PHYSICAL REVIEW A VOLUME 22, NUMBER 5 NOVEMBER 1980

Thomas-Fermi model: The leading correction

Julian Schwinger
Department of Physics, University of California, Los Angeles, California 90024
(Received 14 January 1980)

The correct treatment of strongly bound electrons is grafted smoothly onto the Thomas-Fermi computation of the total binding energy of neutral atoms. This provides a clearcut demonstration of the leading correction of relative order $Z^{-1/3}$ which, with effects of relative order $Z^{-2/3}$, gives an accurate account of the binding energy over a wide range of Z values. There is a brief discussion of relativistic corrections, with results that are somewhat at variance with previous numerical estimates.

INTRODUCTION

The Thomas-Fermi (TF) model was one of the topics I selected for an undergraduate course in quantum mechanics. My level of knowledge of its applications was that of textbooks of the 1950's, along with the monograph cited in Ref. 1; I had no reason to suspect that the particular subject of the binding energies of neutral atoms had attracted any more recent attention. Once again I was struck by the qualitative agreement of the model with empirically estimated total binding energies, for a wide range of Z. The slowly varying nature of the quantitative discrepancy suggested that a simple leading correction could be found. A qualitative argument indicated that it would vary as $Z^{-1/3}$, and the proper numerical factor was obtained by an elementary physical derivation. The resulting remarkable agreement with experiment seemed to merit a small publication. The referee of that paper kindly drew my attention to a communication by Scott[2] in which the same result appeared, identified as a "boundary effect." Of course, the underlying physical ideas are the same—the error of the TF model in giving the electrons an infinite density at the nucleus had always been recognized. But, as to the reliability of the quantitative statement, as derived by Scott (I quote from another reference[3] supplied by the referee), "it seems difficult to give a completely clearcut demonstration of the case." Accordingly, I feel justified in resubmitting my "clearcut demonstration." It will be followed by a discussion of the different approaches, and then by a partial treatment of relativistic effects, which topic does not appear to have received its definitive study (again, there may be publications more recent than the citations of Ref. 3).

QUALITATIVE ARGUMENT

The virial theorem, which equates the total binding energy $-E$ to the total kinetic energy, supplies the following semiclassical phase-space integral over occupied cells:

$$-E = \int 2\frac{(d\vec{r})(d\vec{p})}{(2\pi\hbar)^3}\frac{\vec{p}^2}{2m} = \frac{3}{5}\frac{Z^2e^2}{a}\int_0^\infty dx\,\frac{[f(x)]^{5/2}}{x^{1/2}}. \tag{1}$$

In the latter form, a symbolizes the radial scale of distance,

$$r = ax, \tag{2}$$

with

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

and $f(x)$ is the ratio between the potential energy of an electron and its Coulomb energy with the nucleus,

$$V(r) = -(Ze^2/r)f(x). \tag{4}$$

The function $f(x)$ obeys the differential equation

$$\frac{d^2f(x)}{dx^2} = \frac{[f(x)]^{3/2}}{x^{1/2}}, \tag{5}$$

subject to the boundary conditions

$$f(0) = 1, \quad f(\infty) = 0. \tag{6}$$

An important parameter is the magnitude of the initial slope

$$B = -\frac{df}{dx}(0); \tag{7}$$

numerical integration yields

$$B = 1.011(\pi/2) = 1.588. \tag{8}$$

The integral appearing in the second version of (1) is evaluated as

$$\int_0^\infty dx\,\frac{[f(x)]^{5/2}}{x^{1/2}} = \frac{5}{7}B. \tag{9}$$

Accordingly, the TF value of the total binding en-

ergy is

$$-E = \tfrac{3}{7} B Z^2 e^2/a = 0.7687\, Z^{7/3} e^2/a_0 , \tag{10}$$

where

$$e^2/a_0 = 2(13.61) \tag{11}$$

expressed in eV. Another way of presenting the energy,

$$E = -\tfrac{3}{7} B Z^{7/3} e^2/aZ^{1/3} , \tag{12}$$

leads to the differential relation

$$\frac{\partial E}{\partial Ze} = -B\,\frac{Ze}{a} . \tag{13}$$

This quantity is identified[4] as the average electrostatic potential, produced by the electrons, at the position of the nucleus. The interaction energy, of a single electron near the nucleus with all other electrons, is therefore given by

$$\epsilon_0 = B(Ze^2/a) . \tag{14}$$

The same quantity is also evident in the form of the potential energy (4) at small distances, $r \ll a$, $x \ll 1$:

$$V(r) \cong -(Ze^2/r)(1 - Bx) = -(Ze^2/r) + \epsilon_0 . \tag{15}$$

The validity of the semiclassical evaluation in (1) requires that the particle wavelength be small compared to the radial distance r,

$$\hbar/p \ll r . \tag{16}$$

On using the TF identification of the maximum momentum at a point,

$$(p^2/2m) + V(r) = 0 , \tag{17}$$

that condition becomes

$$(Zr/a_0) f(x) \gg 1 . \tag{18}$$

At small distances ($x \ll 1$) the restriction is

$$r \gg a_0/Z , \tag{19}$$

or

$$x \gg Z^{-2/3} . \tag{20}$$

This suggests that the x integration in (1) should be stopped at a lower limit $\sim Z^{-2/3}$, so that

$$\begin{aligned} \frac{-E}{(3/5)(Z^2e^2/a)} &= \int_{-Z^{-2/3}}^{\infty} dx\, \frac{[f(x)]^{5/2}}{x^{1/2}} \\ &\cong \tfrac{5}{7} B - \int_0^{-Z^{-2/3}} dx\, \frac{1}{x^{1/2}} \\ &= \tfrac{5}{7} B(1 - cZ^{-1/3}) , \end{aligned} \tag{21}$$

with c a constant of order unity.

QUANTITATIVE DERIVATION

We begin by removing from the semiclassical phase-space integral the incorrectly described contribution of strongly bound electrons, those with energies

$$p^2/2m + V(r) < -\epsilon , \tag{22}$$

where the characteristic distance Ze^2/ϵ is small compared with the TF length $a_0 Z^{-1/3}$, but large on the scale of the hydrogenic Bohr radius $a_0 Z^{-1}$:

$$Ze^2/a_0 Z^{-1/3} \ll \epsilon \ll Ze^2/a_0 Z^{-1} . \tag{23}$$

In this domain $x \ll 1$ and the Coulombic potential (15) applies. Then the momentum restriction (22) reads

$$p^2/2m < Ze^2/r - \epsilon' , \quad \epsilon' = \epsilon + \epsilon_0 \cong \epsilon , \tag{24}$$

and the contribution to be removed is

$$\begin{aligned} \int_0^{Ze^2/\epsilon'} 2\,\frac{4\pi r^2 dr}{(2\pi\hbar)^3}\,\frac{4\pi}{10m}\left[2m\left(\frac{Ze^2}{r} - \epsilon'\right)\right]^{5/2} \\ = \frac{Z^2e^2}{a_0} n' , \end{aligned} \tag{25}$$

where

$$n' = \left(\frac{Z^2e^2}{2a_0\epsilon'}\right)^{1/2} \tag{26}$$

is limited by

$$1 \ll n' \ll Z^{1/3} . \tag{27}$$

The correct quantum replacement for the deleted semiclassical contribution is clearly the trace of the operator $p^2/2m$, over all single-particle states of energy less than $-\epsilon$. Inasmuch as those states refer to the Coulombic potential (15), the desired trace is just

$$\sum_n \left\langle \frac{p^2}{2m} \right\rangle_n 2n^2 = \frac{Z^2e^2}{a_0} \sum_n 1 , \tag{28}$$

extended over all n such that

$$-\frac{Z^2e^2}{2a_0}\,\frac{1}{n^2} + \epsilon_0 < -\epsilon \tag{29}$$

or

$$n < n' . \tag{30}$$

Then the required summation (28) equals

$$\frac{Z^2e^2}{a_0}[n'] , \tag{31}$$

where $[n']$ indicates the largest integer contained in n'.

To compare this with (25), we need an asymptotic replacement for the discontinuous function $[n']$, which is of staircase form. The continuous func-

tion n' touches the tops of all the stairs; the function $n'-1$ touches the bottoms. The desired interpolating curve is, evidently, $n'-\frac{1}{2}$. Accordingly, the replacement of (25) with (31) leaves the residue

$$-Z^2e^2/2a_0, \tag{32}$$

and now

$$-E=0.7687\,Z^{7/3}e^2/a_0-\tfrac{1}{2}Z^2e^2/a_0$$

$$=0.7687\,Z^{7/3}(1-0.6504\,Z^{-1/3})e^2/a_0; \tag{33}$$

this correction is of the anticipated form (21). I emphasize the seamless way in which the correct treatment of strongly bound electrons has been grafted onto the TF model. Any value of n' obeying (27) is acceptable, or, inasmuch as the basic parameter $Z^{1/3}$ is supposed to be very large, n' can be chosen as any large Z-independent number.

An estimate of the total binding energy for Hg ($Z=80$, $Z^{1/3}=4.31$) is quoted[5] as (e^2/a_0 units)

$$-E_{\text{expt}}=18.13\times10^3; \tag{34}$$

the TF value is

$$-E_{\text{TF}}=21.20\times10^3, \tag{35}$$

an excess of 17%. The formula (33) gives

$$-E_{\text{theor}}=18.00\times10^3, \tag{36}$$

which is agreement to a fraction of a percent.

The smooth variation of the discrepancy, from one element to another, invites an extension to smaller Z values. For $Z=12$ ($Z^{1/3}=2.29$), the initial discrepancy of 27% is overcompensated by 10% on applying (33). But here one must also include the next level of correction, of relative order $Z^{-2/3}$. Exchange effects, omitted in the simple TF model, contribute to this, as does a small residue of the leading correction. That is discussed in Ref. 3, and we here accept without comment the recommended additional energy term:

$$-0.266\,Z^{5/3}(e^2/a_0). \tag{37}$$

The modified Eq. (33) now reads

$$-E=0.7687\,Z^{7/3}Fe^2/a_0, \tag{38}$$

where the correction factor F is

$$F=1-0.6504\,Z^{-1/3}+0.346\,Z^{-2/3}. \tag{39}$$

The experimental results for $Z=26$ down to $Z=6$ are reproduced with an error not exceeding 1%.

A simplified formula, in the nature of a mnemonic, emerges from the small numerical modifications $0.6504\to\frac{2}{3}$, $0.346\to\frac{1}{3}$. They give

$$F=\tfrac{2}{3}+\tfrac{1}{3}(1-Z^{-1/3})^2, \tag{40}$$

which reproduces all the data from $Z=80$ down to $Z=6$, at the 2% level. Another, somewhat cruder version stems from the numerical replacement $0.7687\to\frac{3}{4}$, namely,

$$-E=(e^2/2a_0)\,Z^{7/3}[1+\tfrac{1}{2}(1-Z^{-1/3})^2]. \tag{41}$$

(As a memory aide, note that it produces the correct value for $Z=1$.) We have another example of what has been called[6] "the principle of unreasonable utility of asymptotic estimates."

DISCUSSION

All the above refers to energy; there is no overt reference to particle number. Now, in order to make contact with the treatment of Scott, we consider particle number explicitly. The TF model identifies the number of electrons as the phase space integral

$$\int 2\,\frac{(d\vec{r})(d\vec{p})}{(2\pi\hbar)^3}=Z\int_0^\infty dx\,x^{1/2}[f(x)]^{3/2}, \tag{42}$$

where, according to the differential equation (5), the latter integral is

$$\int_0^\infty dx\,x\,\frac{d^2f(x)}{dx^2}=\int_0^\infty dx\,\frac{d}{dx}\left(x\,\frac{df(x)}{dx}-f(x)\right)$$

$$=f(0)=1. \tag{43}$$

Again, we proceed to remove the incorrectly described contribution of strongly bound electrons, those obeying (22). This is

$$\int_0^{Ze^2/\epsilon'}2\,\frac{4\pi r^2dr}{(2\pi\hbar)^3}\,\frac{4\pi}{3}\left[2m\left(\frac{Ze^2}{r}-\epsilon'\right)\right]^{3/2}=\tfrac{2}{3}n'^3, \tag{44}$$

where n' is given by (26) and qualified by (27). The quantum replacement of (44) is the summation

$$\sum_{n=1}2n^2 \tag{45}$$

for all $n<n'$, which equals

$$\tfrac{2}{3}([n']+\tfrac{1}{2})[n']([n']+1)=\tfrac{2}{3}([n']+\tfrac{1}{2})^3-\tfrac{1}{6}([n']+\tfrac{1}{2}). \tag{46}$$

We have already remarked on the asymptotic replacement for the discontinuous function $[n']$, namely, $n'-\frac{1}{2}$. Its introduction in (46) gives

$$\tfrac{2}{3}n'^3-\tfrac{1}{6}n', \tag{47}$$

the first term of which agrees with (44). Deleting (44) and substituting (47) therefore has the residue $-\frac{1}{6}n'$; this graft leaves a scar, but it is not one that need concern us. The immediate implication is that the number of electrons with energy above $-\epsilon$ must be increased, by the ill-determined amount $\frac{1}{6}n'$. But the consequent change in energy is of relative order Z^{-1}, one level beyond the two

leading corrections of relative orders $Z^{-1/3}$ and $Z^{-2/3}$.

In arriving at the continuous function (47), we inserted the appropriate continuous curve for the discontinuous function $[n']$, which is not necessarily the right thing to do for the cubic structure of (46). Indeed, the equally weighted average between the two bounding continuous functions n' and $n'-1$ gives

$$\tfrac{2}{3}n'^3+\tfrac{1}{3}n', \tag{48}$$

changing the sign and magnitude of the residual term. In this version the number of electrons with energy greater than $-\epsilon$ must be decreased by $\frac{1}{3}n'$. The proper procedure cannot be clear in the absence of an improved treatment that permits the modification to be performed smoothly, at the Z^{-1} level of accuracy.

Finally to Scott; in place of the (within limits) arbitrary parameter ϵ or n', he chooses the latter to make the TF computation of the number of strongly bound electrons, (44), agree with the correct value (46),

$$\begin{aligned} n' &= \{(2[n']+1)\tfrac{1}{2}[n']([n']+1)\}^{1/3} \\ &\cong [n']+\tfrac{1}{2}-\tfrac{1}{12}1/([n']+\tfrac{1}{2}), \end{aligned} \tag{49}$$

where the indicated asymptotic expansion already yields two-significant-figure accuracy for the value of $n'-[n']$, at $[n']=1$. He then turns to energy (he actually considered $\partial E/\partial Ze$, but no matter) and observes that the replacement of (25) with (31) alters the energy by

$$(Z^2e^2/a_0)(n'-[n']) \tag{50}$$

which, according to (49), for large enough $[n']$ becomes $Z^2e^2/2a_0$. But the explicit reliance on particle number, with its special choices of the energy parameter ϵ, is irrelevant, which perhaps underlies the uneasiness conveyed in the quotation cited in the introductory paragraph. Yet the answer is correct; what has been supplied here is the reassurance that the Scott leading correction to the TF atomic binding energy calculation is right.

RELATIVISTIC CORRECTIONS

The excellent agreement found for $Z=80$ might be surprising. Surely relativistic effects are of some importance at large-Z values? Perhaps, but the question is not really pertinent; the cited "experimental" value uses semiempirical formulas that have no reference to relativistic effects. But the question still merits an answer, one that is not forthcoming in the literature (apart from rough numerical estimates by Scott) but can be supplied, in part at least, by the methods of this paper.

For electrons of energy greater than $-\epsilon$, we consider only the leading relativistic correction to kinetic energy

$$\begin{aligned} \delta E(>-\epsilon) &= \int 2\frac{(d\vec{r})(d\vec{p})}{(2\pi\hbar)^3}\left[-\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)^2\right] \\ &= -\frac{1}{14\pi}\frac{1}{c^2\hbar^3m^3}\int_0^\infty dr\,r^2\{[-2mV(r)]^{7/2}-(-2mV-2m\epsilon)^{7/2}\} \\ &= -\frac{1}{14\pi}\frac{1}{c^2\hbar^3m^3}\int_{Ze^2/\epsilon'}^\infty dr\,r^2\left(2m\frac{Ze^2}{r}f(x)\right)^{7/2} \\ &\quad -\frac{1}{14\pi}\frac{1}{c^2\hbar^3m^3}\int_0^{Ze^2/\epsilon'} dr\,r^2\left[\left(2m\frac{Ze^2}{r}-2m\epsilon_0\right)^{7/2}-\left(\frac{2mZe^2}{r}-2m\epsilon'\right)^{7/2}\right]. \end{aligned} \tag{51}$$

The fractional error involved in omitting ϵ_0 in the second integral of the last form,

$$\epsilon_0/\epsilon' \sim n'^2/Z^{2/3}, \tag{52}$$

is below the level to which we aspire, $Z^{-1/3}$. The evaluation of that second integral, combined with a partial integration of the first one, then yields

$$\begin{aligned} \delta E(>-\epsilon) &= -\frac{5}{4n'}\frac{Z^2e^2}{a_0}(Z\alpha)^2 \\ &\quad +\frac{4}{\pi}\left(\frac{2}{0.8853}\right)^{1/2}\frac{Z^{5/3}e^2}{a_0}(Z\alpha)^2 \\ &\quad \times\int_0^\infty dx\,x^{-1/2}[f(x)]^{5/2}\left(-\frac{df(x)}{dx}\right), \end{aligned} \tag{53}$$

where $\alpha=e^2/\hbar c$.

The differential equation obeyed by $f(x)$ is used to convert the last integral into

$$\begin{aligned} &\int_0^\infty dx\frac{d^2f(x)}{dx}f(x)\left(-\frac{df(x)}{dx}\right) \\ &\quad =-\int_0^\infty dx f(x)\frac{1}{2}\frac{d}{dx}\left(\frac{df(x)}{dx}\right)^2 \\ &\quad =\tfrac{1}{2}B^2-\tfrac{1}{2}\int_0^\infty dx\left(-\frac{df(x)}{dx}\right)^3 \\ &\quad =1.04, \end{aligned} \tag{54}$$

according to a rough numerical integration that produced 0.437 as the value of the integral of $(-df/dx)^3$.

We illustrate the relativistic treatment of the strongly bound electrons moving in the Coulombic potential (15) by retaining only the $(Z\alpha)^2$ fine-structure term implied by the Dirac equation; additional refinements can be added as needed. This gives

$$\delta E(<-\epsilon)=\sum_{n=1}^{[n']}\sum_{j=1/2}^{n-1}{}^{2}(2j+1)m_{nj}\left[-\frac{Z^2e^2}{2a_0}(Z\alpha)^2\left(\frac{1}{n^3}\frac{1}{j+1/2}-\frac{3}{4}\frac{1}{n^4}\right)\right], \tag{55}$$

where

$$m_{nj}=2,\quad j<n-\tfrac{1}{2};\quad m_{nj}=1,\quad j=n-\tfrac{1}{2}. \tag{56}$$

The j summation is

$$\sum_{j=1/2}^{n-1/2}(2j+1)m_{nj}\left(\frac{1}{n^3}\frac{1}{j+1/2}-\frac{3}{4}\frac{1}{n^4}\right)=\frac{1}{n^3}2(2n-1)-\frac{3}{4}\frac{1}{n^4}2n^2=\frac{5}{2}\frac{1}{n^2}-2\frac{1}{n^3} \tag{57}$$

and the subsequent n summations are evaluated, for our purposes, as

$$\sum_{n=1}^{[n']}\frac{1}{n^2}=\frac{\pi^2}{6}-\sum_{[n']+1}^{\infty}\frac{1}{n^2}\cong\frac{\pi^2}{6}-\frac{1}{n'},\qquad \sum_{n=1}^{[n']}\frac{1}{n^3}\cong\zeta(3)=1.202. \tag{58}$$

Accordingly, we have

$$\delta E(<-\epsilon)=-\frac{Z^2e^2}{a_0}(Z\alpha)^2\left(\frac{5}{24}\pi^2-\zeta(3)-\frac{5}{4n'}\right), \tag{59}$$

which joins smoothly with (53) to produce

$$\delta E=-0.854\frac{Z^2e^2}{a_0}(Z\alpha)^2(1-2.33Z^{-1/3}). \tag{60}$$

Applied to $Z=80$, this formula predicts a relativistic correction to the binding energy of (e^2/a_0 units) 0.86×10^3, which is an increase of slightly less than 5%.

It is interesting that the ratio

$$(1-2.33Z^{-1/3})/Z^{1/2} \tag{61}$$

has a maximum value of 0.052 at a little below $Z=60$, and deviates from that value by less than 4% in the interval from $Z=40$ to 90. This provides an approximate replacement for (61), as

$$\delta E\cong-2.4\times10^{-6}Z^{9/2}e^2/a_0, \tag{62}$$

which makes contact with the numerical estimates[2] of Scott. His version has the same form as (62), but with the numerical coefficient 2.4 replaced by 4. Perhaps the number 2.33 in (60) is wrong? Replacing it by unity would increase the correction by a factor close to $\frac{5}{3}$ for $Z=80$. But, then the equivalent fractional power of Z for $1-Z^{-1/3}$ would be about $\frac{1}{9}$, rather than $\frac{1}{2}$. (We also note that $1-0.65Z^{-1/3}$ is well represented over a wide range of Z by the $\frac{1}{15}$ power of Z.) Inasmuch as Scott speaks of "order of magnitude" and "rough estimates," it is not clear whether a significant discrepancy exists, and we leave the question there.

Notes added in proof. I am indebted to L. DeRaad and D. Clark for independent computer calculations that replace my rough number cited after Eq. (54) by 0.353. The rapid variation of the integrand near the origin was not well represented in the simple integration rule I used. That alters the numerical value given in Eq. (54) to 1.084. As a consequence the number 2.33 in Eq. (60) is replaced by 2.43. The appropriately modified discussion of Eq. (61) now produces Eq. (62) with the coefficient 2.3.

Additional clarification is needed on several points. Reassurance can be given that the bulk of the electrons do not contribute to the correction of relative order $Z^{-1/3}$; the paper ascribes that entirely to the strongly bound electrons. Here is a qualitative argument. Improvements in the semiclassical treatment of the kinetic energy should introduce modifications that are roughly measured by $\hbar^2/r^2$, as compared with p^2. That is the content of Eq. (16), with the added remark that it is not p, but p^2, that is significant here. A measure of the fractional change in energy is just the inverse of the left side of Eq. (18). And, for the bulk of the electrons, with $r\sim a_0Z^{-1/3}$, $f(x)\sim1$, this is $\sim Z^{-2/3}$.

Then, it could be questioned whether the discrepancy $\sim n'$ between the exact and TF calculated numbers of strongly bound electrons implies an energy shift of order $n'\epsilon$, which would be larger than the shift of relative order Z^{-1} suggested in the paper. But this effect is already included in the energy calculation of the paper. That is emphasized by writing $n'\epsilon=(Z^2e^2/2a_0)(1/n')$; it is a small part ($n'\gg1$) of the Z^2 term in the energy, the correction of relative order $Z^{-1/3}$.

Finally the question is raised: Why, in discussing relativistic corrections are spin effects ignored for energies $> -\epsilon$? Explicit spin-orbit coupling averages to zero, of course. But there is the s-wave effect proportional to $\nabla^2 V$. However, the same sort of qualitative argument used before shows this to be $\sim Z^{-2/3}$ relative to the leading term.

---

[1]P. Gombás, *Die Statistiche Theories des Atoms und Ihre Anwendungen* (Springer, Wien, 1949).
[2]J. Scott, Philos. Mag. 43, 859 (1952).
[3]N. March, Adv. Phys. 6, 1 (1957).
[4]This is an application of the equality between the derivative of the energy with respect to a parameter and the expectation value of the derivative of the Hamiltonian with respect to that parameter. The relation appeared early in quantum-mechanical history. It is stated explicitly [Eq. (246')] in Pauli's universally known treatise on wave mechanics [in *Handbuch der Physik*, Vol. 24, Part I, edited by H. Geiger and K. Scheel (Springer, Berlin, 1933), p. 83.], where the original work is cited. The equality is now known as Feynman's theorem (1939).
[5]See Ref. 1, p. 174.
[6]Quoted in Phys. Today, 33, 29 (1980).