Brief Reports

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Thomas-Fermi-Scott model: Momentum-space density

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We derive the Scott correction to the atomic electron density in momentum space. The implied corrections to expectation values of powers of the momentum, as well as to the Compton profile, are then obtained.

The well-known failure of the Thomas-Fermi (TF) model in the vicinity of the atomic nucleus requires a special treatment of the strongly bound electrons. This is generally called the Scott correction.[1] It can be incorporated consistently into the TF model, provided the language of potential functionals is employed.[2] Thus one arrives at the Thomas-Fermi-Scott (TFS) model. All physical quantities, for which the contribution from the innermost electrons is dominating or at least substantial, are treated much more realistically in the TFS model than in the TF model. For example, whereas the TF density at the site of the nucleus is infinite, the corresponding TFS prediction is both finite and numerically accurate.[3] In this Brief Report we derive the Scott correction to the density in momentum space and show that it significantly improves the TF result for large momenta. As an immediate application we then find the Scott correction to expectation values of some momentum functions, including in particular the Compton profile.

We take the TFS model in the formulation of Ref. 3 and use the notation and conventions introduced there. The spatial density of an isolated TFS atom,

$$n_{\rm TFS}(r)=n_{\rm TF}(r)+\Delta_s n(r)\ ,$$

is the sum of the TF density,

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

(square roots of negative numbers are understood to be zero), and its Scott correction,

$$\Delta_s n(r)=\left[\sum_{\nu=1}^{[\nu_s]}2\nu^2|\psi_\nu|^2_{\rm av}(r)+Q_s|\psi_{\nu_s}|^2_{\rm av}(r) - \left[1-(\zeta_s-\zeta)\frac{\partial}{\partial\zeta_s}\right] \times\frac{1}{3\pi^2}\{-2[V(r)+\zeta_s]\}^{3/2}\right]_{\rm SP} . \tag{2}$$

Here, $V(r)$ is the spherically symmetric effective potential; ζ is the minimal single-particle binding energy; $|\psi_\nu|^2_{\rm av}(r)$ is the average density of one electron in the νth shell; ν_s plays the role of a continuous principal quantum number; and for the present purpose the parameters ζ_s and Q_s are well approximated by

$$\zeta_s=\frac{Z^2}{2\nu_s^2}+\frac{\partial}{\partial Z}E_{\rm TFS}(Z,N)\ ,$$
$$Q_s=(\zeta_s-\zeta)\frac{2\nu_s^5}{Z^2}\ , \tag{3}$$

where $E_{\rm TFS}(Z,N)$ is the energy of a TFS atom with nuclear charge Z and N electrons. In $\Delta_s n(r)$ it suffices to use the small-r form of $V(r)$,

$$V(r)\simeq-\frac{Z}{r}-\frac{\partial}{\partial Z}E_{\rm TFS}(Z,N)\ . \tag{4}$$

The large square brackets $[f(\nu_s)]_{\rm SP}$ in Eq. (2) symbolize the injunction to evaluate the *smooth part* of this function of ν_s, thereby discarding all oscillatory contributions that arise because the summation over ν terminates at the integer part $[\nu_s]$ of ν_s. For later reference, we report that the density at the site of the nucleus is given by

$$n_0 \equiv n_{\rm TFS}(r=0) = \frac{(2Z)^3}{4\pi}\left[\zeta_R(3)+\frac{1}{Z^2}\left(\frac{\partial}{\partial Z}+\frac{\partial}{\partial N}\right)E_{\rm TFS}(Z,N)\right], \quad (5)$$

where $\zeta_R(z)$ is Riemann's zeta function, and the relation $\zeta = -\partial E_{\rm TFS}(Z,N)/\partial N$ has entered.

Upon recalling that (1) originates in

$$n_{\rm TF}(r)=2\int (d\mathbf{p})(2\pi)^{-3}\eta[-\tfrac{1}{2}p^2-V(r)-\zeta],$$

where

$$\eta(x)=\begin{cases}1 & \text{for } x>0\\ 0 & \text{for } x<0\end{cases}$$

is Heaviside's unit step function, the corresponding TF momentum-space density is immediately found:

$$n_{\rm TF}(p)=2\int (d\mathbf{r})(2\pi)^{-3}\eta[-\tfrac{1}{2}p^2-V(r)-\zeta] = \frac{1}{3\pi^2}[R(p)]^3 \quad (6)$$

with $R(p)$ determined by

$$\tfrac{1}{2}p^2+V(R)+\zeta=0 . \quad (7)$$

Further, the analog of $|\psi_\nu|^2_{\rm av}(r)$ in momentum space is[4]

$$|\psi_\nu|^2_{\rm av}(p)=\frac{8}{\pi^2}\left(\frac{\nu}{Z}\right)^3[1+(\nu p/Z)^2]^{-4} .$$

This, combined with using (6) also for the TF structure in (2), together with (3) and (4), yields

$$\Delta_s n(p)=\left(\frac{4Z}{\pi}\right)^2\left[\sum_{\nu=1}^{[\nu_s]}\frac{(\nu/Z)^5}{[1+(\nu p/Z)^2]^4}-\frac{Z}{6}\left(\frac{(\nu_s/Z)^2}{1+(\nu_s p/Z)^2}\right)^3\right]_{\rm SP} . \quad (8)$$

The general statement[5]

$$\sum_{\nu=1}^{[\nu_s]} f(\nu)=\sum_{\nu=1}^{\infty} f(\nu)-\int_{\nu_s}^{\infty} d\nu\, f(\nu)+O$$

(where O represents oscillatory terms), which holds if both the series and the integral exist, enables us to evaluate the smooth part in (8), as required. The outcome is

$$\Delta_s n(p)=\left(\frac{4Z}{\pi}\right)^2\sum_{\nu=1}^{\infty}\frac{(\nu/Z)^5}{[1+(\nu p/Z)^2]^4}-\frac{1}{3\pi^2}\left(\frac{2Z}{p^2}\right)^3 , \quad (9)$$

which must not and does not depend on ν_s. This is our central result. As is typical for a Scott correction, it is the same for all degrees of ionization.

The ν summation in (9) converges for all $p\neq 0$. For $p=0$ the limiting value is

$$\Delta_s n(p=0)=-\frac{4}{63\pi^2}\frac{1}{Z^3} .$$

This is quite irrelevant compared to $n_{\rm TF}(p)$, which for neutral atoms is

$$n_{\rm TF}(p)\simeq 9/(8\pi p^3)^{1/2} \quad \text{for } p\to 0 . \quad (10)$$

Of course, the TF and TFS predictions for $p\to 0$ are not to be taken seriously because here one is outside the range of validity of these models. A realistic treatment would have to include quantum corrections to the kinetic energy, and the exchange interaction. These developments, however, are not the subject of this Brief Report.

Naturally the Scott correction (9) is most important for large momenta. There one has

$$n_{\rm TF}(p)=\frac{1}{3\pi^2}\left(\frac{2Z}{p^2}\right)^3+\left(\frac{4}{\pi}\right)^2\frac{Z^3}{p^8}\left(\frac{\partial}{\partial Z}+\frac{\partial}{\partial N}\right)E_{\rm TFS}(Z,N)+\cdots ,$$

$$\Delta_s n(p)=-\frac{1}{3\pi^2}\left(\frac{2Z}{p^2}\right)^3+\left(\frac{4}{\pi}\right)^2\frac{Z^5}{p^8}\zeta_R(3)+\cdots ,$$

so that the p^{-6} terms compensate for each other, with the consequence

$$n_{\rm TFS}(p)=n_{\rm TF}(p)+\Delta_s n(p)=\frac{8}{\pi}n_0\frac{Z^2}{p^8}+\cdots , \quad (11)$$

where we make use of (5), and the ellipsis indicates terms of order p^{-10}. This connection between the spatial density at the nucleus and the large-p form of the momentum density, here predicted by the TFS model, can also be derived with the aid of Hartree-Fock arguments.[6]

As a first application of $n_{\rm TFS}(p)$, we consider neutral-atom expectation values of powers of p,

$$\langle p^k\rangle_{\rm TFS}=4\pi\int_0^{\infty}dp\, p^{k+2}n_{\rm TFS}(p) .$$

In view of (10) and (11) the permissible values of k are limited by $-\frac{3}{2}<k<5$. For neutral atoms one has $\zeta=0$, and the difference between the TFS potential and the TF potential is negligible,[7] so that it is quite sufficient to insert

$$V_{\rm TF}(r)=-\frac{Z}{r}F(x), \quad x=Z^{1/3}r/a ,$$

with $a=\frac{1}{2}(3\pi/4)^{2/3}=0.8853$ into (6). This $F(x)$ is the well-known Thomas-Fermi function. We thus find

$$\langle p^k\rangle_{\rm TFS}=\frac{3Z}{3-k}2^k\left(\frac{4Z^2}{3\pi}\right)^{k/3}I_k+\frac{16}{3\pi}\left(\frac{k+1}{2}\right)!\left(\frac{3-k}{2}\right)!\zeta_R(k-2)Z^k , \quad (12)$$

where

$$I_k=\int_0^{\infty}dx\, x^{(3-k)/2}[F(x)]^{(k+1)/2}\left(-\frac{d}{dx}F(x)\right) .$$

Equation (12) is valid for the whole range $-\frac{3}{2}<k<5$, containing the $k=3$ result as a limit. It is explicitly given by

$$\langle p^3\rangle_{\rm TFS}=\frac{32}{9\pi}Z^3\left[\ln\left[\frac{3\pi}{32}Z\right]+3C+\frac{11}{4}-\frac{3}{2}\int_0^\infty dx\frac{d[F(x)]^3}{dx}\ln x\right],$$

where $C=0.5772\ldots$ is Euler's constant and the integral has the numerical value 1.080 1017.

The numerical computation of I_k poses no particular problem. In addition, for integer k, the values can be found in the existing literature (for instance, in Ref. 3). For the sake of completeness, here they are again:

$$I_{-1}=18.3885,\quad I_0=1,\quad I_1=0.307\,717\ ,$$

$$I_2=-\frac{1}{7}\frac{dF}{dx}(0)=0.226\,867,\quad I_3=\frac{1}{3},\quad I_4=1.084\,32\ .$$

This establishes

$$\begin{aligned}\langle p^{-1}\rangle_{\rm TFS}&=9.1759Z^{1/3}+0.0283Z^{-1}\ ,\\ \langle p^{0}\rangle_{\rm TFS}&=Z\ ,\\ \langle p^{1}\rangle_{\rm TFS}&=0.693\,75Z^{5/3}-0.141\,47Z\ ,\\ \langle p^{2}\rangle_{\rm TFS}&=1.5375Z^{7/3}-Z^2=-2E_{\rm TFS}(Z,Z)\ ,\\ \langle p^{3}\rangle_{\rm TFS}&=1.1318Z^3\ln(Z/0.5725)\ ,\\ \langle p^{4}\rangle_{TFS}&=16.449Z^4-16.600Z^{11/3}\ .\end{aligned}\tag{13}$$

Let us remark that $\langle p^2\rangle$ is twice the kinetic energy and equals twice the binding energy (virial theorem), and $\langle p^4\rangle$ is needed when evaluating the leading relativistic energy correction.

The expectation values (13) agree, to the extent to which they can be compared, with those obtained by Dmitrieva and Plindov.[8] These authors point out, quite correctly, that the inclusion of exchange energy and other corrections supplies additional terms to $\langle p^k\rangle$ of the order $Z^{(2k+1)/3}$. Therefore the Scott term ($\sim Z^k$) is the leading correction to $\langle p^k\rangle_{\rm TF}$ only for $k>1$. (As a matter of fact, $\langle p^k\rangle_{\rm TF}$ does not even exist for $k\geq 3$.) This is an illustration of the general observation that the TFS model cannot make reliable predictions about momentum expectation values $\langle f(p)\rangle$ that are sensitive to the contributions from small p values.

Another application of $n_{\rm TFS}(p)$ concerns the Compton profile

$$J(q)=\left\langle\frac{1}{2p}\eta(p^2-q^2)\right\rangle=2\pi\int_{|q|}^\infty dp\,pn(p)\ .$$

In the TFS model one finds

$$J_{\rm TFS}(q)=J_{\rm TF}(q)+\Delta_sJ(q)$$

with the TF contribution

$$J_{\rm TF}(q)=\frac{2}{\pi}\int_0^{R(q)}dr\,r^2[-\tfrac{1}{2}q^2-V(r)-\zeta]$$

[where, as in (7), the upper limit is the distance at which the integrand changes sign] and the Scott correction

$$\Delta_sJ(q)=\frac{16}{3\pi}Z^2\sum_{\nu=1}^\infty\left[\frac{\nu/Z}{1+(\nu q/Z)^2}\right]^3-\frac{4}{3\pi}\frac{Z^3}{q^4}\ .$$

Analogous to (11), the large-q form is

$$J_{\rm TFS}(q)=\frac{8}{3}n_0\frac{Z^2}{q^6}+O(q^{-8})\ .\tag{14}$$

Again, this is identical with the corresponding Hartree-Fock result.[6] Unfortunately, in the large-q range there are no measured Compton profiles, as far as we know, with sufficient precision to either confirm or refute the power law (14). If it indeed holds, it offers—certainly in principle and possibly in practice—a way of measuring the electron density at the site of the nucleus, which quantity is of importance for various physical processes like K capture, to name one.

For $q^2>Z^2$, one can expand $\Delta_sJ(q)$ in powers of Z^2/q^2,

$$\Delta_sJ(q)=\frac{8}{3\pi Z}\sum_{k=1}^\infty(-1)^kk(k-1)\times\zeta_R(2k-1)(Z^2/q^2)^{k+1}\ ,$$

where one uses $(k-1)\zeta_R(2k-1)=\frac{1}{2}$ for $k=1$. It is amusing that for $q^2<Z^2$ there is an asymptotic expansion

$$\Delta_sJ(q)=-\frac{8}{3\pi Z}\sum_{k=-\infty}^{-1}(-1)^kk(k-1)\times\zeta_R(2k-1)(Z^2/q^2)^{k+1}\tag{15}$$

with an identical structure except that now negative k values are summed (and an overall minus sign appears). Equation (15) looks more conventional after using the relation

$$\zeta_R(-l)=\frac{(-1)^l}{l+1}B_{l+1},\quad l=0,1,2,\ldots$$

between Riemann's zeta function and the Bernoulli numbers:

$$\begin{aligned}\Delta_sJ(q)&=\frac{4}{3\pi Z}\sum_{l=0}^\infty(-1)^{l+1}(l+1)B_{2l+4}(q^2/Z^2)^l\\&=\frac{2}{45\pi Z}\left[1+\frac{10}{7}\frac{q^2}{Z^2}+\cdots\right].\end{aligned}$$

This is, of course, quite insignificant compared to the TF contribution, which for small q is given by

$$\begin{aligned}J_{\rm TF}(q)&\simeq\tfrac{1}{2}\langle p^{-1}\rangle_{\rm TF}-9\sqrt{2\pi|q|}\\&=4.59Z^{1/3}-22.56\sqrt{|q|}\ ;\end{aligned}$$

again, at these small q values we are outside the range of validity of the TFS model.

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[1]J. M. S. Scott, Philos. Mag. **43**, 859 (1952); J. Schwinger, Phys. Rev. A **22**, 1827 (1980).
[2]B.-G. Englert and J. Schwinger, Phys. Rev. A **29**, 2331 (1984); for a list of misprints in this paper see Ref. 3, p. 387.
[3]B.-G. Englert, *Semiclassical Theory of Atoms,* Vol. 300 of *Lecture Notes in Physics,* edited by J. Ehlers *et al.* (Springer, Berlin, 1988).
[4]An elegant, concise derivation of the momentum wave functions is given by J. Schwinger, J. Math. Phys. **5**, 1606 (1964).
[5]See Problem 3-4 in Ref. 3.
[6]See, for example, R. Benesch, and V. H. Smith, Jr., in *Wave Mechanics–The First Fifty Years,* edited by W. C. Price *et al.* (Butterworths, London, 1973).
[7]This is demonstrated in Fig. 3-7 of Ref. 3.
[8]I. K. Dmitrieva and G. I. Plindov, J. Phys. (Paris) **44**, 333 (1983).