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Statistical atom: Handling the strongly bound electrons

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We show how the corrections for strongly bound electrons are incorporated into the Thomas-Fermi energy functional, and derive for the density the analog of what is known as Scott's correction to the energy. The scaling properties of this energy functional supply a new, consistent derivation of the Scott term.

INTRODUCTION

The failure of the Thomas-Fermi (TF) model in the vicinity of the nucleus, where it predicts an enormous electron density, has, of course, been well known since the very first papers on the subject by Thomas and Fermi.[1] Surprisingly, it took a quarter of a century until Scott[2] suggested that TF can be significantly improved by a better treatment of the strongly bound electrons. Some 28 years later, one of us gave a clearer derivation of the Scott term.[3] It is the purpose of the present paper, now only three years later, to take the next step—to incorporate the corrections for strongly bound electrons into the energy functional, in such a way that their effect on the density can also be studied.

ENERGY FUNCTIONAL

One starting point of TF theory, and a useful one here, is the following stationary energy functional of the single-particle potential V (atomic units: $e=m=\hbar=1$):

$$E_{\mathrm{TF}}=2\int\frac{(d\vec{r})(d\vec{p})}{(2\pi)^3}\left[\tfrac{1}{2}p^2+V(\vec{r})+\zeta\right]\times\eta\left(-\left[\tfrac{1}{2}p^2+V(\vec{r})+\zeta\right]\right)-\int(d\vec{r})\frac{1}{8\pi}\left[\vec{\nabla}\left[V(\vec{r})+\frac{Z}{r}\right]\right]^2-\zeta N\,, \qquad (1)$$

where η is Heaviside's step function and ζ, the Lagrangian multiplier of the total number N of electrons, is the negative of the largest single-electron energy. The phase-space integral that sums the contributions of all electrons with energy less than $-\zeta$ exhibits $V+\zeta$ as an effective single-particle potential. In the spirit of Ref. 3 we modify E_{TF} by subtracting the contributions of the strongly bound electrons, those with energy less than $-\zeta_s$, where $Z^{4/3}\ll\zeta_s\ll Z^2$ [more about ζ_s later, see Eq. (32)], while adding the correct quantum-mechanical energy of these electrons. This gives the energy

$$E_{\zeta_s}=E_{\mathrm{TF}}-2\int\frac{(d\vec{r})(d\vec{p})}{(2\pi)^3}\left(\tfrac{1}{2}p^2+V+\zeta\right)\eta\left(-\left(\tfrac{1}{2}p^2+V+\zeta_s\right)\right)+\sum_{n=1}^{n_s}2n^2\left[-\frac{Z^2}{2n^2}\right]+\sum_{\substack{n\,(\le n_s),\\ l,m}}2\int(d\vec{r})\left[V+\frac{Z}{r}+\zeta\right]|\psi_{nlm}(\vec{r})|^2 \qquad (2)$$

which treats the difference between $-Z/r$ and $V+\zeta$ for the strongly bound electrons as small. Here, n_s is the number of closed shells of electrons in the Coulombic field of the nucleus, and the ψ_{nlm} are the corresponding wave functions. They enter (2) as the sum

$$\rho_s(\vec{r})\equiv\sum_{\substack{n\,(\le n_s),\\ l,m}}2\,|\psi_{nlm}(\vec{r})|^2 \qquad (3)$$

which is the density of the specially treated strongly bound electrons.

Of course, ζ_s and n_s are related by the fact that $-\zeta_s$ means an energy in between the single-electron energies of the n_sth and the (n_s+1)-th shell:

$$\max_{l,m}\left[-\frac{Z^2}{2n_s^2}+\left\langle V+\frac{Z}{r}\right\rangle_{n_s,l,m}\right]<-\zeta_s<\min_{l,m}\left[-\frac{Z^2}{2(n_s+1)^2}+\left\langle V+\frac{Z}{r}\right\rangle_{n_s+1,l,m}\right], \qquad (4)$$

where

$$\left\langle V+\frac{Z}{r}\right\rangle_{n_s,l,m}=\int(d\vec{r})\left[V(\vec{r})+\frac{Z}{r}\right]|\psi_{n_slm}(\vec{r})|^2\,. \qquad (5)$$

For a spherically symmetric potential $V=V(r)$, as is the situation for an isolated atom, there is no m dependence in (5), and little l dependence is expected. We shall therefore use averages over shells

$$\left\langle V+\frac{Z}{r}\right\rangle_{n_s} \equiv \frac{1}{2n_s^2}\sum_{l,m} 2\int (d\vec{r}\,)\left[V(r)+\frac{Z}{r}\right] \times |\psi_{n_s lm}(\vec{r}\,)|^2 \tag{6}$$

for the limits in (4),

$$-\frac{Z^2}{2n_s^2}+\left\langle V+\frac{Z}{r}\right\rangle_{n_s} < -\zeta_s < -\frac{Z^2}{2(n_s+1)^2}+\left\langle V+\frac{Z}{r}\right\rangle_{n_s+1} . \tag{7}$$

The spherical symmetry of each closed l subshell enables us to do the angular average of the density,

$$|\psi_{n_s}|^2_{\text{av}} = \frac{1}{2n_s^2}\sum_{l,m} 2\,|\psi_{n_s lm}(r,\theta,\phi)|^2 \equiv \frac{Z^3}{4\pi}\phi_{n_s}(Zr) , \tag{8}$$

so that now

$$\left\langle V+\frac{Z}{r}\right\rangle_{n_s} = \int (d\vec{r}\,)\left[V(r)+\frac{Z}{r}\right]|\psi_{n_s}|^2_{\text{av}} , \tag{9}$$

where $|\psi_{n_s}|^2_{\text{av}}$ is only a function of r. In (8) we introduced the radial density functions $\phi_{n_s}(Zr)$ which are normalized according to

$$\int_0^\infty dx\, x^2 \phi_{n_s}(x) = 1 . \tag{10}$$

They are displayed here for the first few n_s:

$$\begin{aligned}
\phi_1(x) &= 4e^{-2x} ,\\
\phi_2(x) &= \tfrac{4}{32}(1-x+\tfrac{1}{2}x^2)e^{-x} ,\\
\phi_3(x) &= \tfrac{4}{243}(1-\tfrac{4}{3}x+\tfrac{8}{9}x^2-\tfrac{16}{81}x^3+\tfrac{4}{243}x^4)e^{-2x/3} .
\end{aligned} \tag{11}$$

We then write the total density in Eq. (3) as

$$\rho_s(r) = \sum_{n=1}^{n_s} 2n^2\,|\psi_n|^2_{\text{av}} \equiv \frac{Z^3}{4\pi}\Phi_s(Zr) , \tag{12}$$

where

$$\Phi_s(Zr) = \sum_{n=1}^{n_s} 2n^2\phi_n(Zr) , \tag{13}$$

which upon integration gives the total number of specially treated strongly bound electrons,

$$N_s = \int (d\vec{r}\,)\rho_s = \sum_{n=1}^{n_s} 2n^2 = \tfrac{2}{3}(n_s+\tfrac{1}{2})^3 - \tfrac{1}{6}(n_s+\tfrac{1}{2}) . \tag{14}$$

Equation (2) is all very well but it disregards the fact that ζ_s is not a uniquely determined quantity. We have to average over all ζ_s that obey the restriction (7), as well as over a small range of n_s, in principle. The fundamental physical quantity is the energy, so it is natural to average uniformly on the energy scale. Then the mean energy is just half the sum of its extreme values,

$$E = \tfrac{1}{2}(E_{\zeta_1}+E_{\zeta_2}) , \tag{15}$$

where ζ_1 (ζ_2) is the upper (lower) bound for ζ_s in (7).

If we now evaluate the momentum integral in (2), we obtain the new energy functional which includes corrections for strongly bound electrons:

$$\begin{aligned}
E = {} & \int (d\vec{r}\,)\left\{-\frac{1}{3\pi^2}\frac{1}{5}[-2(V+\zeta)]^{5/2} - \frac{1}{8\pi}\left[\vec{\nabla}\left[V+\frac{Z}{r}\right]\right]^2\right\} - \zeta N \\
& + \tfrac{1}{2}\sum_{j=1}^{2}\int (d\vec{r}\,)\left[\frac{1}{3\pi^2}\frac{1}{5}[-2(V+\zeta_j)]^{5/2} + \frac{1}{3\pi^2}(\zeta_j-\zeta)[-2(V+\zeta_j)]^{3/2}\right] + \int (d\vec{r}\,)\left[V+\frac{Z}{r}+\zeta\right]\rho_s(r) - Z^2 n_s ;
\end{aligned} \tag{16}$$

the first terms are the TF energy E_{TF}, the remaining ones its modification. Here and in the sequel, square roots of negative numbers are understood to be zero.

Before going on, let us supply evidence in favor of the average (15) by checking that (16) correctly reproduces Scott's correction when it is treated as a small perturbation. For that we use the TF potential V_{TF} in E_{TF}, and just $V=-Z/r$ in the correction terms referring to strongly bound electrons, so that

$$\zeta_j \cong \frac{Z^2}{2n_j^2}, \quad n_1 = n_s, \quad n_2 = n_s+1 , \tag{17}$$

and $[\zeta=0,\ r=(Z/\zeta_j)x]$

$$\begin{aligned}
E &\cong E_{\text{TF}} + \tfrac{1}{2}\sum_j \frac{4\pi}{3\pi^2}\left[\frac{Z}{\zeta_j}\right]^3 (2\zeta_j)^{5/2}\int_0^1 dx\left[\frac{1}{5}\frac{(1-x)^{5/2}}{x^{1/2}} + \frac{1}{2}x^{1/2}(1-x)^{3/2}\right] - Z^2 n_s \\
&= E_{\text{TF}} + Z^2\tfrac{1}{2}\sum_j\left[\frac{Z}{(2\zeta_j)^{1/2}} - n_s\right] = E_{\text{TF}} + \tfrac{1}{2}Z^2 .
\end{aligned} \tag{18}$$

Indeed, there is Scott's term. This derivation, which is very close to that of Ref. 3, does not take into account the change of E_{TF} which is caused by the transition from the TF potential to the one that minimizes (16). We shall do better later, but first we have to look at the implications of the stationary property of the new energy functional (16).

Arbitrary variations of V and ζ give rise to a change of E given by

$$\begin{aligned}\delta E=\delta\zeta&\left[\int(d\vec{r}\,)\left[\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}-\tfrac{1}{2}\sum_j\frac{1}{3\pi^2}[-2(V+\zeta_j)]^{3/2}+\rho_s\right]-N\right]\\&+\int(d\vec{r}\,)\delta V\left[\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}-\tfrac{1}{2}\sum_j\left[\frac{1}{3\pi^2}[-2(V+\zeta_j)]^{3/2}+\frac{1}{\pi^2}(\zeta_j-\zeta)[-2(V+\zeta_j)]^{1/2}\right]\right.\\&\qquad\left.+\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]+\rho_s\right]-\tfrac{1}{2}\sum_j\delta\zeta_jQ_j\ ,\end{aligned}\tag{19}$$

where we have introduced

$$\begin{aligned}Q_j&=-2\frac{\partial E}{\partial\zeta_j}=-\frac{\partial E_{\zeta_j}}{\partial\zeta_j}\\&=\int(d\vec{r}\,)\frac{1}{\pi^2}(\zeta_j-\zeta)[-2(V+\zeta_j)]^{1/2}\ .\end{aligned}\tag{20}$$

According to

$$\zeta_j=\frac{Z^2}{2n_j^2}-\left\langle V+\frac{Z}{r}\right\rangle_{n_j}\tag{21}$$

and (9) we have

$$\delta\zeta_j=-\int(d\vec{r}\,)\delta V\,|\psi_{n_j}|^2_{\mathrm{av}}\ .\tag{22}$$

The vanishing of δE for arbitrary infinitesimal δV and $\delta\zeta$ supplies us therefore with

$$\begin{aligned}N=\int(d\vec{r}\,)&\left[\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}\right.\\&\left.-\tfrac{1}{2}\sum_j\frac{1}{3\pi^2}[-2(V+\zeta_j)]^{3/2}+\rho_s\right]\end{aligned}\tag{23}$$

and

$$-\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]=n\ ,\tag{24}$$

where

$$n=n_{\mathrm{strong}}+\tilde{n}\ ,\tag{25}$$

$$n_{\mathrm{strong}}=\rho_s+\tfrac{1}{2}\sum_jQ_j\,|\psi_{n_j}|^2_{\mathrm{av}}\ ,\tag{26}$$

$$\begin{aligned}\tilde{n}=&\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}\\&-\tfrac{1}{2}\sum_j\left[\frac{1}{3\pi^2}[-2(V+\zeta_j)]^{3/2}\right.\\&\qquad\left.+\frac{1}{\pi^2}(\zeta_j-\zeta)[-2(V+\zeta_j)]^{1/2}\right]\ .\end{aligned}\tag{27}$$

The combination of Eqs. (20), (23), and (25)–(27) tells us that the total number of electrons is equal to the integrated density:

$$N=\int(d\vec{r}\,)n;\tag{28}$$

a basic test of consistency.

DENSITY

At large distances from the nucleus, all terms in the density with explicit reference to the corrections vanish and we are left with the first term of $\tilde{n}$, which is to say, with the TF density

$$n_{\mathrm{TF}}=\frac{1}{3\pi^2}[-2(V+\zeta)]^{3/2}\ .\tag{29}$$

The extrapolation of n_{TF} into the region of strongly bound electrons (where $V\cong-Z/r$) predicts an infinite density at the nucleus,

$$n_{\mathrm{TF}}\cong\frac{1}{3\pi^2}\left[\frac{2Z}{r}\right]^{3/2}\quad\text{as } r\to0\ .\tag{30}$$

A look at the new density makes the improvement obvious, as we find a finite (and positive) value:

$$\begin{aligned}n&\cong n_{\mathrm{strong}}(r=0)\\&=\frac{(2Z)^3}{4\pi}\left[\sum_{n=1}^{n_s}\frac{1}{n^3}+\frac{Q_1}{4n_s^5}+\frac{Q_2}{4(n_s+1)^5}\right]\quad\text{as } r\to0\ .\end{aligned}\tag{31}$$

There is no contribution from $\tilde{n}\sim r^{+1/2}$ at small r.

As an illustration, Fig. 1 shows a plot of both the TF density and the new one for neutral mercury ($Z=N=80$), $n_s=1$. The two sharp edges are produced by the last term in $\tilde{n}$, Eq. (27); thus they are artifacts of the typical TF discontinuity associated with the square root. An improved theory of the statistical atom—we describe it in a companion paper[4]—removes this insufficiency.

The value obtained for $n(r=0)$ in (31) clearly depends on the choice we make for n_s, but there is little room for arbitrariness. Looking back to Eq. (2) we remark that ζ_s is physically restricted to be small on the scale of Bohrian energies and large compared to TF energies, i.e.,

$$Z^2\gg\zeta_s\gg Z^{4/3}\ .\tag{32}$$

On the other hand, ζ_s is bounded by ζ_1 and ζ_2 for which we have the estimates (17), so that

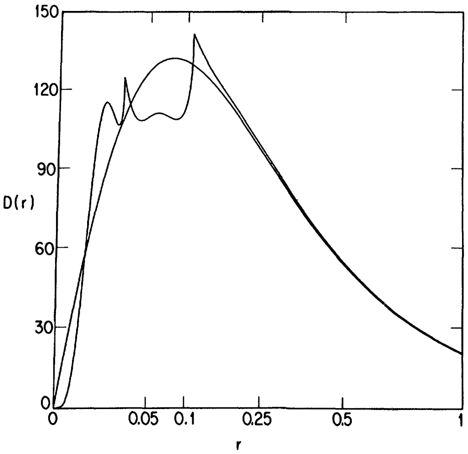

FIG. 1. Comparison of radial densities $D=4\pi r^2 n$ for neutral mercury, $n_s=1$. Smooth curve, TF; curve with structure, new theory. Abscissa is linear in the square root of r.

$$\frac{Z^2}{2n_s^2} \gtrsim \zeta_s \gtrsim \frac{Z^2}{2(n_s+1)^2} \; , \tag{33}$$

or

$$\zeta_s \cong \frac{Z^2}{2(n_s+\frac{1}{2})^2} \cong \tfrac{1}{2}Z^2(\tfrac{3}{2}N_s)^{-2/3} \tag{34}$$

[Eq. (14)]. Insertion of (34) into (32) gives then

$$1 \ll n_s \ll Z^{1/3} \tag{35}$$

and

$$1 \ll N_s \ll Z \sim N \; . \tag{36}$$

The latter simply requires the number of specially treated strongly bound electrons to be a small fraction of the total number.

For realistic values of Z the upper bound for n_s in (35) is not much larger than unity [$Z^{1/3}$: 1→5], indicating that we cannot take (35) too literally, unless we wish to turn our attention to enormous values of Z. This largely forces us to choose $n_s=1$, or at most $n_s=2$, in practical applications. Therefore there will usually be no call for the, in principle necessary, average on n_s. For $n_s=1$, the electron density at the nucleus is just

$$n(r=0)=\frac{(2Z)^3}{4\pi}(1+\tfrac{1}{4}Q_1+\tfrac{1}{128}Q_2), \quad n_s=1 \; . \tag{37}$$

INTEGRATION

The price for the more realistic density at small distances is paid in the form of complications in the differential equation that determines V. Now it is really a system of equations because the right-hand side of Poisson's equation (24) contains not only V but also the parameters ζ_j, Q_j; and they themselves are given as integrals involving V.

For positive ions, $N<Z$, the numerical search for V begins with a reasonable guess for ζ, ζ_1, ζ_2, Q_1, and Q_2. Then starting at a sufficiently large distance (where $n=0$) with the known asymptotic form of V

$$V=-\frac{Z-N}{r} \quad \text{for } r \text{ large} \tag{38}$$

one integrates the differential equation inwards and compares the evaluations of the integrals for ζ_1,ζ_2, and Q_1,Q_2 with the initial guesses, thereby obtaining improved values of these parameters. Further, the test

$$V \overset{?}{\cong} -\frac{Z}{r} \quad \text{as } r\to 0 \tag{39}$$

has to be made, and its outcome leads to an improved ζ. Then one tries again with the new parameters. For a not too bad initial guess, this scheme is rapidly converging.

For neutral atoms, $N=Z$, we know that ζ is zero, but we have less knowledge about the asymptotic form of V. For large r, which means outside the region of strongly bound electrons, the density has the TF form (29) (with $\zeta=0$), and the potential now satisfies the TF equation

$$-\nabla^2 V=\frac{1}{3\pi^2}(-2V)^{3/2} \quad \text{for } r \text{ large} \; . \tag{40}$$

Thus, asymptotically V has to be equal to a rescaled TF potential

$$V(r)=\alpha^4 V_{\mathrm{TF}}(\alpha r) \quad \text{for } r \text{ large} \tag{41}$$

with α close to 1. Again, for given parameters—now α, ζ_1, ζ_2, Q_1, and Q_2—one integrates the differential equation for V inwards and by iteration improves their values.

SCALING

We mentioned the rescaling property of the TF equation (40), which is an invitation to examine scaling in the new theory. This will do the two things for us: first, it supplies reasonable guesses for ζ_1,ζ_2 and Q_1,Q_2; second, a more consistent derivation of Scott's term is achieved.

As it stands, the energy [Eq. (16)] implicitly contains the restriction

$$(rV)\big|_{r\to 0}=-Z \tag{42}$$

because otherwise the integral on the squared gradient does not converge. Therefore, scalings of the type

$$V(r)\to\lambda^{\beta}V(\lambda r) \tag{43}$$

have to be accompanied by a scaling of Z,

$$Z\to\lambda^{\beta-1}Z \; . \tag{44}$$

For convenience, we shall also scale ζ in order to preserve the structure $V+\zeta$; thus

$$\zeta\to\lambda^{\beta}\zeta \; . \tag{45}$$

Since the energy (16) is stationary under infinitesimal variations of V and ζ, all first-order changes stem from scaling Z,

$$\frac{d}{d\lambda}E(\lambda)\Big|_{\lambda=1}=\frac{\partial E}{\partial Z}\frac{d}{d\lambda}(\lambda^{\beta-1}Z)\Big|_{\lambda=1}=(\beta-1)Z\frac{\partial E}{\partial Z} \; . \tag{46}$$

As a first example, we do the scaling for uncorrected TF,

$$E_{\mathrm{TF}}=E_{\mathrm{TF}}^{(1)}+E_{\mathrm{TF}}^{(2)}-\zeta N \tag{47}$$

with

$$E_{\mathrm{TF}}^{(1)}=\int(d\vec{r}\,)\left[-\frac{1}{3\pi^2}\right]\frac{1}{5}[-2(V_{\mathrm{TF}}+\zeta)]^{5/2} \tag{48}$$

and

$$E_{\mathrm{TF}}^{(2)}=\int(d\vec{r}\,)\left[-\frac{1}{8\pi}\right]\left[\vec{\nabla}\left[V_{\mathrm{TF}}+\frac{Z}{r}\right]\right]^2 . \tag{49}$$

The scaling properties of $E_{\mathrm{TF}}^{(1,2)}$ are simple; we get

$$E_{\mathrm{TF}}(\lambda)=\lambda^{5\beta/2-3}E_{\mathrm{TF}}^{(1)}+\lambda^{2\beta-1}E_{\mathrm{TF}}^{(2)}-\lambda^{\beta}\zeta N , \tag{50}$$

which inserted into (46) produces

$$(\tfrac{5}{2}\beta-3)E_{\mathrm{TF}}^{(1)}+(2\beta-1)E_{\mathrm{TF}}^{(2)}-\beta\zeta N=(\beta-1)Z\frac{\partial}{\partial Z}E_{\mathrm{TF}} . \tag{51}$$

This has to hold for any value of β. So we get two independent relations among the energy quantities in (51); e.g., for $\beta=1$ and 4,

$$-\tfrac{1}{2}E_{\mathrm{TF}}^{(1)}+E_{\mathrm{TF}}^{(2)}-\zeta N=0 , \tag{52}$$

$$7E_{\mathrm{TF}}^{(1)}+7E_{\mathrm{TF}}^{(2)}-4\zeta N=3Z\frac{\partial}{\partial Z}E_{\mathrm{TF}} . \tag{53}$$

The latter combines with (47) and the relation

$$\frac{\partial}{\partial N}E_{\mathrm{TF}}=-\zeta \tag{54}$$

to give

$$7E_{\mathrm{TF}}(Z,N)=3\left[Z\frac{\partial}{\partial Z}+N\frac{\partial}{\partial N}\right]E_{\mathrm{TF}}(Z,N) . \tag{55}$$

For neutral atoms, $N=Z$, there is a simple implication of this equation. For, after recognizing that

$$\left[Z\frac{\partial}{\partial Z}+N\frac{\partial}{\partial N}\right]E_{\mathrm{TF}}(Z,N)\,|_{N=Z}=Z\frac{d}{dZ}E_{\mathrm{TF}}(Z,Z) , \tag{56}$$

we obtain

$$7E_{\mathrm{TF}}(Z,Z)=3Z\frac{d}{dZ}E_{\mathrm{TF}}(Z,Z) , \tag{57}$$

or

$$E_{\mathrm{TF}}(Z,Z)=-CZ^{7/3} . \tag{58}$$

The constant C is found from the knowledge of $\zeta=-\partial E_{\mathrm{TF}}/\partial N=0$ for $N=Z$, together with

$$\begin{aligned}Z\frac{\partial}{\partial Z}E_{\mathrm{TF}}=Z\frac{\partial}{\partial Z}E_{\mathrm{TF}}^{(2)}&=\int(d\vec{r}\,)\left[V_{\mathrm{TF}}+\frac{Z}{r}\right]\frac{1}{4\pi}\nabla^2\frac{Z}{r}\\&=-Z\left[V_{\mathrm{TF}}+\frac{Z}{r}\right]\Bigg|_{r=0}\end{aligned} \tag{59}$$

which is simply the potential energy of the nucleus in the field of the electronic cloud. The introduction of Baker's[5] constant B, as defined by

$$V_{\mathrm{TF}}(r)=-\frac{Z}{r}+\frac{B}{a}Z^{4/3}+O(r^{1/2}),\quad a=\frac{1}{2}\left[\frac{3\pi}{4}\right]^{2/3} \tag{60}$$

then gives

$$Z\frac{\partial}{\partial Z}E_{\mathrm{TF}}=-\frac{B}{a}Z^{7/3} , \tag{61}$$

which implies [Eqs. (55) and (56)]

$$E_{\mathrm{TF}}(Z,Z)=-\frac{3}{7}\frac{B}{a}Z^{7/3} . \tag{62}$$

The numerical value of B is

$$B=1.588\,070\ldots , \tag{63}$$

it can only be found by numerical integration of the TF equation. For $N=Z$ the additional lesson from (52) is

$$E_{\mathrm{TF}}=\tfrac{3}{2}E_{\mathrm{TF}}^{(1)}=3E_{\mathrm{TF}}^{(2)}=-0.768\,745Z^{7/3} . \tag{64}$$

For ions, $N<Z$, there is less specific information in these equations. A general statement,

$$E_{\mathrm{TF}}(Z,N)=-\frac{3}{7}\frac{B}{a}Z^{7/3}f(N/Z),\quad f(1)=1 \tag{65}$$

follows simply from (55) and (62), but to know $f(N/Z)$ one has to solve the TF equation for the particular degree of ionization.

Unfortunately, scaling is not quite so simple for the corrected theory. We encounter mainly two complications: the ζ_j do not scale like ζ, and there are additional Z dependences hidden in the Coulombic densities $|\psi_n|^2_{\mathrm{av}}$ and ρ_s. We start with decomposing the energy (16) in a way analogous to (47),

$$E=E^{(1)}+E^{(2)}+E^{(3)}-\zeta N+Z^2n_s , \tag{66}$$

where

$$\begin{aligned}E^{(1)}=\tfrac{1}{2}\sum_j\int(d\vec{r}\,)\Bigg[&-\frac{1}{3\pi^2}\frac{1}{5}[-2(V+\zeta)]^{5/2}\\&+\frac{1}{3\pi^2}\frac{1}{5}[-2(V+\zeta_j)]^{5/2}\\&+\frac{1}{3\pi^2}(\zeta_j-\zeta)[-2(V+\zeta_j)]^{3/2}\Bigg] ,\end{aligned} \tag{67}$$

$$E^{(2)}=\int(d\vec{r}\,)\left[-\frac{1}{8\pi}\right]\left[\vec{\nabla}\left[V+\frac{Z}{r}\right]\right]^2 , \tag{68}$$

$$E^{(3)}=\int(d\vec{r}\,)(V+\zeta)\rho_s(r) . \tag{69}$$

In writing (66) we made use of

$$\left\langle\frac{Z}{r}\right\rangle_n=\int(d\vec{r}\,)\frac{Z}{r}\,|\psi_n|^2_{\mathrm{av}}=\frac{Z^2}{n^2} \tag{70}$$

in the form [Eq. (12)]

$$\int (d\vec{r})\frac{Z}{r}\rho_s(r)=\sum_{n=1}^{n_s} 2n^2\left\langle\frac{Z}{r}\right\rangle_n=2Z^2n_s\ . \tag{71}$$

Another implication of (70) is [Eq. (21)]

$$\zeta_j=-\frac{Z^2}{2n_j^2}-\langle V\rangle_{n_j}\ . \tag{72}$$

Before we can investigate the scaling behavior and Z dependence of the various contributions to E in (66), we have to prepare some tools. Looking back at (8) and (12), we find that $|\psi_n|_{\text{av}}^2$ and ρ_s scale according to [Eq. (44)]

$$\begin{bmatrix} |\psi_n|_{\text{av}}^2 \\ \rho_s \end{bmatrix}(r)\rightarrow\lambda^{3(\beta-1)}\begin{bmatrix} |\psi_n|_{\text{av}}^2 \\ \rho_s \end{bmatrix}(\lambda^{\beta-1}r)\ , \tag{73}$$

as r scales to $\lambda^{\beta-1}r$. Consequently,

$$\begin{aligned}\langle V(r)\rangle_{n_j}&=\int(d\vec{r})V(r)[\,|\psi_{n_j}|_{\text{av}}^2(r)]\\ &\rightarrow\int(d\vec{r})\lambda^\beta V(\lambda r)\lambda^{3(\beta-1)}[\,|\psi_{n_j}|_{\text{av}}^2(\lambda^{\beta-1}r)]\\ &=\int(d\vec{r})\lambda^\beta V(\lambda^{2-\beta}r)[\,|\psi_{n_j}|_{\text{av}}^2(r)]\\ &=\langle\lambda^\beta V(\lambda^{2-\beta}r)\rangle_{n_j}\ ,\end{aligned} \tag{74}$$

which we insert into (72) to produce

$$\begin{aligned}&\frac{d}{d\lambda}[\lambda^{-\beta}\zeta_j(\lambda)]\,|_{\lambda=1}\\ &\quad=\frac{d}{d\lambda}\left.\left[-\lambda^{\beta-2}\frac{Z^2}{2n_j^2}-\langle V(\lambda^{2-\beta}r)\rangle_{n_j}\right]\right|_{\lambda=1}\\ &\quad=(\beta-2)\left[\zeta_j+\left\langle\frac{\partial}{\partial r}[rV(r)]\right\rangle_{n_j}\right]\ .\end{aligned} \tag{75}$$

Similarly, we obtain

$$\begin{aligned}&\frac{d}{d\lambda}E^{(3)}(\lambda)\,|_{\lambda=1}\\ &\quad=\frac{d}{d\lambda}\left.\left[\lambda^\beta\int(d\vec{r})[V(\lambda^{2-\beta}r)+\zeta]\rho_s(r)\right]\right|_{\lambda=1}\\ &\quad=2(\beta-1)E^{(3)}-(\beta-2)\zeta N_s\\ &\qquad-(\beta-2)\int(d\vec{r})\frac{\partial}{\partial r}(rV)\rho_s\ ,\end{aligned} \tag{76}$$

with N_s as given in (14). Now concerning the Z dependence of the Coulombic wave functions, we again consult (8) and (12), and find

$$Z\frac{\partial}{\partial Z}\begin{bmatrix} |\psi_n|_{\text{av}}^2 \\ \rho_s \end{bmatrix}=(3+\vec{r}\cdot\vec{\nabla}\,)\begin{bmatrix} |\psi_n|_{\text{av}}^2 \\ \rho_s \end{bmatrix}\ , \tag{77}$$

with the consequences

$$Z\frac{\partial}{\partial Z}\zeta_j=\zeta_j-\frac{Z^2}{2n_j^2}+\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j} \tag{78}$$

and

$$Z\frac{\partial}{\partial z}E^{(3)}=E^{(3)}-\zeta N_s-\int(d\vec{r})\frac{\partial}{\partial r}(rV)\rho_s\ . \tag{79}$$

We are now ready for examining $E^{(1)}$. In analogy to the TF calculation we have

$$\begin{aligned}E^{(1)}(\lambda)=\lambda^{5\beta/2-3}\tfrac{1}{2}\sum_j\int(d\vec{r})\Bigg[&-\frac{1}{3\pi^2}\frac{1}{5}[-2(V+\zeta)]^{5/2}+\frac{1}{3\pi^2}\frac{1}{5}\{-2[V+\lambda^{-\beta}\zeta_j(\lambda)]\}^{5/2}\\ &+\frac{1}{3\pi^2}[\lambda^{-\beta}\zeta_j(\lambda)-\zeta]\{-2[V+\lambda^{-\beta}\zeta_j(\lambda)]\}^{3/2}\Bigg]\ ,\end{aligned} \tag{80}$$

where we meet ζ_j in just the combination that is differentiated in (75). Accordingly, we get

$$\begin{aligned}\frac{d}{d\lambda}E^{(1)}(\lambda)\,|_{\lambda=1}&=(\tfrac{5}{2}\beta-3)E^{(1)}+\sum_j\frac{\partial E^{(1)}}{\partial\zeta_j}\frac{d}{d\lambda}[\lambda^{-\beta}\zeta_j(\lambda)]\,|_{\lambda=1}\\ &=(\tfrac{5}{2}\beta-3)E^{(1)}-(\beta-2)\tfrac{1}{2}\sum_j Q_j\left[\zeta_j+\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j}\right]\ ,\end{aligned} \tag{81}$$

with Q_j as defined in (20). The Z dependence of $E^{(1)}$ is revealed by

$$Z\frac{\partial}{\partial Z}E^{(1)}=\sum_j\frac{\partial E^{(1)}}{\partial\zeta_j}Z\frac{\partial}{\partial Z}\zeta_j=-\tfrac{1}{2}\sum_j Q_j\left[\zeta_j-\frac{Z^2}{2n_j^2}+\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j}\right]\ . \tag{82}$$

For $E^{(2)}$ we just have to copy the previous results [Eqs. (51) and (59)],

$$\frac{\partial}{\partial\lambda}E^{(2)}(\lambda)\,|_{\lambda=1}=(2\beta-1)E^{(2)} \tag{83}$$

and

$$Z\frac{\partial}{\partial Z}E^{(2)}=-Z\left.\left[V+\frac{Z}{r}\right]\right|_{r=0}\ . \tag{84}$$

Now we are prepared to use (46)—here in the form

$$\frac{d}{d\lambda}[E^{(1)}(\lambda)+E^{(2)}(\lambda)+E^{(3)}(\lambda)]\,|_{\lambda=1}-\beta\zeta N+2(\beta-1)Z^2n_s=(\beta-1)Z\frac{\partial}{\partial Z}(E^{(1)}+E^{(2)}+E^{(3)})+2(\beta-1)Z^2n_s\;. \tag{85}$$

We insert what we found in Eqs. (76), (79), and (81)—(84) and arrive at

$$(\tfrac{5}{2}\beta-3)E^{(1)}+(2\beta-1)E^{(2)}+(\beta-1)E^{(3)}+\int(d\vec{r}\,)\frac{\partial}{\partial r}(rV)\rho_s + \tfrac{1}{2}\sum_j Q_j\left[\zeta_j+\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j}-(\beta-1)\frac{Z^2}{2n_j^2}\right]+\zeta N_s-\beta\zeta N=-(\beta-1)Z\left[V+\frac{Z}{r}\right]\Bigg|_{r=0}\;. \tag{86}$$

Although this must, of course, hold for arbitrary β, only $\beta=4$ is immediately useful, since for this β, $E^{(1)}$ and $E^{(2)}$ are both multiplied by the same factor, 7. We can then replace their sum with the aid of (66). At this stage we have

$$7E=-3Z\left[V+\frac{Z}{r}\right]\Bigg|_{r=0}+4E^{(3)}-\int(d\vec{r}\,)\frac{\partial}{\partial r}(rV)\rho_s-\tfrac{1}{2}\sum_j Q_j\left[\zeta_i+\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j}-3\frac{Z^2}{2n_j^2}\right]-\zeta N_s-3\zeta N+7Z^2n_s\;. \tag{87}$$

For neutral systems, $N=Z$, ζ is zero and all terms on the right-hand side of (87) refer to the region of strongly bound electrons. Upon introducing the counterpart of Baker's constant by writing

$$V(r)=-\frac{Z}{r}+\frac{b}{a}+Z^{4/3}+O(r^2) \tag{88}$$

[cf. Eq. (60)], we can therefore evaluate E in terms of b in an approximate way by neglecting the $O(r^2)$ contribution to V. For the various terms in (87) these approximations are

$$\zeta_j\cong\frac{Z^2}{2n_j^2}-\frac{b}{a}Z^{4/3}\;, \tag{89}$$

$$Q_j\cong2\frac{n_j^5}{Z^2}\left[\frac{Z^2}{2n_j^2}-\frac{b}{a}Z^{4/3}\right]\;, \tag{90}$$

$$\left\langle\frac{\partial}{\partial r}(rV)\right\rangle_{n_j}\cong\frac{b}{a}Z^{4/3}\;, \tag{91}$$

$$\int(d\vec{r}\,)\frac{\partial}{\partial r}(rV)\rho_s\cong\frac{b}{a}Z^{4/3}N_s\;, \tag{92}$$

$$E^{(3)}\cong-2Z^2n_s+\frac{b}{a}Z^{4/3}N_s\;. \tag{93}$$

After inserting them into (87) we have

$$7E\cong-3\frac{b}{a}Z^{7/3}-\frac{b}{a}Z^{4/3}\left[\sum_j n_j^3-3N_s\right]+Z^2\left[-n_s+\tfrac{1}{2}\sum_j n_j\right]\;, \tag{94}$$

or

$$E\cong-\frac{3}{7}\frac{b}{a}Z^{7/3}+\frac{1}{14}Z^2-\frac{2n_s+1}{7}\frac{b}{a}Z^{4/3}\;. \tag{95}$$

In order to make contact with the uncorrected TF energy of (62), we examine the Z dependence of b, about which we already know

$$b(Z\to\infty)=B\;, \tag{96}$$

because in this limit the influence of the corrections on the shape of the potential is negligible. We derive a differential equation for $b(Z)$ by utilizing the identity

$$Z\frac{d}{dZ}E(Z,Z)=\left[Z\frac{\partial}{\partial Z}+N\frac{\partial}{\partial N}\right]E(Z,N)\,|_{N=Z} =Z\frac{\partial}{\partial Z}E(Z,N)\,|_{N=Z}\;, \tag{97}$$

which is based on $\partial E/\partial N=-\zeta=0$ for $N=Z$. On the left-hand side of (97) we use the energy found in (95). The right-hand side is recognized to be also the right-hand side of (85) [or (46)] without the factor $\beta-1$. If we use the approximations (89)—(93), we obtain

$$Z\frac{\partial}{\partial Z}E^{(1)}\cong0\;, \tag{98}$$

$$Z\frac{\partial}{\partial Z}E^{(2)}=-\frac{b}{a}Z^{7/3}\;, \tag{99}$$

$$Z\frac{\partial}{\partial Z}E^{(3)}\cong-2Z^2n_s\;, \tag{100}$$

implying

$$Z\frac{\partial}{\partial Z}E\cong-\frac{b}{a}Z^{7/3}\;. \tag{101}$$

This looks like (61), but now it is only approximately true.

After evaluating the left-hand side of (97) with E from (95), we get the differential equation

$$\left[1+\frac{2n_s+1}{3Z}\right]\frac{\partial(b/a)}{\partial Z}+\frac{4}{9}(2n_s+1)\frac{b/a}{Z^2}=\frac{1}{3}\frac{1}{Z^{1/3}}\;, \tag{102}$$

the solution of which, subject to the asymptotic condition (96) is

$$\frac{b}{a}=\frac{B}{a}\left[1+\frac{2n_s+1}{3Z}\right]^{4/3}-\frac{1}{Z^{1/3}}\left[1+\frac{2n_s+1}{4Z}\right]\;. \tag{103}$$

The last step is to insert this result into (95), which yields

TABLE I. Comparison of approximate predictions with actual values for $Z=N=80$, $n_s=1$. In parentheses are the corresponding deviations for $Z=N=800$, $n_s=1$.

Quantity	Prediction	Actual value	Percent deviation
b	1.407	1.414	−0.47 (−0.40)
ζ_1	2652.0	2788.0	−2.8 (−0.26)
ζ_2	252.1	443.6	−43.0 (−3.0)
Q_1	0.8288	0.8667	−4.4 (−0.86)
Q_2	2.521	5.115	−51.0 (−4.3)
$-E$	18 560	18 340	+ 1.2 (+ 0.27)

$$E=-\frac{3}{7}\frac{B}{a}Z^{7/3}\left[1+\frac{2n_s+1}{3Z}\right]^{7/3}+Z^2\left[\frac{1}{2}+\frac{2n_s+1}{4Z}+\frac{(2n_s+1)^2}{28Z^2}\right] \tag{104}$$

$$\cong -\frac{3}{7}\frac{B}{a}Z^{7/3}+\frac{1}{2}Z^2+O(Z^{4/3})\,. \tag{105}$$

Indeed, it very nicely reproduces Scott's correction. This is the derivation promised after Eq. (18).

On the way to (103) and (104) we received the approximations (89) and (90) for the parameters ζ_j and Q_j. These values, with b from (103), can very well be taken as the necessary "reasonable initial guesses" that we mentioned when describing how the numerical solution of the differential equation for V is achieved. As an illustration we report in Table I how the predictions of Eqs. (103), (89), (90), and (104) compare with the actual numbers obtained by numerical integration. While the deviations for b, ζ, Q_1, and E are rather small, for ζ_2 and Q_2 the predictions are significantly worse. This can be expected because the integrations to be performed for ζ_2 and Q_2 cover a much larger range of r than the ones for ζ_1 and Q_1. In this larger range, (88) is not as good an approximation as for the very small r associated with ζ_1 and Q_1. However, the numbers in parentheses, referring to a Z ten times larger, are, of course, much better.

We finally remark that the described corrections for strongly bound electrons have to be supplemented by an improved treatment of the outer region of the atom, a topic that we are addressing in a companion paper[4] where we discuss a new approach to the statistical atom.

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