Corrections to the Thomas–Fermi Model of the Atom*

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A WKB approximation to the Hartree equations for an atom, taking the $1/r$ singularity of the potential into account, is developed. This in turn allows us to obtain in a systematic way the $Z^{-1/3}$ and $Z^{-2/3}$ corrections to the Thomas–Fermi model of the atom. Such a procedure is used to obtain a finite change density at the nucleus, which agrees well with Hartree–Fock values.

I. INTRODUCTION

It has been recognized for a long time that the Thomas–Fermi equations for a many-electron system may be obtained in a semi-classical approximation to the Hartree or Hartree–Fock self-consistent equations for such a system [1]. A naive expansion, in powers of $\hbar$, of these self-consistent equations leads to corrections of order $Z^{p-2/3}$ to the leading term of the Thomas–Fermi equation but has difficulty in correctly describing the energy functional. It was pointed out by Scott [2] that the leading corrections to the energy are of order $Z^{-1/3}$ compared to the leading term and are independent of the interelectronic repulsion. Scott's derivation did not indicate how to obtain higher order corrections. March and Plaskett [3] solved the Hartree equations, in a WKB approximation, for $Z = 18$ (the self-consistent potential was taken from the solution of the uncorrected Thomas–Fermi equations); they isolated the leading and Scott terms and attributed all of the remainder to the next order correction and obtained the coefficient of the $Z^{-2/3}$ corrections to the leading term. The agreement with observed binding energies was very good. The results for the energy of an atom of $Z$ electrons is (in units of $e^4m/\hbar^2$)

$$-E(Z) = 0.76874Z^{7/3} - 0.5Z^2 + cZ^{2/3}. \quad (1.1)$$

The first term is the original Thomas–Fermi result, the second is the correction due to Scott and the last one is due in part to exchange interactions [4] and in part to $\hbar^2$ corrections to the leading result. The result of Ref. [3] is

$$c = 0.266. \quad (1.2)$$

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A more recent determination of such a fit to Hartree–Fock energies was made by Shakeshaft et al. [5]. These authors found a best value for $c$,

$$c = 0.275 \pm 0.005$$  \hspace{1cm} (1.3)

with this value of $c$ reproduces the Hartree–Fock binding energies to a few parts in $10^{-4}$ for $Z \sim 100$ and is within 8% for $Z = 1$.

Recently, Schwinger [6] obtained both the Scott correction, as well as the coefficient of the $Z^{-2/3}$ term. The theoretical value of $c$ is

$$c = 0.270.$$  \hspace{1cm} (1.4)

which is very close to either (1.20) or (1.3). In Schwinger’s treatment the continuous approximation to the discontinuous function $\lfloor x \rfloor$ (largest integer less than $x$) is taken as $x - \frac{1}{2}$. It is not clear whether the oscillations around this approximation contribute to $c$. As we shall show these oscillations will contribute to higher terms. That higher order terms are likely to be nonanalytic has been noted by Shakeshaft and Spruch [7].

Another quantity for which the Thomas–Fermi approximation gives glaringly wrong results is the charge density at the nucleus. In this approximation it is infinite, whereas in reality it is finite. The methods for correcting the WKB approximation will yield a finite answer which, for larger $Z$, is in good agreement with the Hartree–Fock result.

The reason a straightforward WKB approximation cannot be applied to this problem is that the Coulomb potential near the nucleus varies too rapidly for such an approximation to be valid. Naively, one would expect the Scott term to be absent. A treatment taking into account the singular nature of the potential at the origin restores this term. At first sight one might argue that a smearing out of this singularity would solve the problem. However, a fixed nuclear radius will not do, as the Bohr radius of the $K$ shell behaves as $h^2/Z^2$, and for small $h$ or large $Z$ would lie inside any fixed distance. We need a cutoff depending on $h$ and $Z$. Of course quantum mechanics does provide such a cutoff. Heuristically, we may see it even in a WKB approximation. Langer [8] pointed out that in this approximation, the angular momentum $lh$ should go to $(l + \frac{1}{2})h$ and thus, even for $S$ waves we have a centrifugal barrier providing a cutoff of the right magnitude.

In Section II, we review the Hartree approximation. This approximation is the first term in a WKB expansion in $\hbar$ or equivalently an expansion in the number of loops of a Feynman diagram [9].

The next term is responsible for the exchange interaction energy. The Hartree term itself may be expanded as a power series in $\hbar$, with the attendant difficulties
mentioned earlier. Thus, in principle, we have a formalism for a systematic expansion of the atomic problem. It should be emphasized that in this formalism it is the Hartree term that determines the self-consistent field, and the Dirac exchange term is evaluated with that field as input. Had one started from the Hartree-Fock equations then the sum of the exchange and direct terms would be minimized to obtain the self consistent field, yielding the Thomas-Fermi-Dirac model [10]. The Hartree-Fock approximation is intrinsically a variational approximation, while, as we will show, the Hartree approximation is the first term of a systematic expansion. Of course, to the order we are working in, the Hartree-Fock model is likely to be a better physical approximation.

The WKB solution of the Hartree equation is presented in Section III. The procedure for handling the aforementioned singularity consists of subtracting a similar expression for the situation where the interelectronic repulsion is neglected. This difference has, to the order considered, a straightforward WKB expansion. The exact value for this extra term is then added back. This, together with the exchange interaction, yields (1.4). We also note that any further corrections will be nonanalytic in \( Z^{-1/3} \).

Section IV is devoted to a study of the electronic change density at the nucleus. The Thomas-Fermi density diverges at this point. We subtract the density for a purely hydrogenic system filled to a definite level, obtain a finite Thomas-Fermi approximation to this difference and then add on the exact value for the hydrogenic system. The highest level of this system is determined by the solution of the Thomas-Fermi equations. This procedure describes the leading and \( Z^{-2/3} \) corrections to this change density. For large \( Z \) the Hartree-Fock values are reproduced.

II. Thomas-Fermi Approximation to the Hartree Model

A. A Restatement of the \( N \) Electron Problem

The Hamiltonian, in second quantized form, for an atomic system of electrons interacting with each other and with a nucleus of charge \( Z \) is [11]

\[
H = \int d^3x \left\{ \frac{\hbar^2}{2m} \nabla \psi_\alpha^+(x) \cdot \nabla \psi_\alpha(x) - \frac{Ze^2}{|x|} \psi_\alpha^+(x) \psi_\alpha(x) \right. \\
\left. + \frac{e^2}{2} \psi_\alpha^+(x) \psi_\alpha(x) \int d^3y \frac{1}{|x-y|} \psi_\beta^+(y) \psi_\beta(y) \right\}, \tag{2.1}
\]

\( \psi(x) \) is the Fermi field operator for the electron. In (2.1) and subsequently, repeated indices are summed over. The electron density is

\[
\rho(x) = \psi_\alpha^+(x) \psi_\alpha(x) \tag{2.2}
\]

leading to a number operator

\[
N = \int d^3x \psi_\alpha^+(x) \psi_\alpha(x). \tag{2.3}
\]
It is convenient to treat this problem in the grand canonical formalism and we introduce the operator

$$K = H - \mu N,$$  \hspace{1cm} (2.4)

with $\mu$ the chemical potential. Results for specific $N$'s are obtained by appropriate Legendre transforms between $\mu$ and $N$.

In order to obtain the Hartree equations we eliminate the quartic coupling in (2.1) by introducing a scalar field $\sigma(x)$.

$$K = \int d^3x \left\{ -\frac{1}{2} (\nabla \sigma)^2 + \frac{\hbar^2}{2m} \nabla \psi^+ \nabla \psi - \left( \mu + \frac{Ze^2}{|x|} - \sqrt{4\pi e^2} \sigma \right) \psi^+ \psi \right\}. \hspace{1cm} (2.5)$$

The Euler-Lagrange equations for $u$,

$$\nabla^2 u(x) = -\nabla^2 \rho(x),$$

are used to eliminate $\sigma(x)$ from (2.5) yielding back the Hamiltonian of (2.1).

We note that for a fixed $\sigma(x)$, (2.5) is the Hamiltonian for electrons interacting with the nucleus and with an external potential $\sqrt{4\pi e^2} \sigma(x)$.

B. Hartree Approximation

The Hartree self-consistent approximation results from replacing the right hand side of (2.6) by its ground state expectation value

$$\nabla^2 \sigma = -\sqrt{4\pi e^2} \langle \rho(x) \rangle.$$  \hspace{1cm} (2.6)

The ground state refers to that of electron moving in an external potential determined by $\sigma$, but not interacting with each other. In this ground state all levels up to the chemical potential $\mu$ are filled.

$$\langle \rho(x) \rangle = 2\langle x | \theta \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} - \sqrt{4\pi e^2} \sigma \right] | x \rangle,$$  \hspace{1cm} (2.7)

while the corresponding eigenvalue of $K$, Eq. (2.4), is

$$\mathcal{E}(\mu) = \int d^3x \left\{ -\frac{1}{2} (\nabla \sigma)^2 - \langle x | \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} - \sqrt{4\pi e^2} \sigma \right] + | x \rangle \right\}. \hspace{1cm} (2.8)$$

The subscript $+$ indicates that we project out only the positive eigenvalues of the operator.

Hartree equations (2.6) and (2.7) are the equations for the self-consistent field $\sigma(x)$. In the language of Feynman diagrams, the solution of these equations corresponds to a summation of one loop diagrams, or equivalently is the first term in
a WKB expansion in $\hbar$ [9]. The higher terms in this expansion represent exchange energies, correlation energies, etc. The exchange energy is [4, 6]

$$\mathcal{E}_{\text{exch}}(\mu) = \frac{1}{2} \int d^3x \, d^3y \, \frac{e^2}{|x - y|} \sum_{\mathcal{E} < \mu} \langle \phi_{E,\alpha}(x) \times \phi_{E',\alpha}(y) \phi_{E',\beta}(x) \rangle. \tag{2.9}$$

$\phi_{E,\alpha}$ is an eigenfunction of the self-consistent Hartree Hamiltonian with energy eigenvalue $E$ and spin $\alpha$. The summations in (2.9) may be carried out in a formal way. We obtain

$$\mathcal{E}_{\text{exch}}(\mu) = -\frac{1}{2} \int d^3x \, d^3y \, \frac{e^2}{|x - y|} \langle x | \theta \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} \right] y \rangle \langle y | \frac{1}{2} \frac{\hbar^4 \nabla^2}{m^2} \rangle \tag{2.10}$$

As we shall show, this term is of order $Z^{-2/3}$ compared to the direct energy given in (2.8).

C. Thomas–Fermi Approximation

As in the matrix element is (2.7) cannot be obtained in analytic form for arbitrary $\sigma(x)$, the Hartree equations are solved iteratively. We shall develop a method of evaluating the matrix elements appearing in (2.7) and (2.8). It is a variant of the WKB approximation. These matrix elements may be obtained from

$$G(x, x'; \eta) = \langle x | e^{i\eta/H} e^{\frac{\hbar^2\nabla^2}{2m} V(x)} | x' \rangle, \quad V(x) = -\frac{Ze^2}{|x|} + \sqrt{4\pi e^2} \sigma(x). \tag{2.11}$$

Knowing this matrix element we find

$$\langle x | \theta \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} - V(x) \right] x' \rangle = \frac{1}{2\pi i} \int \frac{d\eta}{\eta - i\epsilon} G(x, x'; \eta);$$

$$\langle x | \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} - V(x) \right] x \rangle = -\frac{i\hbar}{2\pi i} \int \frac{d\eta}{(\eta - i\epsilon)^2} G(x, x; \eta). \tag{2.12}$$

Equation (2.11) may be viewed as the propagator for a Schrödinger particle moving from $x'$ to $x$ in time $\eta$. It has a standard Feynman path integral representation [12]

$$G(x, x'; \eta) = \int |dQ| \exp \frac{i}{\hbar} \int_0^\eta \left[ \frac{m}{2} \dot{Q}^2 - V(Q) + \mu \right] dt. \tag{2.13}$$

In the above we integrate over all classical trajectories joining $x'$ to $x$ in time $\eta$. Let us first concentrate on the diagonal, $x = x'$ element. One path is the constant one

$$Q(t) = x. \tag{2.14}$$
We expand the integrand around this path, keeping up to terms of second order

\begin{equation}
Q(t) = x + q(t),
\end{equation}

\begin{equation}
G(x, x'; \eta) = \int [dq] \exp \left[ \frac{i}{\hbar} \int_0^n \left[ \frac{m}{2} q^2 - V(x) - \nabla_i V(x) q_i \right. \right. \\
\left. \left. - \frac{1}{2} \nabla_i \nabla_j V(x) q_i q_j + \cdots + \mu \right] dt \right]
\end{equation}

\begin{equation}
= \int [dq] \exp \left[ \frac{i}{\hbar} \int_0^n \frac{m}{2} q^2 - V(x) + \mu \right] dt
\end{equation}

\begin{equation}
\times \left\{ 1 - \frac{i}{\hbar} \int_0^n \nabla_i V(x) q_i dt - \frac{i}{2\hbar} \int_0^n \nabla_i \nabla_j V(x) q_i q_j dt \right\}
\end{equation}

\begin{equation}
- \frac{1}{\hbar^2} \left( \int_0^n \nabla_i V(x) q_i dt \right)^2 + \cdots \right\}.
\end{equation}

The path integration is now governed by a free particle Lagrangian and can be evaluated explicitly. We need

\begin{equation}
\langle q_i(t) q_j(t') \rangle = \delta_{ij} \left( \frac{-i}{2m} \right) \left[ |t - t'| - t - t' + \frac{2\eta t'}{\eta} \right]
\end{equation}

to obtain

\begin{equation}
G(x, x'; \eta) = \frac{1}{\hbar^3} \left[ \frac{m}{2\pi i(\eta - i\epsilon)} \right]^{3/2} e^{i\eta H(\eta - i\epsilon)}
\end{equation}

\begin{equation}
\times \left[ 1 + \frac{\eta^2 \nabla^2 V}{12m} - \frac{i\eta^3}{24\hbar} (\nabla V)^2 + \cdots \right].
\end{equation}

Upon rescaling \( \eta \) to \( \eta/\hbar \) we see that the two terms involving the potential are of order \( \hbar^2 \) compared to the term independent of \( V \). Terms involving higher derivatives or products of more gradient terms will yield higher powers of \( \hbar \). Combining (2.18) with (2.12) we obtain

\begin{equation}
\langle x | \theta \left[ \mu + \hbar^2 \nabla^2 - V(x) \right] | x \rangle = \frac{1}{\pi^2 \hbar^3} \left( \frac{m}{2} \right)^{3/2} \left\{ \frac{4}{3} |\mu - V(x)|^{3/2} 
\end{equation}

\begin{equation}
+ \frac{\hbar^2}{12m} \frac{\nabla^2 |\mu - V(x)|}{|\mu - V(x)|^{1/2}} - \frac{\hbar^7}{48m} \frac{|\nabla |\mu - V(x)|}{|\mu - V(x)|^{3/2}} + \cdots \right\}
\end{equation}
and
\[
\langle x | \left[ \mu + \frac{\hbar^2}{2m} \nabla^2 - V(x) \right]_+ | x \rangle = \frac{1}{\pi^2 \hbar^2} \left( \frac{m}{2} \right)^{3/2} \left\{ \frac{8}{15} [\mu - V(x)]^{3/2}_+ \\
+ \frac{\hbar^2}{6m} [\nabla^2 [\mu - V(x)]_+]_+ + \frac{\hbar^2}{24m} [\nabla [\mu - V(x)]_+]_+^2 + \cdots \right\}.
\]

The first term on the right in (2.19) and (2.20) represents the usual Thomas–Fermi approximation. Equation (2.19) has been derived previously [1].

We note that, as with all WKB approximations, the validity of this one depends on how slowly the potentials vary. Equation (2.11) reminds us that \( V(x) \) has a Coulomb singularity at \( x \sim 0 \) and this approximation becomes suspect in this region. Specifically, the \( \hbar^2 \) terms in (2.19) behave as \( r^{-5/2} \) at the origin and are integrable while the corresponding terms in (2.20) behave as \( r^{-7/2} \) and are not integrable. This is the difficulty discussed in the introduction. The resolution of this problem is the subject of the next section.

Before closing this section we will obtain an approximation to the off diagonal matrix elements needed for the determination of the exchange energy.

Inserting a complete set of momentum states into the matrix elements appearing in (2.10) and to leading order in \( \hbar \), neglecting the noncommutativity of \( x \) and \( V \), we obtain

\[
\langle x | \theta \left[ \mu + \frac{\hbar^2 \nabla^2}{2m} - V(x) \right] | y \rangle = \int \frac{d^3p}{(2\pi\hbar)^3} e^{i \cdot (x-y) / \hbar} \theta \left[ \mu - \frac{p^2}{2m} - V(x) \right].
\]

Inserting the expression into (2.10), we obtain the exchange energy

\[
\mathcal{E}_{\text{exch}}(\mu) = -\frac{16\pi e^2 m^2}{(2\pi\hbar)^4} \int d^3x \left[ \mu + \frac{Ze^2}{|x|} - \sqrt{4\pi e^2 \sigma} \right]^2.
\]

### III. Corrections to the Thomas–Fermi Energy

#### A. Elimination of the 1/r Singularity

As noted earlier, the \( 1/r \) Coulombic term in \( V(x) \) yields an infinite contribution to the energy in (2.20). The potential varies too fast for the WKB approximation to be valid. The strategy we shall employ is to calculate the difference of (2.20) and similar
expressions with $V(x)$ purely Coulombic, and then add the exact expression for the Coulomb case.

The difference of matrix elements

$$
\Delta(x) = \langle x | \left[ \mu + \frac{\hbar^2}{2m} \nabla^2 - V(x) \right]_+ | x \rangle
- \langle x | \left[ \bar{\mu} + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} \right]_+ | x \rangle
$$

(3.1)

has an expansion in $\hbar$ which to order $\hbar^2$ is integrable at $x = 0$. As we project out only the positive eigenvalues of the above operators we may encounter rapid variations for large $x$. $\bar{\mu}$ is chosen to minimize these. We shall find that for the neutral atom and to the order we will study $\mu = 0$ and thus $\bar{\mu}$ will likewise be zero. Writing an expression similar to (2.20) for the second term above, subtracting the two terms and integrating the $\hbar^2$ terms by parts, we obtain

$$
2 \int d^3x \Delta(x) = \frac{2}{\pi^2 \hbar^4} \left( \frac{m}{2} \right)^{3/2} \int d^3x \left\{ \frac{8}{15} [\mu - V(x)]^{5/2} + \frac{8}{15} \left[ \bar{\mu} + \frac{Ze^2}{|x|} \right]^{5/2} + \frac{\hbar^2}{12m} \nabla^2 (-\sqrt{4\pi e^2} \sigma(x)) |\mu - V(x)|^{1/2} \right\}.
$$

(3.2)

Although to the order in $\hbar$ we shall be interested if the above difference is sufficient to obtain a finite result we shall indicate the procedures necessary to go to higher orders. In effect what we do is subtract, from (2.20), as many terms as necessary, in a power series in $\sigma$ around the pure Coulomb term. For example, had we been interested in terms of order $\hbar^4$ we would study

$$
\Delta(x) = \langle x | \left[ \mu + \frac{\hbar^2}{2m} \nabla^2 - V(x) \right]_+ | x \rangle - \langle x | \left[ \bar{\mu} + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} \right]_+ | x \rangle
- (\mu - \bar{\mu} - \sqrt{4\pi e^2} \sigma(x)) \langle x | \theta \left[ \bar{\mu} + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} \right] | x \rangle.
$$

(3.3)

Equation (3.3) has a finite expansion to order $\hbar^4$.

B. Energies without Electron Repulsion

The integral of the second term in (3.1) is just the energy of noninteracting electrons in a Coulomb field of charge $Ze$ and at a chemical potential $\bar{\mu}$.

$$
\int d^3x \langle x | \left[ \bar{\mu} + \frac{\hbar^2 \nabla^2}{2m} + \frac{Ze^2}{|x|} \right]_+ | x \rangle = \sum_{n=1}^{N} n^2 \left[ \bar{\mu} + \frac{Z^2 e^4 m}{2\hbar^2 n^2} \right]
$$

(3.4)
(\(n^2\) is the degeneracy of each level with principal quantum number \(n\)). \(N\) is the highest level filled whose energy is less than \(\tilde{\mu}\),

\[
N = \left\lfloor \left( -\frac{Z^2e^4m}{2\hbar^2\tilde{\mu}} \right)^{1/2} \right\rfloor,  \tag{3.5}
\]

where by \(|a|\) we mean the largest integer smaller than \(a\). The summation in (3.4) can be performed easily and we find

\[
(3.4) = \tilde{\mu} \left( \frac{N^3}{3} + \frac{N^2}{2} + \frac{N}{6} \right) + \frac{Z^2e^4m}{2\hbar^2} N.  \tag{3.6}
\]

Introducing \(\zeta\), the difference between \((-Ze^2m/2\hbar^2\tilde{\mu})^{1/2}\) and \(N\),

\[
N = \left( -\frac{Z^2e^4m}{2\hbar^2\tilde{\mu}} \right)^{1/2} - \zeta, \tag{3.7}
\]

we obtain

\[
(3.4) = \frac{2}{3} \left( \frac{Z^2e^4m}{2\hbar^2} \right)^{3/2} \frac{1}{(-\tilde{\mu})^{1/2}} - \frac{1}{2} \left( \frac{Z^2e^4m}{2\hbar^2} \right) + O(\sqrt{-\tilde{\mu}}). \tag{3.8}
\]

In the limit \(\tilde{\mu} \to 0\) this expression is independent of \(\zeta\).

We shall also need the explicit value of the integral involving \(\tilde{\mu}\) in (3.2). This integration is straightforward and yields

\[
-\frac{1}{\pi^2\hbar^3} \left( \frac{m}{2} \right)^{3/2} \frac{8}{15} \int d^3x \left[ \frac{\mu}{|x|} + \frac{Ze^2}{|x|} \right]^{5/2} = -\frac{2}{3} \left( \frac{Z^2e^4m}{2\hbar^2} \right)^{3/2} (-\tilde{\mu})^{-1/2}, \tag{3.9}
\]

namely, the first term in (3.8).

Combining (3.9), (3.8), (3.2), and (3.1), and taking the limit \(\tilde{\mu} \to 0\), we obtain a finite expression for

\[
2 \int \langle x \mid \mu + \frac{h^2}{2m} \nabla^2 - V(x) \mid x \rangle d^3x = \frac{2}{\pi^2\hbar^3} \left( \frac{m}{2} \right)^{3/2} \int d^3x \left\{ \frac{8}{15} [\mu - V(x)]^{5/2} + \frac{h^2}{12m} \nabla^2 (\sqrt{4\pi e^2 \sigma(x)}) [\mu - V(x)]^{1/2} \right\} \tag{3.10}
\]

This is the basic result of this treatment. It is a correct expression to order \(\hbar^2\). The last term is responsible for the Scott correction.

If we attempt to calculate higher order terms, as, for example, by the use of (3.3),
and as neither $\mu$ nor $\tilde{\mu}$ will be zero the answers will have a $\zeta$ dependence and this will be nonanalytic in $Z^{-1/3}$.

C. Solution to Order $\hbar^2$

Before bringing all these results together it is convenient to rescale all the variables to dimensionless form. Introduce

\[
b = \left( \frac{3\pi}{4} \right)^{2/3} \frac{\hbar^2}{2me^2},
\]
\[
x = bZ^{-1/3}y,
\]
\[
\mu = \frac{Z^{4/3}e^2}{4\pi b} \tilde{\mu},
\]
\[
\sigma = \frac{e}{\sqrt{4\pi}} \frac{Z^{4/3}}{b} \tilde{\sigma}.
\]

We separate the energies into direct and exchange terms

\[
\mathcal{E} = \frac{Z^{7/3}e^2}{4\pi b} \left[ \mathcal{E}_{\text{dir}} + \mathcal{E}_{\text{exch}} \right]
\]

with

\[
\mathcal{E}_{\text{dir}} = \int d^3y \left\{ -\frac{1}{2} (\nabla \tilde{\sigma})^2 - \frac{2}{5} \left[ \frac{\tilde{\mu}}{4\pi} + \frac{1}{y} - \tilde{\sigma} \right] \right\}_{+}^{5/2}
\]
\[
- \frac{1}{2} \frac{1}{(6\pi Z)^{2/3}} \nabla^2 (-\tilde{\sigma}) \left[ \frac{\tilde{\mu}}{4\pi} + \frac{1}{y} \right] \right\}_{+}^{1/2}
\]
\[
+ \frac{\pi}{4} \frac{1}{(6\pi Z)^{2/3}} Z^{-1/3}
\]

and

\[
\mathcal{E}_{\text{exch}} = -\frac{9}{4} \frac{1}{(6\pi Z)^{2/3}} \int \left[ \frac{\tilde{\mu}}{4\pi} + \frac{1}{y} - \tilde{\sigma} \right]_{+}^{2} d^3y.
\]

$\tilde{\sigma}(y)$ is determined by minimizing $\mathcal{E}_{\text{dir}}$ only.

\[
\nabla^2 \tilde{\sigma} + \left[ \frac{\tilde{\mu}}{4\pi} + \frac{1}{y} - \tilde{\sigma} \right]_{+}^{3/2} + \frac{1}{2} \frac{1}{(6\pi Z)^{2/3}}
\]
\[
\times \left\{ \frac{\nabla^2 (-\tilde{\sigma})}{[\tilde{\mu}/4\pi + 1/y - \tilde{\sigma}]_{+}^{1/2}} - \frac{1}{4} \frac{1}{[1/y - \tilde{\sigma}]_{+}^{3/2}} \right\} = 0.
\]
The relation between $N$ and $\mu$ is obtained by differentiating $\mathcal{E}_{\text{dir}}$ and $\mathcal{E}_{\text{exch}}$ with respect to $\bar{\mu}$.

$$
\frac{N}{Z} = \frac{1}{4\pi} \int d^3y \left\{ \left[ \frac{\bar{\mu}}{4\pi} + \frac{1}{y} - \bar{\sigma} \right]^{3/2} + \frac{1}{4} \frac{1}{(6\pi Z)^{2/3}} \frac{\nabla^2(-\bar{\sigma})}{\bar{\mu}/4\pi + 1/y - \bar{\sigma}} \right\} + \frac{9}{2} \frac{\bar{\mu}}{(6\pi Z)^{2/3}} \left[ \frac{\bar{\mu}}{4\pi} + \frac{1}{y} - \bar{\sigma} \right]^{1/2} \left( 1 - 4\pi \frac{\partial \bar{\sigma}}{\partial \bar{\mu}} \right)
$$

(3.16)

The term involving the derivative of $\bar{\sigma}$ with respect to $\bar{\mu}$ is due to the fact that the exchange term does not participate in the determination of $\bar{\sigma}$.

Equation (3.15) determines the self-consistent potential $\bar{\sigma}$. It is highly nonlinear and probably has many solutions. We shall be interested in is the one generated by the $Z^{-2/3}$ corrections to the classical Thomas–Fermi solution. To this order, $\bar{\sigma}$ is finite at the origin, implying a $y^{-3/2}$ singularity for the charge density. It is easy to see that there is a second class of solutions with $\bar{\sigma} \sim 1/y$ at the origin, resulting in a finite charge density. This solution is not obtainable in a perturbation series in $Z^{-2/3}$ around the lowest order solution, and thus falls outside the spirit of this approach. We would not recover the classical Thomas–Fermi model in the $Z \rightarrow \infty$ limit. It is amusing to note that if we do set $\bar{\sigma} = 1/y + \rho(x)$, we obtain the variational equation of the Thomas–Fermi–von Weizacker model [10], albeit with a coefficient nine times smaller than the one originally proposed by von Weizacker and about a factor 2/3 smaller than a phenomenologically determined term [10, 13].

We are primarily interested in the energy of atomic system for fixed $N$. We use (3.16) to eliminate $\bar{\mu}$ and (2.8) to find $E(N)$. The situation simplifies considerably for the neutral atom, $N = Z$. For the neutral atom, the first order Thomas–Fermi theory yields $\bar{\mu} = 0$, therefore for the present case $\bar{\mu} \sim Z^{-3/3}$. Separating $\bar{\sigma}$ into $\bar{\sigma}_0 + Z^{-2/3} \bar{\sigma}_1$, with $\bar{\sigma}_0$ determined by the first order theory, we obtain

$$
E(Z) = \frac{Z^{7/3} e^2}{4\pi b} \left[ \int d^3y \right] - \frac{1}{2} (\nabla \bar{\sigma}_0)^2 - \frac{2}{5} \left[ \frac{1}{y} - \bar{\sigma}_0 \right]^{5/2} + \frac{1}{2} \frac{\nabla^2(-\bar{\sigma}_0)}{(6\pi Z)^{2/3}} \left[ \frac{1}{y} - \bar{\sigma}_0 \right]^{1/2} - \frac{9}{4} \frac{1}{(6\pi Z)^{2/3}} \left[ \frac{1}{y} - \bar{\sigma}_0 \right]^{2} + \frac{\pi}{4} \frac{1}{(6\pi)^{2/3}} Z^{-1/3}
$$

and $\bar{\sigma}_0$ is determined by

$$
\nabla^2 \bar{\sigma}_0 + \left[ \frac{1}{y} - \bar{\sigma}_0 \right]^{3/2} = 0.
$$

(3.18)
The use of the above equation simplifies the expression for the energy

\[ E(Z) = \frac{Z^{7/3}e^2}{4\pi b} \left[ \int d^3y \left\{ -\frac{1}{2} \left( \nabla \tilde{\sigma}_0 \right)^2 - \frac{2}{y} \left[ \frac{1}{y} - \tilde{\sigma}_0 \right] \right\} \right]^{5/2} \]

\[ - \left( \frac{1}{2} + \frac{9}{4} \right) \frac{1}{(6\pi Z)^{2/3}} \left[ \frac{1}{y} - \tilde{\sigma}_0 \right]^{2/3} + \frac{\pi}{4} (6\pi)^{2/3} Z^{-1/3} \].

The third term in the above has been written in a form distinguishing the direct and exchange corrections. Inserting the numerical solutions for \( \tilde{\sigma}_0 \) gives the result of (1.4).

IV. Corrections to the Electron Density at the Nucleus

The Thomas–Fermi approximation to the electron density as well as the corrections to the density, though integrable at the origin are infinite at that point. This result is unphysical as the true density is finite. The purpose of this section will be to modify the Thomas–Fermi approximation so as to obtain such a finite density. We shall also compare these to Hartree–Fock results.

We wish to subtract from (2.7) a density for a purely hydrogenic system, such that the Thomas–Fermi approximation to this difference will be finite at the origin. Thus we consider

\[ P(X) - \rho_{\text{H}}(X) = \int \frac{d^3y}{L} \sum_{n} \hat{P} + \frac{Z e^2}{2m} \left( \frac{1}{y} - \tilde{\sigma}_0 \right) \int \frac{d^3y}{L} \sum_{n} \hat{P} \]

\[ = \frac{1}{2} \left( \frac{9}{4} \right) \frac{1}{(6\pi Z)^{2/3}} \left[ \frac{1}{y} - \tilde{\sigma}_0 \right]^{2/3} + \frac{\pi}{4} (6\pi)^{2/3} Z^{-1/3} \].

The hydrogenic term is evaluated at a chemical potential \( \mu' \), different from the one considered in the previous section. As we shall not be interested in the behavior of the density at large \( x \), \( \mu' \) does not have to be sent to zero when \( \mu \) is, and in fact will be chosen to insure that (4.1) is finite at \( x = 0 \).

The leading Thomas–Fermi approximation to (4.1) is (cf. (2.19))

\[ \rho(x) - \rho_{\text{H}}(x) = \frac{8}{3\pi^2} \left( \frac{m}{2} \right)^{3/2} \left\{ \left[ \mu + \frac{Ze^2}{|x|} - \sqrt{4\pi e^2 \sigma(x)} \right] \right\}^{3/2} \]

\[ - \left[ \mu' + \frac{Ze^2}{|x|} \right]^{3/2} \].

Choosing

\[ \mu' = \mu - \sqrt{4\pi e^2 \sigma(0)} \]

yields a finite value for (4.2) at \( x = 0 \).
\[ \rho_e(x) \] may be evaluated exactly. It is the electron density for noninteracting electrons bound to a charge \( Ze \) and filled up to a level

\[ N' = \left\lfloor \frac{Z^2 e^4 m}{2 \hbar^2 u'} \right\rfloor^{1/2} \]  

(4.4)

(Again the bracket denotes the largest integer smaller than the quantity in the bracket). For \( x = 0 \) this density is [14]

\[ \rho_e(0) = \frac{1}{c} \left( \frac{Z e^2 m}{\hbar^2} \right)^3 \sum_{n=1}^{N'} \frac{1}{n^3} \].  

(4.5)

To leading orders in \( Z^{-1/3} \), we find that for the neutral atom

\[ \rho(x) = \frac{1}{x} \left( \frac{Z e^2 m}{\hbar^2} \right)^3 \left[ 1.20 - \frac{1}{2} \left\{ 2^2 \sqrt{4 \pi e^2 \sigma(0)} \right\} \right] \].  

(4.6)

For the neutral atom \( \bar{\sigma}(0) = 1.588 \) [15], giving

\[ \pi \rho(0) \left( \frac{Z e^2 m}{\hbar^2} \right) = 1.20 - \frac{1.79}{Z^{2/3}}. \]  

(4.7)

In Table I we compare this result to Hartree–Fock values [16]. We see that we find a good description of this quantity down to \( Z = 50 \). In this picture the charge density at the nucleus is determined by \( N' \) hydrogenic wave functions, where \( N' \) is determined from the solution of the Thomas–Fermi equation.

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