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Statistical atom: Some quantum improvements

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The Thomas-Fermi model is improved by simultaneously introducing three different quantum corrections. The first concerns the nonlocality of quantum mechanics; we go beyond the von Weizsäcker approach by including arbitrary powers of the gradient of the single-particle potential. The second is a special treatment of the strongly bound electrons, which removes the incorrect statistical description of the vicinity of the nucleus. In the third we generalize Dirac's way of handling the exchange interaction by, again, including gradient effects to arbitrary order. All this is done in the framework of a "potential-functional method" and results in a new differential equation for the potential. The comparison of numerical results with both experimental and Hartree-Fock data for the mean-squared distance indicates a superiority of the new statistical theory over the Hartree-Fock theory, at least for the description of the outer reaches of the atom.

INTRODUCTION

Two different attitudes have evolved toward the Thomas-Fermi (TF) statistical model and its variants associated with the names of Dirac and von Weizsäcker. One is highly mathematical, rich in theorems about received formulations;[1] the other is more physical, aware of the inherent errors of the model and dedicated to its improvement, while striving to maintain its essential simplicity. Both approaches are valuable, but there is danger in judging one by the standards of the other. This paper is a further contribution toward the quantitative improvement of the statistical model through the incorporation of quantal refinements. One aspect of that improvement is displayed in Fig. 1. It presents the total binding energy of neutral atoms, comparing integral-Z Hartree-Fock (HF) calculations[2] with continuous curves, first of the TF model,[3] then with the leading correction of relative order $Z^{-1/3}$,[4] and finally with the inclusion of corrections of relative order $Z^{-2/3}$.[5] The remaining deviations, which are indiscernible in Fig. 1, are presented in Fig. 2 in a manner that displays quite regular oscillations as a function of $Z^{1/3}$. We intend to address the latter behavior on another occasion.[6]

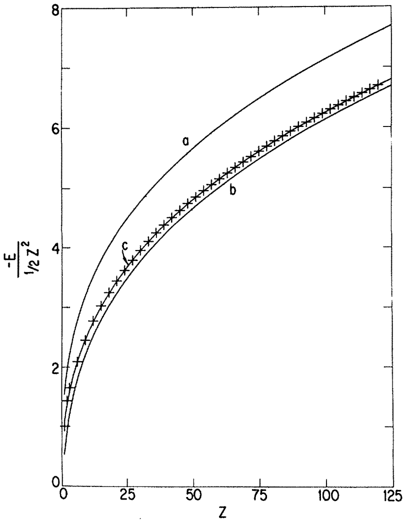

FIG. 1. Comparison of calculations of the total binding energy. Crosses: HF data (for $Z=1,2,3,6,9,\ldots,120$). Curve *a* original TF; curve *b* TF with corrections of relative order $Z^{-1/3}$; curve *c* TF with corrections of relative orders $Z^{-1/3}$ and $Z^{-2/3}$.

The improvement in total binding-energy calculations stems primarily from the corrected treatment of the strongly bound electrons near the nucleus, for which the TF model is seriously in error. An accompanying paper[7] develops this in detail, with emphasis on the implications for the particle density. The other region of failure of the TF model is at large distances. We have already discussed one improvement in the description of the outer reaches of the atom[8]—it gave not unreasonable values for the diamagnetic susceptibilities of the inert-gas configurations—but which had the serious flaw of ascribing a sharp boundary to ions and atoms. This paper is designed to remove that deficiency by introducing a better quantal description of the weakly bound electrons occupying the

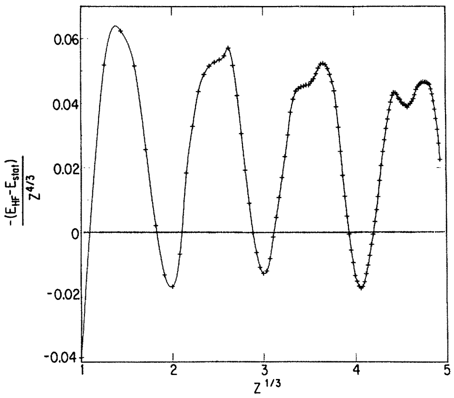

FIG. 2. Deviation between curve *c* of Fig. 1 and the HF data (crosses, all Z here).

outer atomic regions. At the same time, the accurate quantum treatment of strongly bound electrons near the nucleus is incorporated more consistently into the general formulation.

As in Ref. 8, we use the single-particle potential as the fundamental quantity from which everything else is derived. It should be emphasized that this differs from the so-called "density-functional formalism,"[9] where—as indicated by its name—this role is played by the density. The advantage of our strategy becomes obvious as soon as one recalls that the potential is a much smoother spatial function than the particle density; according to Poisson's equation, it is the Laplacian of the potential that has as much structure as the density. Consequently, an approximation that expresses all quantities in terms of the potential and its derivatives should be significantly more reliable than a similar one based on the density.

QUANTUM CORRECTION

In a previous paper[5] there appeared under this heading the sentences: "The correction we now consider is a property of the bulk of electrons. It expresses the inadequacy of the semiclassical approximation that relates the particle density at a point to just the potential energy at that point. There is a particularly simple way of looking at this effect. It begins in one spatial dimension." There follows the remark that in a small range of coordinate x, and with a suitable change of origin, the potential can be presented in the oscillator form (we now use atomic units: $e=m=\hbar=1$)

$$V(x)=V_0+\tfrac{1}{2}\omega^2x^2\ , \tag{1}$$

for which the dynamic evolution is well known (it is here stated for $x'=x$),

$$\begin{aligned}\langle xt\,|\,x0\rangle &= \left[\frac{\omega}{2\pi i\sin(\omega t)}\right]^{1/2} e^{-iV_0t}e^{-i\omega x^2\tan(\omega t/2)}\\ &=\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp\left\{-i\left[\tfrac{1}{2}p^2\frac{\sin(\omega t)}{\omega}+V_0t\right.\right.\\ &\qquad\left.\left.+\ \omega x^2\tan\left[\frac{\omega t}{2}\right]\right]\right\}\ . \end{aligned}\tag{2}$$

It has already been remarked that

$$\langle xt\,|\,x0\rangle\cong\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp[-i(\tfrac{1}{2}p^2+V(x))t] \qquad \text{for } \omega t\ll 1 \tag{3}$$

is the semiclassical limit. The earlier paper also took the next step of retaining the cubic term in the expansion of the trigonometric functions. We now go beyond what was done there by retaining these additional terms in the exponent, rather than regarding all such effects as small. This yields

$$\langle xt\,|\,x0\rangle\cong\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp\left[-i\left\{\left[\frac{1}{2}p^2+V(x)\right]t+\frac{1}{24}\left[\left[\frac{dV}{dx}\right]^2-2\left[p\frac{d}{dx}\right]^2V\right]t^3\right\}\right]\ . \tag{4}$$

The principal justification for taking this seriously comes from the consideration of the "edge of the atom," the region where $V(x)$ (more generally, with an additive constant) changes from negative values (classically allowed region) to positive values (classically forbidden region). Let the transition point be labeled $x=0$, with the potential in its neighborhood approximated by that for a constant force (familiar in the WKB description of wave functions near turning points)

$$V(x)=-Fx\ . \tag{5}$$

The known quantum-dynamical solution of this problem is

$$\langle xt\,|\,x0\rangle=\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp\{-i[(\tfrac{1}{2}p^2-Fx)t+\tfrac{1}{24}F^2t^3]\}\ . \tag{6}$$

It is identical with what (4) yields for the linear potential (5). This outcome also suggests that the term involving the second derivative of the potential in the exponential of (4) is of lesser importance, permitting further expansion.

The three-dimensional generalization of (4), presented as a matrix element of the time-evolution operator for the one-particle Hamiltonian H (we add the constant ζ) is

$$\begin{aligned}\langle\vec{r}\,|\,e^{-i(H+\zeta)t}\,|\,\vec{r}\rangle &\cong\int\frac{(d\vec{p})}{(2\pi)^3}\exp\left[-i[\tfrac{1}{2}\vec{p}^{\,2}+V(\vec{r})+\zeta]t\right.\\ &\qquad\left.-\frac{i}{24}[(\vec{\nabla}V)^2-2(\vec{p}\cdot\vec{\nabla})^2V]t^3\right]\end{aligned}\tag{7}$$

and (the factor 2 is the spin multiplicity)

$$\mathrm{Tr}\,e^{-i(H+\zeta)t}\cong 2\int\frac{(d\vec{r})(d\vec{p})}{(2\pi)^3}\exp\left[-i[\tfrac{1}{2}\vec{p}^{\,2}+V(\vec{r})+\zeta]t-\frac{i}{8}[(\vec{\nabla}V)^2-2(\vec{p}\cdot\vec{\nabla})^2V]\frac{t^3}{3}\right]\ , \tag{8}$$

which exhibits the quantum correction in the framework of a classical phase-space integral.

In preparation for a more useful representation of the exponential function of t^3, we remark that

$$e^{-iy^3/3}=\int_{-\infty}^{+\infty}dx\,e^{ixy}\mathrm{Ai}(x)\ , \tag{9}$$

where $\mathrm{Ai}(x)$ is the Airy function,[10] given explicitly by the integral

$$\mathrm{Ai}(x)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}dx\,e^{-ixy}e^{-iy^3/3}$$
$$=\frac{1}{\pi}\int_0^{\infty}dy\cos(xy+\tfrac{1}{3}y^3)\ . \tag{10}$$

It is familiar that $\mathrm{Ai}(x)$ is oscillatory for $x<0$ and exponentially decreasing for $x>0$ with the relevant variable proportional to $|x|^{3/2}$. We also infer, on setting $y=0$ in (9), that

$$\int_{-\infty}^{+\infty}dx\,\mathrm{Ai}(x)=1\ , \tag{11}$$

which permits one to introduce a definition of Airy averaging:

$$\langle f(x)\rangle=\int_{-\infty}^{+\infty}dx\,\mathrm{Ai}(x)f(x)\ . \tag{12}$$

In this notation, we have

$$\langle e^{ixy}\rangle=e^{-iy^3/3}\ , \tag{13}$$

which has the special consequences

$$\langle x\rangle=0\ ,\quad \langle x^2\rangle=0\ ,\quad \langle x^3\rangle=2\ . \tag{14}$$

On employing (9) and (12), we can now present (8) as

$$\mathrm{Tr}e^{-i(H+\zeta)t}\cong 2\int\frac{(d\vec{\mathrm{r}})(d\vec{\mathrm{p}})}{(2\pi)^3}\langle e^{-i[h_x(\vec{\mathrm{r}},\vec{\mathrm{p}})+\zeta]t}\rangle\ , \tag{15}$$

where

$$h_x(\vec{\mathrm{r}},\vec{\mathrm{p}})=\tfrac{1}{2}\vec{\mathrm{p}}^{\,2}+V(\vec{\mathrm{r}})$$
$$-\tfrac{1}{2}x[(\vec{\nabla}V)^2-2(\vec{\mathrm{p}}\cdot\vec{\nabla})^2V]^{1/3}(\vec{\mathrm{r}}) \tag{16}$$

which identifies the effective, quantum-corrected, semiclassical spectrum of H. We use it to write immediately the sum over all values of $H'+\zeta$, such that

$$-\zeta_s<H'<-\zeta\ . \tag{17}$$

This is [$\eta(z)$ is the Heaviside step function]

$$E_{\zeta\zeta_s}=\mathrm{Tr}(H+\zeta)[\eta(-H-\zeta)-\eta(-H-\zeta_s)]$$
$$\cong 2\int\frac{(d\vec{\mathrm{r}})(d\vec{\mathrm{p}})}{(2\pi)^3}$$
$$\times\langle(h_x+\zeta)[\eta(-h_x-\zeta)-\eta(-h_x-\zeta_s)]\rangle\ . \tag{18}$$

Now we follow the suggestion that an expansion in powers of the second derivative of V is acceptable:

$$[(\vec{\nabla}V)^2-2(\vec{\mathrm{p}}\cdot\vec{\nabla})^2V]^{1/3}$$
$$\cong|\vec{\nabla}V|^{2/3}-\tfrac{2}{3}|\vec{\nabla}V|^{-4/3}(\vec{\mathrm{p}}\cdot\vec{\nabla})^2V+\cdots\ . \tag{19}$$

We shall retain only the indicated terms, with the permissible replacement

$$(\vec{\mathrm{p}}\cdot\vec{\nabla})^2V\rightarrow\tfrac{1}{3}p^2\nabla^2V\ . \tag{20}$$

On introducing the symbols

$$z=-\tfrac{1}{2}p^2-V-\zeta+\tfrac{1}{2}x|\vec{\nabla}V|^{2/3}\ ,$$
$$z_s=-\tfrac{1}{2}p^2-V-\zeta_s+\tfrac{1}{2}x|\vec{\nabla}V|^{2/3}=z-(\zeta_s-\zeta)\ , \tag{21}$$

and recalling that the delta function is produced by differentiation of the step function:

$$\frac{d}{dz}\eta(z)=\delta(z)\ , \tag{22}$$

we get the approximation

$$E_{\zeta\zeta_s}\cong 2\int\frac{(d\vec{\mathrm{r}})(d\vec{\mathrm{p}})}{(2\pi)^3}\langle\{[-z+\tfrac{1}{9}x|\vec{\nabla}V|^{-4/3}(p^2\nabla^2V)][\eta(z)-\eta(z_s)]-\tfrac{1}{9}x|\vec{\nabla}V|^{-4/3}(p^2\nabla^2V)(\zeta_s-\zeta)\delta(z_s)\}\rangle\ . \tag{23}$$

The differential equation obeyed by the Airy function,

$$\frac{d^2}{dx^2}\mathrm{Ai}(x)=x\mathrm{Ai}(x)\ , \tag{24}$$

is used in producing the equivalent Airy averages,

$$\langle xf(x)\rangle=\left\langle\frac{d^2}{dx^2}f(x)\right\rangle\ . \tag{25}$$

One application, which generalizes (14), is the recurrence relation

$$\langle x^{k+1}\rangle=k(k-1)\langle x^{k-2}\rangle\ . \tag{26}$$

Now observe that

$$\frac{d}{dx}\eta(z)=\tfrac{1}{2}|\vec{\nabla}V|^{2/3}\delta(z) \tag{27}$$

and

$$p^2\frac{d^2}{dx^2}\eta(z)=-\tfrac{1}{4}|\vec{\nabla}V|^{4/3}\vec{\mathrm{p}}\cdot\frac{\partial}{\partial\vec{\mathrm{p}}}\delta(z)\ , \tag{28}$$

with similar relations for $\eta(z_s)$ and $\delta(z_s)=\eta'(z_s)$. After partial integration with respect to $\vec{\mathrm{p}}$ we are left with

$$E_{\zeta\zeta_s}\cong 2\int\frac{(d\vec{\mathrm{r}})(d\vec{\mathrm{p}})}{(2\pi)^3}\langle\{-z[\eta(z)-\eta(z_s)]+\tfrac{1}{12}(\nabla^2V)[\delta(z)-\delta(z_s)-(\zeta_s-\zeta)\delta'(z_s)]\}\rangle\ . \tag{29}$$

FIRST QUANTUM CORRECTION

Before continuing, it is advisable to check that the first quantum correction that is contained in this more general expression reproduces what is already known. For that purpose we must carry out an expansion of

$$-z[\eta(z)-\eta(z_s)]=-z\eta(z)+z_s\eta(z_s)+(\zeta_s-\zeta)\eta(z_s)\ , \tag{30}$$

in powers of

$$\delta z=\delta z_s=\tfrac{1}{2}x|\vec{\nabla}V|^{2/3}\ , \tag{31}$$

that exhibits the cubic term $[\langle x\rangle=\langle x^2\rangle=0]$. No expansion is required for the term already possessing $\nabla^2 V$ as a factor. Now,

$$\frac{d}{dz}[z\eta(z)]=\eta(z) \tag{32}$$

inasmuch as $z\delta(z)=0$, and therefore (the notation is a reminder that z and z_s are altered by the same amount)

$$\frac{\partial^3}{\partial(z,z_s)^3}\{-z[\eta(z)-\eta(z_s)]\}$$
$$=-\delta'(z)+\delta'(z_s)+(\zeta_s-\zeta)\delta''(z_s)\ . \tag{33}$$

This produces the energy correction

$$\delta E_{\text{qu}}=2\int\frac{(d\vec{\mathrm{r}})(d\vec{\mathrm{p}})}{(2\pi)^3}$$
$$\times\{-\tfrac{1}{24}(\vec\nabla V)^2[\delta'(z)-\delta'(z_s)-(\zeta_s-\zeta)\delta''(z_s)]$$
$$+\tfrac{1}{12}(\nabla^2 V)[\delta(z)-\delta(z_s)-(\zeta_s-\zeta)\delta'(z_s)]\} \tag{34}$$

in which z and z_s now mean

$$z=\tfrac{1}{2}[2(-V-\zeta)-p^2]\equiv\tfrac{1}{2}(P^2-p^2)\ ,$$
$$z_s=\tfrac{1}{2}[2(-V-\zeta_s)-p^2]\equiv\tfrac{1}{2}(P_s^2-p^2)\ , \tag{35}$$

displaying the maximum classical momenta associated with the upper and lower energy bounds ζ and ζ_s.

We should notice the significance of the combinations appearing in Eq. (34), as expressed in terms of a variable z' that analogously involves a parameter ζ' intermediate between ζ_s and ζ:

$$f(z)-f(z_s)-(\zeta_s-\zeta)f'(z_s)$$
$$=\int_\zeta^{\zeta_s}d\zeta'(\zeta'-\zeta)\frac{d^2}{d\zeta'^2}f(z')\ . \tag{36}$$

This form conveys the strong cancellation that occurs at small distances where both z and z_s become very large ($V\cong -Z/r$) with a fixed difference between them. To show this cancellation in action, we use the integrals

$$2\int\frac{(d\vec{\mathrm{p}})}{(2\pi)^3}\delta[\tfrac{1}{2}P^2-\tfrac{1}{2}p^2]=\begin{cases}\dfrac{1}{\pi^2}P\ , & P^2>0\\ 0\ , & P^2\le 0\end{cases} \tag{37}$$

$$2\int\frac{(d\vec{\mathrm{p}})}{(2\pi)^3}\delta'[\tfrac{1}{2}P^2-\tfrac{1}{2}p^2]=\begin{cases}\dfrac{1}{\pi^2}\dfrac{1}{P}\ , & P^2>0\\ 0\ , & P^2\le 0\end{cases} \tag{38}$$

to produce

$$\delta E_{\text{qu}}=\int(d\vec{\mathrm{r}})\frac{1}{24\pi^2}\left[-(\vec\nabla V)^2\int_\zeta^{\zeta_s}d\zeta'(\zeta'-\zeta)\frac{d^2}{d\zeta' 2}\frac{1}{[2(-V-\zeta')]^{1/2}}\right.$$
$$\left.+2(\nabla^2 V)\int_\zeta^{\zeta_s}d\zeta'(\zeta'-\zeta)\frac{d^2}{d\zeta'^2}[2(-V-\zeta')]^{1/2}\right]\ . \tag{39}$$

First we dispose of the delta function at the origin in $\nabla^2 V$. Of course, $[2(-V)]^{1/2}$ is singular at that point. But, the two derivatives with respect to ζ' wipe that term out. Indeed, the whole structure of the second derivative, $\sim[2(-V-\zeta')]^{-3/2}$, is thoroughly zero at the origin. Then there is the connection between the two contributions. Note that

$$-(\vec\nabla V)^2[2(-V-\zeta')]^{-1/2}=-\nabla^2\{\tfrac{1}{3}[2(-V-\zeta')]^{3/2}\}$$
$$-(\nabla^2 V)[2(-V-\zeta')]^{1/2}\ . \tag{40}$$

We now have the option of integrating the Laplacian term over all space with a null result, or, of excising a small sphere around the origin (in which event there is no delta-function term) with the same outcome. In short, the first term of (39) is the negative of half the second one. That leaves just

$$\delta E_{\text{qu}}=\int(d\vec{\mathrm{r}})\frac{1}{24\pi^2}(\nabla^2 V)$$
$$\times\int_\zeta^{\zeta_s}d\zeta'(\zeta'-\zeta)\frac{d^2}{d\zeta'^2}[2(-V-\zeta')]^{1/2}\ , \tag{41}$$

wherein use of Poisson's equation ($\nabla^2 V=-4\pi n$, $r>0$) and the recognition that, with all singularities at the origin removed, ζ_s can in good approximation be made arbitrarily large, yields ($\zeta=0$)

$$\delta E_{\text{qu}}=\int(d\vec{\mathrm{r}})\frac{1}{24\pi^2}(-4\pi n)[2(-V)]^{1/2}\ , \tag{42}$$

in agreement with Eq. (43) of Ref. 5.

QUANTUM CORRECTION (CONTINUED)

While we opted in favor of $\nabla^2 V$ in seeking δE_{qu}, we proceed conversely with $\nabla^2 V$ in (29), choosing to produce a functional just of V and $|\vec\nabla V|$. First, a qualitative argument. To the extent that $\nabla^2 V$ is related to the density, it is most significant in the interior of the atom, far from the "edge" where $|\vec\nabla V|$ becomes important. And when we do approach the edge, $|\vec\nabla V|$ is essentially constant. All this means that, in writing

$$\int(d\vec{\mathrm{r}})(\nabla^2 V)[\delta(z)-\delta(z_s)-(\zeta_s-\zeta)\delta'(z_s)]$$
$$=-\int(d\vec{\mathrm{r}})\vec\nabla V\cdot\vec\nabla[\delta(z)-\delta(z_s)-(\zeta_s-\zeta)\delta'(z_s)] \tag{43}$$

we feel justified in evaluating the gradient of z and z_s as

$$\vec{\nabla}(z,z_s)\cong-\vec{\nabla}V\,, \tag{44}$$

leading to the replacement of (43) by

$$\int(d\vec{r})\,|\,\vec{\nabla}V\,|^2[\delta'(z)-\delta'(z_s)-(\zeta_s-\zeta)\delta''(z_s)]\,. \tag{45}$$

We thus arrive at

$$\begin{aligned}E_{\zeta\zeta_s}\cong2\int\frac{(d\vec{r})(d\vec{p})}{(2\pi)^3}\langle\{&-z[\eta(z)-\eta(z_s)]\\&+\tfrac{1}{12}\,|\,\vec{\nabla}V\,|^2[\delta'(z)-\delta'(z_s)\\&-(\zeta_s-\zeta)\delta''(z_s)]\}\rangle\,.\end{aligned} \tag{46}$$

AIRY INTEGRALS

All the momentum integrals that appear here can be expressed in terms of the Airy function and its derivative. We deal with these integrals as a set, exploiting their relationship through differentiation. To convey this compactly, we shall introduce positive and negative powers of derivatives:

$$\delta''(z)=\frac{d}{dz}\delta'(z),\quad \delta'''(z)=\left[\frac{d}{dz}\right]^2\delta'(z)\,, \tag{47}$$

and

$$\begin{aligned}\delta(z)&=\left[\frac{d}{dz}\right]^{-1}\delta'(z)\,,\\ \eta(z)&=\left[\frac{d}{dz}\right]^{-2}\delta'(z)\,,\\ z\eta(z)&=\left[\frac{d}{dz}\right]^{-3}\delta'(z)\,.\end{aligned} \tag{48}$$

Then, in view of the linear dependence of z on the constant $-\zeta$, we can write

$$\begin{aligned}&2\int\frac{(d\vec{p})}{(2\pi)^3}\left\langle\left[\frac{d}{dz}\right]^{-n}\delta'(z)\right\rangle\\&\quad=\left[\frac{d}{d(-\zeta)}\right]^{-n}\frac{1}{\pi^2}\langle[2(-V-\zeta+\tfrac{1}{2}x\,|\,\vec{\nabla}V\,|^{2/3})]^{-1/2}\rangle\end{aligned} \tag{49}$$

which utilizes the known integral (38), where one has only to replace $-\zeta$ with $-\zeta+\frac{1}{2}x\,|\,\vec{\nabla}V\,|^{2/3}$ and apply Airy averaging. We reexpress this in terms of the variable

$$y=\frac{2(V+\zeta)}{|\,2\vec{\nabla}V\,|^{2/3}}\,, \tag{50}$$

which has the property of being negative (positive) in the classically allowed (forbidden) region, to get

$$\begin{aligned}&2\int\frac{(d\vec{p})}{(2\pi)^3}\left\langle\left[\frac{d}{dz}\right]^{-n}\delta'(z)\right\rangle\\&\quad=\frac{2}{\pi}\,|\,2\vec{\nabla}V\,|^{2(n-1/2)/3}2^{-n}F_n(y)\,,\end{aligned} \tag{51}$$

where

$$F_n(y)=\frac{1}{2\pi}\left[-\frac{d}{dy}\right]^{-n}\langle(2^{-2/3}x-y)^{-1/2}\rangle\,. \tag{52}$$

Similar statements evaluate the integrals involving z_s in terms of

$$y_s=\frac{2(V+\zeta_s)}{|\,2\vec{\nabla}V\,|^{2/3}}=y+(\zeta_s-\zeta)\frac{2}{|\,2\vec{\nabla}V\,|^{2/3}}\,. \tag{53}$$

An immediate recurrence relation for these functions is

$$-\frac{d}{dy}F_n(y)=F_{n-1}(y)\,. \tag{54}$$

To produce another relation we first remark that, for $n\geq0$, (52) has the following explicit significance:

$$F_n(y)=\frac{(-\frac{1}{2})!}{(n-\frac{1}{2})!}\frac{1}{2\pi}\langle(2^{-2/3}x-y)^{n-1/2}\rangle\,, \tag{55}$$

which can be checked against (54). Now observe that

$$\begin{aligned}\langle(2^{-2/3}x-y)^{n+1/2}\rangle&=\langle(2^{-2/3}x-y)(2^{-2/3}x-y)^{n-1/2}\rangle\\&=\left[\frac{1}{4}\frac{d^2}{dy^2}-y\right]\langle(2^{-2/3}x-y)^{n-1/2}\rangle\,,\end{aligned} \tag{56}$$

on applying the Airy averaging relation of (25). Accordingly,

$$\begin{aligned}(n+\tfrac{1}{2})F_{n+1}(y)&=\left[\frac{1}{4}\frac{d^2}{dy^2}-y\right]F_n(y)\\&=\tfrac{1}{4}F_{n-2}(y)-yF_n(y)\,,\end{aligned} \tag{57}$$

which is compatible with (54) and therefore also valid for $n<0$. Now, beginning with a knowledge of $F_0(y)$, we first use (54) to compute successively $F_{-1}(y),F_{-2}(y)$, $F_{-3}(y),\ldots$; then we apply (57) for a purely algebraic computation of $F_1(y)$, $F_2(y),F_3(y),\ldots$.

To find $F_0(y)$, consider $[\mathrm{Ai}(y)]^2$. It is given by

$$\begin{aligned}[\mathrm{Ai}(y)]^2=\frac{1}{(2\pi)^2}\int_{-\infty}^{+\infty}&dt\,dt'e^{-iy(t+t')}\\&\times e^{-i(t^3+t'^3)/3}\end{aligned} \tag{58}$$

or, on changing variables,

$$t=\tfrac{1}{2}\sigma+\tau\,,\quad t'=\tfrac{1}{2}\sigma-\tau\,, \tag{59}$$

by

$$\begin{aligned}[\mathrm{Ai}(y)]^2=\frac{1}{(2\pi)^2}\int_{-\infty}^{+\infty}&d\sigma\,d\tau\,e^{-i(\tau^2+y)\sigma}\\&\times e^{-i(2^{-2/3}\sigma)^3/3}\,.\end{aligned} \tag{60}$$

The use of (13) converts this into

$$
\begin{aligned}
[\mathrm{Ai}(y)]^2 &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\tau \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\sigma \langle e^{-i(\tau^2+y-2^{-2/3}x)\sigma}\rangle \\
&= \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\tau \langle \delta(\tau^2+y-2^{-2/3}x)\rangle \\
&= \frac{1}{2\pi}\langle (2^{-2/3}x-y)^{-1/2}\rangle \; . \qquad (61)
\end{aligned}
$$

In short,

$$F_0(y)=[\mathrm{Ai}(y)]^2 \; . \qquad (62)$$

We now produce

$$
\begin{aligned}
F_{-1}(y) &= -2\mathrm{Ai}(y)\mathrm{Ai}'(y) \; , \\
F_{-2}(y) &= 2\{y[\mathrm{Ai}(y)]^2+[\mathrm{Ai}'(y)]^2\} \; ,
\end{aligned} \qquad (63)
$$

and then

$$
\begin{aligned}
F_1(y) &= -y[\mathrm{Ai}(y)]^2+[\mathrm{Ai}'(y)]^2 \; , \\
F_2(y) &= \tfrac{2}{3}\{y^2[\mathrm{Ai}(y)]^2-\tfrac{1}{2}\mathrm{Ai}(y)\mathrm{Ai}'(y) \\
&\quad -y[\mathrm{Ai}'(y)]^2\} \; , \qquad (64) \\
F_3(y) &= \tfrac{4}{5}\{(\tfrac{3}{8}-y^3)[\mathrm{Ai}(y)]^2+\tfrac{1}{2}y\,\mathrm{Ai}(y)\mathrm{Ai}'(y) \\
&\quad +y^2[\mathrm{Ai}'(y)]^2\} \; .
\end{aligned}
$$

These functions are plotted in Fig. 3.

The asymptotic behavior of the functions $F_n(y)$, $n \geq 0$, for very large values of $|y|$ is independent of Airy averaging and is that of the classical limit:

$$F_n(y) \sim \frac{(-\frac{1}{2})!}{(n-\frac{1}{2})!}\frac{1}{2\pi}(-y)^{n-1/2} \text{ for } -y \gg 1 \; , \qquad (65)$$

$$F_n(y) \sim 0 \text{ for } y \gg 1 \; . \qquad (66)$$

These results should also emerge from the asymptotic form of Airy's function,

$$
\begin{aligned}
\mathrm{Ai}(y) &\sim \pi^{-1/2}|y|^{-1/4} \\
&\quad \times \cos\left[\frac{2}{3}|y|^{3/2}-\frac{\pi}{4}\right] \text{ for} -y \gg 1 \; , \\
\mathrm{Ai}(y) &\sim \tfrac{1}{2}\pi^{-1/2}y^{-1/4}e^{-2y^{3/2}/3} \text{ for } y \gg 1 \; .
\end{aligned} \qquad (67)
$$

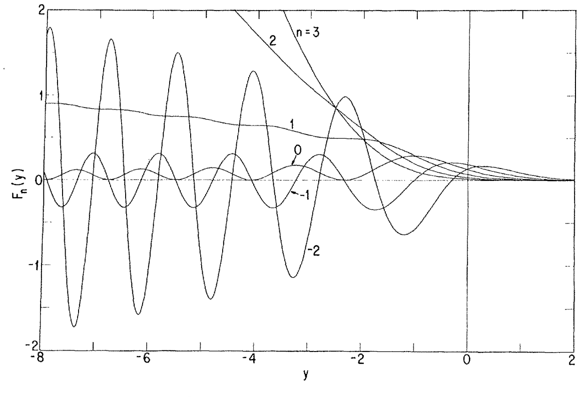

FIG. 3. Plot of the $F_n(y)$ for $n=3,2,1,0,-1,-2$.

Indeed they do, but there is an interesting point here. First notice that

$$
\begin{aligned}
F_0(y) &= [\mathrm{Ai}(y)]^2 \\
&\sim \frac{1}{\pi}\frac{1}{|y|^{1/2}}\left[\cos\left[\frac{2}{3}|y|^{3/2}-\frac{\pi}{4}\right]\right]^2 \\
&\qquad \text{for } -y \gg 1 \qquad (68)
\end{aligned}
$$

which coincides with the classical value [Eq. (65)] $(1/2\pi)|y|^{-1/2}$ only after averaging over the oscillations of the squared cosine function in (68). In contrast, consider $F_1(y)$, where one also needs

$$
\begin{aligned}
\mathrm{Ai}'(y) &\sim |y|^{1/2}\left[\pi^{-1/2}|y|^{-1/4}\right. \\
&\qquad \left.\times \sin\left[\frac{2}{3}|y|^{3/2}-\frac{\pi}{4}\right]\right] \\
&\qquad \text{for } -y \gg 1 \qquad (69)
\end{aligned}
$$

resulting in

$$
\begin{aligned}
F_1(y) &\sim |y|\frac{1}{\pi}|y|^{-1/2}\left[\sin^2\left[\frac{2}{3}|y|^{3/2}-\frac{\pi}{4}\right]\right. \\
&\qquad \left. + \cos^2\left[\frac{2}{3}|y|^{3/2}-\frac{\pi}{4}\right]\right] \\
&= \frac{1}{\pi}|y|^{1/2} \text{ for } -y \gg 1 \qquad (70)
\end{aligned}
$$

without the necessity of averaging over oscillations. The same situation holds for the leading terms of F_2 and F_3, as is evident from the recurrence relation (57). In this connection it should also be noticed that the leading terms of F_{-1} and F_{-2} are entirely oscillatory.

STRONGLY BOUND ELECTRONS

We have evaluated

$$E_{\zeta\zeta_s}=\mathrm{Tr}(H+\zeta)[\eta(-H-\zeta)-\eta(-H-\zeta_s)] \qquad (71)$$

by a statistical method, one that includes some quantum corrections. Now we compute

$$E_s=\mathrm{Tr}(H+\zeta)\eta(-H-\zeta_s) \; , \qquad (72)$$

the sum over all values of $H'+\zeta$ for which

$$H'<-\zeta_s \; , \qquad (73)$$

by using the exact energies in the Coulomb potential. More precisely, we write the particle potential V as

$$V(\vec{r})=-\frac{Z}{r}+\left[V(\vec{r})+\frac{Z}{r}\right] \qquad (74)$$

and regard the latter part as a small perturbation, leading to the energy value

$$\mathscr{E}_{nlm}=-\frac{Z^2}{2n^2}+\left\langle\left[V+\frac{Z}{r}\right]\right\rangle_{nlm} \; . \qquad (75)$$

This treatment should be justified if the energy at which the quantum calculation is connected with the (improved) semiclassical calculation is such that

$$\frac{Z}{Z^{-1}} \gg \zeta_s \gg \frac{Z}{Z^{-1/3}} \tag{76}$$

which is to say that the largest principal quantum number n_s of the quantum treatment is in the range

$$1 \ll n_s \ll Z^{1/3} . \tag{77}$$

The quantum energy E_s is then given by

$$E_s = -Z^2 n_s + 2 \sum_{n,l,m} \left\langle V + \frac{Z}{r} + \zeta \right\rangle_{nlm} , \tag{78}$$

where, to be accurate, n_s and ζ_s are related by

$$\begin{aligned} -\zeta_1 \equiv -\frac{Z^2}{2n_s^2} + \left\langle V + \frac{Z}{r} \right\rangle_{n_s} &< -\zeta_s \\ < -\frac{Z^2}{2(n_s+1)^2} + \left\langle V + \frac{Z}{r} \right\rangle_{n_s+1} &\equiv -\zeta_2 \end{aligned} \tag{79}$$

in which, in principle, $\langle \cdots \rangle_{n_s}$ ($\langle \cdots \rangle_{n_s+1}$) is the largest (smallest) value found for this set of states. Only a slight dependence on the particular choice of angular quantum numbers is expected, however, and therefore we shall average away the angular dependence of the squared wave functions:

$$\begin{aligned} \left\langle V + \frac{Z}{r} \right\rangle_{n_s} &= \int (d\vec{r}) \left[V + \frac{Z}{r} \right] \frac{1}{2n_s^2} \\ &\quad \times \sum_{l,m} 2 \, | \psi_{n_s lm}(r,\theta,\phi) |^2 \\ &\equiv \int (d\vec{r}) \left[V + \frac{Z}{r} \right] | \psi_{n_s} |^2_{\mathrm{av}}(r) , \end{aligned} \tag{80}$$

and indeed this averaged density depends only on r because of the spherical symmetry of closed Coulombic l subshells. It is important to appreciate that no particular value of ζ_s in the range (79) is implied and, indeed, an averaging process that smoothes the transition between the two regions is to be understood.

The number of specially treated electrons is

$$N_s = \sum_{n=1}^{n_s} 2n^2 = \tfrac{1}{3} n_s (n_s+1)(2n_s+1) , \tag{81}$$

in view of which we rewrite (77) as

$$1 \ll N_s \ll Z . \tag{82}$$

This is to say that N_s must be a small fraction of the total number of electrons. For most practical applications this means $n_s = 1$, or at most $n_s = 2$.

For a system of N electrons, the combination of $E_{\zeta\zeta_s}$ and E_s approximates the single-particle energy E_1 plus ζN, or

$$\begin{aligned} E_1 &= \mathrm{Tr}(H+\zeta)\eta(-H-\zeta) - \zeta N \\ &\cong \tfrac{1}{2} \sum_{j=1}^{2} E_{\zeta\zeta_j} + E_s - \zeta N . \end{aligned} \tag{83}$$

Here the above-mentioned average over the various values of ζ_s is performed with uniform weight on the energy scale, which effectively uses half the sum of the extreme values. Evidence in favor of this being a reasonable way of averaging over ζ_s is presented in a companion paper,[7] dedicated to the details of the special treatment of strongly bound electrons.

Notice that

$$\frac{\partial E_1}{\partial \zeta} = \mathrm{Tr}\eta(-H-\zeta) - N = 0 , \tag{84}$$

which equates the number of electrons with the number of states having single-particle energy $H' < -\zeta$, all such states being occupied.

EXCHANGE

The Fermi-Dirac antisymmetry of coordinate wave functions for parallel spin states requires that the electrostatic energy of the electrons, as expressed in terms of the particle density $n(\vec{r})$,

$$E_{\mathrm{es}} = \tfrac{1}{2} \int (d\vec{r})(d\vec{r}\,') \frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} , \tag{85}$$

be supplemented by an exchange term

$$E_{\mathrm{ex}} = -\tfrac{1}{2} \int (d\vec{r})(d\vec{r}\,') \frac{1}{2} \frac{n(\vec{r},\vec{r}\,')n(\vec{r}\,',\vec{r})}{|\vec{r}-\vec{r}\,'|} \tag{86}$$

involving a nondiagonal density. In the semiclassical phase-space treatment,

$$n(\vec{r},\vec{r}\,') = \int \frac{(d\vec{p})}{(2\pi)^3} e^{i\vec{p}\cdot(\vec{r}-\vec{r}\,')} n(\bar{\vec{r}},\vec{p}) , \quad \bar{\vec{r}} = \tfrac{1}{2}(\vec{r}+\vec{r}\,') \tag{87}$$

and

$$n(\vec{r}) = n(\vec{r},\vec{r}) = \int \frac{(d\vec{p})}{(2\pi)^3} n(\vec{r},\vec{p}) \tag{88}$$

which produces the total number of electrons as

$$N = \mathrm{Tr}\eta(-H-\zeta) \cong \int \frac{(d\vec{r})(d\vec{p})}{(2\pi)^3} n(\vec{r},\vec{p}) . \tag{89}$$

In the extreme semiclassical limit (TF) and without reference to strongly bound electrons, it is clear that

$$n(\vec{r},\vec{p}) = 2\eta(-\tfrac{1}{2}p^2 - V - \zeta) \tag{90}$$

being the selection (with spin multiplicity 2) of all states of energy below $-\zeta$, the counterpart of $\eta(-H-\zeta)$. As with the energy density, there are quantum modifications of this form, and the special treatment of strongly bound electrons will introduce the parameters ζ_s on somewhat the same footing as ζ. At the moment, it is sufficient to appreciate that the momentum dependence of $n(\vec{r},\vec{p})$ involves $\frac{1}{2}p^2 + \zeta$ (and $\frac{1}{2}p^2 + \zeta_s$), which dependence, harkening back to Eq. (3), we take in the elementary Fourier form $\exp[-i(\frac{1}{2}p^2+\zeta)t]$ where ζ is also a stand-in for ζ_s.

To set the stage for applying these remarks, we exhibit the exchange energy as

$$E_{\mathrm{ex}} = \int (d\vec{r}) \mathscr{E}_{\mathrm{ex}}(\vec{r}) \tag{91}$$

in which the exchange energy density is

$$\mathscr{E}_{\mathrm{ex}}(\vec{r})=-\tfrac{1}{4}\int(d\vec{\rho})\frac{1}{|\vec{\rho}|}\int\frac{(d\vec{p})}{(2\pi)^3}\frac{(d\vec{p}\,')}{(2\pi)^3}e^{i(\vec{p}-\vec{p}\,')\cdot\vec{\rho}}\times n(\vec{r},\vec{p})n(\vec{r},\vec{p}\,')\ . \qquad (92)$$

Notice that the variables $\vec{r}$ and $\vec{\rho}$ used here signify the $\vec{r}$ and $\vec{r}-\vec{r}\,'$ of (87). Now we represent $n(\vec{r},\vec{p})$ and $n(\vec{r},\vec{p}\,')$ by the typical Fourier terms from which they are constructed. This directs us to the integral

$$\int\frac{(d\vec{p})}{(2\pi)^3}\frac{(d\vec{p}\,')}{(2\pi)^3}\exp[i(\vec{p}-\vec{p}\,')\cdot\vec{\rho}]\exp[-i(\tfrac{1}{2}\vec{p}^{\,2}+\zeta)t]\exp[-i(\tfrac{1}{2}\vec{p}\,'^{2}+\zeta)t']$$
$$=\left[\int\frac{(d\vec{p})}{(2\pi)^3}\frac{(d\vec{p}\,')}{(2\pi)^3}\exp[-i(\tfrac{1}{2}\vec{p}^{\,2}+\zeta)t]\exp[-i(\tfrac{1}{2}\vec{p}\,'^{2}+\zeta)t']\right]\exp\left[i\frac{\vec{\rho}^{\,2}}{2}\left[\frac{1}{t}+\frac{1}{t'}\right]\right] \qquad (93)$$

as produced by suitable translations of the two momentum variables. Now we perform the ρ integration:

$$-\tfrac{1}{4}\int(d\vec{\rho})\frac{1}{|\vec{\rho}|}\exp\left[i\frac{\vec{\rho}^{\,2}}{2}\left[\frac{t+t'}{tt'}\right]\right]$$
$$=-\frac{\pi}{2}\int_0^\infty d\rho^2\exp\left[\frac{i}{2}\rho^2\frac{t+t'}{tt'}\right]$$
$$=-\pi i\frac{tt'}{t+t'}\ . \qquad (94)$$

For the final steps, first note that differentiation of (93) with respect to ζ (ζ_s) would supply the factor $-i(t+t')$, converting (94) into $\pi(-it)(-it')$. Then we remark that the factors $-it$ and $-it'$ are just what is produced by differentiating the individual exponentials with respect to ζ. With those individual exponentials understood as the basic elements of $n(\vec{r},\vec{p})$ and $n(\vec{r},\vec{p}\,')$, respectively, we have arrived at the result

$$\frac{\partial}{\partial(\zeta,\zeta_s)}\mathscr{E}_{\mathrm{ex}}(\vec{r})=\pi\left[\frac{\partial}{\partial(\zeta,\zeta_s)}n(\vec{r})\right]^2\ . \qquad (95)$$

Before continuing, we test this for the simple TF theory, where

$$n(\vec{r})=2\int\frac{(d\vec{p})}{(2\pi)^3}\eta(-V-\zeta-\tfrac{1}{2}p^2)$$
$$=\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2} \qquad (96)$$

and

$$\frac{\partial}{\partial\zeta}n(\vec{r})=-\frac{1}{\pi^2}[2(-V-\zeta)]^{1/2}\ . \qquad (97)$$

This leads to

$$\frac{\partial}{\partial\zeta}\mathscr{E}_{\mathrm{ex}}=\frac{1}{\pi^3}[2(-V-\zeta)] \qquad (98)$$

and

$$\mathscr{E}_{\mathrm{ex}}=-\frac{1}{4\pi^3}[2(-V-\zeta)]^2=-\frac{1}{4\pi^3}(3\pi^2n)^{4/3} \qquad (99)$$

which is its well-known[5] value ($E_{\mathrm{ex}}=\frac{9}{2}\delta E_{\mathrm{qu}}$).

We can regard (95) as providing information about the manner in which E_{ex} depends differentially on the density,

$$\delta E_{\mathrm{ex}}=\int(d\vec{r})\delta n(\vec{r})V_{\mathrm{ex}}(\vec{r}) \qquad (100)$$

thereby defining the exchange potential $V_{\mathrm{ex}}(\vec{r})$. We infer that

$$V_{\mathrm{ex}}(\vec{r})=\pi\frac{\partial}{\partial(\zeta,\zeta_s)}n(\vec{r})\ . \qquad (101)$$

In the TF example, where

$$E_{\mathrm{ex}}=-\frac{1}{4\pi^3}\int(d\vec{r})(3\pi^2n)^{4/3}\ , \qquad (102)$$

$$\delta E_{\mathrm{ex}}=-\frac{1}{\pi}\int(d\vec{r})\delta n(3\pi^2n)^{1/3}\ , \qquad (103)$$

the implied exchange potential,

$$V_{\mathrm{ex}}=-\frac{1}{\pi}(3\pi^2n)^{1/3}=-\frac{1}{\pi}[2(-V-\zeta)]^{1/2}\ , \qquad (104)$$

is indeed what is produced by (101), according to (97).

We are now going to consider simplified versions of the particle density that incorporate quantum modifications of the Airy type. First we ignore the special treatment of the strongly bound electrons. Then, not bothering with a derivation, we simply look back at the structure of

$$z=-\tfrac{1}{2}p^2-V-\zeta+\tfrac{1}{2}x\,|\vec{\nabla}V|^{2/3} \qquad (105)$$

and recognize the appropriate modification[11] of the TF form (96):

$$n(\vec{r})=\frac{1}{3\pi^2}\langle[2(-V-\zeta+\tfrac{1}{2}x\,|\vec{\nabla}V|^{2/3})]^{3/2}\rangle$$
$$=\frac{1}{2\pi}|2\vec{\nabla}V|F_2(y) \qquad (106)$$

according to (50) and (55). The exchange potential then derived from (101) is

$$V_{\mathrm{ex}}=-|2\vec{\nabla}V|^{1/3}F_1(y)\ . \qquad (107)$$

Then we go on to construct the exchange energy density proceeding from

$$\frac{\partial\mathscr{E}_{\mathrm{ex}}}{\partial\zeta}=\pi\left[\frac{1}{\pi}V_{\mathrm{ex}}\right]^2=\frac{1}{\pi}|2\vec{\nabla}V|^{2/3}[F_1(y)]^2 \qquad (108)$$

or

$$\frac{\partial\mathscr{E}_{\mathrm{ex}}}{\partial y}=\frac{1}{2\pi}|2\vec{\nabla}V|^{4/3}[F_1(y)]^2\ . \qquad (109)$$

What is needed here is provided by a general relation that is derived by multiplying the recurrence relation (57) with $F_{n+1}(y)$:

$$(n+\tfrac{1}{2})F_{n+1}^2=\tfrac{1}{4}F_{n+1}\frac{d^2}{dy^2}F_n-yF_{n+1}F_n$$
$$=\frac{1}{4}\frac{d}{dy}\left[F_{n+1}\frac{d}{dy}F_n\right]+\frac{1}{8}\frac{d}{dy}F_n^2$$
$$+\frac{1}{2}y\frac{d}{dy}F_{n+1}^2\ , \qquad (110)$$

or

$$(n+1)F_{n+1}^2=\frac{d}{dy}(-\tfrac{1}{4}F_{n+1}F_{n-1}+\tfrac{1}{8}F_n^2+\tfrac{1}{2}yF_{n+1}^2)\ . \qquad (111)$$

The special implication of $n=-1$ is immediately checked; indeed,

$$-\tfrac{1}{4}F_0F_{-2}+\tfrac{1}{8}F_{-1}^2+\tfrac{1}{2}yF_0^2=0\ . \qquad (112)$$

What we want is the example

$$F_1^2=\frac{d}{dy}(-\tfrac{1}{4}F_1F_{-1}+\tfrac{1}{8}F_0^2+\tfrac{1}{2}yF_1^2)\ , \qquad (113)$$

leading to

$$\mathscr{E}_{\text{ex}}(\vec{r})=\frac{1}{2\pi}\,|\,2\vec{\nabla}V\,|^{4/3}(-\tfrac{1}{4}F_1F_{-1}+\tfrac{1}{8}F_0^2+\tfrac{1}{2}yF_1^2)(y)\ , \qquad (114)$$

a structure that does not lend itself to further simplification by introducing the explicit forms of the F_n.

THE EDGE

One easily checks, with the aid of the asymptotic formula (65), that, for $-y\gg1$, all these quantities assume their TF forms. And, of course, they all tend rapidly to zero for increasing positive values of y. What is the situation now at the edge, to which we assign the nominal meaning $y=0$? We need the values of

$$\text{Ai}(0)=\frac{1}{\pi}\text{Re}\int_0^\infty dy\,e^{-iy^3/3}$$
$$=\frac{3^{-1/6}}{2\pi}(-\tfrac{2}{3})!=0.355\,03\ldots \qquad (115)$$

and

$$-\text{Ai}'(0)=\frac{1}{\pi}\text{Re}\int_0^\infty dy\,iye^{-iy^3/3}$$
$$=\frac{3^{1/6}}{2\pi}(-\tfrac{1}{3})!=0.258\,82\ldots \qquad (116)$$

which are related by

$$-\text{Ai}(0)\text{Ai}'(0)=\frac{3^{-1/2}}{2\pi}=0.091\,888\ldots\ . \qquad (117)$$

We note the values

$$F_{-2}(0)=0.1340\ ,\quad F_{-1}(0)=0.1837\ ,\quad F_0(0)=0.1260 \qquad (118)$$

from which the $F_n(0)$ follow from the recurrence relation

$$(n+\tfrac{1}{2})F_{n+1}(0)=\tfrac{1}{4}F_{n-2}(0)\ . \qquad (119)$$

Then, some edge values are

$$V_{\text{ex}}\,|_{y=0}=-\,|\,2\vec{\nabla}V\,|_{y=0}^{1/3}F_1(0)=-0.0670\,|\,2\vec{\nabla}V\,|_{y=0}^{1/3}\ ,$$
$$n\,|_{y=0}=\frac{1}{2\pi}\,|\,2\vec{\nabla}V\,|_{y=0}F_2(0)=0.004\,87\,|\,2\vec{\nabla}V\,|_{y=0}\ . \qquad (120)$$

ENERGY

First we review the situation without exchange. The single-particle energy E_1 is not the total energy E inasmuch as the electrostatic interaction energy of the electrons is counted twice. That electrostatic energy is

$$E_{\text{es}}=\tfrac{1}{2}\int(d\vec{r})(d\vec{r}\,')\frac{n(\vec{r})n(\vec{r}\,')}{|\,\vec{r}-\vec{r}\,'\,|}$$
$$=\tfrac{1}{2}\int(d\vec{r})n(\vec{r})\left[V_{\text{es}}+\frac{Z}{r}\right]\ , \qquad (121)$$

where

$$V_{\text{es}}(\vec{r})+\frac{Z}{r}=\int(d\vec{r}\,')\frac{1}{|\,\vec{r}-\vec{r}\,'\,|}n(\vec{r}\,') \qquad (122)$$

obeys the Poisson equation

$$-\nabla^2\left[V_{\text{es}}(\vec{r})+\frac{Z}{r}\right]=4\pi n(\vec{r})\ . \qquad (123)$$

The introduction of the latter into (121), with a partial integration, supplies the following version of E_{es}:

$$E_{\text{es}}=\frac{1}{8\pi}\int(d\vec{r})\left[\vec{\nabla}\left[V_{\text{es}}+\frac{Z}{r}\right]\right]^2\ . \qquad (124)$$

Now the total energy of the system is given by

$$E=E_1-\frac{1}{8\pi}\int(d\vec{r})\left[\vec{\nabla}\left[V_{\text{es}}+\frac{Z}{r}\right]\right]^2\ . \qquad (125)$$

The advantage of this form is its stationary property for variations of V_{es}. That involves the definition of the density based on the variation in E_1 of the single-particle potential V:

$$\delta E_1=\int(d\vec{r})\delta V(\vec{r})n(\vec{r})\ . \qquad (126)$$

In the present situation, $V(\vec{r})$ is $V_{\text{es}}(\vec{r})$ and the variation of E yields

$$\delta E=\int(d\vec{r})\delta V_{\text{es}}\left[n+\frac{1}{4\pi}\nabla^2\left[V_{\text{es}}+\frac{Z}{r}\right]\right]=0\ . \qquad (127)$$

Now we include the effect of exchange. It changes the single-particle potential into

$$V(\vec{r})=V_{\text{es}}(\vec{r})+V_{\text{ex}}(\vec{r})\ . \qquad (128)$$

We must also add E_{ex}, in constructing E, but avoid double counting. This is accomplished by

$$E=E_1+E_{\rm ex}-\int (d\vec r)nV_{\rm ex}-\frac{1}{8\pi}\int (d\vec r)\left[\vec\nabla\left[V_{\rm es}+\frac{Z}{r}\right]\right]^2 . \qquad (129)$$

First, the significance of the combination involving the exchange energy and the exchange potential can be appreciated by considering

$$\begin{aligned}\delta\left[E_{\rm ex}-\int (d\vec r)nV_{\rm ex}\right]&=\int (d\vec r)\delta n\, V_{\rm ex}-\int (d\vec r)(\delta n\, V_{\rm ex}+n\,\delta V_{\rm ex})\\&=-\int (d\vec r)\delta V_{\rm ex}n \qquad (130)\end{aligned}$$

according to the definition (100). Then, quite simply, we get

$$\begin{aligned}\delta E&=\int (d\vec r)\delta V n-\int (d\vec r)\delta V_{\rm ex}n+\frac{1}{4\pi}\int (d\vec r)\delta V_{\rm es}\nabla^2\left[V_{\rm es}+\frac{Z}{r}\right]\\&=\int (d\vec r)\delta V_{\rm es}\left[n+\frac{1}{4\pi}\nabla^2\left[V_{\rm es}+\frac{Z}{r}\right]\right] , \qquad (131)\end{aligned}$$

which reaffirms the equivalence of the stationary property with the electrostatic Poisson equation.

PARTICLE DENSITY

We proceed to construct $n(\vec r)$, starting from the single-particle energy according to (126). The single-particle energy is produced by [Eq. (83)]

$$E_1=\sum_{j=1}^{2}\tfrac{1}{2}E_{\zeta\zeta_j}+E_s-\zeta N , \qquad (132)$$

its parts being displayed, respectively, in Eqs. (46) and (78). The introduction of the various momentum integral evaluations [Eq. (51)] into (46) gives

$$\sum_{j=1}^{2}\tfrac{1}{2}E_{\zeta\zeta_j}=-\int (d\vec r)\frac{1}{4\pi}|2\vec\nabla V|^{5/3}\times[\mathcal{F}_3(V,|\vec\nabla V|)-\tfrac{1}{6}\mathcal{F}_0(V,|\vec\nabla V|)] \qquad (133)$$

in which the $\mathcal{F}_n$ are the ζ_s-averaged functions

$$\mathcal{F}_n(V,|\vec\nabla V|)=\sum_{j=1}^{2}\tfrac{1}{2}[F_n(y)-F_n(y_j)-(y_j-y)F_{n-1}(y_j)] . \qquad (134)$$

For convenient reference we also note that [Eq. (78)]

$$E_s=-Z^2n_s+2\sum_{\substack{n\,(\le n_s),\\ l,m}}\int (d\vec r)\left[V(\vec r)+\frac{Z}{r}+\zeta\right]\times|\psi_{nlm}(\vec r)|^2 ; \qquad (135)$$

and the ζ_j entering y_j in (134) are [Eq. (79)]

$$\zeta_j=\frac{Z^2}{2n_j^2}-\left\langle V+\frac{Z}{r}\right\rangle_{n_j} , \quad n_1=n_s , \quad n_2=n_s+1 ; \qquad (136)$$

the quantum-mechanical expectation value herein refers to the angular average of (80),

$$\left\langle V+\frac{Z}{r}\right\rangle_{n_j}=\int (d\vec r)\left[V+\frac{Z}{r}\right]|\psi_{n_j}|^2_{\rm av} , \qquad (137)$$

where $|\psi_{n_j}|^2_{\rm av}$ depends only on r.

The variable $V(\vec r)$ enters in three ways into E_1: explicitly as $V(\vec r)$ and as $\vec\nabla V(\vec r)$, and implicitly in the ζ_j, for, as $V(\vec r)$ is altered, ζ_j is correspondingly modified,

$$\delta\zeta_j=-\int (d\vec r)\delta V(\vec r)|\psi_{n_j}|^2_{\rm av} . \qquad (138)$$

The effect on $E_{\zeta\zeta_j}$ which enters through

$$\frac{\partial y_j}{\partial\zeta_j}=2|2\vec\nabla V|^{-2/3} \qquad (139)$$

is given by

$$\begin{aligned}\frac{\partial E_{\zeta\zeta_j}}{\partial\zeta_j}&=-\int (d\vec r)\frac{1}{2\pi}|2\vec\nabla V|(y_j-y)\times[F_1(y_j)-\tfrac{1}{6}F_{-2}(y_j)]\\&=-\int (d\vec r)\frac{1}{3\pi}|2\vec\nabla V|(y_j-y)\times[F_1(y_j)-y_jF_0(y_j)]\\&\equiv -Q_j . \qquad (140)\end{aligned}$$

The recurrence relation (54) has been used in the form

$$-\frac{\partial}{\partial y_j}[F_n(y_j)+(y_j-y)F_{n-1}(y_j)]=(y_j-y)F_{n-2}(y_j) , \qquad (141)$$

and (57), with $n=0$, is responsible for the second version of (140). Accordingly, this contribution to δE_1 is

$$\delta_{\zeta_j}E_1=\int (d\vec r)\delta V(\vec r)\tfrac{1}{2}Q_j|\psi_{n_j}|^2_{\rm av} . \qquad (142)$$

Next we consider the explicit dependence on V, as produced in $E_{\zeta\zeta_j}$ by

$$\delta_V y=\delta_V y_j=2|2\vec\nabla V|^{-2/3}\delta V , \qquad (143)$$

which implies, through (54), that

$$\delta_V\mathcal{F}_n=-2|2\vec\nabla V|^{-2/3}\mathcal{F}_{n-1}\delta V . \qquad (144)$$

We get

$$\delta_V\sum_{j=1}^{2}\tfrac{1}{2}E_{\zeta\zeta_j}=\int (d\vec r)\delta V(\vec r)\frac{1}{2\pi}|2\vec\nabla V|(\mathcal{F}_2-\tfrac{1}{6}\mathcal{F}_{-1}) . \qquad (145)$$

The consideration of explicit $\vec\nabla V$ dependence begins with the observation that

$$\delta_{\vec{\nabla} V} | 2\vec{\nabla} V |^{n/3} = \frac{2n}{3} | 2\vec{\nabla} V |^{(n/3)-2} \delta(\vec{\nabla} V)^2 , \qquad (146)$$

with the implications (y also stands for y_j)

$$\delta_{\vec{\nabla} V} y = -\tfrac{4}{3} | 2\vec{\nabla} V |^{-2} y \delta(\vec{\nabla} V)^2 , \qquad (147)$$

$$\begin{aligned} \delta_{\vec{\nabla} V} F_n(y) &= 4yF_{n-1}(y) \tfrac{1}{3} | 2\vec{\nabla} V |^{-2} \delta(\vec{\nabla} V)^2 \\ &= \tfrac{1}{3} | 2\vec{\nabla} V |^{-2} [F_{n-3}(y) - (4n-2)F_n(y)] \\ &\quad \times \delta(\vec{\nabla} V)^2 ; \end{aligned} \qquad (148)$$

the last step, once again, made use of the recurrence relation (57). Then, after realizing that the change in $\mathcal{F}_n$ is

$$\delta_{\vec{\nabla} V} \mathcal{F}_n = \tfrac{1}{3} | 2\vec{\nabla} V |^{-2} [\mathcal{F}_{n-3} - (4n-2)\mathcal{F}_n] \delta(\vec{\nabla} V)^2 , \qquad (149)$$

we obtain from (133) that

$$\begin{aligned} \delta_{\vec{\nabla} V} \sum_{j=1}^{2} \tfrac{1}{2} E_{\zeta\zeta_j} &= \int (d\vec{r}) \delta(\vec{\nabla} V)^2 \frac{1}{4\pi} \frac{1}{3} | 2\vec{\nabla} V |^{-1/3} (\mathcal{F}_0 + \tfrac{1}{6}\mathcal{F}_{-3}) \\ &= \int (d\vec{r}) \delta V \vec{\nabla} \cdot \left[-\vec{\nabla} V \frac{1}{4\pi} \frac{2}{3} | 2\vec{\nabla} V |^{-1/3} \right. \\ &\qquad \left. \times (\mathcal{F}_0 + \tfrac{1}{6}\mathcal{F}_{-3}) \right] , \end{aligned} \qquad (150)$$

where a partial integration produces the latter form.

When we add to these variational contributions that of (135),

$$\begin{aligned} \delta E_s &= \int (d\vec{r}) \delta V(\vec{r}) 2 \sum_{\substack{n\,(\le n_s),\\ l,m}} | \psi_{nlm} |^2 \\ &= \int (d\vec{r}) \delta V(\vec{r}) \sum_{n=1}^{n_s} 2n^2 | \psi_n |^2_{\text{av}} \\ &\equiv \int (d\vec{r}) \delta V(\vec{r}) \rho_s(r) , \end{aligned} \qquad (151)$$

we arrive at the density

$$n(\vec{r}) = n_{\text{strong}}(r) + \tilde{n}(\vec{r}) , \qquad (152)$$

where [Eqs. (142) and (151)]

$$n_{\text{strong}} = \rho_s + \sum_{j=1}^{2} \tfrac{1}{2} Q_j | \psi_{n_j} |^2_{\text{av}} , \qquad (153)$$

and [Eqs. (145) and (150)]

$$\begin{aligned} \tilde{n} &= \frac{1}{2\pi} | 2\vec{\nabla} V | (\mathcal{F}_2 - \tfrac{1}{6}\mathcal{F}_{-1}) \\ &\quad - \frac{1}{6\pi} \vec{\nabla} \cdot [\vec{\nabla} V | 2\vec{\nabla} V |^{-1/3} (\mathcal{F}_0 + \tfrac{1}{6}\mathcal{F}_{-3})] . \end{aligned} \qquad (154)$$

The count of the number of electrons is now given by

$$\begin{aligned} N &= \int (d\vec{r}) n \\ &= \int (d\vec{r}) \frac{1}{2\pi} | 2\vec{\nabla} V | (\mathcal{F}_2 - \tfrac{1}{6}\mathcal{F}_{-1}) \\ &\quad + \sum_{j=1}^{2} \tfrac{1}{2} Q_j + \sum_{n=1}^{n_s} 2n^2 \end{aligned} \qquad (155)$$

or, using the definition of the Q_j [Eq. (140)], in terms of the energy (133),

$$\begin{aligned} N &= \int (d\vec{r}) \frac{1}{2\pi} | 2\vec{\nabla} V | (\mathcal{F}_2 - \tfrac{1}{6}\mathcal{F}_{-1}) \\ &\quad + \int (d\vec{r}) \left[\frac{\partial}{\partial\zeta_1} + \frac{\partial}{\partial\zeta_2} \right] \frac{1}{4\pi} | 2\vec{\nabla} V |^{5/3} (\mathcal{F}_3 - \tfrac{1}{6}\mathcal{F}_0) \\ &\quad + \tfrac{1}{3} n_s (n_s + 1)(2n_s + 1) . \end{aligned} \qquad (156)$$

Now, according to (84) and (132), this number should also be

$$N = \frac{\partial}{\partial\zeta} \left[\sum_{j=1}^{2} \tfrac{1}{2} E_{\zeta\zeta_j} + E_s \right] . \qquad (157)$$

Indeed it is, for on using the fact that, with respect to the integrand of (133), an infinitesimal change of V is equivalent to an equal change of every ζ, or

$$\frac{\partial}{\partial\zeta} = \frac{\partial}{\partial V} - \left[\frac{\partial}{\partial\zeta_1} + \frac{\partial}{\partial\zeta_2} \right] , \qquad (158)$$

we get [Eq. (145)]

$$\frac{\partial}{\partial\zeta} \sum_{j=1}^{2} \tfrac{1}{2} E_{\zeta\zeta_j} = \int (d\vec{r}) \left[\frac{1}{2\pi} | 2\vec{\nabla} V | (\mathcal{F}_2 - \tfrac{1}{6}\mathcal{F}_{-1}) + \left[\frac{\partial}{\partial\zeta_1} + \frac{\partial}{\partial\zeta_2} \right] \frac{1}{4\pi} | 2\vec{\nabla} V |^{5/3} (\mathcal{F}_3 - \tfrac{1}{6}\mathcal{F}_0) \right] , \qquad (159)$$

and [Eq. (135)]

$$\frac{\partial}{\partial\zeta} E_s = N_s = \tfrac{1}{3} n_s (n_s + 1)(2n_s + 1) . \qquad (160)$$

DIFFERENTIAL EQUATION

The differential equation that will enable us to find the potential for given Z and N is, of course, the Poisson equation (123),

$$-\frac{1}{4\pi} \nabla^2 \left[V - V_{\text{ex}} + \frac{Z}{r} \right] = n , \qquad (161)$$

where n is now expressed in terms of V and its derivatives in (152)–(154), and the exchange potential is related to the density through [Eq. (101)]

$$V_{\text{ex}} = \pi \left[\frac{\partial}{\partial\zeta} + \frac{\partial}{\partial\zeta_1} + \frac{\partial}{\partial\zeta_2} \right] n = \pi \frac{\partial}{\partial V} n ; \qquad (162)$$

the last equality is an implication of (158).

Before continuing the discussion of these equations, with their plethora of Airy functions, we need to make contact with the differential equations of Ref. 8 [Eqs. (14) and (20) there], which represents an extrapolation of the first quantum correction and the exchange effect toward the outer reaches of the atom. Accordingly, we introduce the classical limits, with leading quantum corrections, where significant, of the various quantities appearing here. Let us note first what supplements the classical limit given for $F_n(y)$ in (65). Returning to (55), we recognize that the first quantum correction will be obtained by writing the initial terms of an expansion:

$$F_n(y)=\frac{(-\frac{1}{2})!}{(n-\frac{1}{2})!}\frac{1}{2\pi}\left[(-y)^{n-1/2}+\frac{1}{3!}\frac{1}{2}\left[\frac{d}{d(-y)}\right]^3(-y)^{n-1/2}+\cdots\right] \quad \text{for } -y \ll 1 \tag{163}$$

which employs the Airy average $\langle x^3\rangle=2$.

Inasmuch as the equation to be contacted is initially based on the state of affairs in the dense interior of the atom, we do not include the corrections for strongly bound electrons—which is to replace the $\mathcal{F}_n$ in (154) by $F_n(y)$, and to discard n_{strong} [Eq. (153)], so that

$$n\cong\frac{1}{2\pi}\,|2\vec{\nabla}V|\,[F_2(y)-\tfrac{1}{6}F_{-1}(y)] -\frac{1}{6\pi}\vec{\nabla}\cdot\{\vec{\nabla}V\,|2\vec{\nabla}V\,|^{-1/3}[F_0(y)+\tfrac{1}{6}F_{-3}(y)]\} \tag{164}$$

is now the density—and we regard quantum and exchange effects as small, requiring the omission of corrections to corrections. Thus, for the exchange potential we are content with the simple version of (104)

$$V_{\text{ex}}\cong-\frac{1}{\pi}[2(-V-\zeta)]^{1/2}\,, \tag{165}$$

and in the density (164) we retain only the leading terms of the expansion (163). That expansion refers to nonnegative values of the integer n only, and therefore we employ the recurrence relation (57) to express $F_{-1}(y)$ and $F_{-3}(y)$ in terms of F_0,F_1,F_2. This leads us to

$$n\cong-\frac{1}{3\pi}\,|2\vec{\nabla}V\,|yF_1(y) -\frac{1}{6\pi}\vec{\nabla}\cdot\{\vec{\nabla}V\,|2\vec{\nabla}V\,|^{-1/3}[4yF_2(y)+\tfrac{8}{3}y^2F_1(y) +\tfrac{2}{3}F_0(y)]\}\,. \tag{166}$$

Upon utilizing (163) we get $[y=2(V+\zeta)\,|2\vec{\nabla}V\,|^{-2/3}]$

$$n\cong\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2}+\frac{1}{24\pi^2}(\vec{\nabla}V)^2[2(-V-\zeta)]^{-3/2} -\frac{1}{6\pi}\vec{\nabla}\cdot\left[\vec{\nabla}V\frac{1}{2\pi}[2(-V-\zeta)]^{-1/2}\right], \tag{167}$$

which, with the observation that

$$\vec{\nabla}\cdot\{\vec{\nabla}V[2(-V-\zeta)]^{-1/2}\}=-\nabla^2[2(-V-\zeta)]^{1/2} \tag{168}$$

and

$$\begin{aligned}(\vec{\nabla}V)^2[2(-V-\zeta)]^{-3/2} &=\vec{\nabla}V\cdot\vec{\nabla}[2(-V-\zeta)]^{-1/2}\\ &=-\nabla^2[2(-V-\zeta)]^{+1/2}-\nabla^2V[2(-V-\zeta)]^{-1/2}\,,\end{aligned} \tag{169}$$

is turned into

$$n\cong\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2} +\frac{1}{6\pi}\left[-\frac{1}{4\pi}\nabla^2V\right][2(-V-\zeta)]^{-1/2} +\frac{1}{24\pi^2}\nabla^2[2(-V-\zeta)]^{+1/2}\,. \tag{170}$$

The last term supplements the exchange potential (165) by one-sixth, if we bring it over to the other side of the Poisson equation.

At this stage we have

$$-\frac{1}{4\pi}\nabla^2\left[V+\frac{7}{6\pi}[2(-V-\zeta)]^{1/2}+\frac{Z}{r}\right] \cong\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2}\left[1+\left[\frac{-\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]}{\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2}}\right]\frac{1}{6\pi}[2(-V-\zeta)]^{-1/2}\right]. \tag{171}$$

The inclusion of Z/r into the Laplacian on the right-hand side does not change anything because the resulting delta function is multiplied by an expression that vanishes at the origin. And, with this form, we are invited to introduce the TF evaluation

$$-\frac{1}{4\pi}\nabla^2\left[V+\frac{Z}{r}\right]=\frac{1}{3\pi^2}[2(-V-\zeta)]^{3/2}\,, \tag{172}$$

and obtain

$$-\nabla^2\left[V+\frac{7}{6\pi}[2(-V-\zeta)]^{1/2}+\frac{Z}{r}\right]\cong\frac{4}{3\pi}[2(-V-\zeta)]^{3/2}\left[1+\frac{1}{6\pi}[2(-V-\zeta)]^{-1/2}\right]$$
$$\cong\frac{4}{3\pi}\left[[2(-V-\zeta)]^{1/2}\left[1+\frac{1}{18\pi}[2(-V-\zeta)]^{-1/2}\right]\right]^3$$
$$=\frac{4}{3\pi}\left[[2(-V-\zeta)]^{1/2}+\frac{1}{18\pi}\right]^3 . \tag{173}$$

Now, if we change the variable V to $\overline{V}$, in accordance with

$$(V+\zeta)+\frac{7}{6\pi}[2(-V-\zeta)]^{1/2}=\overline{V}-\frac{1}{2}\left[\left[\frac{11}{9\pi}\right]^2-\left[\frac{7}{6\pi}\right]^2\right] , \tag{174}$$

or

$$[2(-V-\zeta)]^{1/2}=\left[-2\overline{V}+\left[\frac{11}{9\pi}\right]^2\right]^{1/2}+\frac{7}{6\pi} , \tag{175}$$

we get

$$-\nabla^2\left[\overline{V}+\frac{Z}{r}\right]=\frac{4}{3\pi}\left\{\left[-2\overline{V}+\left[\frac{11}{9\pi}\right]^2\right]^{1/2}+\frac{11}{9\pi}\right\}^3 \tag{176}$$

which, indeed, is the desired differential equation of Ref. 8. Although Eq. (176) has proved to describe the outer region of weakly bound electrons in a significantly better way than the TF model, it suffers from the major deficiency of ascribing a sharp edge to ions and atoms. It was with an eye on the boundary condition for $\overline{V}$ at that edge, that we chose the additive constant in (174) or, equivalently, in (176). (For more detail, one should consult Ref. 8.) This drawback is removed in the new theory, where the Airy function effects a smooth transition through the edge of the atom.

After these remarks we return to Eqs. (161) and (162). To construct the differential equation for V, one first has to differentiate the density, according to (162), in order to obtain an explicit expression for the exchange potential in terms of V and its derivatives. Then the Laplacian of V_{ex} is needed in Poisson's equation (161). It is clear that this will result in a differential equation of higher order for V, unless simplifications are introduced which are based upon the knowledge of the limits of validity of such relations as (162). All this leads to a second-order differential equation for V, which, under the circumstance of spherical symmetry, as is the situation for an isolated atom, reads

$$-\nabla^2\left[V+\frac{Z}{r}\right]=\left[1-|2\vec{\nabla}V|^{-1/3}(\tfrac{8}{3}\mathscr{F}_0-\tfrac{2}{9}\mathscr{F}_{-3}-\tfrac{1}{27}\mathscr{F}_{-6})+\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla}V|^{-5/3}(\tfrac{8}{3}\mathscr{F}_{-2}+\tfrac{10}{9}\mathscr{F}_{-5}+\tfrac{1}{27}\mathscr{F}_{-8})\right]^{-1}$$
$$\times\left[4\pi n_{\text{strong}}+|2\vec{\nabla}V|(2\mathscr{F}_2+\mathscr{F}_{-1}-\tfrac{1}{9}\mathscr{F}_{-4})\right.$$
$$\left.-\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla}V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{-3}+\tfrac{5}{27}\mathscr{F}_{-6})-\frac{1}{r^2}|2\vec{\nabla}V|^{+1/3}(\mathscr{F}_{-2}+\tfrac{1}{2}\mathscr{F}_{-5}+\tfrac{1}{54}\mathscr{F}_{-8})\right] . \tag{177}$$

Since the detailed derivation of (177) is rather lengthy and technical, we prefer to present it in a separate paper,[12] which also contains an exhaustive discussion of numerical results. Here we confine ourselves to a graphical comparison of mean-squared distances,

$$\overline{r^2}=\frac{1}{N}\int(d\vec{r})r^2n(\vec{r}) , \tag{178}$$

for which experimental data are supplied by the measurements of molar diamagnetic susceptibilities,

$$-\chi_m=\left[\frac{1}{\text{“137”}}\right]^2N_Aa_0^3I=4.752\times10^{-6}I , \tag{179}$$

where, expressed in atomic units,

$$I=\tfrac{1}{6}\int(d\vec{r})r^2n(\vec{r})=\frac{N}{6}\overline{r^2} . \tag{180}$$

Figure 4 shows nine histograms, one each for the $\overline{r^2}$

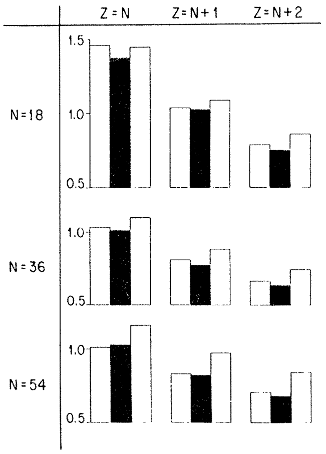

FIG. 4. Histograms comparing statistical, experimental, and HF data for the mean-squared distance, see text.

values belonging to the noble-gas atoms with $N=Z=18,36,54$ and to the related ions with $Z=N+1$, $N+2$. The blackened center columns represent the experimental data[13] while the left ones indicate the results of the new statistical calculation. To the right of the experimental columns stand those belonging to Hartree-Fock calculations.[13] The surprisingly poor performance of HF is obvious: all HF predictions exceed the experimental numbers, by up to 24%. With the single exception of the argon atom ($N=Z=18$), the statistically calculated $\overline{r^2}$ values reproduce the experimental ones better—frequently much better—than the HF numbers do. And, even for argon the relative "failure" of the new statistical theory can possibly be blamed on deficiencies in computational procedure; for details see Ref. 12.

FINAL REMARKS

The new statistical theory of atoms presented above turned out to be superior to the HF approach at larger distances. This is the domain of chemistry, and there is where we see the immediate application of the new methods. Not only can one expect better results than a HF calculation would produce, but the statistical treatment should also enable one to attack problems that cannot be handled by HF because of their complexity; a large molecule illustrates such a situation. Of course, the new methods of dealing with quantum corrections, strongly bound electrons, and the exchange interaction should improve matters wherever TF ideas have been applied before, e.g., in solid-state and nuclear physics.

We think that there may be also a lesson for the "mean-field approximations" of high-energy physics (which lack "quality control") although making the connection probably requires a reformulation in terms of many-particle Green's functions. We intend to return to this topic elsewhere.

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[13] For references see Ref. 12.