac{d}{dq'}\Big[\frac{1}{q'^{1/3} x_o(q')}\Big] \quad .
\end{aligned} \tag{2-252}
$$

The latter equality is verified by performing a partial integration. Since $-f_q'(o)$ increases with increasing q, we learn here that

$$\frac{d}{dq}[q^{1/3} x_o(q)] < o \quad . \tag{2-253}$$

We observe in these relations, that in studying ions the central quantity is $x_o(q)$. It is basically available from solving numerically the differential equation for $f_q(x)$, Eq.(59):

$$f''_q(x) = \frac{[f_q(x)]^{3/2}}{x^{1/2}} \tag{2-254}$$

with the boundary conditions (60):

$$f_q(o) = 1 \ , \quad f_q(x_o(q)) = o \ , \quad -x_o(q) f_q'(x_o(q)) = q \quad . \tag{2-255}$$

Nevertheless, in the two limiting situations $q \lesssim 1$ and $q \gtrsim o$ it is possible to make precise statements about the analytic dependence of $x_o(q)$ on 1-q(=N/Z), or, q, respectively. Let us first concentrate on highly ionized atoms, $q \lesssim 1$.

Highly ionized TF atoms. In the limit of extremely high ionization, $N/Z \rightarrow o$, the interelectronic interaction becomes insignificant as compared to the nucleus-electron interaction. In this situation V is simply the Coulomb potential -Z/r, and we are dealing with Bohr atoms, which have been studied in the first Chapter. We concluded already, in Eq.(46), that then

$$E_{TF}(Z,N) = -Z^2(\tfrac{3}{2}N)^{1/3} \quad \text{for} \quad N/Z \rightarrow o \quad . \tag{2-256}$$

As a statement about e(q) this reads

$$e(q) = a[\tfrac{3}{2}(1-q)]^{1/3} = \tfrac{3}{4}(\tfrac{\pi}{2})^{2/3}(1-q)^{1/3}$$

$$\text{for } q \to 1 \quad . \tag{2-257}$$

After employing Eq.(246) we find

$$x_o(q) = [\frac{16}{\pi}(1-q)]^{2/3} \quad \text{for} \quad q \to 1 \quad , \tag{2-258}$$

which is recognized to be Eq.(1-35) when $\zeta=(Z^{4/3}/a)(q/x_o)$, etc., is inserted there.

If N/Z is not that small, Eq.(257) and (258) acquire corrections that account for the repulsion among the electrons. A systematic treatment proceeds from noting that f(x) is not the best suited parametrization of the potential for the present purpose. It is advantageous to introduce another function $\phi(t)$ by means of[15]

$$V(r) + \zeta = -\frac{Z-N}{r}\phi(r/r_o) \quad , \tag{2-259}$$

or, recalling $\zeta = (Z-N)/r_o$ [Eq.(55)] ,

$$V + \zeta = -\zeta\frac{\phi(t)}{t} \quad , \quad t=r/r_o = x/x_o \quad . \tag{2-260}$$

Because of the great similarity between the definition of f(x) in (57) and the one of $\phi(t)$ in (259), the two functions are simply related to each other:

$$f(x) = q\,\phi(x/x_o) \quad , \quad \phi(t) = \frac{1}{q} f(tx_o) \quad . \tag{2-261}$$

Consequently, $\phi(t)$ obeys the differential equation

$$\phi''(t) = \lambda\frac{[\phi(t)]^{3/2}}{t^{1/2}} \quad , \tag{2-262}$$

and is subject to

$$\phi(o) = \frac{1}{q} \quad , \quad \phi(1) = o \quad , \quad \phi'(1) = -1 \quad , \tag{2-263}$$

where $\lambda=\lambda(q)$ is given by

$$\lambda(q) = q^{1/2}[x_o(q)]^{3/2} \quad . \tag{2-264}$$

As a consequence of (258), λ is small for $q \lesssim 1$:

$$\lambda \cong \frac{16}{\pi}(1-q) = \frac{16}{\pi}\,\frac{N}{Z} \quad \text{for} \quad \frac{N}{Z} = 1-q \gtrsim 0 \quad . \tag{2-265}$$

Why is it fitting to switch from f(x) to $\phi(t)$? The reason is that the appearance of λ in (262) offers the possibility of expanding $\phi(t)$ in powers of λ, whereby the smallness of λ promises a good convergence of the expansion.

The differential equation (262) and the boundary conditions at $t>1$ in (263) can be combined into the integral equation

$$\phi_\lambda(t) = 1 - t + \lambda \int_t^1 dt'\,(t'-t)\,\frac{[\phi_\lambda(t')]^{3/2}}{t'^{1/2}} \quad . \tag{2-266}$$

where we wrote $\phi_\lambda(t)$ in order to emphasize the λ dependence of ϕ. After solving this equation for a chosen λ, the corresponding value of q emerges from

$$\frac{1}{q} = \phi_\lambda(0) = 1 + \lambda \int_0^1 dt\; t^{1/2}[\phi_\lambda(t)]^{3/2} \quad . \tag{2-267}$$

In the first place, one obtains 1/q as a function of λ, from which $\lambda(q)$ is to be found in an additional step. Then Eq.(248), here in the form

$$e(q) = \int_q^1 dq'\,\frac{q'^{7/3}}{[\lambda(q')]^{2/3}} \quad , \tag{2-268}$$

supplies the desired e(q). The evaluation of this integral is eased by writing it as an integration over λ instead of q, since then $q(\lambda)$ enters, not $\lambda(q)$. The rewriting begins with

$$\begin{aligned} e(q) &= \int_{\lambda(q)}^{0} d\lambda'\,\frac{dq(\lambda')}{d\lambda'}\,\frac{[q(\lambda')]^{4/3}}{\lambda'^{2/3}} \\ &= \frac{3}{7}\int_0^{\lambda(q)} d\,\lambda'\;\lambda'^{-2/3}\,\frac{d}{d\lambda'}\left(1-[q(\lambda')]^{7/3}\right) \quad ; \end{aligned} \tag{2-269}$$

in view of this implication of Eq.(265) :

$$\lambda^{-2/3}\left(1-[q(\lambda)]^{7/3}\right) = \lambda^{-2/3}\left(1-[1-\tfrac{\pi}{16}\lambda+\ldots]^{7/3}\right) =$$

$$= \frac{7\pi}{48}\lambda^{1/3} + O(\lambda^{4/3}) \; ; \; = o \quad \text{for} \quad \lambda = o \quad , \tag{2-270}$$

a partial integration can be performed with the outcome

$$e(q) = \frac{3}{7}\,\frac{1-q^{7/3}}{[\lambda(q)]^{2/3}} + \frac{2}{7}\int_{o}^{\lambda(q)} d\lambda'\,\frac{1-[q(\lambda')]^{7/3}}{\lambda'^{5/3}} \quad . \tag{2-271}$$

An alternative expression makes use of (251); here it reads

$$e(q) = \frac{3}{7}\,\frac{q^{4/3}}{[\lambda(q)]^{2/3}}\,(-\phi'_\lambda(o)-q) \quad , \tag{2-272}$$

where

$$-\phi'_\lambda(o) = 1 + \lambda\int_{o}^{1} dt\,\frac{[\phi_\lambda(t)]^{3/2}}{t^{1/2}} \tag{2-273}$$

is the initial slope of $\phi_\lambda(t)$. Note that the equivalence of (271) and (272) allows to relate $\phi'_\lambda(o)$ to $\phi_\lambda(o) = 1/q(\lambda)$ [this is Eq.(267)]:

$$-\phi'_\lambda\;(o) = [\phi_\lambda(o)]^{4/3}\{1 + \frac{2}{3}\lambda^{2/3}\int_{o}^{\lambda} d\lambda'\,\frac{1-[\phi_{\lambda'}(o)]^{-7/3}}{\lambda'^{\,5/3}}\} \;, \tag{2-274}$$

which is a useful equation for checking against algebraic mistakes.

Let us now, indeed, expand $\phi_\lambda(t)$ in powers of λ,

$$\phi_\lambda(t) = 1 - t + \sum_{k=1}^{\infty}\lambda^k\,\phi_k(t) \quad . \tag{2-275}$$

This, inserted into (266), implies

$$\sum_{\ell=1}^{\infty}\lambda^\ell\phi_\ell(t) = \lambda\int_{t}^{1} dt'(t'-t)\;t'^{-1/2}[1-t'+\sum_{k=1}^{\infty}\lambda^k\;\phi_k(t')]^{3/2} . \tag{2-276}$$

The technique that produced the recurrence relation for the s_ℓ in Eq. (174) can be applied here, too. We find

$$\phi_1(t) = \int_{t}^{1} dt'(t'-t)t'^{-1/2}(1-t')^{3/2} \quad , \tag{2-277}$$

and

$$\phi_\ell(t) = \int_t^1 dt'(t'-t)t'^{-1/2} \sum_{j=1}^{\ell-1} \binom{3/2}{j} (1-t')^{3/2-j}$$

$$\times \sum_{k_1=1}^{\ell-j} \cdots \sum_{k_j=1}^{\ell-j} \phi_{k_1}(t') \cdots \phi_{k_j}(t') \delta_{\ell-1, k_1+\ldots+k_j} \tag{2-278}$$

$$\text{for} \quad \ell=2,\ 3,\ \ldots \quad .$$

The first few $\phi_\ell(t)$ can be expressed in terms of elementary functions; unfortunately, the degree of algebraic complexity increases rapidly. Let us, therefore, confine ourselves to explicitly stating only $\phi_1(t)$ as it emerges from (277) :

$$\phi_1(t) = (\tfrac{1}{8} - \tfrac{3}{4}t)\arccos(t^{1/2}) + (\tfrac{1}{8} + \tfrac{2}{3}t - \tfrac{1}{6}t^2)t^{1/2}(1-t)^{1/2}. \tag{2-279}$$

In particular, we have

$$\phi_1(o) = \int_o^1 dt\ t^{1/2}(1-t)^{3/2} = \frac{\pi}{16} \quad , \tag{2-280}$$

$$-\phi_1'(o) = \int_o^1 dt\ t^{-1/2}(1-t)^{3/2} = \frac{3\pi}{8} \quad .$$

Equation (279) is utilized in

$$\phi_2(o) = \frac{3}{2} \int_o^1 dt\ t^{1/2}(1-t)^{1/2}\ \phi_1(t) = \frac{2}{15} - \frac{3\pi^2}{256} \quad , \tag{2-281}$$

and

$$-\phi_2'(o) = \frac{3}{2} \int_o^1 dt\ t^{-1/2}(1-t)^{1/2}\ \phi_1(t) = \frac{1}{3} - \frac{3\pi^2}{256} \quad . \tag{2-282}$$

We are now prepared to employ Eq.(267) in order to find the leading corrections to (265), (257), and (258). From

$$\begin{aligned}\frac{1}{q} = \frac{1}{1-(1-q)} &= 1 + (1-q) + (1-q)^2 + \ldots \\ &= \phi_\lambda(o) = 1 + \phi_1(o)\lambda + \phi_2(o)\lambda^2 + \ldots \quad ,\end{aligned} \tag{2-283}$$

we get

$$\lambda(q) = \frac{1}{\phi_1(o)}\ (1-q)[1+(1-\frac{\phi_2(o)}{[\phi_1(o)]^2})(1-q)\ +\ \ldots\ ]$$

$$= \frac{16}{\pi}(1-q)[1+(4-\frac{512}{15\pi^2})(1-q)\ +\ \ldots\ ]\quad , \tag{2-284}$$

or

$$\lambda(q) = \frac{16}{\pi}\ \frac{N}{Z}\ [1+(4-\frac{512}{15\pi^2})\ \frac{N}{Z} + O((\frac{N}{Z})^2)]\quad \text{for } N/Z<<1\quad . \tag{2-285}$$

Then, using either one of the Eqs. (268), (269), or (271), we find

$$e(q) = \frac{3}{4}(\frac{\pi}{2})^{2/3}(1-q)^{1/3}[1-(1-\frac{256}{45\pi^2})(1-q)\ +\ \ldots\ ]$$

$$= \frac{3}{4}(\frac{\pi}{2})^{2/3}(\frac{N}{Z})^{1/3}[1-(1-\frac{256}{45\pi^2})\ \frac{N}{Z} + O((\frac{N}{Z})^2)]\quad . \tag{2-286}$$

Also, from (264) or (246),

$$x_o(q) = [\frac{16}{\pi}(1-q)]^{2/3}[1+(3-\frac{1024}{45\pi^2})(1-q)\ +\ \ldots\ ]$$

$$= (\frac{16}{\pi}\ \frac{N}{Z})^{2/3}[1+(3-\frac{1024}{45\pi^2})\ \frac{N}{Z} + O((\frac{N}{Z})^2)]\quad . \tag{2-287}$$

The numerical versions thereof are

$$\lambda = 5.093\ \frac{N}{Z}(1+0.5416\ \frac{N}{Z} + \ldots)\quad ,$$

$$e = 1.0135(\frac{N}{Z})^{1/3}(1-0.4236\ \frac{N}{Z} + ..)\quad , \tag{2-288}$$

$$x_o = 2.960(\frac{N}{Z})^{2/3}(1+0.6944\ \frac{N}{Z} + \ldots)\quad .$$

Here then is the modification of Eq. (46) that we promised at that time:

$$E_{TF}(Z,N) = -Z^2(\frac{3}{2}N)^{1/3}[1-(1-\frac{256}{45\pi^2})\frac{N}{Z} + \ldots] \tag{2-289}$$

for N<<Z ;

it is obtained by inserting (287) into (240).

A simple check of consistency is provided by (253). This states

$$\frac{d}{dq}\,\lambda(q) < 0 \quad , \tag{2-290}$$

or,

$$\frac{d}{d(N/Z)}\,\lambda(q=1-N/Z) > 0 \quad . \tag{2-291}$$

A quick look at (285) shows that this is true, indeed.

We close this section on highly ionized TF atoms with a discussion of the relative sizes of E_{kin}, E_{ee}, and E_{Ne}. In order to be able to apply Eq.(238), we need ζN. It is given by

$$\begin{aligned} \zeta N &= -N\frac{\partial}{\partial N}\,E_{TF}(Z,N) \\ &= \frac{1}{3}Z^2\left(\frac{3}{2}N\right)^{1/3}\left[1-\left(4-\frac{1024}{45\pi^2}\right)\frac{N}{Z}+\ldots\right] \quad , \end{aligned} \tag{2-292}$$

so that Eqs.(236) and (234) produce

$$\begin{aligned} E_{ee} &= -\frac{1}{3}E_{TF} - \zeta N \\ &= Z^2\left(\frac{3}{2}N\right)^{1/3}\left[\left(1-\frac{256}{45\pi^2}\right)\frac{N}{Z}+\ldots\right] \quad . \end{aligned} \tag{2-293}$$

The interaction energy of the electrons with the nucleus is given by [see Eq.(230)]

$$\begin{aligned} E_{Ne} &= Z\frac{\partial}{\partial Z}\,E_{TF}(Z,N) \\ &= -2Z^2\left(\frac{3}{2}N\right)^{1/3}\left[1-\left(\frac{1}{2}-\frac{128}{45\pi^2}\right)\frac{N}{Z}+\ldots\right] \quad , \end{aligned} \tag{2-294}$$

whereas the kinetic energy is simply the negative of E_{TF}, as is expressed in Eq.(235). Consequently,

$$\frac{E_{ee}}{-E_{Ne}} = \left(\frac{1}{2}-\frac{128}{45\pi^2}\right)\frac{N}{Z} + O\left(\left(\frac{N}{Z}\right)^2\right) \quad , \tag{2-295}$$

which states that E_{ee} is negligible in the limit of extremely high ionization. [We have already made use of this (physically obvious) fact repeatedly; see, for example, Eq. (256).] Together with the neutral-atom statement of (238), we have, therefore,

$$\frac{E_{ee}}{-E_{Ne}} = \begin{cases} 1/7 & \text{for} \quad N = Z \\ 0.2118\frac{N}{Z} & \text{for} \quad N \ll Z \end{cases} \quad . \tag{2-296}$$

Likewise, one obtains

$$\frac{E_{kin}}{-E_{Ne}} = \begin{cases} 3/7 & \text{for} \quad N = Z \\ \frac{1}{2}(1-0.2118\frac{N}{Z}) & \text{for} \quad N \ll Z \end{cases} \quad , \tag{2-297}$$

and

$$\frac{E_{ee}}{E_{kin}} = \begin{cases} 1/3 & \text{for} \quad N = Z \\ 0.4236\frac{N}{Z} & \text{for} \quad N \ll Z \end{cases} \quad . \tag{2-298}$$

Weakly ionized TF atoms. As λ increases, $\phi_\lambda(t)$ grows larger for all $t<1$, as is evident from Eq. (262), or Eq. (266). Thus $q=1/\phi_\lambda(o)$ decreases, finally reaching $q=o$ for the critical value

$$\Lambda = \lambda(q)\Big|_{q\to o} \quad . \tag{2-299}$$

Consequently,

$$\begin{aligned} x_o(q) &= q^{-1/3}[\lambda(q)]^{2/3} \\ &\cong \Lambda^{2/3}\, q^{-1/3} \quad \text{for} \quad q\to o \quad , \end{aligned} \tag{2-300}$$

so that Eq. (247) implies

$$e(q) \cong \frac{3}{7}B - \frac{3}{7}\Lambda^{-2/3}\, q^{7/3} \quad \text{for} \quad q\to o \quad . \tag{2-301}$$

Accordingly, we have in the limit of very weak ionization

$$E_{TF}(Z,N) \cong -\frac{3}{7}\frac{Z^{7/3}}{a}[B - \Lambda^{-2/3}\, q^{7/3}] =$$

$$= -\frac{3}{7}\frac{1}{a}[B\ Z^{7/3} - \Lambda^{-2/3}(Z-N)^{7/3}] \tag{2-302}$$

$$\text{for}\quad N \lesssim Z\ .$$

If we insert Eq.(301) into the inequalities of (242), suitably chosen trial functions f(x) and g(x) supply bounds on $\Lambda^{-2/3}$. Details are given in Problem 10, from where we cite

$$0.0946 < \Lambda^{-2/3} < 0.1008\ , \tag{2-303}$$

or,

$$\Lambda^{-2/3} = 0.0977 \pm 0.0031\ , \tag{2-304}$$

which tells us that $\Lambda^{-2/3}$ is about six percent of B. A weakly ionized TF atom has, therefore, practically the same binding energy that has the neutral atom. In other words: the outermost electrons contribute very little to the total binding energy of the atom.

In the limit $q\to o$, the relation between f(x) and $\phi(t)$ becomes singular. We cannot give sense to the right hand side of

$$f_q(x)\Big|_{q\to o} = F(x) = q\ \phi_{\lambda(q)}(x/x_o(q))\Big|_{q\to o} \tag{2-305}$$

[Eq.(261)], because $x_o(q\to\infty) = \infty$ squeezes $t=x/x_o(q)$ into an infinitesimal vicinity of $t=o$. There is, nevertheless, a sensible limit to $\phi_\lambda(t)$ as λ approaches Λ. We write $\Phi(t)$ for this $\phi_\Lambda(t)$. It obeys the differential equation

$$\Phi''(t) = \Lambda\ \frac{[\Phi(t)]^{3/2}}{t^{1/2}}\ , \tag{2-306}$$

and is subject to

$$\Phi(1) = o\ ,\quad \Phi'(1) = -1\ , \tag{2-307}$$

and

$$\Phi(t) \to \infty \quad \text{as} \quad t \to o\ . \tag{2-308}$$

Although $\Phi(t)$ is somehow corresponding to the situation of neutral TF atoms, the trouble of Eq.(305) signifies that it cannot be used as a parametrization of the potential V(r). Fortunately, there is still a use for Eqs.(306) through (308), in as much as they offer a simple and highly precise method for calculating Λ . Here is how it goes: $\Phi(t)$ possesses an expansion in powers of αt^{σ}, with a yet undetermined constant α and

$$\sigma = 7 + \gamma = \frac{1}{2}(7+\sqrt{73}) \quad , \qquad (2\text{-}309)$$

of the form

$$\Phi(t) = \frac{144/\Lambda^2}{t^3}[1-\alpha t^{\sigma} + \frac{9}{12+4\sigma^2}(\alpha t^{\sigma})^2 + \ldots] \quad , \qquad (2\text{-}310)$$

which is, of course, an immediate analog to Eqs.(180), (193), (192), and (190). The coefficients of the powers of αt^{σ} obey the recurrence relation (196) after replacing γ by σ. The (numerical) range of convergence of this series is $\alpha t^{\sigma} \lesssim 0.6$, or, anticipating that α is close to unity, $t \lesssim 0.94$. On the other hand, $\Phi(t)$ can also be expanded in powers of $(1-t)^{1/2}$,

$$\begin{aligned}\Phi(t) = (1-t) + \frac{4\Lambda}{35}(1-t)^{7/2} + \frac{2\Lambda}{63}(1-t)^{9/2} \\ + \frac{\Lambda}{66}(1-t)^{11/2} + \frac{\Lambda^2}{175}(1-t)^6 + \ldots \quad ,\end{aligned} \qquad (2\text{-}311)$$

this series being convergent for $(1-t)^{1/2} \lesssim 0.35$, or, $t \gtrsim 0.88$, when Λ is within the bounds of (303). There is a range of t around t=0.9 where both expansions are converging. This allows to determine Λ and α numerically by forcing the two expansions to agree within the accuracy to which they represent solutions to Eq.(306). Such a calculation[16] resulted in

$$\Lambda = 32.729416116173 \qquad (2\text{-}312)$$

and

$$\alpha = 1.0401806573862 \quad . \qquad (2\text{-}313)$$

Naturally, physics does not need this many decimals; they are reported only in order to demonstrate the marvelous precision of this simple method. Please note that one cannot compute B and ß in a similar way, because the expansions (164) and (193) converge for $x \lesssim 0.15$ and $x \gtrsim 30$, respectively. There is no overlap.

The Λ of (312) yields

$$\Lambda^{-2/3} = 0.0977330 \quad , \tag{2-314}$$

so that we obtain, from Eq.(302),

$$-E_{TF}(Z,N) \cong 0.768745\, Z^{7/3} - 0.047310(Z-N)^{7/3}$$

$$\text{for} \quad N \lesssim Z \quad . \tag{2-315}$$

The correction to the neutral atom binding energy is rather small; even for $N=Z/2$ it is only about one percent.

Since Λ is large, the series of Eq.(275) does not converge rapidly (if at all) for weakly ionized atoms, and the switching from $f(x)$ to $\phi(t)$ is pointless in this situation. Here we make use of the fact that the difference between $F(x)$ and $f_q(x)$ is small, when $q \gtrsim o$ and $x<x_o(q)$. In particular, $f_q'(o)$ does not differ significantly from $-B$, so that $f_q'(o)+B$ is a possibly useful expansion parameter. We use it in making the ansatz

$$f_q(x) = F(x) + \sum_{k=1}^{\infty} [f_q'(o) + B]^k \, f_k(x) \quad , \tag{2-316}$$

where the $f_k(x)$ are subject to

$$f_k(o) = o \quad \text{for} \quad k=1,2,\ldots \tag{2-317}$$

and

$$f_1'(o) = 1 \quad , \quad f_k'(o) = o \quad \text{for} \quad k=2,3,\ldots \quad . \tag{2-318}$$

To first order in $f_q'(o)+B$, the differential equation obeyed by $f_q(x)$ requires[17]

$$\left[\frac{d^2}{dx^2} - \frac{3}{2}\left[\frac{F(x)}{x}\right]^{1/2}\right] f_1(x) = o \quad . \tag{2-319}$$

One solution is

$$f_o(x) = F(x) + \frac{1}{3} x F'(x) = \frac{1}{3x^2} \frac{d}{dx}(x^3 F(x)) \quad , \tag{2-320}$$

because

$$\left[\frac{d^2}{dx^2} - \frac{3}{2}\left[\frac{F(x)}{x}\right]^{1/2}\right]\left[\frac{1}{3x^2}\frac{d}{dx}x^3\right]F(x)$$

$$= \left(\frac{1}{3x^2}\frac{d}{dx}x^3\right)\left[\frac{d^2}{dx^2} - \left[\frac{F(x)}{x}\right]^{1/2}\right]F(x) = o \quad . \tag{2-321}$$

However, inasmuch as

$$f_o(1) = 1 \quad , \quad f_o'(1) = -\frac{4}{3}B \quad , \tag{2-322}$$

$f_o(x)$ is not proportional to $f_1(x)$. The Wronskian of the differential equation (319) relates the two functions to each other:

$$f_o(x)\, f_1'(x) - f_o'(x)\, f_1(x) = 1 \quad . \tag{2-323}$$

This is equivalent to

$$\frac{d}{dx}\frac{f_1(x)}{f_o(x)} = [f_o(x)]^{-2} \quad , \tag{2-324}$$

which has the consequence

$$f_1(x) = f_o(x) \int_o^x \frac{dx'}{[f_o(x')]^2} \quad . \tag{2-325}$$

This does, indeed, satisfy the requirements $f_1(o)=o$ and $f_1'(o)=1$, so that we need not add a multiple of $f_o(x)$ on the right hand side.

For large x, we have

$$f_o(x) = \frac{1}{3x^2}\frac{d}{dx}[144\, G\,(y(x))] = \frac{(12)^2}{3x^2}\frac{d}{dx}[1-y(x) + \ldots]$$

$$\cong \frac{(12)^2}{3}\frac{\gamma y(x)}{x^3} = \frac{(12)^2}{3}\gamma\beta\, x^{-(\gamma+3)} \quad , \tag{2-326}$$

which uses Eqs.(180), (187), (184), and (192). This inserted into (323) or, equivalently, (326) produces

$$f_1(x) \cong \frac{1}{48\beta}\frac{1}{\gamma(\gamma+\sigma)}\, x^{\sigma-3} \quad \text{for large } x \tag{2-327}$$

$[\sigma = 7+\gamma$, Eq. (309)].

In deriving Eq. (319) the first order approximation $(1+\varepsilon)^{3/2} \cong 1+\frac{3}{2}\varepsilon$ has been used for $\varepsilon=[f'_q(o)+B]f_1(x)/F(x)$. Consequently,

$$f_q(x) \cong F(x) + [f'_q(o)+B]f_1(x) \qquad (2\text{-}328)$$

must not be applied to $x \cong x_o$, where $\varepsilon \cong -1$. We can, however, supplement (328) with

$$f_q(x) \cong q(1-\frac{x}{x_o}) \qquad (2\text{-}329)$$

which is valid for $x \cong x_o$: [This is obviously no more than the first term of Eq. (311) as it analogously appears in $\phi_\lambda(t)$]. Let us now join the two approximations for $f_q(x)$, Eqs. (328) and (329), at a certain $x=x_1$. The three unknown quantities $x_o(q)$, $x_1(q)$, and $f'_q(o)+B$ are determined from the requirement that $f_q(x)$ and its two first derivatives are continuous at $x=x_1$. This can be done explicitly in the limiting situation of very small q, since then both $x_o(q)$ and $x_1(q)$ are large, which allows to employ the large-x forms of $F(x)$ and $f_1(x)$. Thus, we have the three algebraic equations

$$\begin{aligned}
f_q:&\quad \frac{144}{x_1^3} + [f'_q(o)+B]\,\frac{x_1^{\sigma-3}}{48\beta\gamma(\gamma+\sigma)} = q(1-\frac{x_1}{x_o}) \quad ,\\
f'_q:&\quad -\frac{432}{x_1^4} + [f'_q(o)+B]\,\frac{(\sigma-3)x_1^{\sigma-4}}{48\beta\gamma(\gamma+\sigma)} = -q/x_o \quad , \qquad (2\text{-}330)\\
f''_q:&\quad \frac{(12)^3}{x_1^5} + [f'_q(o)+B]\,\frac{18\,x_1^{\sigma-5}}{48\beta\gamma(\gamma+\sigma)} = o \quad ;
\end{aligned}$$

the last one uses $(\sigma-3)(\sigma-4)=18$. These three equations imply

$$\frac{x_1}{x_o} = \frac{\sigma+3/2}{\sigma+2} = \frac{\gamma+17/2}{\gamma+9} = \frac{37+\sqrt{73}}{48} = 0.9488 \quad , \qquad (2\text{-}331)$$

and

$$x_o = \frac{\sigma+2}{\sigma+3/2}\,[96(\sigma+2)]^{1/3}\,q^{-1/3} = 10.32\,q^{-1/3} \quad , \qquad (2\text{-}332)$$

as well as

$$-f'_q(o) = B + \frac{1}{2}(96)^{-(\gamma+1)/3}\,\beta\gamma(\gamma+\sigma)(\sigma+2)^{-\sigma/3}\,q^{\sigma/3} =$$

$$= B + 8.05 \times 10^{-3}\, q^{2.59} \quad , \tag{2-333}$$

whereby identities like $\sigma=\gamma+7$ and $\gamma\sigma=6$ have been used. Of course, since these results are based upon the simple approximations (328) and (329) we should not take them too seriously. Nevertheless, their structure is certainly right. For instance, Eq.(332) says that the combination $q^{1/3}x_o(q)$ approaches a constant as $q\to o$. This much we know already - the constant is $\Lambda^{2/3}=10.2320$. The estimate for $\Lambda^{2/3}$ obtained in (332) differs from the actual value by less than one percent.

Something new is to be learned from Eq.(333). As a preparation, we differentiate Eq.(252) with respect to q:

$$\frac{d}{dq}[-f_q'(o)] = q^{7/3}\,\frac{d}{dq}\Big[\frac{1}{q^{1/3}x_o(q)}\Big] = q^{7/3}\,\frac{d}{dq}[\lambda(q)]^{-2/3} \quad ; \tag{2-334}$$

the latter equality is a consequence of the definition of $\lambda(q)$ in Eq.(264). Now Eq.(333) implies that

$$q\,\frac{d}{dq}[\lambda(q)]^{-2/3} \sim q^{(\sigma-7)/3} = q^{\gamma/3} \quad . \tag{2-335}$$

We infer that

$$\lambda(q) = \Lambda\,[1+(\text{powers of } q^{\gamma/3})] \tag{2-336}$$

for values of q not too large. Then, of course,

$$x_o(q) = \Lambda^{2/3}\,q^{-1/3}[1+(\text{powers of } q^{\gamma/3})] \quad , \tag{2-337}$$

and

$$e(q) = \frac{3}{7}B - \frac{3}{7}\,\Lambda^{-2/3}\,q^{7/3}[1+e_1q^{\gamma/3} + e_2q^{2\gamma/3} + \ldots] \quad , \tag{2-338}$$

which is an implication of (337) when it is inserted into Eq.(247). The challenge consists in calculating the coefficients e_1, e_2, ..., which determine the corresponding coefficients in (336) and (337). In particular, Eq.(246) supplies

$$x_o(q) = \Lambda^{2/3}\,q^{-1/3}[1+\frac{\sigma}{7}e_1q^{\gamma/3}+\frac{\sigma+\gamma}{7}e_2q^{2\gamma/3}+\ldots]^{-1} = \tag{2-339}$$

$$= \Lambda^{2/3}\, q^{-1/3}[1 - \tfrac{\sigma}{7}e_1 q^{\gamma/3} + ((\tfrac{\sigma}{7}e_1)^2 - \tfrac{\sigma+\gamma}{7}e_2)q^{2\gamma/3} + \ldots] \ .$$

Then

$$\lambda(q) = [q^{1/3}x_o(q)]^{3/2} \tag{2-340}$$

$$= \Lambda[1 - \tfrac{3\sigma}{14}e_1\, q^{\gamma/3} + \tfrac{3}{2}(\tfrac{5}{4}(\tfrac{\sigma}{7}e_1)^2 - \tfrac{\sigma+\gamma}{7}e_2)q^{2\gamma/3} + \ldots] \ ,$$

and from combining (251) and (246) with (338)

$$-f_q'(o) = \tfrac{7}{3}e(q) + \frac{q^2}{x_o(q)} = (\tfrac{7}{3} - q\tfrac{d}{dq})e(q) \tag{2-341}$$

$$= -q^{10/3}\,\frac{d}{dq}[q^{-7/3}\ e(q)]$$

$$= q^{10/3}\,\frac{d}{dq}(-\tfrac{3}{7}B\, q^{-7/3} + \tfrac{3}{7}\,\Lambda^{-2/3}[1+e_1q^{\gamma/3}+e_2q^{2\gamma/3}+\ldots]),$$

or,

$$-f_q'(o) = B + \tfrac{\gamma}{7}\,\Lambda^{-2/3}\,q^{\sigma/3}[e_1 + 2e_2\, q^{\gamma/3} + \ldots] \ . \tag{2-342}$$

The comparison with (333) yields a first estimate for e_1:

$$e_1 \cong 0.75 \ , \tag{2-343}$$

which, in view of the crudeness of the approximation used in arriving at (333), cannot be expected to have more significance than stating the order of magnitude. (We shall see below that the actual value is about ten percent larger.)

A systematic computation of e_1, e_2, ... starts from the expansion (316). Comparing powers of $f_q'(o)+B$ in the differential equation obeyed by $f_q(x)$ produces

$$f_\ell''(x) = \sum_{j=1}^{\ell}\binom{3/2}{j}\frac{[F(x)]^{3/2-j}}{x^{1/2}}\sum_{k_1=1}^{\ell-j+1}\cdots\sum_{k_j=1}^{\ell-j+1}f_{k_1}(x)\ldots$$

$$\times\ldots f_{k_j}(x)\,\delta_{\ell,k_1+\ldots+k_j} \ . \tag{2-344}$$

The $j=1$ term on the right hand side is brought over to the left, so that

$$\left[\frac{d^2}{dx^2} - \frac{3}{2}\sqrt{F(x)/x}\right] f_\ell(x) = \sum_{j=2}^{\ell} \binom{3/2}{j} \frac{[F(x)]^{3/2-j}}{x^{1/2}} \sum_{k_1=1}^{\ell-j+1} \cdots \sum_{k_j=1}^{\ell-j+1} f_{k_1}(x) \cdots \times \cdots f_{k_j}(x)\,\delta_{\ell,k_1+\cdots+k_j} \quad . \qquad (2\text{-}345)$$

This right hand side contains $f_1(x)$, ..., $f_{\ell-1}(x)$ but not $f_\ell(x)$. The solutions to the corresponding homogeneous differential equation are $f_0(x)$ and $f_1(x)$, given in Eqs. (320) and (325). With their aid we can construct Green's function $G(x,x')$ which satisfies

$$\left[\frac{d^2}{dx^2} - \frac{3}{2}\sqrt{F(x)/x}\right] G(x,x') = \delta(x-x') \quad ,$$
$$G(x,x') = 0 \quad \text{and} \quad \frac{\partial}{\partial x} G(x,x') = 0 \quad \text{for} \quad x=0 \quad . \qquad (2\text{-}346)$$

It is given by

$$G(x,x') = [f_0(x')f_1(x) - f_0(x)f_1(x')]\,\eta(x-x') \quad . \qquad (2\text{-}347)$$

Thus

$$f_\ell(x) = \int_0^x dx' \, [f_0(x')f_1(x) - f_0(x)f_1(x')] \times \left[\left(\frac{d^2}{dx'^2} - \frac{3}{2}\sqrt{F(x')/x'}\right) f_\ell(x')\right] \quad , \qquad (2\text{-}348)$$

where we refrained from explicitly inserting the right hand side of (345).

The use of Eq. (348) does not lie primarily in explicitly calculating $f_2(x)$, $f_3(x)$, etc. but in studying their structure. Recall that $F(x)$ can be written as

$$F(x) = \frac{144}{x^3}\, G(y(x)) = \frac{144}{x^3}\left[1 + \sum_{k=1}^{\infty} c_k [y(x)^k]\right] \qquad (2\text{-}349)$$

which is repeating Eqs. (180) and (193). As a consequence, $f_o(x)$ has the form

$$f_o(x) = \frac{144}{x^3}\,\frac{1}{3}\,\gamma\, y(x)\,[1+(\text{powers of } y(x))] \quad . \tag{2-350}$$

Inserted into (325) this implies

$$f_1(x) = \frac{144}{x^3}\,\frac{3}{(12)^4}\,\frac{1}{\beta\gamma(\gamma+\sigma)}\,x^\sigma\,[1+(\text{powers of } y(x))] \quad , \tag{2-351}$$

of which we have seen the leading term in (327). Now we employ the recurrence formula (348) to conclude that

$$f_\ell(x) = \frac{144}{x^3}\left[-\frac{3}{(12)^4}\,\frac{1}{\beta\gamma(\gamma+\sigma)}\,x^\sigma\right]^\ell d_\ell\,[1+(\text{powers of } y(x))] \quad , \tag{2-352}$$

where the constants d_ℓ obey

$$d_1 = -1 \tag{2-353}$$

and

$$d_\ell = \frac{2\gamma}{(\ell\sigma+\gamma)(\ell-1)} \sum_{j=2}^{\ell} \binom{3/2}{j} \sum_{k_1=1}^{\ell-j+1} \cdots \sum_{k_j=1}^{\ell-j+1} d_{k_1}\cdots d_{k_j}\,\delta_{\ell,k_1+\ldots+k_j} \quad . \tag{2-354}$$

This we recognize to be the recursion for the c_k of Eq. (196), after γ and σ are interchanged. Consequently, the d_ℓ's are the coefficients that appear in the expansion of Eq. (310). That is

$$\Phi(t) = \frac{144/\lambda_o^2}{t^3}\,[\,1+\sum_{k=1}^{\infty} d_k\,(\alpha\, t^\sigma)^k\,] \quad . \tag{2-355}$$

This connection between the $f_\ell(x)$'s and $\Phi(t)$, which is, of course, not accidental, is the clue to computing e_1, e_2, ... of Eq. (338). We reveal its significance by inserting Eqs. (349) and (352) into the ansatz (316),

$$f_q(x) = \frac{144}{x^3}[1+\sum_{k=1}^{\infty}(-[f_q'(0)+B]\frac{3}{(12)^4}\,\frac{[x_o(q)]^\sigma}{\beta\gamma(\gamma+\sigma)})^k\,(\frac{x}{x_o(q)})^{k\sigma} d_k] +$$

$$+\ldots \quad , \qquad (2\text{-}356)$$

where the ellipsis indicates the terms containing "powers of $y(x)$." After introducing h_q by

$$-f_q'(0) = B + \tfrac{1}{3}(12)^4\alpha\beta\gamma(\gamma+\sigma)[h_q/x_0(q)]^\sigma \quad , \qquad (2\text{-}357)$$

Eq.(355) is employed:

$$f_q(x) = \frac{144}{x^3}\left[1+\sum_{k=1}^{\infty} d_k\left(\alpha\left[h_q\frac{x}{x_0(q)}\right]^\sigma\right)^k\right]$$

$$+\ldots \qquad (2\text{-}358)$$

$$= q\left[\frac{\Lambda}{\lambda(q)}\right]^2 h_q^3\, \Phi\left(h_q\frac{x}{x_0(q)}\right) + \ldots \quad ,$$

where $[\lambda(q)]^2 = q[x_0(q)]^3$ is used. What is exhibited in (358) is the part of $f_q(x)$ that goes with the zeroth power of $y(x)$. Likewise, an arbitrary power of $y(x)$, say $[y(x)]^m$ contributes

$$[y(x)]^m\,\frac{144}{x^3}\left[c_m + (\text{powers of } \alpha(h_q x/x_0(q))^\sigma)\right]$$

$$\equiv q\left[\frac{\Lambda}{\lambda(q)}\right]^2 h_q\, c_m[y(x)]^m\, \psi_m\left(h_q\frac{x}{x_0(q)}\right) \qquad (2\text{-}359)$$

to $f_q(x)$. The functions $\psi_m(t)$ thus defined are such that

$$\psi_m(t) = \frac{144/\Lambda^2}{t^3}\left[1 + (\text{powers of } \alpha t^\sigma)\right] \quad . \qquad (2\text{-}360)$$

We can now make explicit what supplements Eq.(358):

$$f_q(x) = q\left[\frac{\Lambda}{\lambda(q)}\right]^2 h_q^3\left[\Phi\left(h_q\frac{x}{x_0(q)}\right) + \sum_{m=1}^{\infty} c_m[y(x)]^m\,\psi_m\left(h_q\frac{x}{x_0(q)}\right)\right]$$

$$(2\text{-}361).$$

Whereas (316) is an expansion that is expected to converge rapidly for x not too close to $x_0(q)$, the series of (361) is the faster convergent the smaller $y(x)$ is. This identifies large values of x (i.e., $x \lesssim x_0$) as the domain of application.

It is instructive to make contact with the original definition of $\Phi(t)$,

$$\Phi(t) = \phi_{\lambda(q)}(t)\Big|_{q\to o} = \frac{1}{q}\, f_q(tx_o(q))\Big|_{q\to o} \qquad (2\text{-}362)$$

[see the comment to Eq.(305)]. Since

$$y(tx_o(q))\Big|_{q\to o} = \beta(tx_o(q))^{-\gamma}\Big|_{q\to o} = o \quad , \qquad (2\text{-}363)$$

the combination of Eqs.(361) and (362) reads

$$\Phi(t) = h_q^3\, \Phi(h_q t)\Big|_{q\to o} \quad , \qquad (2\text{-}364)$$

from which we learn that

$$h_q\Big|_{q\to o} = 1 \ . \qquad (2\text{-}365)$$

This tells us what e_1 is. Equations (342) and (357) together say

$$\begin{aligned} e_1 + 2e_2\, q^{\gamma/3} + \ldots &= -[f_q'(o)+B]\, \frac{7}{\gamma}\, \Lambda^{2/3}\, q^{-\sigma/3} \\ &= \frac{7}{3}(12)^4 \alpha\beta(\gamma+\sigma)\, \Lambda^{2/3} \left[\frac{h_q}{q^{1/3}x_o(q)}\right]^{\sigma} \quad , \end{aligned} \qquad (2\text{-}366)$$

or, after making use of $q^{1/3}x_o(q)=[\lambda(q)]^{2/3}$,

$$e_1 + 2e_2\, q^{\gamma/3} + \ldots = \frac{7}{3}\left(\frac{12}{\Lambda}\right)^4 \alpha\beta(\gamma+\sigma)\, \Lambda^{-2\gamma/3} \left(h_q\left[\frac{\Lambda}{\lambda(q)}\right]^{2/3}\right)^{\sigma} \ . \qquad (2\text{-}367)$$

Now the limit $q\to o$ identifies

$$e_1 = \frac{7}{3}\left(\frac{12}{\Lambda}\right)^4 \alpha\beta(\gamma+\sigma)\, \Lambda^{-2\gamma/3} \quad . \qquad (2\text{-}368)$$

With α, β, and Λ from (313), (204), and (312), respectively, the numerical value of e_1 is roughly 10% larger than the estimate of (343):

$$e_1 = 0.825908 \quad . \tag{2-369}$$

Note that Eq.(368) reveals the physical significance of α and β; that of B and Λ has been clear since Eqs.(67) and (301).

The requirement $f_q(x=x_o(q))=o$ relates h_q to $y_o(q)$, given by

$$\begin{aligned} y_o(q) &\equiv y(x_o(q)) = \beta[x_o(q)]^{-\gamma} \\ &= \beta\Lambda^{-2\gamma/3}\, q^{\gamma/3}[\frac{\Lambda}{\lambda(q)}]^{2\gamma/3} \quad , \end{aligned} \tag{2-370}$$

inasmuch as $x = x_o(q)$ in Eq.(361) yields

$$\Phi(h_q) + \sum_{m=1}^{\infty} c_m[y_o(q)]^m\, \psi_m(h_q) = o. \tag{2-371}$$

With the aid of $\Phi'(1) = -1$ [which is Eq.(307)], we find to first order in $y_o(q)$, or, $q^{\gamma/3}$, respectively:

$$\begin{aligned} h_q &= 1 + c_1\, y_o(q)\, \psi_1(1) + \mathcal{O}(y_o(q))^2) \\ &= 1 - \beta\, \Lambda^{-2\gamma/3}\, \psi_1(1)q^{\gamma/3} + \mathcal{O}(q^{2\gamma/3}) \quad , \end{aligned} \tag{2-372}$$

where $c_1 = -1$ has been used. In conjunction with Eq.(340) this has the consequence

$$\begin{aligned} (h_q[\frac{\Lambda}{\lambda(q)}]^{2/3})^{\sigma} &= (1+(\frac{\sigma}{7}e_1 - \beta\Lambda^{-2\gamma/3}\, \psi_1(1))q^{\gamma/3} + \ldots)^{\sigma} \\ &= 1 + \sigma(\frac{\sigma}{7}e_1 - \beta\Lambda^{-2\gamma/3}\, \psi_1(1))q^{\gamma/3} + \ldots \quad , \end{aligned} \tag{2-373}$$

so that the order $q^{\gamma/3}$ in Eq.(367) is

$$2e_2 = \sigma e_1(\frac{\sigma}{7}e_1 - \beta\Lambda^{-2\gamma/3}\, \psi_1(1)) \quad . \tag{2-374}$$

To proceed further, we need to know $\psi_1(1)$.

The insertion of Eq.(361) into the differential equation obeyed by $f_q(x)$ produces

$$[\frac{d^2}{dt^2} - \frac{3}{2}\, \Lambda\sqrt{\Phi(t)/t}]\, t^{-\gamma}\, \psi_1(t) = o \quad , \tag{2-375}$$

when terms linear in y(x) are identified. This is quite analogous to Eq.(319), so that

$$\psi_o(t) \equiv t^\gamma[\Phi(t)+\frac{1}{3}t\ \Phi'(t)] \tag{2-376}$$

is one solution of (375), the one corresponding to $f_o(x)$ of (320). The Wronskian of $\psi_1(t)$ with $\psi_o(t)$ is

$$\psi_o(t)\psi_1'(t) - \psi_o'(t)\psi_1(t) = \frac{1}{3}(\frac{12}{\Lambda})^4\alpha\sigma(\sigma+\gamma)t^{2\gamma} \quad , \tag{2-377}$$

which makes use of Eq.(360) and the small t form of $\psi_o(t)$,

$$\begin{aligned}\psi_o(t) &= t^\gamma \frac{1}{3t^2}\frac{d}{dt}(t^3\Phi(t)) \\ &= \frac{1}{3}t^{-(2-\gamma)}(\frac{12}{\Lambda})^2\frac{d}{dt}[1-\alpha t^\sigma+d_2(\alpha t^\sigma)^2+...] \\ &= -\frac{1}{3}(\frac{12}{\Lambda})^2\alpha\sigma t^{\sigma+\gamma-3}[1-2d_2\alpha t^\sigma+..] \quad .\end{aligned} \tag{2-378}$$

Equation (377) now implies

$$\psi_1(t) = \psi_o(t)[\psi_1(1)/\psi_o(1) - \frac{1}{3}(\frac{12}{\Lambda})^4\alpha\sigma(\sigma+\gamma)\int_t^1 dt'(\frac{t'^\gamma}{\psi_o(t')})^2] \quad , \tag{2-379}$$

where $\psi_1(1)$ is determined by the t→o form of $\psi_1(t)$, statet in Eq.(360). In connection with (378) this requires that the square brackets in (379) possess the form

$$\begin{aligned}&-\frac{3}{\alpha\sigma}t^{-(\sigma+\gamma)}[1+\text{(powers of }\alpha t^\sigma)] \\ &= \psi_1(1)/\psi_o(1) - \frac{3}{\alpha\sigma}(\sigma+\gamma)\int_t^1 dt'[-\frac{1}{3}(\frac{12}{\Lambda})^2\alpha\sigma\frac{t'^\gamma}{\psi_o(t')}]^2 \\ &= \psi_1(1)/\psi_o(1) - \frac{3}{\alpha\sigma}(\sigma+\gamma)\int_t^1 dt'\ t^{-2(\sigma-3)}(1+4d_2\alpha t^\sigma) \\ &\quad - \frac{3}{\alpha\sigma}(\sigma+\gamma)\int_t^1 dt'\{[-\frac{1}{3}(\frac{12}{\Lambda})^2\alpha\sigma\frac{t'^\gamma}{\psi_o(t')}]^2 - t^{-2(\sigma-3)}(1+4d_2\alpha t^\sigma)\}.\end{aligned} \tag{2-380}$$

In the latter version, the second integral is no longer singular at t=o, since the integrand has the structure

$$\{\ \ldots\} = \alpha^2 t'^6 [\text{const.} + (\text{powers of } \alpha t^\sigma)] \quad , \tag{2-381}$$

which integrates to

$$\int_t^1 dt' \ \{\ \ldots\} = \int_o^1 dt' \ \{\ \ldots\} + \alpha^2 t^7 [\text{const.} + (\text{powers of } \alpha t^\sigma)]$$

$$= \int_o^1 dt' \ \{\ldots\} + t^{-(\sigma+\gamma)} (\alpha t^\sigma)^2 [\text{const.} + (\text{powers of } \alpha t^\sigma)] \ . \tag{2-382}$$

The first integral in (380) is

$$-\frac{3}{\alpha\sigma}(\sigma+\gamma)\left[\frac{1-t^{7-2\sigma}}{7-2\sigma} + 4d_2\alpha\,\frac{1-t^{7-\sigma}}{7-\sigma}\right] \tag{2-383}$$

$$= \frac{3}{\alpha\sigma}\left(1+4d_2\,\frac{\sigma+\gamma}{\gamma}\,\alpha\right) - \frac{3}{\alpha\sigma}\,t^{-(\sigma+\gamma)}\left(1+4d_2\,\frac{\sigma+\gamma}{\gamma}\,\alpha t^\sigma\right) \quad .$$

The consequence of (380) is therefore

$$\psi_1(1)/\psi_o(1) + \frac{3}{\alpha\sigma}\left(1+4d_2\,\frac{\sigma+\gamma}{\gamma}\,\alpha\right)$$

$$-\frac{3}{\alpha\sigma}(\sigma+\gamma)\int_o^1 dt\left\{\left[-\frac{1}{3}\left(\frac{12}{\Lambda}\right)^2\alpha\sigma\,\frac{t^\gamma}{\psi_o(t)}\right]^2 - \frac{1+4d_2\alpha t^\sigma}{t^{\sigma+\gamma+1}}\right\} = o \quad . \tag{2-384}$$

With the aid of $\psi_o(1) = -1/3$ and, from (310) or (354),

$$d_2 = \frac{9}{12+4\sigma^2} = \frac{9/2}{\sigma(2\sigma+\gamma)} = \frac{3}{4}\,\frac{\gamma}{2\sigma+\gamma} \quad , \tag{2-385}$$

this says

$$\psi_1(1) = \frac{1}{\alpha\sigma}\left(1+3\,\frac{\sigma+\gamma}{2\sigma+\gamma}\,\alpha\right)$$

$$+\frac{\sigma+\gamma}{\alpha\sigma}\int_o^1 dt\left\{\frac{1+3\frac{\sigma+\gamma}{2\sigma+\gamma}\alpha t^\sigma}{t^{\sigma+\gamma-1}} - \left[\frac{1}{3}\left(\frac{12}{x_o}\right)^2\alpha\sigma\,\frac{t^\gamma}{\psi_o(t)}\right]^2\right\} \ . \tag{2-386}$$

This expression does not lend itself to further algebraic simplifications.

The numerical value of $\psi_1(1)$, obtained by a method analogous to the one that produced Λ and α in Eqs. (312) and (313), is

$$\psi_1(1) = 0.3216868353717 \quad , \tag{2-387}$$

which illustrates once more the high precision of the algorithm. The Wronskian (377), at t=1, is employed in finding

$$\begin{aligned}\psi_1'(1) &= (4+\gamma)\psi_1(1) - (\frac{12}{\Lambda})^4 \alpha\sigma(\sigma+\gamma) \\ &= 0.2869164052321 \quad ,\end{aligned} \tag{2-388}$$

whereas the differential equation (375) supplies

$$\begin{aligned}\psi_1''(1) &= 2\gamma\psi_1'(1) - \gamma(\gamma+1)\psi_1(1) \\ &= 0.002936027410 \quad .\end{aligned} \tag{2-389}$$

The algebraic statements of (388) and (389) can be combined into

$$\psi_1(1) = 2(\frac{12}{\Lambda})^4 \alpha(\sigma+\gamma) + \frac{1}{6}\psi_1''(1) \quad , \tag{2-390}$$

where, because of the smallness of $\psi_1''(1)$, the latter part is only about 0.15% of the sum. In conjunction with Eq. (368), this implies

$$\beta\Lambda^{-2\gamma/3}\psi_1(1) = \frac{6}{7}e_1 + \frac{1}{6}\beta\Lambda^{-2\gamma/3}\psi_1''(1) \quad , \tag{2-391}$$

which we insert into (374) to find

$$e_2 = \frac{\sigma+6}{14} e_1^2 [1 - \frac{1}{\sigma-6} \frac{\psi_1''(1)}{2(\frac{12}{\Lambda})^4 \alpha(\sigma+\gamma)}] \quad ; \tag{2-392}$$

here, the $\psi_1''(1)$ term represents a 0.5% correction to

$$e_2 \cong \frac{\sigma+6}{14} e_1^2 = 0.671015 \quad , \tag{2-393}$$

resulting in

$$e_2 = 0.667554 \quad . \tag{2-394}$$

Naturally, the subsequent coefficients in (338) can be computed the same way.

The results of this section are summarized in

$$-E_{TF}(Z,N) = 0.768745\ Z^{7/3}$$
$$-0.047310(Z-N)^{7/3}[1+0.825908(1-N/Z)^{0.257334}$$
$$+0.667554(1-N/Z)^{0.514668}$$
$$+\ldots] \quad , \qquad (2\text{-}395)$$

which is the weak-ionization analog to the high-ionization result of Eq.(289)[and its supplement of Problem 7].

One last remark is in order. How could we get around without making explicit use of the requirement $-x_o(q)f_q'(x_o(q)) = q$? As applied to (361) it reads

$$h_q\Phi'(h_q) + \sum_{m=1}^{\infty} c_m[y_o(q)]^m[h_q\psi_m'(h_q) - \gamma m\,\psi_m(h_q)]$$
$$= -\left[\frac{\lambda(q)}{\Lambda}\right]^2 h_q^{-3} \quad . \qquad (2\text{-}396)$$

Indeed, this together with (371) gives $\lambda(q)$ as a function of $y_o(q)$, which can be converted into $\lambda(q)$ as a function of q, whereafter Eq.(340) identifies e_1, e_2, etc. Fortunately, we came to know the relation between $f_q'(o)$ and h_q in Eq.(356), so that we could avoid the more tedious (though, of course, equivalent) procedure based upon Eq.(396).

Arbitrarily ionized TF atoms. We have spent some time on studying the analytic form of such quantities like e(q), $x_o(q)$, and $-f_q'(o)$ as functions of q - both for $q\lesssim 1$ and for $q\gtrsim o$, which are the situations of highly and weakly ionized atoms, respectively. These considerations, however, did not tell us how good are few-terms approximations as in Eqs. (289) and (395). Let us, therefore, make the comparison with the results of numerical integrations of the differential equation obeyed by $f_q(x)$ for various values of q.

We present in Table 2 the outcome of such calculations for the nineteen q values 0.95,0.90,...,0.05 , supplemented by what we know for q=1 and q=o. The fractional binding energy

$$e(q)/e(o) = E_{TF}(Z,N)/E_{TF}(Z,Z) \qquad (2\text{-}397)$$

is additionally plotted, as a function of q, in Fig.4. We observe that

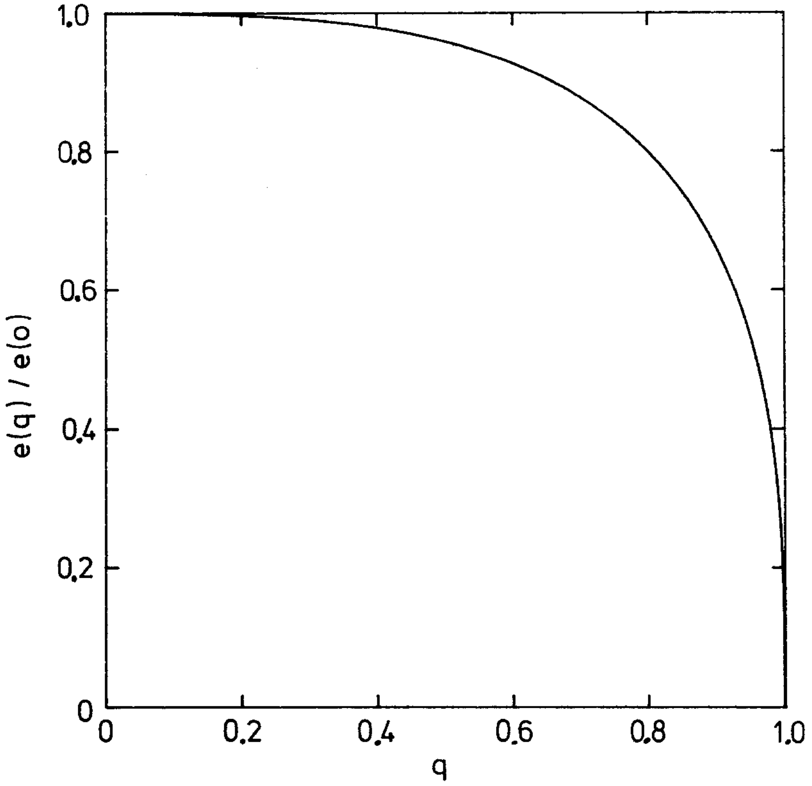

Fig.2-4. The fractional binding energy e(q)/e(o) *as a function of* q.

removing 30% of the electrons from the neutral atom, reduces the binding energy only by 1%; a reduction by 10% requires the removal of 65% of the electrons. Even when only 5% of the electrons are left, the binding energy is still more than 50% of the neutral-atom one. Here is the quantitative version of the qualitative remark that the innermost electrons contribute most to the binding energy, the outermost least.

From Eq.(286), (241) and Problem 7 we find that, for N<<Z,

$$\frac{e(q)/e(o)}{1.489(N/Z)^{1/3}} = 1 - 0.4236\,\frac{N}{Z} + 0.0909\left(\frac{N}{Z}\right)^2 + \dots \quad . \qquad (2\text{-}398)$$

The successive approximations that this represents are compared to the

Table 2-2. TF quantities $x_o(q)$, $-f_q'(o)$, and $e(q)/e(o)$ for N/Z= 1-q = 0, 0.05, ..., 1.

N/Z	$x_o(q)$	$-f_q'(o)$	e(q)/e(o)
0	0	∞	0
0.05	0.416269	3.020996	0.537084
0.10	0.685790	2.233243	0.662517
0.15	0.934348	1.952470	0.742539
0.20	1.179253	1.813524	0.800221
0.25	1.428919	1.734116	0.844082
0.30	1.689292	1.684993	0.878380
0.35	1.965691	1.653119	0.905616
0.40	2.263681	1.631819	0.927406
0.45	2.589715	1.617337	0.944875
0.50	2.951825	1.607410	0.958847
0.55	3.360561	1.600602	0.969946
0.60	3.830452	1.595965	0.978668
0.65	4.382486	1.592853	0.985410
0.70	5.048683	1.590815	0.990503
0.75	5.881272	1.589530	0.994227
0.80	6.973385	1.588763	0.996824
0.85	8.513784	1.588345	0.998508
0.90	10.92728	1.588149	0.999475
0.95	16.10273	1.588081	0.999908
1	∞	B=1.588071	1

actual values in Fig.2-5. We see that the quadratic approximation reproduces the actual data almost perfectly even for $N \lesssim Z$. [Incidentally, the inclusion of the next term, $0.0024369(N/Z)^3$,[18] would make the deviation unrecognizable in Fig.5.]

In contrast, the performance of the weak ionization expansion [Eqs.(338), (369), and (394)],

$$\frac{1-e(q)/e(o)}{0.06154q^{7/3}} = 1 + 0.8259\, q^{\gamma/3} + 0.6676\, q^{2\gamma/3} + \dots \quad ,(2\text{-}399)$$

is significantly worse; see Fig.6. Obviously, the coefficients in this expansions do not get small as rapidly as the ones in (398). One needs a few more terms in (399) for a high quality approximation over a large

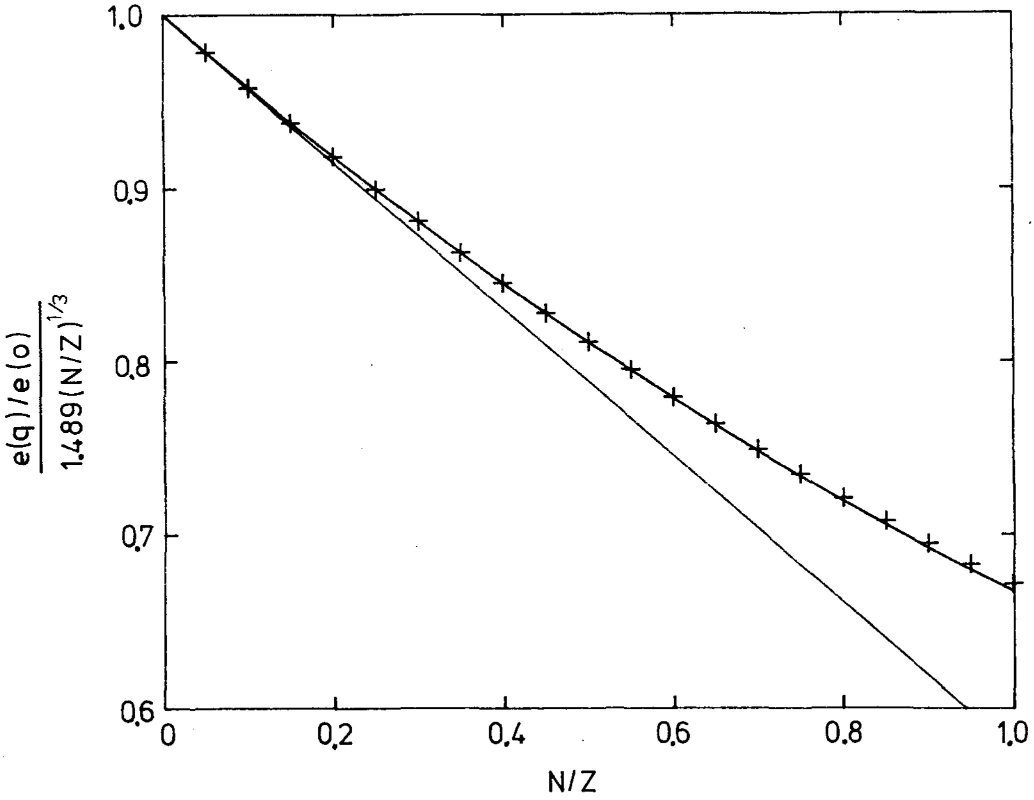

Fig.2-5. Comparison of the linear and quadratic approximations of Eq.(398) with the actual numbers (crosses).

range of $q^{\gamma/3}$. At this time, only the numerical value of $e_3 = 0.550086$ has been calculated[19], whereas e_4, e_5, ... are not known as yet. This value for e_3 leads to the dashed curve in Fig.6.

Validity of the TF model. The detailed discussion of the TF model, which touched upon all its important aspects, has made us familiar with the properties of TF atoms. In order to improve the description we must now find out what the deficiencies of the model are.

The approximations that define the model are those which brought us from Eq.(40) to Eq.(41). They are: (i) the (highly) semiclassical evaluation of the trace in E_{IP} according to the recipy of Eq.(1-43); and (ii) the disregard of electron-electron interactions except for the (direct) electrostatic one (in particular, we did not care for the exchange energy). Of the two, the first one is the more serious one, because it leads to an incorrect treatment of the most strongly

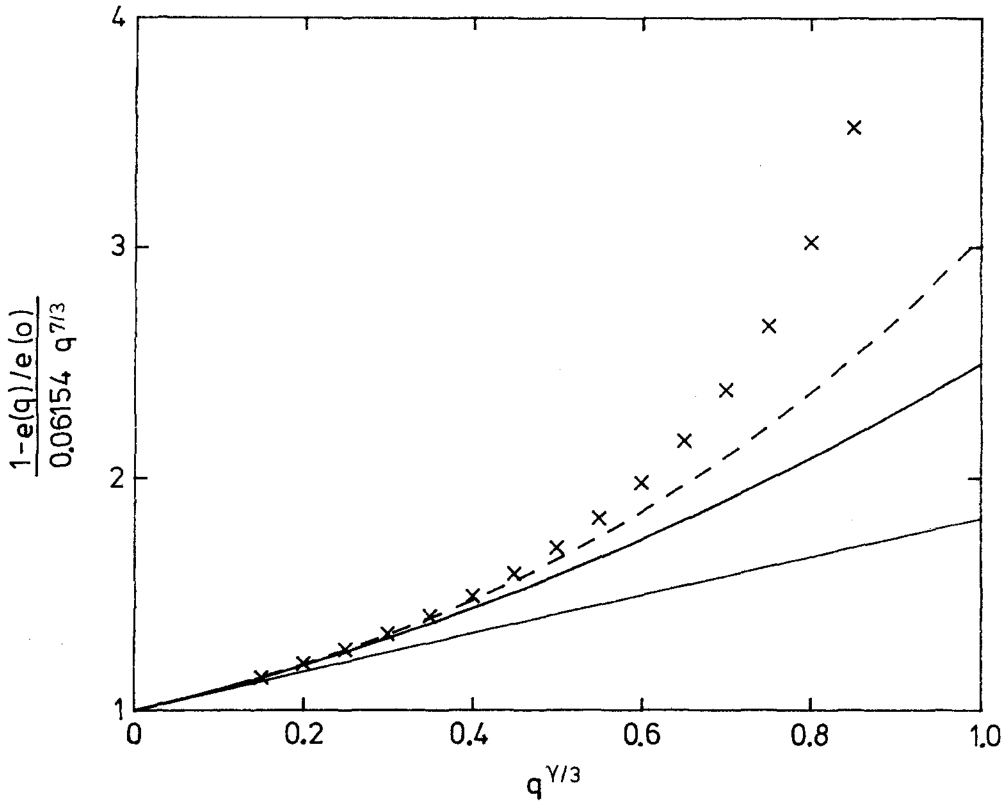

Fig.2-6. Comparison of the linear and quadratic approximations of Eq.(399) with the actual numbers (crosses). The dashed curve is the corresponding cubic approximation.

bound electrons, the ones close to the nucleus that contribute most to the energy. To make this point, let us recall that the application of Eq.(1-43)(i.e., the evaluation of traces of unordered operators by phase space integrals) is justified when commutator terms, as they appear in the ordering process, are negligible. In the present context this requires that the commutator of the momentum and the potential, which equals i times the gradient of the potential, be "small." Small compared to what? Physically, this gradient is small if the potential does not change significantly over the range important for an electron. Since the quantum standard of length, associated with an individual electron, is its deBroglie wave length, λ, a small gradient means

$$|\lambda \vec{\nabla} V| \ll |V| \quad . \tag{2-400}$$

Substantial changes in V occur on a scale set by the distance r, so that criterion (400) requires that

$$\lambda \ll r \quad . \tag{2-401}$$

On the other hand, λ is the inverse momentum (we ignore factors of two and pi for this kind of reasoning), which in turn is given by the square root of the potential, see Eq.(42). In short, we have, as criterion for the validity of the TF model, the relation

$$r \sqrt{|V+\zeta|} \gg 1 \quad . \tag{2-402}$$

Upon introducing TF variables, this reads

$$Z^{1/3} \ |x\ f_q(x)|^{1/2} \gg 1 \quad . \tag{2-403}$$

First, we learn here that, for a given x, the TF model is reliable only if Z is large enough. Second, there is information about the regions where the approximation cannot be trusted.

At short distances, $f_q(x)$ practically equals unity, and the left-hand side of (403) is of the order of one, when $x \sim Z^{-2/3}$, or $r \sim 1/Z$. Consequently, there is an inner region of strong binding where the TF approximation fails. Indeed, the innermost electrons are described incorrectly in the TF model.

Then, near the edge of the atom at $x=x_o$, $f_q(x)$ has the linear form of Eq.(329). Now the left-hand side of (403) is of the order of one, when $|x-x_o| \sim Z^{-2/3}/q^2$, or $|r-r_o| \sim 1/(Zq^2)$. Thus we find the outer region of weak binding to be also treated inadequately in the TF model. The situation is, of course not basically different for neutral atoms, although the argument has to be modified. For q=o, the TF function F(x) appears in (403). Its large-x form $F(x) \sim 1/x^3$ implies that the criterion is not satisfied, once x is of the order $Z^{1/3}$, or $r \sim 1$.

In Figs.7 and 8 plots of the radial densities

$$D(r) = 4\pi r^2 n(r) \tag{2-404}$$

are used to illustrate these observations concerning the validity of the TF model. Please note that the regions of failure shrink with increasing Z. We conlcude that (in some sense) the TF approximation becomes exact for $Z \to \infty$.[20]

Nice, but in the real world Z isn't that large, the more so $Z^{1/3}$, which obviously is the relevant parameter. It ranges merely from

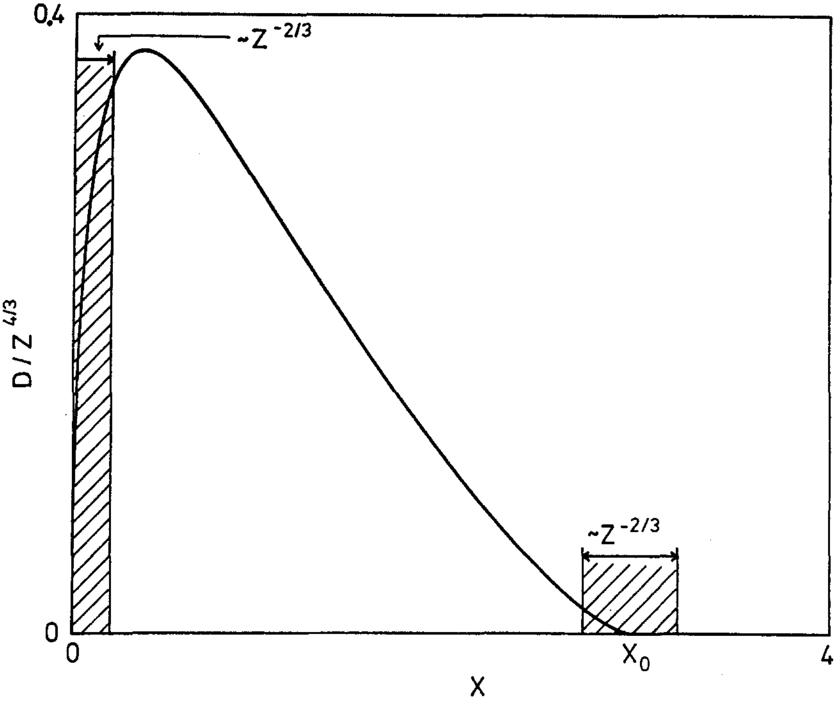

Fig.2-7. Regions of reliability and failure of the TF model in an ionized atom (q=1/2), illustrated by the radial density as a function of the TF variable x.

one to roughly five over the whole Periodic Table. Clearly, modifications aimed at improving the TF model are called for. All following Chapters are devoted to their discussion. The TF atom is thereby the leading approximation, and the supplements to the TF model will all be regarded as small corrections. For this reason it was necessary to spend so much time with a detailed study of the TF model.

It is important to appreciate that the density, which was used in Figs.7 and 8, is the right quantity to plot for this purpose. The TF prediction (51)

$$n_{TF}(r) = \frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} \tag{2-405}$$

$$\cong \frac{1}{3\pi^2}(2Z/r)^{3/2} \quad \text{for} \quad r\to o$$

is clearly very much in error at small distances. Also, for an ion of

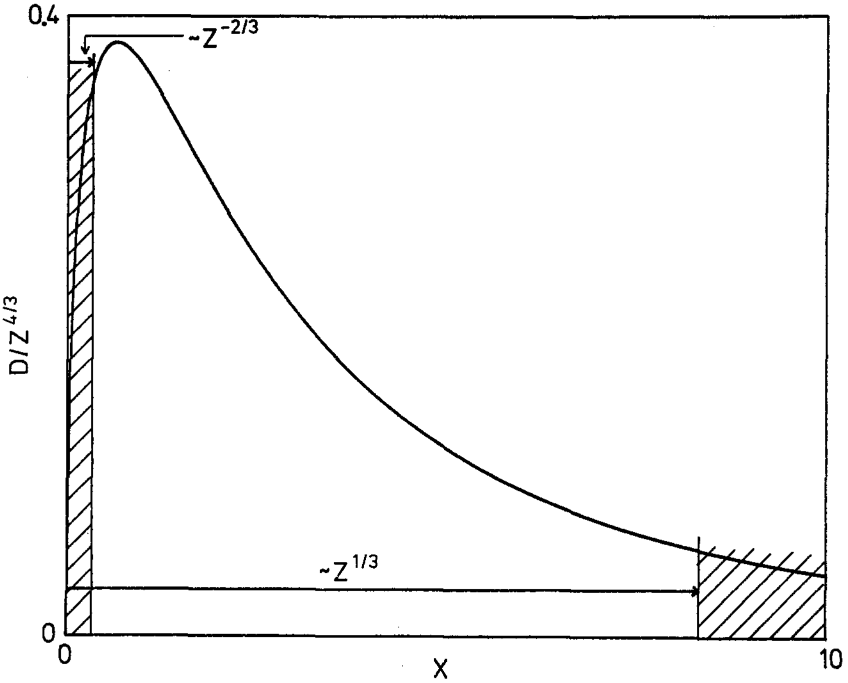

Fig.2-8. Like Fig.7, for a neutral atom.

degree of ionization q, we obtain

$$n_{TF}(r) \cong \frac{1}{3\pi^2}[2Zq(1-r/r_o)]^{3/2} \quad \text{for} \quad r \lesssim r_o \ , \qquad (2\text{-}406)$$

$$n_{TF}(r) = o \quad \text{for} \quad r > r_o$$

for the density around the edge of the atom. This is a sharp boundary instead of the quantum-mechanically correct smooth transition into the classically forbidden domain, where the real density decreases exponentially. In the situation of neutral atoms, the large-r behavior of the density is

$$n_{TF}(r) \cong \frac{1}{3\pi^2}[\,2\,\frac{Z}{r}\,\frac{144}{x^3}\,]^{3/2} = \frac{243}{8}\pi\frac{1}{r^6} \ , \qquad (2\text{-}407)$$

where the large-x form of F(x) is employed. Again, this is not the correct exponential dependence on the distance.

The principal lesson consists in stating that the real density is not of the form

$$n = n_{TF} + (\text{ a small correction}) . \tag{2-408}$$

As a consequence, the TF density functional of Eq.(95) cannot be used as the starting point when looking for corrections. In contrast, the TF potential is very much like the real effective potential, inasmuch as it behaves like $-Z/r$ for $r\to o$ and like $-(Z-N)/r$ for $r\to\infty$, being structureless in between. The structure is in the second derivative of the potential (related to the density), not in the potential itself. Therefore, we must find modifications of the TF potential functional of Eq. (45) in order to overcome the insufficiencies of the TF model. If this is so, why does the vast majority of people working on TF theory use the language of density functionals? As far as I can see, the reasons are historical ones. In the original work by Thomas and Fermi[21] the principal variable was the density, whereas the effective potential played the role of an auxiliary quantity. This remained so over the years in basically all presentations of the subject, of which Gombás' textbook[22] is the most prominent one. Then, in 1964, the socalled Hohenberg-Kohn theorem[23] (of which we shall sketch a proof in the next section) triggered the development of a density functional formalism. Because of this theorem, density functionals appear to be well founded theoretically, in contrast to formulations based upon the concept of the effective potential, which is widely regarded as an intuitive approach (our introduction certainly is in this spirit) lacking a "rigorous" theoretical foundation. In the following section, which continues the "general formalism" that we left after Eq.(40), we shall see that this preconception is wrong. The potential functional is as well defined as the density functional, and for the reasons given above it is the preferable formulation in atomic physics.

Density and potential functionals. For a proof of the aforementioned Hohenberg-Kohn theorem (we shall state it below), we return to the many particle Hamilton operator of Eq.(1-7), where we replace the nucleus-electron potential $-Z/r$ by an arbitrary external potential $V_{ext}(\vec{r})$, and split H_{mp} into the kinetic energy operator H_{kin}, and the interaction energy operators H_{ext} and H_{ee}:

$$H_{mp} = \sum_{j=1}^{N} \frac{1}{2} p_j^2 + \sum_{j=1}^{N} V_{ext}(r_j) + \frac{1}{2}\sum_{j,k=1}^{N}{}' \frac{1}{r_{jk}} =$$

$$= H_{kin} + H_{ext} + H_{ee} \quad . \tag{2-409}$$

Different ground states $|\psi_o\rangle$ will correspond to differing choices of V_{ext}. In order to simplify the argument, we shall assume that, except for the irrelevant possibility of a reorientation of all spins, the ground states are unique (a slight, and otherwise innocuous, change of the external potential would destroy any degeneracy anyhow). Thus, the density in the ground state,

$$\begin{aligned} n(\vec{r}') &= \int (d\vec{r}_2')(d\vec{r}_3')\ldots(d\vec{r}_N') \quad |\langle \vec{r}';\vec{r}_2',\vec{r}_3',\ldots,\vec{r}_N'|\psi_o\rangle|^2 \\ &+ \int (d\vec{r}_1')(d\vec{r}_3')\ldots(d\vec{r}_N') \quad |\langle \vec{r}_1',\vec{r}';\vec{r}_3',\ldots,\vec{r}_N'|\psi_o\rangle|^2 \\ &+ \ldots \\ &+ \int (d\vec{r}_1')\ldots(d\vec{r}_{N-1}') \quad |\langle \vec{r}_1',\vec{r}_2',\ldots,\vec{r}_{N-1}',\vec{r}'|\psi_o\rangle|^2 \\ &= N\int (d\vec{r}_2')\ldots(d\vec{r}_N') \quad |\langle \vec{r}';\vec{r}_2',\ldots,\vec{r}_N'|\psi_o\rangle|^2 \end{aligned} \tag{2-410}$$

(the latter equality makes use of the antisymmetry of the wave function, and a trace affecting the spin indices only is understood implicitly), is a functional of the external potential V_{ext}.

Two different external potentials, V_{ext} and $\tilde{V}_{ext}$, will lead to two different ground states $|\psi_o\rangle$ and $|\tilde{\psi}_o\rangle$, since the respective Schrödinger equations are different. (The situation $\tilde{V}_{ext} = V_{ext}$ + const. is not interesting, since we consider only potentials that are physically different). The expectation values of H_{mp} and $\tilde{H}_{mp}$ are minimized by $|\psi_o\rangle$ and $|\tilde{\psi}_o\rangle$, respectively, so that

$$\langle\psi_o|H_{mp}|\psi_o\rangle - \langle\tilde{\psi}_o|\tilde{H}_{mp}|\tilde{\psi}_o\rangle < \langle\tilde{\psi}_o|H_{mp}-\tilde{H}_{mp}|\tilde{\psi}_o\rangle \tag{2-411}$$

and

$$\langle\psi_o|H_{mp}|\psi_o\rangle - \langle\tilde{\psi}_o|\tilde{H}_{mp}|\tilde{\psi}_o\rangle > \langle\psi_o|H_{mp}-\tilde{H}_{mp}|\psi_o\rangle \quad , \tag{2-412}$$

which are combined into

$$\langle\psi_o|H_{mp}-\tilde{H}_{mp}|\psi_o\rangle < \langle\tilde{\psi}_o|H_{mp}-\tilde{H}_{mp}|\tilde{\psi}_o\rangle \quad . \tag{2-413}$$

Now we insert

$$H_{mp} - \tilde{H}_{mp} = H_{ext} - \tilde{H}_{ext} = \sum_{j=1}^{N} (V_{ext}(\vec{r}_j) - \tilde{V}_{ext}(\vec{r}_j)) \tag{2-414}$$

and obtain

$$<\psi_o|H_{mp} - \tilde{H}_{mp}|\psi_o> = \sum_{j=1}^{N} \int (d\vec{r}_1') \ldots (d\vec{r}_N') (V_{ext}(\vec{r}_j') - \tilde{V}_{ext}(\vec{r}_j'))$$

$$\times |<\vec{r}_1', \ldots, \vec{r}_N'|\psi_o>|^2$$

$$= \int (d\vec{r}') [V_{ext}(\vec{r}') - \tilde{V}_{ext}(\vec{r}')] n(\vec{r}') \quad , \tag{2-415}$$

and likewise for $|\tilde{\psi}_o>$. The implication of (413) is therefore

$$\int (d\vec{r}') [V_{ext}(\vec{r}') - \tilde{V}_{ext}(\vec{r}')][n(\vec{r}') - \tilde{n}(\vec{r}')] < o \quad , \tag{2-416}$$

from which we conclude that $n \neq \tilde{n}$. Different external potentials not only produce different ground states but also different ground-state densities. Consequently, a given n corresponds to a certain V_{ext} which is uniquely determined by n. In other words: V_{ext} is a functional of n. And since the ground state $|\psi_o>$ is a functional of V_{ext}, it can be regarded as a functional of n as well. Then the expectation values of H_{kin} and H_{ee} in the ground states are also functionals of the density. Here then is the Hohenberg-Kohn theorem: there exist universal (i.e., independent of V_{ext}) functionals of the density $E_{kin}(n)$ and $E_{ee}(n)$, so that the ground-state energy equals

$$E(n) = E_{kin}(n) + \int (d\vec{r}') V_{ext}(\vec{r}') n(\vec{r}') + E_{ee}(n) \quad , \tag{2-417}$$

where n is the ground-state density. The minimum property of $<\psi|H_{mp}|\psi>$ implies that the energy E(n) is minimized by the correct ground-state density; trial densities $\tilde{n}$, which must be subject to the normalization

$$\int (d\vec{r}') \tilde{n}(\vec{r}') = N \quad , \tag{2-418}$$

yield larger energies $E(\tilde{n})$ than the ground-state energy E(n). It is useful to include the constraint (418) into the energy functional by means of

$$E(n,\zeta) = E_{kin}(n) + \int (d\vec{r}') V_{ext}(\vec{r}') n(\vec{r}') + E_{ee}(n) -$$

$$-\zeta\,(\,N - \int(d\vec{r})n\,) \quad , \tag{2-419}$$

since this $E(n,\zeta)$ is stationary under arbitrary variations of both the density n and the Lagrangian multiplier ζ.

Before proceeding to construct the related potential functional, a few remarks are in order. The Hohenberg-Kohn theorem is a very general one; in particular, the specific forms of H_{kin} and H_{ee} never enter. The price for the generality is paid in form of a total lack of knowledge concerning the structure of the density functionals $E_{kin}(n)$ and $E_{ee}(n)$. The theorem states no more than their existence. Obviously, the detailed form of these functionals must depend upon the specific H_{kin} and H_{ee} that are investigated [one could, for instance, consider relativistic corrections to the kinetic energy, or, in applications to nuclear physics, reflect upon fermion-fermion interactions different from the Coulomb form of (409)]. Also, no technical procedure is known that would enable us to perform the step from H_{mp} to $E(n)$. One must rely upon some physical insight, when constructing functionals that approximate the actual $E(n)$.

The kinetic energy in the ground state of H_{mp} of (409) is the expectation value

$$E_{kin} = \langle\psi_o|H_{kin}|\psi_o\rangle = \langle\psi_o|\sum_{j=1}^{N}\frac{1}{2}p_j^2|\psi_o\rangle \quad , \tag{2-420}$$

which, in configuration space, appears as

$$\begin{aligned} E_{kin} &= \frac{1}{2}N\int(d\vec{r}\,')\int(d\vec{r}_2^{\,\prime})\ldots(d\vec{r}_N^{\,\prime})\vec{\nabla}'\psi_o^*(\vec{r}\,',\vec{r}_2^{\,\prime}\ldots,\vec{r}_N^{\,\prime}) \\ &\qquad\qquad \cdot\vec{\nabla}'\psi_o(\vec{r}\,',\vec{r}_2^{\,\prime},\ldots,\vec{r}_N^{\,\prime}) \qquad (2\text{-}421) \\ &= \int(d\vec{r}\,')(d\vec{r}\,'')\frac{1}{2}\delta\,(\vec{r}\,'-\vec{r}\,'')\ \vec{\nabla}'\cdot\vec{\nabla}''\ n^{(1)}(\vec{r}\,';r'') \ . \end{aligned}$$

Here, once more, the antisymmetry of the wave function has been used, and we have introduced the one-particle density matrix

$$n^{(1)}(\vec{r}\,';\vec{r}\,'') = N\int(d\vec{r}_2^{\,\prime})\ldots(d\vec{r}_N^{\,\prime})\psi_o^*(\vec{r}\,'',\vec{r}_2^{\,\prime},..,\vec{r}_N^{\,\prime})\psi_o(\vec{r}\,',\vec{r}_2^{\,\prime},..,\vec{r}_N^{\,\prime}) \quad , \tag{2-422}$$

which is an immediate generalization of (410), so that the density itself is the diagonal part of $n^{(1)}(\vec{r}\,';\vec{r}\,'')$,

$$n(\vec{r}') = n^{(1)}(\vec{r}';\vec{r}') \quad . \tag{2-423}$$

Let us now attempt to interpret $n^{(1)}(\vec{r}';\vec{r}")$ as the matrix element of an effective density operator,

$$n^{(1)}(\vec{r}';\vec{r}") = 2\langle\vec{r}'|\eta(-\frac{1}{2}p^2 - V(\vec{r}) - \zeta)|\vec{r}"\rangle \quad . \tag{2-424}$$

(A more careful discussion hereof will be presented in Chapter Four.) The effective potential $V(\vec{r})$ that appears here is unspecified at this stage, except for remarking that it is a functional of the density, $n(\vec{r})$, because the density matrix on the left-hand side is such a functional. The factor of two is the spin multiplicity which we now choose to make explicit instead of further assuming that a trace on spin indices is left implicit. Note that V is determined without the option of adding a constant, since Eq.(423) has to hold for the given density.

The diagonal version of Eq.(424) showed up earlier, in Eq. (20). We are clearly back to the picture of particles moving independently in an effective potential V. The notation established then is useful here, too. In particular, we introduce the independent particle Hamilton operator

$$H(\vec{r},\vec{p}) = \frac{1}{2}p^2 + V(\vec{r}) \tag{2-425}$$

just as in Eq.(3). The kinetic energy of (421) is then rewritten as

$$\begin{aligned} E_{kin} &= \int(d\vec{r}')(d\vec{r}")[\tfrac{1}{2}\vec{\nabla}'\cdot\vec{\nabla}"\ \delta(\vec{r}'-\vec{r}")]n^{(1)}(\vec{r}';\vec{r}") \\ &= \int(d\vec{r}')(d\vec{r}")\ \langle\vec{r}"|\tfrac{1}{2}p^2\ |\vec{r}'\rangle\ 2\ \langle\vec{r}'|\eta(-H-\zeta)|\vec{r}"\rangle \\ &= \mathrm{tr}\ \tfrac{1}{2}p^2\ \eta(-H-\zeta) \quad , \end{aligned} \tag{2-426}$$

where we remember that the trace operation includes multiplying by the spin factor. The quantity E_1 of Eq.(7),

$$E_1 = \mathrm{tr}(H+\zeta)\eta(-H-\zeta) \tag{2-427}$$

is a functional of $V+\zeta$, thus a functional of n, as $V=V(n)$. The kinetic energy (426) is contained in (427),

$$\begin{aligned} E_{kin} &= E_1 - \mathrm{tr}(V+\zeta)\eta(-H-\zeta) \\ &= E_1 - \int(d\vec{r}')(V(\vec{r}')+\zeta)n(\vec{r}') \quad . \end{aligned} \tag{2-428}$$

This we insert into (419) and arrive at

$$E(n,\zeta) = E_1(V+\zeta) - \int(d\vec{r}')(V(\vec{r}') - V_{ext}(\vec{r}'))n(\vec{r}') \\ + E_{ee}(n) - \zeta N \quad . \tag{2-429}$$

In the present context, V is still regarded as a functional of n. Therefore, (429) is the same functional as in (419), we have done no more than reorganize the right-hand side. Consequently, the functional (429) is stationary under variations of n and ζ around their correct values, just as (419) is stationary. An infinitesimal variation of ζ induces a change in $E(n,\zeta)$ given by

$$\delta_\zeta E(n,\zeta) = (\frac{\partial}{\partial\zeta}E_1(V+\zeta) - N)\delta\zeta = o \quad ; \tag{2-430}$$

it is, indeed, zero for the same reasons that implied Eq.(13). Now consider a variation of the density:

$$\begin{aligned} \delta_n E(n,\zeta) &= \int(d\vec{r}')\delta_n V(\vec{r}')n(\vec{r}') - \int(d\vec{r}')\delta_n V(\vec{r}')n(\vec{r}') \\ &- \int(d\vec{r}')(V(\vec{r}') - V_{ext}(\vec{r}'))\delta n(\vec{r}') \\ &+ \int(d\vec{r}')\delta n(\vec{r}')\ V_{ee}(\vec{r}') \\ &= \int(d\vec{r}')[-V(\vec{r}') + V_{ext}(\vec{r}') + V_{ee}(\vec{r}')]\delta n(\vec{r}') \quad , \end{aligned} \tag{2-431}$$

where Eqs.(14) and (25) have been employed. The stationary property of $E(n,\zeta)$ thus implies

$$V = V_{ext} + V_{ee} \quad . \tag{2-432}$$

In words: the effective potential equals the sum of the external potential and the effective interaction potential, V_{ee}, defined by Eq.(25),

$$\delta_n E_{ee}(n) = \int(d\vec{r}')\delta n(\vec{r}')V_{ee}(\vec{r}') \quad . \tag{2-433}$$

Note in particular, that V is always a local (i.e., momentum independent) potential.

So far, V has been regarded as a functional of the density. Because of the circumstance that the contributions in (431), that originate in variations of V, take care of themselves, we can equally well treat V as an independent variable. The energy functional

$$E(V,n,\zeta) = E_1(V+\zeta) - \int(d\vec{r}\,')(V-V_{ext})n + E_{ee}(n) - \zeta N \qquad (2\text{-}434)$$

is obviously stationary under independent infinitesimal variations of V,n, and ζ. If we do not want to have both V and n as independent quantities, we have the option of eliminating one of the two. The step from (434) back to (419) is done by first solving Eq. (20) for V, thereby expressing the potential in terms of the density, and then using this V(n) in (434). Likewise, to obtain a functional of the potential alone, one has to use Eq. (432), in which V_{ee} is a functional of the density, to express n as a functional of V. This n(V) then eliminates the density from (434) leaving us with a potential functional $E(V,\zeta)$.

Let us illustrate these ideas with the respective TF functionals. Starting from

$$E_{TF}(V,n,\zeta) = \int(d\vec{r})\left(-\frac{1}{15\pi^2}\right)[-2(V+\zeta)]^{5/2} - \int(d\vec{r})\left(V+\frac{Z}{r}\right)n$$
$$+\frac{1}{2}\int(d\vec{r})(d\vec{r}\,')\frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} - \zeta N \ , \qquad (2\text{-}435)$$

where V_{ext} is now the potential energy of an electron with the nucleus, $-Z/r$, we get the density funcitonal of Eq. (95), after first inverting [Eq. (51)]

$$n = \frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2} \qquad (2\text{-}436)$$

to

$$V = -\frac{1}{2}(3\pi^2 n)^{2/3} - \zeta \ , \qquad (2\text{-}437)$$

which then allows to rewrite the first and second term in (435) accordingly. On the other hand, if

$$V = -\frac{Z}{r} + \int(d\vec{r}\,')\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \qquad (2\text{-}438)$$

is solved for n,

$$n = -\frac{1}{4\pi}\nabla^2\left(V+\frac{Z}{r}\right) \qquad (2\text{-}439)$$

(this is, of course, Poisson's equation), we can eliminate n from the second and third term in (435) and are led to the TF potential functional of Eq. (45). Of course, within the framework of the TF model, the three functionals $E(V,n,\zeta)$, $E(n,\zeta)$, and $E(V,\zeta)$ are perfectly equivalent, but I repeat: as a basis for improvements over the TF approximation, the potential functional is the preferable one.

We have investigated earlier the scaling properties of the TF model. Let us now see, what one can state about the behavior of the exact density functionals $E_{kin}(n)$ and $E_{ee}(n)$ under scale transformations of the density,

$$n(\vec{r}\,')\to n_\mu(\vec{r}\,') = \mu^3\, n(\mu\vec{r}\,') \quad . \tag{2-440}$$

The TF approximations to E_{kin} and E_{ee} scale in the manner that one would intuitively expect:

$$\begin{aligned}\left(E_{kin}(n)\right)_{TF} &= \int (d\vec{r}\,')\, \frac{1}{10\pi^2}\left(3\pi^2 n(\vec{r}\,')\right)^{5/3} \\ &\to \mu^{-3}\int(d\mu\vec{r}\,')\, \frac{1}{10\pi^2}\left(3\pi^2\mu^3 n(\mu\vec{r}\,')\right)^{5/3} \\ &= \mu^2\left(E_{kin}(n)\right)_{TF} \quad ,\end{aligned} \tag{2-441}$$

and likewise

$$\begin{aligned}\left(E_{ee}(n)\right)_{TF} &= \frac{1}{2}\int (d\vec{r}\,')(d\vec{r}\,'')\, \frac{n(\vec{r}\,')n(\vec{r}\,'')}{|\vec{r}\,'-\vec{r}\,''|} \\ &\to \mu\left(E_{ee}(n)\right)_{TF} \quad .\end{aligned} \tag{2-442}$$

For the exact functionals, the equations

$$E_{kin}(n_\mu) = \mu^2\, E_{kin}(n) \tag{2-443}$$

and

$$E_{ee}(n_\mu) = \mu\, E_{ee}(n) \tag{2-444}$$

do <u>not</u> hold, however; even their combination

$$E_{kin}(n_\mu) + E_{ee}(n_\mu) = \mu^2\, E_{kin}(n) + \mu\, E_{ee}(n) \tag{2-445}$$

is only true if $\mu=1+\varepsilon$ with an infinitesimal ε. This surprising observation has been made only recently, by Levy and Perdew.[24] Please note that the statement (445) is, indeed, only needed for such $\mu\cong 1$, in order to derive the virial theorem

$$2\, E_{kin}(n) = - E_{ee}(n) + \int (d\vec{r}\,')n(\vec{r}\,')\vec{r}\,'\cdot\vec{\nabla}'\, V_{ext}(\vec{r}\,') \tag{2-446}$$

from the minimum property of the density functional (417).

As a first step towards proving these remarks about Eqs.(443) through (445), we recall that to any given density there correspond uniquely a certain external potential and a certain ground state. Let us keep the notation V_{ext} and $|\psi_o>$ for the ones related to the actual ground-state density n, and write V^{μ}_{ext} and $|\psi_o^{\mu}>$ for the ones that go with the scaled density n_{μ}. Thus $|\psi_o^{\mu}>$ obeys

$$(H_{kin} + H^{\mu}_{ext} + H_{ee})\,|\psi_o^{\mu}> = E_o^{\mu}\,|\psi_o^{\mu}> \quad , \tag{2-447}$$

where E_o^{μ} is the ground-state energy for n_{μ}. Clearly, if we transform $|\psi_o>$ according to

$$<\vec{r}_1',\ldots,\vec{r}_N'|\psi_o> \to \mu^{3N/2}\ <\mu\vec{r}_1',\ldots,\mu\vec{r}_N'|\psi_o> \quad , \tag{2-448}$$

then the density is scaled as in Eq.(440). Inasmuch as

$$\mu^{3N/2}\ <\mu\vec{r}_1',\ \ldots,\ \mu\vec{r}_N'| = <\vec{r}_1',\ \ldots,\vec{r}_N'|U(\mu) \quad , \tag{2-449}$$

where the unitary operator $U(\mu)$ is given by

$$U(\mu) = \exp\{\, i\ \frac{1}{2}\sum_{j=1}^{N} (\vec{r}_j\cdot\vec{p}_j+\vec{p}_j\cdot\vec{r}_j)\ \log\mu\,\} \quad , \tag{2-450}$$

we can read (448) as

$$|\psi_o> \to U(\mu)\,|\psi_o> \quad . \tag{2-451}$$

The point is that this scaled $|\psi_o>$ is not equal to $|\psi_o^{\mu}>$. This emerges from considering the Schrödinger equation obeyed by $U(\mu)\,|\psi_o>$, which is immediately obtained from the one satisfied by $|\psi_o>$. We have

$$U(\mu)\,(H_{kin} + H_{ext} + H_{ee})\ U^{-1}(\mu)\ U(\mu)\,|\psi_o> = E_oU(\mu)\,|\psi_o>. \tag{2-452}$$

The action of U upon $\vec{r}_j$ and $\vec{p}_j$ is simply

$$U(\mu)\,\vec{r}_j\,U^{-1}(\mu) = \mu\,\vec{r}_j \quad ,$$
$$U(\mu)\,\vec{p}_j\,U^{-1}(\mu) = \frac{1}{\mu}\,\vec{p}_j \quad , \qquad (2\text{-}453)$$

so that

$$U(\mu)\,H_{kin}\,U^{-1}(\mu) = \frac{1}{\mu^2}\,H_{kin} \quad ,$$
$$U(\mu)\,H_{ee}\,U^{-1}(\mu) = \frac{1}{\mu}\,H_{ee} \quad , \qquad (2\text{-}454)$$

and

$$U(\mu)\,H_{ext}\,U^{-1}(\mu) = \sum_{j=1}^{N} V_{ext}(\mu\vec{r}_j) \quad . \qquad (2\text{-}455)$$

Consequently,

$$(H_{kin} + \mu^2 U(\mu) H_{ext} U^{-1}(\mu) + \mu H_{ee}) U(\mu) |\psi_o\rangle = \mu^2 E_o U(\mu) |\psi_o\rangle \quad , \qquad (2\text{-}456)$$

which, in view of the factor μ multiplying H_{ee}, is not of the form required for $|\psi_o^{\mu}\rangle$ in Eq.(447). Thus, indeed

$$U(\mu)|\psi_o\rangle \neq |\psi_o^{\mu}\rangle \quad , \qquad (2\text{-}457)$$

for $\mu \neq 1$. Nevertheless, $|\psi_o^{\mu}\rangle$ and $U(\mu)|\psi_o\rangle$ are not unrelated. In particular, they give rise to the same density, $n_{\mu}(\vec{r})$, when inserted into (410). This implies the equality

$$\langle\psi_o^{\mu}\,|\,H_{ext}^{\mu}\,|\,\psi_o^{\mu}\rangle = \langle\psi_o|\,U^{-1}(\mu)\,H_{ext}^{\mu}\,U(\mu)|\psi_o\rangle \quad , \qquad (2\text{-}458)$$

and for the same reason

$$\langle\psi_o\,|\,H_{ext}\,|\psi_o\rangle = \langle\psi_o^{\mu}|\,U(\mu)\,H_{ext}\,U^{-1}(\mu)|\psi_o^{\mu}\rangle \quad . \qquad (2\text{-}459)$$

We are now prepared to employ the minimum property of the expectation value of the Hamilton operator of Eq.(447) in the form

$$\langle\psi_o^{\mu}|(H_{kin} + H_{ext}^{\mu} + H_{ee})|\psi_o^{\mu}\rangle \leq$$

$$\leqq \langle\psi_o|\ U^{-1}(\mu)(H_{kin}+H^{\mu}_{ext}+H_{ee})U(\mu)\ \psi_o\rangle \quad , \qquad (2\text{-}460)$$

which, as a consequence of Eqs.(454) and (458), says

$$E_{kin}(n_\mu) + E_{ee}(n_\mu) \leqq \mu^2\ E_{kin}(n) + \mu\ E_{ee}(n) \quad . \qquad (2\text{-}461)$$

The equal sign holds only for $\mu=1$, in the first place. Since the right hand side always exceeds the left hand one for $\mu\neq1$, however, the two sides must agree up to first order in $\varepsilon=\mu-1$, at least, so that the equal sign actually applies to $\mu=1+\varepsilon$ with an infinitesimal ε. This is the statement we made at Eq.(445). Another way of expressing the same fact is

$$\frac{d}{d\mu}[E_{kin}(n_\mu) + E_{ee}(n_\mu)]\Big|_{\mu=1} = 2\ E_{kin}(n) + E_{ee}(n) \quad . \qquad (2\text{-}462)$$

We can also exploit the minimum property of the expectation value of the Hamilton operator of Eq.(456). Here we have

$$\langle\psi_o\ |\ U^{-1}(\mu)(H_{kin}+\ \mu^2\ U(\mu)H_{ext}\ U^{-1}(\mu)\ +\ \mu H_{ee})U(\mu)\ |\psi_o\rangle$$

$$\leqq \langle\psi^{\mu}_o\ |\ (H_{kin}+\ \mu^2 U(\mu)H_{ext}\ U^{-1}(\mu)+\mu H_{ee})\ |\psi^{\mu}_o\rangle \quad , \qquad (2\text{-}463)$$

or with (454) and (459),

$$\mu^2\ E_{kin}(n)\ +\ \mu^2\ E_{ee}(n)\ \leqq E_{kin}(n_\mu)\ +\ \mu\ E_{ee}(n_\mu) \quad , \qquad (2\text{-}464)$$

where, again, the equal sign is true for all μ's that differ from unity at most infinitesimally.

Equations (461) and (464) can be combined into two statements about E_{kin} and E_{ee} individually, namely

$$(\mu-1)[E_{ee}(n_\mu)\ -\ \mu\ E_{ee}(n)]\ \geqq o \qquad (2\text{-}465)$$

and

$$(\mu-1)[E_{kin}(n_\mu)\ -\ \mu^2\ E_{kin}(n)]\ \leqq o \quad . \qquad (2\text{-}466)$$

It seems natural to assume that the left-hand sides in (465) and (466) are of second order in $\varepsilon=\mu-1$ for small ε. If this were true, these equations would mean that

$$\frac{d}{d\mu} E_{ee}(n_\mu)\Big|_{\mu=1} - E_{ee}(n) > 0 \tag{2-467}$$

and

$$\frac{d}{d\mu} E_{kin}(n_\mu)\Big|_{\mu=1} - 2\, E_{kin}(n) < 0 \quad . \tag{2-468}$$

As a matter of fact, we shall see below that equal signs have to be written in (467) and (468) instead of ">" and "<". Consequently, the left-hand sides in (465) and (466) are, at least, of order ε^4, the respective square brackets of order ε^3. Therefore, also in Eq.(461) the equality sign holds up to order ε^3, at least. These remarks go beyond the results of Ref.24, where Levy and Perdew stopped at stating (465) and (466).

For a proof of what has just been said, we have to turn to the potential functional $E_1(V+\zeta)$. In Eq.(216) we found that the TF approximation to E_1 responds like

$$\left(E_1(V+\zeta)\right)_{TF} \rightarrow \mu^{5\nu/2-3} \left(E_1(V+\zeta)\right)_{TF} \quad , \tag{2-469}$$

when V and ζ are scaled according to Eqs.(211) and (214),

$$V(\vec{r}) \rightarrow \mu^\nu V(\mu\vec{r}) \quad , \quad \zeta \rightarrow \mu^\nu \zeta \quad . \tag{2-470}$$

Although the exact $E_1(V+\zeta)$ does not behave like (469) for arbitrary ν, it does so for $\nu=2$:

$$E_1(V+\zeta) \rightarrow \mu^2 E_1(V+\zeta) \tag{2-471}$$

for

$$\begin{aligned} V(\vec{r}) &\rightarrow V_\mu(\vec{r}) = \mu^2 V(\mu\vec{r}) \quad , \\ \zeta &\rightarrow \mu^2 \zeta \quad . \end{aligned} \tag{2-472}$$

We demonstrate this by first observing that

$$\begin{aligned} &\eta(-\tfrac{1}{2} p^2 - \mu^2 V(\mu\vec{r}) - \mu^2 \zeta) \\ &= \eta(-\tfrac{1}{2}(\vec{p}/\mu)^2 - V(\mu\vec{r}) - \zeta) \\ &= U(\mu)\ \eta(-\tfrac{1}{2} p^2 - V(\vec{r}) - \zeta)\ U^{-1}(\mu) \quad , \end{aligned} \tag{2-473}$$

where $U(\mu)$ now denotes the one-particle version of (450),

$$U(\mu) = \exp\{i\,\tfrac{1}{2}(\vec{r}\cdot\vec{p} + \vec{p}\cdot\vec{r})\log\mu\} \quad . \tag{2-474}$$

This is used in

$$\begin{aligned} E_1(V+\zeta) &= \mathrm{tr}(\tfrac{1}{2}p^2 + V(\vec{r})+\zeta)\eta(-\tfrac{1}{2}p^2 - V(\vec{r})-\zeta) \\ &\to \mathrm{tr}(\tfrac{1}{2}p^2 + \mu^2 V(\mu\vec{r})+\mu^2\zeta)\eta(-\tfrac{1}{2}p^2 - \mu^2 V(\mu\vec{r})-\mu^2\zeta) \\ &= \mu^2 \mathrm{tr}\; U(\mu)\,(\tfrac{1}{2}p^2 + V(\vec{r})+\zeta)\eta(-\tfrac{1}{2}p^2 - V(\vec{r})-\zeta)U^{-1}(\mu) \\ &= \mu^2\; E_1(V+\zeta) \quad , \end{aligned} \tag{2-475}$$

or

$$E_1(V_\mu + \mu^2\zeta) = \mu^2\; E_1(V+\zeta) \quad , \tag{2-476}$$

indeed. [The invariance of the trace under cyclic permutations has been employed in the last step of (475).]

Before proceeding, it is instructive to show where the attempt of repeating the argument for $\nu\neq 2$ fails. The analog of (473) would require an operator (not necessarily a unitary one), $U_\nu(\mu)$, such that

$$\begin{aligned} U_\nu(\mu)\;\vec{r}\;U_\nu^{-1}(\mu) &= \mu\vec{r} \quad , \\ U_\nu(\mu)\;\vec{p}\;U_\nu^{-1}(\mu) &= \mu^{-\nu/2}\;\vec{p} \quad . \end{aligned} \tag{2-477}$$

Unfortunately, there is no such operator, except for $\nu=2$, as emerges from considering the commutator of the transformed quantities:

$$\mu^{1-\nu/2}\; i\,\overleftrightarrow{1} = [\mu\vec{r},\mu^{-\nu/2}\;\vec{p}] = U_\nu[\vec{r},\vec{p}]U_\nu^{-1} = i\,\overleftrightarrow{1} \quad . \tag{2-478}$$

This is a contradiction, unless $\nu=2$.

In the section about the scaling properties of the TF model we remarked that a scaling transformation of the effective potential $V(\vec{r})$ must be accompanied by a corresponding transformation of the external potential $V_{ext}(\vec{r})$. In that earlier context, this was achieved by changing Z appropriately [Eq.(213)], because the only V_{ext} considered then was the Coulomb potential $-Z/r$. In the more general present discussion, we preserve the structure $V-V_{ext}$ by scaling V_{ext} like V in Eq.(473),

$$V_{ext}(\vec{r}) \to V_{ext,\mu}(\vec{r}) = \mu^2\; V_{ext}(\mu\vec{r}) \quad . \tag{2-479}$$

The density is, of course, scaled as in (440). Under these simultaneous transformations of V,n,ζ, and V_{ext}, the potential-density functional of (434) behaves as described by

$$E(V,n,\zeta) \rightarrow E_\mu(V,n,\zeta) = E(V_\mu,n_\mu,\mu^2\zeta)$$
$$= \mu^2\{E_1(V+\zeta) - \int(d\vec{r}\,')(V(\vec{r}\,') - V_{ext}(\vec{r}\,'))n(\vec{r}\,')-\zeta N\}$$
$$+ E_{ee}(n_\mu) \quad . \tag{2-480}$$

Since $E(V,n,\zeta)$ is stationary under infinitesimal variations of V,n, and ζ, all first order changes must originate in the scaling of V_{ext}. [The same argument was also applied to $E_{TF}(\mu)$ of Eq. (219).] Thus,

$$\frac{d}{d\mu} E_\mu(V,n,\zeta)\Big|_{\mu=1} = \int(d\vec{r}\,')n(\vec{r}\,')\frac{\partial}{\partial\mu}V_{ext,\mu}(\vec{r}\,')\Big|_{\mu=1} \quad , \tag{2-481}$$

or with (479),

$$\frac{d}{d\mu} E_\mu(V,n,\zeta)\Big|_{\mu=1} = \int(d\vec{r}\,')n(\vec{r}\,')[2\,V_{ext}(\vec{r}\,')+\vec{r}\,'\cdot\vec{\nabla}'V_{ext}(\vec{r}\,')] . \tag{2-482}$$

On the other hand, Eq. (480) implies

$$\frac{d}{d\mu} E_\mu(V,n,\zeta)\Big|_{\mu=1} = 2\,\{E_1(V+\zeta)- \int(d\vec{r}\,')(V(\vec{r}\,')-V_{ext}(\vec{r}\,'))$$
$$\times\, n(\vec{r}\,')-\zeta N\}+ \frac{d}{d\mu}E_{ee}(n_\mu)\Big|_{\mu=1} \quad . \tag{2-483}$$

The equivalence of these two right-hand sides, combined with the virial theorem (446), yields

$$\frac{d}{d\mu} E_{ee}(n_\mu)\Big|_{\mu=1} - E_{ee}(n) = 2\,E_{kin}(n)-2\{E_1(V+\zeta)-\int(d\vec{r}\,')Vn-\zeta N\} \quad . \tag{2-484}$$

The last step consists of recognizing that for the actual V,n, and ζ, the contents of the curly brackets equals the kinetic energy. This emerges from Eq. (428). Consequently, the right-hand side is zero. We arrive at

$$\frac{d}{d\mu} E_{ee}(n_\mu)\Big|_{\mu=1} = E_{ee}(n) \quad , \tag{2-485}$$

and as a consequence of (462),

$$\frac{d}{d\mu} E_{kin}(n_\mu)\Big|_{\mu=1} = 2\, E_{kin}(n) \quad . \tag{2-486}$$

Indeed, the statements following Eq. (468) are justified.

Please be aware of the following mental trap. If the density is eliminated from $E(V,n,\zeta)$, so that we are left with the potential functional $E(V,\zeta)$, one could think that the resulting kinetic energy,

$$E_{kin}(V,\zeta) = E_1(V+\zeta) - \int(d\vec{r}\,')V(\vec{r}\,')n(\vec{r}\,') - \zeta N \tag{2-487}$$

scales according to

$$E_{kin}(V_\mu,\mu^2\zeta) = \mu^2\, E_{kin}(V,\zeta) \quad , \tag{2-488}$$

inasmuch as [Eq. (14)]

$$\delta_V\, E_1(V+\zeta) = \int(d\vec{r}\,')\delta V(\vec{r}\,')n(\vec{r}\,') \quad , \tag{2-489}$$

together with (471), implies

$$n(\vec{r}\,') \rightarrow \mu^3\, n(\mu\vec{r}\,') \quad , \tag{2-490}$$

if V and ζ are scaled as in (472). This is not so, however, because the potential functional that is to be inserted into Eq. (487) for $n(\vec{r}\,')$ is not the one obtained from (489), but the one that emerges from

$$\delta_n\, E_{ee}(n) = \int(d\vec{r}\,')\delta n(\vec{r}\,')[V(\vec{r}\,') - V_{ext}(\vec{r}\,')] \tag{2-491}$$

[Eqs. (432) and (433)]. In the TF approximation, for instance, this is the Poisson equation

$$n(\vec{r}\,') = -\frac{1}{4\pi}\nabla'^2(V(\vec{r}\,') - V_{ext}(\vec{r}\,')) \tag{2-492}$$

in which the scaling of V and V_{ext} [Eqs. (472) and (479)] produces

$$n(\vec{r}\,') \rightarrow \mu^4\, n(\mu\vec{r}\,') \quad , \tag{2-493}$$

different from the desired form of (490). Therefore, Eq. (488) is not true, not even for μ's that differ from unity by an infinitesimal amount.

The kinetic energy by itself is not a central quantity in the potential functional formalism. What we have just seen is an illustration of this remark.

Relation between the TF approximation and Hartree's method. Somewhere at the beginning of Chapter One there is the promise to discuss the connection between TF theory and HF theory "to some extent in Chapter Two." This time has finally come.

Hartree's[25] basic idea consists in approximating the ground-state wave-function by a product in which each factor refers to just one of the electrons:

$$\langle \vec{r}_1{}', \vec{r}_2{}', \ldots, \vec{r}_N{}' | \psi_o \rangle \cong \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\ldots\psi_N(\vec{r}_N) \quad . \tag{2-494}$$

The ψ_j's are supposed to be orthonormal,

$$\int (d\vec{r}\,')\ \psi_j{}^*(\vec{r}\,')\ \psi_k(\vec{r}\,') = \delta_{jk} \quad , \tag{2-495}$$

so that the wave function (494) is properly normalized to unity. The requirement of antisymmetry is not satisfied by (494). Consequently, exchange effects are not treated correctly. In the present context, where we want to make contact with the original TF model, neglecting exchange is consistent. We are actually talking about Hartree's approximation, not about the Hartree-Fock model, which does include exchange. This restriction is not essential for the discussion. The argument can be repeated for a comparison of HF theory with the proper extension of the TF model that includes the exchange interaction, which will be derived in Chapter Four. At this moment we are content with the simple TF model and Hartree's ansatz (494).

With Eq. (494) we obtain approximations to the expectation values of the three parts of the many-particle Hamilton operator (409). These are given by

$$\begin{aligned} E_{kin} &= \langle \psi_o | H_{kin} | \psi_o \rangle \\ &\cong \sum_{j=1}^{N} \int (d\vec{r}\,')\ \frac{1}{2}\ \vec{\nabla}'\psi_j{}^*(\vec{r}\,')\cdot\vec{\nabla}'\psi_j(\vec{r}\,') \quad , \end{aligned} \tag{2-496}$$

and

$$E_{ext} = \langle \psi_o | H_{ext} | \psi_o \rangle \quad \cong$$

$$\cong \sum_{j=1}^{N} \int (d\vec{r}\,')\ \psi_j{}^*(\vec{r}\,')\ V_{ext}(\vec{r}\,')\ \psi_j(\vec{r}\,') \tag{2-497}$$

as well as

$$E_{ee} = \langle\psi_o \mid H_{ee} \mid \psi_o\rangle$$

$$\cong \sum_{j=1}^{N} \tfrac{1}{2}\int (d\vec{r}\,')\,\psi_j{}^*(\vec{r}\,')\,[\sum_{\substack{k=1\\k\neq j}}^{N} \int (d\vec{r}\,'')\,\psi_k{}^*(\vec{r}\,'')\frac{1}{|\vec{r}\,'-\vec{r}\,''|}\psi_k(\vec{r}\,'')]$$

$$\times\ \psi_j(\vec{r}\,') \quad . \tag{2-498}$$

Since the description does not pay attention to the exchange energy, we do not have to be pedantic either when it comes to excluding the self-energy. In other words: it is perfectly consistent to include the k=j term in Eq.(498). The approximation to the ground-state energy is then

$$E = \langle\psi_o|H_{mp}|\psi_o\rangle \cong E_{Hartree}$$

$$= \sum_{j=1}^{N} \int (d\vec{r}\,')\,\{\tfrac{1}{2}\vec{\nabla}'\psi_j{}^*(\vec{r}\,')\cdot\vec{\nabla}'\psi_j(\vec{r}\,')+\psi_j{}^*(\vec{r}\,')V_{ext}(\vec{r}\,')\psi_j(\vec{r}\,')$$

$$+\ \tfrac{1}{2}\psi_j{}^*(\vec{r}\,')\,[\sum_{k=1}^{N}\int (d\vec{r}\,'')\,\psi_k{}^*(\vec{r}\,'')\frac{1}{|\vec{r}\,'-\vec{r}\,''|}\ \psi_k(\vec{r}\,'')]\,\psi_j(\vec{r}\,')\} \quad . \tag{2-499}$$

The as yet undetermined ψ_j's are now chosen such that $E_{Hartree}$ is stationary under infinitesimal variations of them. Thus

$$\sum_{j=1}^{N}\int (d\vec{r}\,')\,\delta\psi_j{}^*(\vec{r}\,')\,\{-\ \tfrac{1}{2}\nabla'^{\,2} + V_{ext}(\vec{r}\,') + \sum_{k=1}^{N}\int (d\vec{r}\,'')\,\psi_k{}^*(\vec{r}\,'')\frac{1}{|\vec{r}\,'-\vec{r}\,''|}$$

$$\times\ \psi_k(\vec{r}\,'')\}\psi_j(\vec{r}\,') = o \quad . \tag{2-500}$$

The variations $\delta\psi_j{}^*$ are not arbitrary but subject to

$$\int (d\vec{r}\,')\,\delta\psi_j{}^*(\vec{r}\,')\ \psi_k(\vec{r}\,') = o \quad , \tag{2-501}$$

which is a consequence of the orthonormalization (495). Therefore, Eq. (500) implies

$$\{-\frac{1}{2}\nabla'^2 + V_{ext}(\vec{r}\,') + \sum_{k=1}^{N} \int (d\vec{r}\,'')\, \psi_k{}^*(\vec{r}\,'') \frac{1}{|\vec{r}\,'-\vec{r}\,''|} \psi_k(\vec{r}\,'')\}\psi_j(\vec{r}\,') \tag{2-502}$$
$$= \sum_{\ell=1}^{N} \varepsilon_{j\ell}\ \psi_\ell(\vec{r}\,') \quad ,$$

where the constants $\varepsilon_{j\ell}$ are the Lagrange mulitpliers of the constraints (495). The single-particle wave-functions ψ_j and the $\varepsilon_{j\ell}$ are to be determined simultaneously from Eqs.(502) and (495).

The hermitian property of the differential operator $\{\ldots\}$ in (502) is employed in demonstrating that the matrix $(\varepsilon_{j\ell})$ is hermitian:

$$\varepsilon_{j\ell} = \int (d\vec{r}\,')\ \psi_\ell{}^*(\vec{r}\,')\{\ldots\}\ \psi_j(\vec{r}\,') \tag{2-503}$$
$$= \int (d\vec{r}\,')\ \psi_j(\vec{r}\,')\{\ldots\}\ \psi_\ell{}^*(\vec{r}\,') = \varepsilon^*_{\ell j} \quad .$$

Another observation is the nonuniqueness of the solution to (502) and (495). If ψ_j and $\varepsilon_{j\ell}$ are one solution, then

$$\tilde{\psi}_j = \sum_{\ell=1}^{N} u_{j\ell}\ \psi_\ell \tag{2-504}$$

and

$$\tilde{\varepsilon}_{j\ell} = \sum_{k,m=1}^{N} u_{jk}\ \varepsilon_{km}\ u^*_{\ell m} \tag{2-505}$$

is another one, whereby $(u_{j\ell})$ is any unitary matrix,

$$\sum_{m=1}^{N} u^*_{mj}\ u_{mk} = \delta_{jk} \quad . \tag{2-506}$$

It is essential here that the density, that appears in (502), is invariant under such a unitary transformation:

$$\tilde{n}(\vec{r}\,') = \sum_{k=1}^{N} \tilde{\psi}_k{}^*(\vec{r}\,')\ \tilde{\psi}_k(\vec{r}\,') \quad =$$

$$= \sum_{k=1}^{N} \psi_k^*(\vec{r}\,')\ \psi_k(\vec{r}\,') = n(\vec{r}\,') \quad . \tag{2-507}$$

[The approximate wave-function (494) is obviously not invariant under (504). This is nothing to worry about, because as soon as (494) is antisymmetrized, the effect of (504) reduces to the mulitplication by a phase-factor.]

Since $(\varepsilon_{j\ell})$ is hermitian, we can choose $(u_{j\ell})$ such that $(\tilde{\varepsilon}_{j\ell})$ is diagonal,

$$\tilde{\varepsilon}_{j\ell} = \tilde{\varepsilon}_j\ \delta_{j\ell} \quad . \tag{2-508}$$

Then Eq. (502) is Schrödinger's equation in appearance,

$$\{-\tfrac{1}{2}\nabla'^2 + V(\vec{r}\,')\}\,\tilde{\psi}_j(\vec{r}\,') = \tilde{\varepsilon}_j\ \tilde{\psi}_j(\vec{r}\,') \quad , \tag{2-509}$$

where the effective single-particle potential V is

$$V(\vec{r}\,') = V_{ext}(\vec{r}\,') + \sum_{k=1}^{N}\int (d\vec{r}\,'')\,\psi_k^*(\vec{r}\,'')\frac{1}{|\vec{r}\,'-\vec{r}\,''|}\ \psi_k(r'') \quad , \tag{2-510}$$

which is equivalent to

$$\sum_{k=1}^{N} \psi_k^*(\vec{r}\,')\psi_k(\vec{r}\,') = -\frac{1}{4\pi}\ \nabla'^2(V(\vec{r}\,')-V_{ext}(\vec{r}\,')) \ . \tag{2-511}$$

Let us now look at the Hartree energy. It is

$$\begin{aligned} E_{Hartree} &= \sum_{j=1}^{N}\int (d\vec{r}\,')\,\psi_j^*(\vec{r}\,')\{-\tfrac{1}{2}\nabla'^2 + V_{ext}(\vec{r}\,') \\ &\qquad + \tfrac{1}{2}(V(\vec{r}\,') - V_{ext}(\vec{r}\,'))\}\psi_j(\vec{r}\,') \\ &= \sum_{j=1}^{N}\int (d\vec{r}\,')\,\psi_j^*(\vec{r}\,')\ \sum_{\ell=1}^{N} \varepsilon_{j\ell}\ \psi_\ell(\vec{r}\,') \\ &\qquad -\tfrac{1}{2}\int (d\vec{r}\,')\,(V(\vec{r}\,') - V_{ext}(\vec{r}\,'))\sum_{j=1}^{N}\psi_j^*(\vec{r}\,')\psi_j(\vec{r}\,') \quad , \end{aligned} \tag{2-512}$$

where both (502) and (510) have been used. With the aid of the orthonormality of the ψ_j's and with Eq. (511) we obtain

$$E_{\text{Hartree}} = \sum_{j=1}^{N} \varepsilon_{jj} - \frac{1}{8\pi}\int (d\vec{r}\,')\,[\vec{\nabla}'(V(\vec{r}\,') - V_{\text{ext}}(\vec{r}\,'))]^2 \quad . \tag{2-513}$$

This will look even more like the TF potential functional after we use

$$\sum_{j=1}^{N} \varepsilon_{jj} = \sum_{j=1}^{N} \tilde{\varepsilon}_{jj} = \sum_{j=1}^{N} \tilde{\varepsilon}_{j} \quad , \tag{2-514}$$

in conjunction with the fact that the $\tilde{\varepsilon}_j$ are the N smallest eigenvalues of the single-particle Hamilton operator

$$H = \frac{1}{2}p^2 + V(\vec{r}) \quad , \tag{2-515}$$

to write

$$\sum_{j=1}^{N} \varepsilon_{jj} = \operatorname{tr} H\,\eta(-H-\zeta) \quad , \tag{2-516}$$

where, of course, ζ is such that the count of occupied states equals the number of electrons:

$$N = \operatorname{tr} \eta(-H-\zeta) \quad . \tag{2-517}$$

If we combine (516) and (517) in the now familiar way,

$$\begin{aligned}\sum_{j=1}^{N} \varepsilon_{jj} &= \operatorname{tr}(H+\zeta)\eta(-H-\zeta) - \zeta N \\ &= E_1(V+\zeta) - \zeta N \quad ,\end{aligned} \tag{2-518}$$

then

$$E_{\text{Hartree}} = E_1(V+\zeta) - \frac{1}{8\pi}\int (d\vec{r}\,')\,[\vec{\nabla}'(V(\vec{r}\,') - V_{\text{ext}}(\vec{r}\,'))]^2 - \zeta N. \tag{2-519}$$

It becomes clear now what the fundamental difference is between the TF approach and Hartree's method. The latter asks: what are the optimal single-particle wave functions to be used in (494)?

The answer is given by the Hartree equations (502).[26] But suppose we do not care that much for the ψ_j's. Then we can equally well put the question: what is the best effective potential in (519)? We reply immediately: the TF potential, if $E_1(V+\zeta)$ is evaluated in the semiclassical limit. Does this mean that the TF model is an approximation to Hartree's description? No, it is rather the other way round: the Hartree picture contains more detail than it should. In view of all the approximations made before arriving at (519), there is absolutely no point in being extremely precise when evaluating $E_1(V+\zeta)$.

Summing up: the TF model and Hartree's method are really two independent, though related, approaches. None is a priori the better or worse one. Whereas I do not want to go as far as Lieb does ["... TF theory is well defined.(...) - a state of affairs in marked contrast to that of HF theory."[27]], I do have the impression that in applying TF methods one is more conscious about the physical approximations that enter the development.

In one respect the Hartree detour over the single-particle wave functions is superior to the TF phase-space integral: the Schrödinger equation (509) treats the strongly bound electrons correctly without any further ado. We shall see in the next Chapter how the TF model can be modified, in a simple way, in order to handle these innermost electrons properly. With this improvement the TF description is in no way inferior to Hartree's.

Please do not miss how naturally we have been led to a potential functional, Eq.(519), not to a density functional. Here is, once more, support for our view that TF theory is best thought of as formulated in terms of the effective potential. Then the density is not a fundamental but a derived quantity.

Problems

2-1. For the generalization of the independent-particle Hamilton operator of Eq.(3) to

$$H = \frac{1}{2}(\vec{p} - \alpha\vec{A}(\vec{r}))^2 + V(\vec{r}) \quad ,$$

where $\alpha = \frac{e^2}{\hbar c} = 1/137.036...$ is Sommerfeld's fine structure constant and $\vec{A}$ is an effective vector potential (in atomic units), show that the analogs of (14) and (20) are

$$\delta_{\vec{A}}\, E_{IP} = \delta_{\vec{A}}\, E_1 = -\,\alpha\int(d\vec{r}\,')\,\delta\vec{A}(\vec{r}\,')\cdot\vec{j}(\vec{r}\,') \quad ,$$

and

$$\vec{j}(\vec{r}\,') = 2\langle\vec{r}\,'|\tfrac{1}{2}[(\vec{p}-\alpha\vec{A})\,\eta(-H-\zeta)+\eta(-H-\zeta)\,(\vec{p}-\alpha\vec{A})]\,|\vec{r}\,'\rangle \ .$$

Then generalize Eq.(25) to read

$$\delta E_{ee} = \int(d\vec{r}\,')\,[\delta n(\vec{r}\,')V_{ee}(\vec{r}\,') - \alpha\delta\vec{j}\cdot\vec{A}_{ee}] \quad .$$

Next conclude that, instead of (30), the stationary energy expression is now

$$E = E_{IP} - \int(d\vec{r}\,')V_{ee}(\vec{r}\,')n(\vec{r}\,')+\alpha\int(d\vec{r}\,')\vec{A}_{ee}(\vec{r}\,')\cdot\vec{j}(\vec{r}\,') + E_{ee} \ ,$$

since

$$\vec{A} = \vec{A}_{ext} + \vec{A}_{ee} \quad ,$$

with a given external vector potential $\vec{A}_{ext}$. How does the TF version of E_1 depend on $\vec{A}$?

2-2. Another application of the stationary property of the electrostatic potential functional of Eq.(78). Instead of $\Phi(\vec{r})$, insert $\Phi(\vec{r}\,')$, where $\vec{r}\,'$ is related to $\vec{r}$ through an infinitesimal translation by $\delta\vec{\varepsilon}$ and an infinitesimal rotation around $\delta\vec{\omega}$,

$$\vec{r} = \vec{r}\,' + \delta\vec{\varepsilon} + \delta\vec{\omega}\times\vec{r}\,' \quad .$$

Use $(d\vec{r}) = (d\vec{r}\,')$ and $(\vec{\nabla}\Phi(\vec{r}\,'))^2 = (\vec{\nabla}'\Phi(\vec{r}\,'))^2$ to write the primed energy as

$$E' = \int(d\vec{r}\,')\,[\rho(\vec{r}\,'+\delta\vec{\varepsilon}+\delta\vec{\omega}\times\vec{r}\,')\Phi(\vec{r}\,') - \frac{1}{8\pi}(\vec{\nabla}'\Phi(\vec{r}\,'))^2]$$

$$\leqq E = \int(d\vec{r})\,[\rho(\vec{r})\Phi(\vec{r}) - \frac{1}{8\pi}(\vec{\nabla}\Phi(\vec{r}))^2] \quad ,$$

where the equal sign holds to first order in $\delta\vec{\varepsilon}$ and $\delta\vec{\omega}$. Conclude, that the self force vanishes [Eq.(86)], and also the self torque,

$$\int(d\vec{r})\,\rho(\vec{r})\,\vec{r}\times(-\vec{\nabla}\Phi(\vec{r})) = 0 \quad .$$

2-3. Write a computer program for the TF function F(x) as outlined around Eq.(200). Use it to confirm

$$\int_0^\infty dx\, F(x) = 1.80006394 \quad ,$$

$$\int_0^\infty dx[F(x)]^2 = 0.61543464 \quad ,$$

$$\int_0^\infty dx[-F'(x)]^3 = 0.35333456 \quad ,$$

$$\int_0^\infty dx\sqrt{F(x)/x} = 3.915933 \quad .$$

2-4. With the computer program of Problem 3 check that the maximum of xF(x) occurs at x=2.104025280, where F(x)=0.2311514708.

2-5. This maximum of xF(x) is relatively broad, so that

$$F''(x)/[F(x)]^2 = [x\,F(x)]^{-1/2} \cong \text{constant} \quad .$$

An approximation to F(x) is therefore represented by the solution of

$$\tilde{F}''(x) = \frac{6}{\tilde{x}^2}[\tilde{F}(x)]^2 \quad , \qquad \tilde{x} = \text{const.} \ ,$$

subject to $\tilde{F}(o)=1$, $\tilde{F}(\infty)=o$, and (to fix the value of $\tilde{x}$)

$$\int_0^\infty dx\; x^{1/2}[\tilde{F}(x)]^{3/2} = 1 \quad .$$

Find this $\tilde{F}(x)$.[28] How good is this approximation when it is employed in calculating the numbers of Problems 3 and 4?

2-6. Insert $\phi_\lambda(o)$ of Eq.(283) into Eq.(274) to find $\phi_1'(o)$ and $\phi_2'(o)$ as the coefficients in

$$\phi_\lambda'(o) = -1 + \phi_1'(o)\,\lambda + \phi_2'(o)\,\lambda^2 + \ldots \quad .$$

Compare with Eqs.(280) and (281).

2-7. Find $\phi_2(t)$ from Eq.(278); then evaluate $\phi_3(o)$. Use it to show that

(i) in Eq. (285):

$$O((N/Z)^2) = (12 - \frac{21067}{60\pi^2} + \frac{524288}{255\pi^4})(\frac{N}{Z})^2 + O((N/Z)^3) \quad ;$$

(ii) in Eqs. (286) and (289):

$$O((N/Z)^2) = (\frac{2}{3} + \frac{223}{30\pi^2} - \frac{262144}{2025\pi^4})(\frac{N}{Z})^2 + O((N/Z)^3) \quad ;$$

(iii) in Eq. (287):

$$O((N/Z)^2) = (\frac{22}{3} - \frac{19019}{90\pi^2} + \frac{2883584}{2025\pi^4})(\frac{N}{Z})^2 + O((N/Z)^3) \quad .$$

2-8. Use the recurrence relation (278) to show that

$$\phi_\ell(t) \sim (1-t)^{(5\ell+2)/2} \qquad \text{for} \quad t \lesssim 1 \quad .$$

Look back at Eq. (311) and notice that, indeed, the first occurence of Λ is in the $(1-t)^{7/2}$-term, and of Λ^2 in the $(1-t)^6$-term.

2-9. Show that, for $\lambda > \Lambda$, $\phi_\lambda(t)$ has a pole, at $t = t_\lambda > o$, of the form

$$\phi(t) \cong \frac{400}{\lambda^2} \frac{t_\lambda}{(t-t_\lambda)^2} \qquad \text{for} \quad t \cong t_\lambda \quad .$$

As $\lambda \to \infty$, $t_\lambda \to 1$, so that $\phi''_\lambda(t) \cong \lambda[\phi(t)]^{3/2}$ for $t_\lambda < t \leqq 1$. Use this to demonstrate that

$$1 - t_\lambda \cong \int_o^\infty \frac{d\phi}{\sqrt{1 + \frac{4}{5}\lambda\phi^{5/2}}} = (\frac{61.9}{\lambda})^{2/5} \quad ,$$

for $\lambda >> \Lambda$.

2-10. Upper and lower bounds to $\Lambda^{-2/3}$ can be obtained from Eq. (301) when it is combined with the inequalities of (242). A suitable trial function f(x) is given by

$$f(x) = \begin{cases} F(x) & \text{for} \quad o \leqq x \leqq x_1 \\ \frac{q}{x_o}(x_2 - x) & \text{for} \quad x_1 \leqq x \end{cases} \quad ,$$

where q is fixed, x_o is arbitrary, and x_1 and x_2 are such that f(x) and its derivative are continuous. For $q \gtrsim o$, x_1 is sufficiently large to justify the use of the asymptotic form (179) for $F(x \geq x_1)$. Show that this implies

$$x_2 = \frac{4}{3} x_1 \qquad \text{and} \qquad x_1^4 = \frac{432}{q/x_o} \quad .$$

Then derive

$$\frac{2}{5} \int_o^\infty dx \, \frac{[f(x)]^{5/2}}{x^{1/2}} = \frac{2}{7} B - \frac{2}{35} \frac{(12)^5}{x_1^7} + \frac{2}{5} \left(\frac{q}{x_o}\right)^{5/2} \left(\frac{4}{3}\right)^3 x_1^3 \left(\frac{5\pi - 9\sqrt{3}}{48}\right) \quad ,$$

and

$$\frac{1}{2} \int_o^\infty dx [f'(x) + \frac{q}{x_o}]^2 = \frac{1}{7} B - \frac{3}{56} \frac{(12)^5}{x_1^7} - \frac{q}{x_o} + \frac{5}{6} \left(\frac{q}{x_o}\right)^2 x_1 \quad .$$

Putting everything together you should have

$$\frac{3}{7} B - \frac{(12)^5}{x_1^7} \left[\frac{30}{7} - \frac{8\pi}{3\sqrt{3}} + \frac{3}{4} \frac{x_o}{x_1}\right]$$

$$> \frac{3}{7} B - \frac{3}{7} \Lambda^{-2/3} q^{7/3} \quad , \qquad \text{for} \quad q \to o \; .$$

It is then useful to switch from x_o to a new independent parameter, λ, by setting $x_o \equiv \lambda^{2/3} q^{-1/3}$. Check that then $x_1 = (432)^{1/4} \lambda^{1/6} q^{-1/3}$, so that, for all $\lambda > o$,

$$\Lambda^{-2/3} > \frac{7}{3} \lambda^{-2/3} - \frac{8}{3^{5/4}} \left(\frac{56\pi}{3\sqrt{3}} - 30\right) \lambda^{-7/6} \quad .$$

Optimize λ and find the lower bound on $\Lambda^{-2/3}$ of (303). Show that, for this optimal λ, the ratio x_2/x_o does not equal unity. Consequently, the trial $f(x)$ does not change its sign at $x = x_o$, as the actual $f(x)$ does. Impose $x_2 = x_o$ and demonstrate that a lower bound on $\Lambda^{-2/3}$ emerges, which is worse than the previous one.
For an upper bound on $\Lambda^{-2/3}$ use the trial function

$$g(x) = \begin{cases} F'(x) + q/x_o & \text{for } o \leq x \leq x_1 \\ -q/x_o (1 - x/x_2) & \text{for } x_1 \leq x \leq x_2 \\ o & \text{for } x_2 \leq x \end{cases} \quad .$$

Make sure that g is continuous and obeys Eq. (243). Then evaluate the g-functional of (242). You should get

$$\Lambda^{-2/3} < \frac{1}{60}\left[\frac{6t}{(5t-1)(3-t)}\right]^{7/3}\left(1-\frac{1}{2}t\right)^{1/3}\left[\frac{1}{9}\left(\frac{35}{t}-16+191t-74t^2\right)\right.$$

$$\left.+\frac{7}{4}t^{1/3}\left(1-\frac{1}{2}t\right)^{1/3}\left(1-t^{4/3}\right)\right] ,$$

where the range of $t=x_1/x_2$ is $\frac{1}{5}<t\leqq 1$. Find (numerically) the optimal value for t and thus the upper bound on $\Lambda^{-2/3}$ of (303).

2-11. Insert Eq. (316) into

$$\Phi(t) = \frac{1}{q} f_q(t\, x_o(q))\Big|_{q\to o}$$

and derive (352).

2-12. Derive Eq. (462) directly from Eqs. (433), (432), and (428).

2-13. Because of the homogeneity and isotropy of the physical three-dimensional space, the density functionals $E_{kin}(n)$ and $E_{ee}(n)$, which appear in Eq. (417), have the same numerical value for $n(\vec{r}\,')$ and the infinitesimally translated and rotated $\tilde{n}(\vec{r}\,') = n(\vec{r}\,' + \delta\vec{\varepsilon} + \delta\vec{\omega}\times\vec{r}\,')$. Combine this with the stationary property of (417) to show that there is no net force,

$$\int(d\vec{r}\,')n(\vec{r}\,')(-\vec{\nabla}' V_{ext}(\vec{r}\,')) = o \quad ,$$

and no net torque,

$$\int(d\vec{r}\,')n(\vec{r}\,')\vec{r}\,' \times (-\vec{\nabla}' V_{ext}(\vec{r}\,')) = o \quad ,$$

exerted on the system by the external potential. Are you reminded of Problem 2?

2-14. Show that the density functional of the kinetic energy is given by

$$E_{kin}(n) = \int(d\vec{r})\,\frac{1}{8}\,(\vec{\nabla}n)^2/n \quad ,$$

if there is only one electron. This does scale like (443). Why is there no contradiction to the general statement that E_{kin} does not obey (443)?