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# New statistical atom: A numerical study

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The new differential equation for the statistical atom is derived and discussed in detail. Numerical results are presented which provide evidence for the validity of all approximations that have entered the formalism. A comparison of experimental data for diamagnetic susceptibilities with theoretical predictions shows that the new statistical atom significantly surpasses its Hartree-Fock competitor.

## INTRODUCTION

This paper supplements the immediately preceding one.[1] It contains a detailed derivation of the new differential equation for the single-electron potential of the statistical atom. There follows a discussion of the properties of this equation and, in particular, of its implications concerning both the vicinity of the nucleus and the outer regions occupied by the weakly bound electrons. Then we explain the numerical procedure that has been employed for solving the differential equation. Finally, numerical results are presented for the inert-gas atoms argon, krypton, and xenon, as well as for the related singly and doubly charged ions. Throughout this paper we use the notation defined in Ref. 1, and refer to this paper as I; e.g., (161) of I refers to Eq. (161) of Ref. 1.

## DIFFERENTIAL EQUATION

The fundamental equation of electrostatics, Poisson's equation (161) of I [see also (131) of I],

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

equates the negative Laplacian of the electrostatic potential of the electrons to their density, multiplied by $4\pi$. In Ref. 1 we found an expression for $n$ in terms of $V$, its gradient, and its Laplacian [Eqs. (152)–(154) of I]. We also recall that the exchange potential is related to the density through [Eq. (162) of I]

$$V_{\text{ex}}=\pi\frac{\partial}{\partial V}n\ . \tag{2}$$

While we were content to make contact with an earlier calculation[2] in Ref. 1, where we checked the semiclassical limit of the combination of Eqs. (1) and (2), we now construct the new differential equation for the single-particle potential $V$. This will lead us to the result already reported in Eq. (177) of I.

We start by rewriting the electron density in such a way as to facilitate the recognition of those parts that have to be taken into account in Eq. (2). Upon carrying out the differentiation in $\tilde{n}$ [Eq. (154) of I] we notice that it splits into two parts

$$\tilde{n}=\tilde{n}_1+\tilde{n}_2\ , \tag{3}$$

of which the first one contains only terms in $V$ and $\vec{\nabla}V$,

$$\begin{aligned}\tilde{n}_1&=\frac{1}{2\pi}\,|2\vec{\nabla}V|\,(\mathscr{F}_2-\tfrac{1}{6}\mathscr{F}_{-1})-\frac{1}{6\pi}(\vec{\nabla}V)^2\,|2\vec{\nabla}V|^{-1/3}\frac{\partial}{\partial V}(\mathscr{F}_0+\tfrac{1}{6}\mathscr{F}_{-3})\\&=\frac{1}{2\pi}\,|2\vec{\nabla}V|\,(\mathscr{F}_2-\tfrac{1}{6}\mathscr{F}_{-1})+\frac{1}{12\pi}\,|2\vec{\nabla}V|\,(\mathscr{F}_{-1}+\tfrac{1}{6}\mathscr{F}_{-4})\\&=-\frac{1}{4\pi}\,|2\vec{\nabla}V|^3\frac{\partial}{\partial(\vec{\nabla}V)^2}(\mathscr{F}_2-\tfrac{1}{6}\mathscr{F}_{-1})\ ,\end{aligned} \tag{4}$$

whereas the second one possesses second derivatives of $V$, too:

$$\begin{aligned}\tilde{n}_2&=-\frac{1}{6\pi}(\vec{\nabla}^2V)\,|2\vec{\nabla}V|^{-1/3}(\mathscr{F}_0+\tfrac{1}{6}\mathscr{F}_{-3})-\frac{1}{6\pi}[\vec{\nabla}V\cdot\vec{\nabla}(\vec{\nabla}V)^2]\frac{\partial}{\partial(\vec{\nabla}V)^2}[\,|2\vec{\nabla}V|^{-1/3}(\mathscr{F}_0+\tfrac{1}{6}\mathscr{F}_{-3})]\\&=-\frac{1}{6\pi}(\vec{\nabla}^2V)\,|2\vec{\nabla}V|^{-1/3}(\mathscr{F}_0+\tfrac{1}{6}\mathscr{F}_{-3})-\frac{1}{3\pi}[\vec{\nabla}V\cdot(\vec{\nabla}\vec{\nabla}V)\cdot\vec{\nabla}V]\,|2\vec{\nabla}V|^{-7/3}(\mathscr{F}_{-3}+\tfrac{1}{18}\mathscr{F}_{-6})\ .\end{aligned} \tag{5}$$

In (4) and (5) we made use of the differentiation rules (144), (146), and (149) of I.

It is time to recall that the derivation of (2) [or (101) of I] did not pay attention to the term $(\vec{p}\cdot\vec{\nabla})^2V$ of (7) in I, but merely used the momentum dependence $\frac{1}{2}p^2+\zeta$. Consequently, for consistency in calculating $V_{\text{ex}}$ we have to discard all contributions to the density that contain, or originate in, second derivatives of the potential. This concerns not only $\tilde{n}_2$, but also the $\mathscr{F}_{-1}$ term in the final form of (4) because it ultimately stems from the Laplacian part of $E_{\zeta\zeta_s}$ in (29) of I. In short, we compute the exchange potential as

$$V_{\text{ex}}=\pi\frac{\partial}{\partial V}\left[-\frac{1}{4\pi}\,|2\vec{\nabla}V|^3\frac{\partial}{\partial(\vec{\nabla}V)^2}\mathscr{F}_2\right] \tag{6}$$

which results in [Eqs. (149) and (144) of I]

$$V_{\text{ex}}=-\,|2\vec{\nabla}V|^{1/3}(\mathscr{F}_1-\tfrac{1}{6}\mathscr{F}_{-2})\,. \tag{7}$$

We remark that after dropping the contributions that refer to the strongly bound electrons, we do not reproduce (107) of I for which a simplified density [Eq. (106) of I] was used. Both the density and the exchange potential have one additional term which is created by the variation of $\vec{\nabla}V$ in the energy [Eq. (150) of I] and could not have been anticipated earlier. However, these extra terms do not contribute in the TF limit ($-y\gg1$).

Having found the exchange potential, we face the question of what to do with its Laplacian in the Poisson equation (1). Were we to actually evaluate the Laplacian of (7) as it stands, we would end up with a third-order differential equation for $V$. But if one wants, as we do, to maintain the basic simplicity of TF, one ingredient of which is the low order of the differential equation, one will aim at a second-order differential equation and look for a sensible approximation of $\nabla^2V_{\text{ex}}$.

Since we cannot tinker with the divergence in the Laplacian without destroying the boundary conditions of $V$, we really need an approximation of the gradient of the exchange potential,

$$\vec{\nabla}V_{\text{ex}}=\vec{\nabla}V\frac{\partial V_{\text{ex}}}{\partial V}+\vec{\nabla}(\vec{\nabla}V)^2\frac{\partial V_{\text{ex}}}{\partial(\vec{\nabla}V)^2}\,. \tag{8}$$

So it comes down to replacing

$$\vec{\nabla}(\vec{\nabla}V)^2=2\vec{\nabla}\vec{\nabla}V\cdot\vec{\nabla}V \tag{9}$$

by something that no longer contains second derivatives of the potential. Although not essential, spherical symmetry helps here. With the aid of

$$\vec{\nabla}V=\frac{\vec{r}}{r}\frac{\partial V}{\partial r}\,, \tag{10}$$

$$\vec{\nabla}\vec{\nabla}V=\frac{\vec{r}}{r}\frac{\vec{r}}{r}\frac{\partial^2V}{\partial r^2}+\left[\overleftrightarrow{1}-\frac{\vec{r}}{r}\frac{\vec{r}}{r}\right]\frac{1}{r}\frac{\partial V}{\partial r}\,, \tag{11}$$

(9) turns into

$$2\vec{\nabla}\vec{\nabla}V\cdot\vec{\nabla}V=2\frac{\partial^2V}{\partial r^2}\vec{\nabla}V=2\left[\nabla^2V-\frac{2}{r}\frac{\partial V}{\partial r}\right]\vec{\nabla}V\,, \tag{12}$$

and (8) now reads

$$\vec{\nabla}V_{\text{ex}}=\vec{\nabla}V\left[\left[\frac{\partial V_{\text{ex}}}{\partial V}-\frac{4}{r}\frac{\partial V}{\partial r}\frac{\partial V_{\text{ex}}}{\partial(\vec{\nabla}V)^2}\right]+2\nabla^2V\frac{\partial V_{\text{ex}}}{\partial(\vec{\nabla}V)^2}\right]. \tag{13}$$

There are, of course, a number of options for the approximation of $\nabla^2V$ herein. For simplicity, let us make the choice $\nabla^2V\cong0$. Then

$$\begin{aligned}\vec{\nabla}V_{\text{ex}}&\cong(\vec{\nabla}V)\left[\frac{\partial V_{\text{ex}}}{\partial V}-\frac{4}{r}\frac{\partial V}{\partial r}\frac{\partial V_{\text{ex}}}{\partial(\vec{\nabla}V)^2}\right]\\&=(\vec{\nabla}V)\left[\,|2\vec{\nabla}V|^{-1/3}(2\mathscr{F}_0-\tfrac{1}{3}\mathscr{F}_{-3})\right.\\&\qquad\left.-\frac{4}{r}\frac{\partial V}{\partial r}\,|2\vec{\nabla}V|^{-5/3}(\tfrac{1}{3}\mathscr{F}_{-2}+\tfrac{1}{18}\mathscr{F}_{-5})\right],\end{aligned} \tag{14}$$

and by utilizing (9)—(12) and the differentiation rules (144), (146), and (149) of I we get the ingredients of the Laplacian of the exchange potential,

$$\nabla^2V_{\text{ex}}\cong\left[(\vec{\nabla}V)^2\frac{\partial}{\partial V}+\vec{\nabla}V\cdot\vec{\nabla}(\vec{\nabla}V)^2\frac{\partial}{\partial(\vec{\nabla}V)^2}+\vec{\nabla}V\cdot\frac{\vec{r}}{r}\frac{\partial}{\partial r}+\nabla^2V\right]\left[\frac{\partial V_{\text{ex}}}{\partial V}-\frac{4}{r}\frac{\partial V}{\partial r}\frac{\partial V_{\text{ex}}}{\partial(\vec{\nabla}V)^2}\right], \tag{15}$$

which are

$$(\vec{\nabla}V)^2\frac{\partial}{\partial V}[\,\cdots\,]=-\,|2\vec{\nabla}V|(\mathscr{F}_{-1}-\tfrac{1}{6}\mathscr{F}_{-4})+\frac{1}{r}\frac{\partial V}{\partial r}\,|2\vec{\nabla}V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{-3}+\tfrac{1}{9}\mathscr{F}_{-6})\,,$$

$$\begin{aligned}\vec{\nabla}V\cdot\vec{\nabla}(\vec{\nabla}V)^2\frac{\partial}{\partial(\vec{\nabla}V)^2}[\,\cdots\,]&=\frac{1}{r}\frac{\partial V}{\partial r}\,|2\vec{\nabla}V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{-3}+\tfrac{1}{9}\mathscr{F}_{-6})+\frac{1}{r^2}\,|2\vec{\nabla}V|^{+1/3}(\tfrac{2}{3}\mathscr{F}_{-2}+\tfrac{4}{9}\mathscr{F}_{-5}+\tfrac{1}{54}\mathscr{F}_{-8})\\&\quad-(\nabla^2V)\left[\,|2\vec{\nabla}V|^{-1/3}(\tfrac{1}{3}\mathscr{F}_{-3}+\tfrac{1}{18}\mathscr{F}_{-6})\right.\\&\qquad\left.+\frac{1}{r}\frac{\partial V}{\partial r}\,|2\vec{\nabla}V|^{-5/3}(\tfrac{4}{3}\mathscr{F}_{-2}+\tfrac{8}{9}\mathscr{F}_{-5}+\tfrac{1}{27}\mathscr{F}_{-8})\right],\end{aligned} \tag{16}$$

$$\vec{\nabla} V \cdot \frac{\vec{r}}{r}\frac{\partial}{\partial r}[\cdots] = \frac{1}{r^2}\,|2\vec{\nabla} V|^{+1/3}(\tfrac{1}{3}\mathscr{F}_{-2}+\tfrac{1}{18}\mathscr{F}_{-5})\ .$$

Thus

$$\begin{aligned}\nabla^2 V_{\text{ex}} \cong {} & -|2\vec{\nabla} V|(\mathscr{F}_{-1}-\tfrac{1}{6}\mathscr{F}_{-4})+\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla} V|^{-1/3}(\tfrac{4}{3}\mathscr{F}_{-3}+\tfrac{2}{9}\mathscr{F}_{-6})+\frac{1}{r^2}|2\vec{\nabla} V|^{+1/3}(\mathscr{F}_{-2}+\tfrac{1}{2}\mathscr{F}_{-5}+\tfrac{1}{54}\mathscr{F}_{-8}) \\ & +\nabla^2 V\left[|2\vec{\nabla} V|^{-1/3}(2\mathscr{F}_{0}-\tfrac{2}{3}\mathscr{F}_{-3}-\tfrac{1}{18}\mathscr{F}_{-6})-\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla} V|^{-5/3}(\tfrac{8}{3}\mathscr{F}_{-2}+\tfrac{10}{9}\mathscr{F}_{-5}+\tfrac{1}{27}\mathscr{F}_{-8})\right]. \end{aligned} \tag{17}$$

This and the density (152) of I, in which $\tilde{n}$ is [Eqs. (3)—(5), and (9)—(12)]

$$\begin{aligned}\tilde{n} = {} & \frac{1}{4\pi}|2\vec{\nabla} V|(2\mathscr{F}_{2}+\tfrac{1}{18}\mathscr{F}_{-4})+\frac{1}{4\pi}\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla} V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{-3}+\tfrac{1}{27}\mathscr{F}_{-6}) \\ & -\frac{1}{4\pi}(\nabla^2 V)|2\vec{\nabla} V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{0}+\tfrac{4}{9}\mathscr{F}_{-3}+\tfrac{1}{54}\mathscr{F}_{-6}) \end{aligned} \tag{18}$$

are now inserted into the Poisson equation (1), and solving for $\nabla^2 V$ supplies us finally with the differential equation for $V$:

$$\begin{aligned}-\nabla^2\left[V+\frac{Z}{r}\right] = {} & \left[1-|2\vec{\nabla} V|^{-1/3}(\tfrac{8}{3}\mathscr{F}_{0}-\tfrac{2}{9}\mathscr{F}_{-3}-\tfrac{1}{27}\mathscr{F}_{-6})+\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla} V|^{-5/3}(\tfrac{8}{3}\mathscr{F}_{-2}+\tfrac{10}{9}\mathscr{F}_{-5}+\tfrac{1}{27}\mathscr{F}_{-8})\right]^{-1} \\ & \times\left[4\pi n_{\text{strong}}+|2\vec{\nabla} V|(2\mathscr{F}_{2}+\mathscr{F}_{-1}-\tfrac{1}{9}\mathscr{F}_{-4})-\frac{1}{r}\frac{\partial V}{\partial r}|2\vec{\nabla} V|^{-1/3}(\tfrac{2}{3}\mathscr{F}_{-3}+\tfrac{5}{27}\mathscr{F}_{-6})\right. \\ & \left.-\frac{1}{r^2}|2\vec{\nabla} V|^{+1/3}(\mathscr{F}_{-2}+\tfrac{1}{2}\mathscr{F}_{-5}+\tfrac{1}{54}\mathscr{F}_{-8})\right], \end{aligned} \tag{19}$$

which we have already reported in (177) of I.

We are ready to admit that this, although being an extension of the TF equation, no longer has any striking resemblance to it. However, there are common features: first, it is a second-order differential equation; second, it is *one* equation for *all* systems, as compared to Hartree-Fock formulations, where going from $N$ to $N+1$ changes the number of functions to be found; third, different $N$ and $Z$ enter the problem via the boundary conditions, without direct effect on the differential equation.

There are enormous differences, too. But they are of a more technical nature. In the case of the TF equation, the numerical challenge was merely to find $\zeta$ and $V$ such that the differential equation along with the boundary conditions, for given $N$ and $Z$,

$$rV \rightarrow \begin{cases} -Z & \text{as } r\rightarrow 0 \\ -(Z-N) & \text{as } r\rightarrow\infty \end{cases} \tag{20}$$

was satisfied. Now, we encounter additional complications because of the special treatment of the strongly bound electrons. For fixed $n_s$, the four new parameters $\zeta_1,\zeta_2,Q_1,Q_2$—each of them being given by an integral involving the potential—also have to be adjusted. This is not a new quality, however; it is just an increase in the number of parameters from one ($\zeta$ in TF theory) to five. Our companion paper[3] on the correlations for strongly bound electrons in the TF model discusses how to handle these parameters. The main change from what is done there comes from the abundance of Airy functions in the new differential equation (19). That makes it numerically more involved (and more expensive), but again this is not a fundamental departure from the TF equation.

## SMALL DISTANCES

When approaching the origin we encounter the strong cancellations that have been already briefly discussed following Eq. (36) of I. In the $\mathscr{F}_n$ [Eq. (134) of I)], $y$ and the $y_j$ are for small $r$ given by

$$y,y_j \cong 2\left[-\frac{Z}{r}\right]\left|\frac{2Z}{r^2}\right|^{-2/3} = -(2Zr)^{1/3}\ , \tag{21}$$

whereas their difference is

$$\begin{aligned}\Delta y_j \equiv y_j - y \cong 2(\zeta_j-\zeta)\left|\frac{2Z}{r^2}\right|^{-2/3} \\ = \frac{\zeta_j-\zeta}{2Z^2}(2Zr)^{4/3}\ . \end{aligned} \tag{22}$$

This implies that the $\mathscr{F}_n$, for $r\rightarrow 0$, behave like

$$\begin{aligned}\mathscr{F}_n = \sum_{j=1}^{2}\tfrac{1}{2}[F_n(y_j-\Delta y_j)-F_n(y_j)-\Delta y_j F_{n-1}(y_j)] &= \sum_{j=1}^{2}\frac{1}{2}\left[\frac{1}{2!}(\Delta y_j)^2 F_{n-2}(y_j)+\frac{1}{3!}(\Delta y_j)^3 F_{n-3}(y_j)+\cdots\right] \\ &\cong \tfrac{1}{8}(2Zr)^{8/3}F_{n-2}(0)\sum_{j=1}^{2}\frac{1}{2}\left[\frac{\zeta_j-\zeta}{Z^2}\right]^2 . \end{aligned} \tag{23}$$

We insert this into the differential equation for $V$ [Eq. (19)] and learn that at the origin the demoninator is 1 while the numerator has contributions from $n_{\text{strong}}$ and from its last term, which possesses the factor $(-1/r^2)|2\vec{\nabla}V|^{+1/3} \sim r^{-8/3}$. Thus

$$-\nabla^2\left[V+\frac{Z}{r}\right]\cong 4\pi n_{\text{strong}}(r=0)-\tfrac{1}{8}(2Z)^3[F_{-4}(0)+\tfrac{1}{2}F_{-7}(0)+\tfrac{1}{54}F_{-10}(0)]\sum_{j=1}^{2}\frac{1}{2}\left[\frac{\zeta_j-\zeta}{Z^2}\right]^2 \quad \text{as } r\to 0\,. \tag{24}$$

Upon recalling that

$$F_{-1}(0)=-2\,\text{Ai}(0)\text{Ai}'(0)=\frac{3^{-1/2}}{\pi} \tag{25}$$

and employing the recurrence relation (119) of I, we find

$$\begin{aligned}-\nabla^2\left[V+\frac{Z}{r}\right] &\cong 4\pi n_{\text{strong}}(r=0)\\ &\quad+\frac{3^{1/2}}{2\pi}(2Z)^3\sum_{j=1}^{2}\frac{1}{2}\left[\frac{\zeta_j-\zeta}{Z^2}\right]^2 \quad \text{as } r\to 0\,.\end{aligned} \tag{26}$$

An implication of both this and (23) is the vanishing of $\tilde{n}$ [Eq. (18)] at the origin. Therefore, the electronic density at that point is entirely given by $n_{\text{strong}}$:

$$\begin{aligned}n(r=0)&=n_{\text{strong}}(r=0)\\ &=\left[\rho_s+\sum_{j=1}^{2}\tfrac{1}{2}Q_j\,|\psi_{n_j}|^2_{\text{av}}\right]\Bigg|_{r=0}\,.\end{aligned} \tag{27}$$

With the aid of the following familiar property of the Coulombic densities:

$$|\psi_n|^2_{\text{av}}|_{r=0}=\frac{(2Z)^3}{4\pi}\frac{1}{2n^5}\,, \tag{28}$$

$$\begin{aligned}\rho_s(r=0)&=\sum_{n=1}^{n_s}2n^2|\psi_n|^2_{\text{av}}|_{r=0}\\ &=\frac{(2Z)^3}{4\pi}\sum_{n=1}^{n_s}\frac{1}{n^3}\,,\end{aligned} \tag{29}$$

we get from (27)

$$n(r=0)=\frac{(2Z)^3}{4\pi}\left[\sum_{n=1}^{n_s}\frac{1}{n^3}+\frac{Q_1}{4n_s^5}+\frac{Q_2}{4(n_s+1)^5}\right]. \tag{30}$$

The first term in the large parentheses is the contribution of the specially treated strongly bound electrons, while the terms containing the $Q_j$ represent the statistically handled bulk of electrons.

As we remarked in Ref. 1, for most practical applications $n_s$ equals 1, under which circumstance (30) reads as follows:

$$n(r=0)=\frac{(2Z)^3}{4\pi}(1+\tfrac{1}{4}Q_1+\tfrac{1}{128}Q_2) \quad \text{for } n_s=1\,. \tag{31}$$

## LARGE DISTANCES

Now we turn to the region of large distances where all terms that refer to the strongly bound electrons are effectively zero. Thus, all $\mathcal{F}_n$'s are now just $F_n(y)$'s, and $n_{\text{strong}}$ is absent. By "large $r$" we mean distances sufficiently far beyond the edge. That becomes more concrete by stating that the potential $V$ is small compared to $\zeta$, allowing the approximation

$$y=2(V+\zeta)|2\vec{\nabla}V|^{-2/3}\cong 2\zeta|2\vec{\nabla}V|^{-2/3}\,. \tag{32}$$

Then, the combination of (62) from I with the asymptotic form for the Airy functions [Eq. (67) of I] produces, more precisely than (66) of I,

$$F_0(y)\cong\frac{1}{4\pi}y^{-1/2}\exp(-\tfrac{4}{3}y^{3/2}) \quad \text{for } y\gg 1 \tag{33}$$

which by differentiation or integration yields

$$\begin{aligned}F_n(y)&=\left[-\frac{d}{dy}\right]^{-n}F_0(y)\\ &\cong\frac{1}{2\pi}(4y)^{-(n+1)/2}\exp(-\tfrac{4}{3}y^{3/2}) \quad \text{for } y\gg 1\end{aligned} \tag{34}$$

or, if we make use of (32),

$$\begin{aligned}F_n(y)&\cong\frac{1}{2\pi}(8\zeta)^{-(n+1)/2}|2\vec{\nabla}V|^{(n+1)/3}\\ &\quad\times\exp\left[-\frac{2}{3}\frac{(2\zeta)^{3/2}}{|\vec{\nabla}V|}\right], \quad r \text{ large}\,.\end{aligned} \tag{35}$$

The asymptotic boundary condition in (20) implies that, for ions, $|\vec{\nabla}V|$ approaches zero like $1/r^2$ and even faster for neutral atoms. Consequently, in a sum of $F_n$'s the one $F_n$ with the most negative index dominates.

A first example for the application of all these preparatory remarks is the gradient of the exchange potential [Eq. (14)],

$$\begin{aligned}\vec{\nabla}V_{\text{ex}}&\cong(\vec{\nabla}V)\left[|2\vec{\nabla}V|^{-1/3}[-\tfrac{1}{3}F_{-3}(y)]-\frac{4}{r}\frac{\partial V}{\partial r}|2\vec{\nabla}V|^{-5/3}\tfrac{1}{18}F_{-5}(y)\right]\\ &\cong(\vec{\nabla}V)\left[-\frac{1}{6\pi}\right](8\zeta)|2\vec{\nabla}V|^{-1}\left[1+\frac{8\zeta}{3}\frac{1}{r}|2\vec{\nabla}V|^{-1}\right]\exp\left[-\frac{2}{3}\frac{(2\zeta)^{3/2}}{|\vec{\nabla}V|}\right], \quad r \text{ large}\end{aligned} \tag{36}$$

wherein we used $\partial V/\partial r = |\vec{\nabla} V|$. It is clear that in calculating the gradient of the electrostatic potential, $V_{\text{es}} = V - V_{\text{ex}}$, there $V_{\text{ex}}$ is negligible compared to $V$. Thus, asymptotically we find

$$4\pi n = -\nabla^2 \left[ V - V_{\text{ex}} + \frac{Z}{r} \right] \cong -\nabla^2 V \,, \tag{37}$$

where the density $n \cong \tilde{n}$ is now approximately given by [Eq. (18)]

$$\begin{aligned} 4\pi\tilde{n} \cong {} & |2\vec{\nabla} V| \tfrac{1}{18} F_{-4}(y) + \frac{1}{r}\frac{\partial V}{\partial r} |2\vec{\nabla} V|^{-1/3} \tfrac{1}{27} F_{-6}(y) \\ & -(\nabla^2 V)|2\vec{\nabla} V|^{-1/3} \tfrac{1}{54} F_{-6}(y) \,. \end{aligned} \tag{38}$$

Again we dispose of the term involving $\nabla^2 V$ because it is negligible when added to the other $\nabla^2 V$ in (37). At this stage, on inserting (35) and $\partial V/\partial r = |\vec{\nabla} V|$, we have

$$\begin{aligned} -\nabla^2 V \cong {} & \frac{1}{36\pi}(8\zeta)^{3/2} \left[ 1 + \frac{8\zeta}{3}\frac{1}{r} |2\vec{\nabla} V|^{-1} \right] \\ & \times \exp\left[ -\frac{2}{3}\frac{(2\zeta)^{3/2}}{|\vec{\nabla} V|} \right] . \end{aligned} \tag{39}$$

After noticing that the second term in this sum asymptotically outweighs the first one, we are led to

$$\begin{aligned} -\nabla^2 V \cong 4\pi n \cong {} & \frac{4}{27\pi}(2\zeta)^{5/2} \frac{1}{r|\vec{\nabla} V|} \\ & \times \exp\left[ -\frac{2}{3}\frac{(2\zeta)^{3/2}}{|\vec{\nabla} V|} \right], \quad r \text{ large} \,. \end{aligned} \tag{40}$$

The message of this equation is twofold. For $N < Z$, it tells us that beyond the edge of the ion the density drops off very rapidly:

$$n \cong \frac{1}{27\pi^2}(2\zeta)^{5/2} \frac{r}{Z-N} \exp\left[ -\frac{2}{3}(2\zeta)^{3/2} \frac{r^2}{Z-N} \right] . \tag{41}$$

For $N = Z$, the main information contained in (40) is, besides the large-distance behavior of the density, the assurance that there is no contradiction in assuming that for neutral atoms $\zeta$ is positive (though small), not zero.

We conclude this section by demonstrating why $\zeta$ cannot be zero for $N = Z$. This could be done by investigating the asymptotic properties of $\nabla^2 V$ once more, but we prefer a simpler, physical argument. It starts with observing that in this case $y$ would certainly be negative for large $r$, with two possible limits:

$$y = 2V|2\vec{\nabla} V|^{-2/3} \rightarrow \begin{cases} y_0 \le 0, & \text{(42a)} \\ -\infty, & \text{(42b)} \end{cases} \quad \text{as } r \rightarrow \infty \,.$$

Now we look at the asymptotic form of the exchange potential [Eq. (7)]

$$\begin{aligned} V_{\text{ex}} & \cong -|2\vec{\nabla} V|^{1/3}[F_1(y) - \tfrac{1}{6}F_{-2}(y)] \\ & = V\frac{2}{(-y)|2\vec{\nabla} V|^{+1/3}} \{ \tfrac{2}{3}[\text{Ai}'(y)]^2 - \tfrac{4}{3} y [\text{Ai}(y)]^2 \} \,, \end{aligned} \tag{43}$$

where we inserted the explicit forms of $F_1$ and $F_{-2}$ given in (63) and (64) of I. The Airy function factor is obviously positive for all $y < 0$. Thus, in order to prevent $V_{\text{ex}}$ from growing large as compared to $V$, which would be physically unacceptable in the asymptotic low-density domain, possibility (42b) has to be realized. We can then make use of the large-$|y|$ behavior of the Airy functions [Eqs. (67) and (69) of I] and arrive at

$$V_{\text{ex}} \cong V\frac{2}{\pi}\frac{1}{|y|^{1/2}|2\vec{\nabla} V|^{1/3}}[1 + \tfrac{1}{3}\sin(\tfrac{4}{3}|y|^{2/3})] \,. \tag{44}$$

Here, $V_{\text{ex}}$ becomes a very small fraction of $V$ for large $r$, but the rapid oscillations of the sine function cause $\vec{\nabla} V_{\text{ex}}$ to be arbitrarily larger than $\vec{\nabla} V$. Again we encounter an unphysical behavior. So (42b) is equally discredited.

The lesson learned from this discussion is that, indeed, $\zeta$ is positive for neutral atoms. Consequently, $\zeta = 0$ applies to a negative ion, for which $y$ is asymptotically a large positive number, and there is no problem with the exchange potential (43).

## NUMERICAL PROCEDURE

The numerical search for the potential $V$, along with the parameters $\zeta, \zeta_j, Q_j$, begins with an appropriate choice of variables. For that, we remark that under scaling transformations of the type

$$\begin{aligned} & V(r) \rightarrow \lambda^{\beta} V(\lambda r) \,, \\ & \zeta \rightarrow \lambda^{\beta} \zeta \,, \end{aligned} \tag{45}$$

$y$ transforms according to

$$y(r) \rightarrow \lambda^{(\beta-2)/3} y(\lambda r) \,, \tag{46}$$

which is simplest for $\beta = 2$. This observation enables us to make an optimal choice for the argument of the function giving the ratio between the potential $V$ and the Coulomb energy of an electron with the nucleus,$^4$

$$V(r) = -\frac{Z}{r} f(x) = -Z^{1+\alpha} \frac{f(x)}{x}, \quad x = Z^{\alpha} r \,. \tag{47}$$

For, since (47) looks like a scaling (45) with $Z^{\alpha} \sim \lambda$ and $Z^{1+\alpha} \sim \lambda^{\beta}$, we have the relation

$$\alpha = \frac{1}{\beta - 1} \,; \tag{48}$$

thus for $\beta = 2$,

$$\alpha = 1 \,. \tag{49}$$

The function $f$ is therefore most conveniently chosen as

$$V(r) = -\frac{Z}{r} f(Zr) = -Z^2 \frac{f(x)}{x}, \quad x = Zr \tag{50}$$

where $f(x)$ still possesses an implicit $Z$ dependence, of course. For original TF the basic scaling has $\beta=4$, so that $\alpha=\frac{1}{3}$, $x\sim Z^{1/3}r$ there. More detail on scaling in TF is given in the mentioned companion paper.[3] In analogy to (50) we also introduce a function $g(x)$ that goes with the derivative of $V(r)$,

$$\frac{\partial}{\partial r}V(r)=Z^3\frac{g(x)}{x^2}\ . \tag{51}$$

It is simply related to $f(x)$ by a Legendre transformation,

$$g(x)=f(x)-x\frac{d}{dx}f(x)\ . \tag{52}$$

The new variable $x=Zr$ is also particularly advantageous in view of the known $Z$ dependence of the Coulombic densities $|\psi_{n_j}|^2_{\text{av}}$ and $\rho_s$:

$$|\psi_{n_j}|^2_{\text{av}}=\frac{Z^3}{4\pi}\phi_{n_j}(Zr)\ , \tag{53}$$

$$\rho_s(r)=\frac{Z^3}{4\pi}\Phi_s(Zr)\ , \tag{54}$$

where

$$\Phi_s(x)=\sum_{n=1}^{n_s}2n^2\phi_n(x)\ , \tag{55}$$

which introduces the density functions $\phi_n(x)$. Here is a list of the first few:

$$\begin{aligned}\phi_1(x)&=4e^{-2x}\ ,\\ \phi_2(x)&=\tfrac{4}{32}(1-x+\tfrac{1}{2}x^2)e^{-x}\ ,\\ \phi_3(x)&=\tfrac{4}{243}(1-\tfrac{4}{3}x+\tfrac{8}{9}x^2-\tfrac{16}{81}x^3+\tfrac{4}{243}x^4)e^{-2x/3}\ .\end{aligned} \tag{56}$$

As a consequence of the normalization of $|\psi_{n_j}|^2_{\text{av}}$, they are normalized to unity,

$$\int_0^\infty dx\,x^2\phi_n(x)=1\ . \tag{57}$$

Upon inserting (50) and (53) into (136) of I we find the explicit $Z$ dependence of $\zeta_j$ to be simply given by an overall factor $Z^2$,

$$\zeta_j=Z^2\left[\frac{1}{2n_j^2}+\int_0^\infty dx\,x^2\frac{f(x)-1}{x}\phi_{n_j}(x)\right]\ . \tag{58}$$

This invites the definition of distances $x_j$ according to

$$\zeta_j=\frac{Z^2}{x_j}\ , \tag{59}$$

supplemented by

$$\zeta=\frac{Z^2}{x_0}\ , \tag{60}$$

which leads to

$$\begin{aligned}y&=-\left[f(x)-\frac{x}{x_0}\right]\left[\frac{2x}{[g(x)]^2}\right]^{1/3}\ ,\\ y_j&=-\left[f(x)-\frac{x}{x_j}\right]\left[\frac{2x}{[g(x)]^2}\right]^{1/3}\ .\end{aligned} \tag{61}$$

Thus, the arguments of all the $F_n$ have no explicit $Z$ dependence. One simple implication thereof is that $Q_j$ also does not contain $Z$ explicitly,

$$Q_j=\tfrac{8}{3}\int_0^\infty dx\,|g(x)|(y_j-y)\times[F_1(y_j)-y_jF_0(y_j)] \tag{62}$$

[Eq. (140) of I]. Another one is that in the new variables, the exchange potential (7) is a function of $x$, multiplied by a single factor of $Z$,

$$V_{\text{ex}}=-Z\left|\frac{2g(x)}{x^2}\right|^{1/3}(\mathscr{F}_1-\tfrac{1}{6}\mathscr{F}_{-2})\ . \tag{63}$$

We can therefore conclude that, for the bulk of electrons, $V_{\text{ex}}$ is smaller than $V$ by roughly a factor of $1/Z$.

The density, being of the dimension $1/r^3$, has, of course, a factor $Z^3$. This becomes obvious when utilizing Eqs. (47), (51), and (53)–(55) to rewrite (152)–(154) of I as

$$\begin{aligned}n=&\frac{Z^3}{4\pi}\left[\Phi_{n_s}(x)+\sum_{j=1}^{2}\tfrac{1}{2}Q_j\phi_{n_j}(x)\right]\\ &+\frac{Z^3}{2\pi}\left|2\frac{g(x)}{x^3}\right|(\mathscr{F}_2-\tfrac{1}{6}\mathscr{F}_{-1})\\ &-\frac{Z^3}{6\pi}\frac{\partial}{\partial x}\left[\frac{g(x)}{x^2}\left|\frac{2g(x)}{x^2}\right|^{-1/3}(\mathscr{F}_0+\tfrac{1}{6}\mathscr{F}_{-3})\right]\ .\end{aligned} \tag{64}$$

The differential equation for $V$, Eq. (19), will now be expressed in terms of $f(x)$ by employing

$$-\nabla^2V(r)=\frac{Z}{r}\frac{\partial^2}{\partial r^2}\left[-\frac{r}{Z}V(r)\right]=Z^4\frac{1}{x}\frac{d^2}{dx^2}f(x)\ . \tag{65}$$

Not wanting to copy (19) we just remark that $f(x)$ obeys a differential equation of the structure

$$\frac{d^2}{dx^2}f(x)=\frac{a(x)}{Z-b(x)}\ , \tag{66}$$

which does contain $Z$ explicitly in the denominator, while $a(x)$ and $b(x)$ depend on $Z$ only implicitly. This is a consequence of the extra factor $Z$ in $V$ as compared to $V_{\text{ex}}$. Contrary to simple TF, it is impossible in the new theory to derive a universal (i.e., $Z$-independent) differential equation.

For given $N$ and $Z$, the numerical challenge is to find a solution to (66), subject to the boundary conditions of (20),

$$\begin{aligned}f(0)&=g(0)=1\ ,\\ f(\infty)&=g(\infty)=1-\frac{N}{Z}\ ,\end{aligned} \tag{67}$$

together with the five parameters $\zeta,\zeta_{1,2},Q_{1,2}$, four of which themselves are given in terms of integrals involving $f(x)$ and $g(x)$.

For positive ions, $N<Z$, one begins by making a guess for $\zeta,\zeta_j,Q_j$. Then starting with the known asymptotic values of $f$ and $g$, (67), at a distance $x$ so large that the right-hand side of (66) is numerically zero, one integrates the differential equation inwards to $x=0$ and evaluates

the integrals for $Q_j$ and $\zeta_j$. The comparison with the initial guesses leads to improved values for these parameters. The test

$$f(0)\overset{?}{=}1 \tag{68}$$

supplies information about $\zeta$, again yielding a better value. Then, with the new set of parameters one integrates once more, and by iteration finally finds $f(x)$ as well as $\zeta,\zeta_j,Q_j$.

Unfortunately, this procedure is not applicable to neutral systems because the asymptotic forms of $f(x)$ and $g(x)$ for large values of $x$ are unknown, so that initial values for the numerical inward integration are not available. (This is different from the situation of Ref. 3, where one knew that the neutral-atom potential at large distances is a rescaled TF potential.) Since a simple outward integration, beginning with $f(0)=1$ and a guess for $(df/dx)(0)$, would be unstable because of its sensitivity to round-off errors, and since a mixed strategy of integrating in both directions from an intermediate distance would introduce two more numerical parameters (e.g., $f$ and $g$ at the intermediate point), we resort to extrapolating the $N=Z$ data from results obtained for ions in the manner described above. For this extrapolation we use the five ions which have fixed $N$ and

$$Z-N=2,1,\tfrac{1}{2},\tfrac{1}{5},\tfrac{1}{10}\ , \tag{69}$$

of which the first two are physical systems interesting in themselves.

## NUMERICAL RESULTS

We report numerical results for the inert gases $Z=N=18,36,54$, and for the related ions with $Z=N+1,N+2$.

The first step towards finding the potential $V$—and all the quantities derived from it, such as the exchange potential and the density—for these concrete systems is to decide how many of the electrons are to be treated in the special manner designed for strongly bound electrons. In practice, the choice is between correcting for one shell ($n_s=1$, $N_s=2$) or for two ($n_s=2$, $N_s=10$). It has to be made in such a way that the condition [Eq. (82) of I]

$$1 \ll N_s \ll Z \cong N \tag{70}$$

is satisfied. However, we are now dealing with realistic, and therefore rather modest, values of $Z$ and $N$, and it is quite impossible to take (70) very seriously. The best one can do is to opt for that $N_s$ which, on a logarithmic scale, is halfway between 1 and $Z$. Another way of stating this is to say that we choose that $N_s$ which is closest to the square root of $Z$ ($\cong N$). For $N=18$ and 54, the answer is unambiguous: $n_s=1$ and 2, respectively. In the case of the $N=36$ systems, both $N_s=2$ and 10 are equally distant from 6, the square root of $N$ (or $Z$); we vote for $n_s=1$, $N_s=2$ in order to avoid the danger of overcorrecting for the strongly bound electrons.

We start our survey of results with a very close look at one representative system, serving as an illustration of all—the rubidium ion ($N=36$, $Z=37$). For it we obtained these values of the parameters:

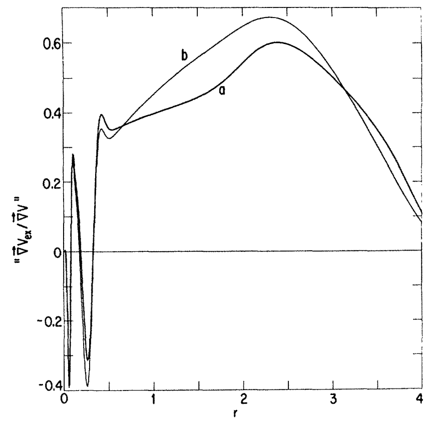

FIG. 1. Comparison of the multipliers of $\vec{\nabla}V$ in Eq. (13) (for curve $a$) and Eq. (14) (for curve $b$), for $\mathrm{Rb}^+$.

$$\zeta=0.32989\ ,$$
$$\zeta_1=526.57,\quad \zeta_2=63.425\ , \tag{71}$$
$$Q_1=0.6132,\quad Q_2=3.971\ .$$

Of particular interest are the actual numbers for $\zeta_1$ and $\zeta_2$ because they tell us whether it is justifiable to use the simple Coulombic densities for the strongly bound electrons. To extract that information out of $\zeta_1$ and $\zeta_2$, we first remark that, as a consequence of Eq. (26), the potential $V$ has the small-distance form

$$V=-\frac{Z}{r}+C+O(r^2)\ , \tag{72}$$

where the constant $C$ is, of course, related to the initial slope of $f(x)$ [Eq. (50)] by

$$C=-Z^2f'(0)\ . \tag{73}$$

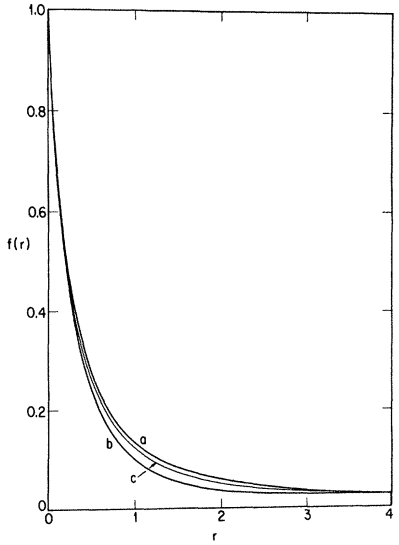

FIG. 2. $f$ functions belonging to the following potentials. Curve $a$: $V$, curve $b$: $V_{es}=V-V_{ex}$, curve $c$: $V_{\mathrm{TF}}$, for $\mathrm{Rb}^+$.

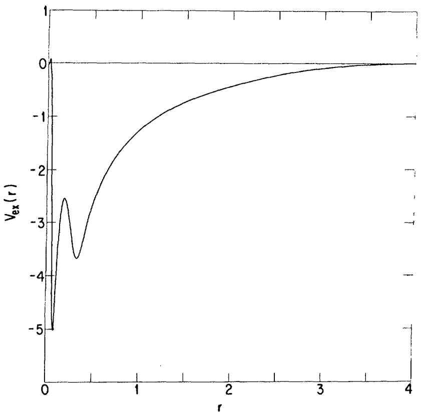

FIG. 3. Exchange potential for $Rb^+$ as a function of the distance from the nucleus.

Only the $O(r^2)$ term gives rise to deformations of the Coulomb wave functions. Consequently, we have to ask how big is this term in the domain of the specially treated strongly bound electrons. A quantitative answer to this question employs the definition of the $\zeta_j$ [Eq. (136) of I],

$$\zeta_j = \frac{Z^2}{2n_j^2} - \left\langle V + \frac{Z}{r} \right\rangle_{n_j} = \frac{Z^2}{2n_j^2} + Z^2 f'(0) - \langle O(r^2) \rangle_{n_j} , \tag{74}$$

to express $f'(0)$ in terms of $\zeta_j$:

$$-f'(0) = \frac{1}{2n_j^2} - \frac{1}{Z^2}[\zeta_j + \langle O(r^2) \rangle_{n_j}] \cong \frac{1}{2n_j^2} - \frac{\zeta_j}{Z^2} = \begin{cases} 0.1154 & \text{for } j=1 \\ 0.0787 & \text{for } j=2. \end{cases} \tag{75}$$

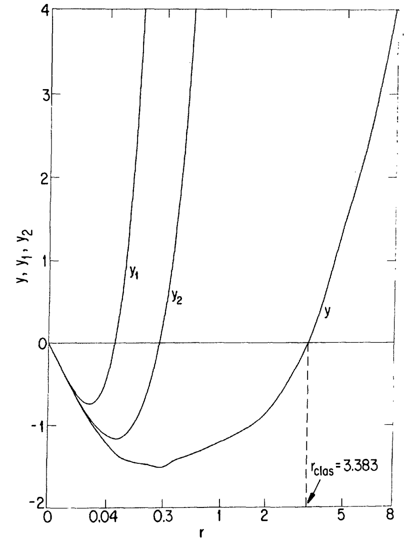

FIG. 4. $y, y_1, y_2$ for $Rb^+$ as a function of $r$. Abscissa is linear in the cubic root of $r$.

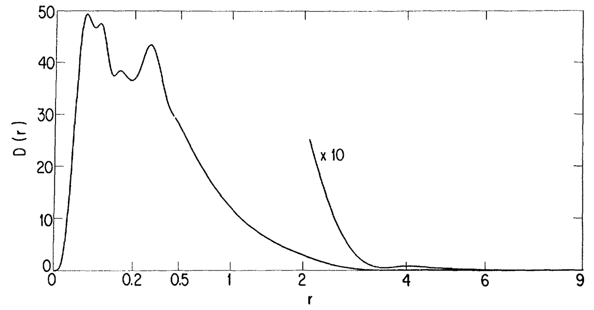

FIG. 5. Radial electron density in $Rb^+$, tail amplified by 10. Abscissa is linear in the square root of $r$.

We compare this with the numerical result for the initial slope of $f$, $-f'(0)=0.1412$, and see a reasonable agreement for the first shell and a somewhat worse situation for the second one. Since the latter does not contribute very much to the whole description we feel entirely justified in using Coulombic densities for the strongly bound electrons, or, in other words, in treating $V+Z/r$ as a small perturbation for those electrons.

Another check for internal consistency concerns the approximation for the gradient of the exchange potential, Eqs. (13) and (14). In Fig. 1, we give a graphical presentation of the multipliers of $\vec{\nabla} V$ in these two equations, as a function of $r$. The difference of the two curves is relatively small, and where it is largest, one is already practically outside the ion—there $\vec{\nabla} V$ is small. Again we have sufficient justification for the applied approximation.

In Fig. 2 we show, as a function of $r$, the $f$ functions belonging to $V$ [cf. Eq. (50)] and, analogously, to the electrostatic potential $V_{es} = V - V_{ex}$, and, for comparison, to the corresponding TF potential $V_{TF}$. One notices that all these functions are very smooth and practically structureless. This justifies our remarks, in the Introduction of Ref. 1, about the advantage of potential functionals over density functionals.

Since we are at it, why not take a look at $V_{ex}$ itself, Fig. 3? With the exception of extremely small $r$, where one cannot believe it anyhow, we notice that the exchange potential is attractive—an obvious consequence of the minus

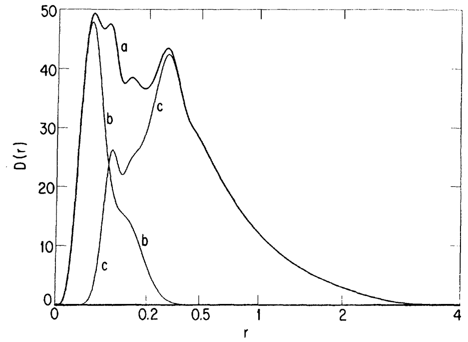

FIG. 6. Radial electron density in $Rb^+$. Curve $a$, $D(r)$; curve $b$, $D_{\text{strong}}(r)$; curve $c$, $\tilde{D}(r)$. Abscissa is linear in the square root of $r$.

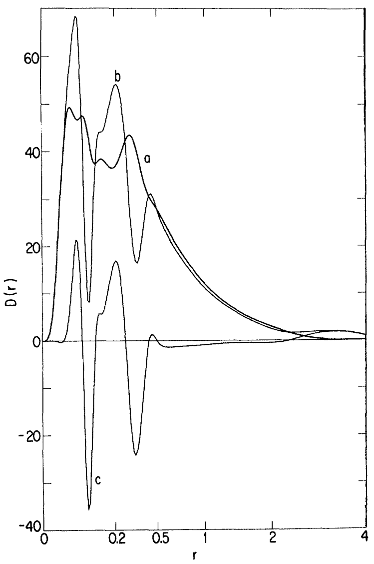

FIG. 7. Radial electron density in Rb$^+$. Curve $a$, $D(r)$; curve $b$, $D_V(r)$; curve $c$, $D_{V_{\text{ex}}}(r)$. Abscissa is linear in the square root of $r$.

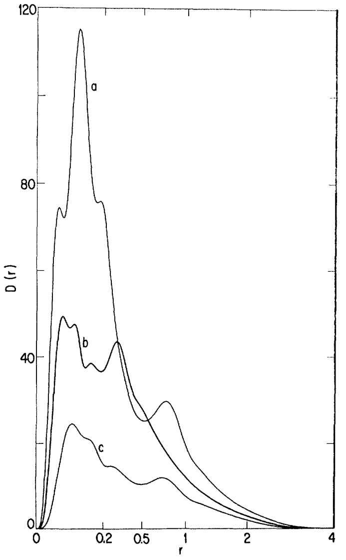

FIG. 8. Radial electron density in, curve $a$, Cs$^+$; curve $b$, Rb$^+$; curve $c$, K$^+$. Abscissa is linear in the square root of $r$.

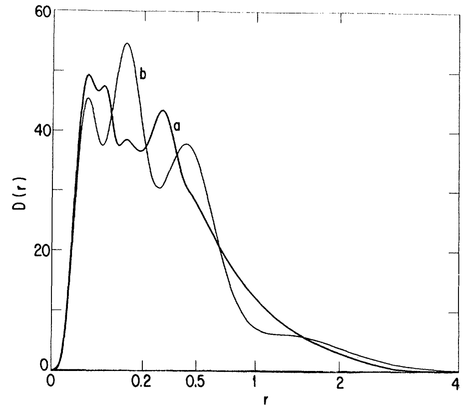

FIG. 9. Radial electron density in Rb$^+$. Curve $a$, new statistical calculation; curve $b$, HF calculation. Abscissa is linear in the square root of $r$.

sign in (86) of I, reflecting the antisymmetry of the two-electron wave functions. Furthermore, one sees that $V_{\text{ex}}$ has very little structure implying that the oscillatory part in (7), $F_{-2}(y)$ in $\mathcal{F}_{-2}$ (cf. Fig. 3 of I), goes only through very few ups and downs. Consequently, $y(r)$ cannot become very negative in the interior of the ion. Indeed, the plot of $y$ along with $y_1$ and $y_2$ in Fig. 4 confirms this observation: $y(r)$ is nowhere less than $-1.6$. Incidentally, we note that $y_1$ and $y_2$ are, of course, always greater than $y$, both turning positive still far inside the ion (roughly at $r=0.055$ and 0.26, respectively), while $y$ stays negative up to $r=3.383$, which is the classical radius of the Rb$^+$ ion. For $r\to 0$, according to (21), all $y$'s are proportional to the cubic root of $r$—straight lines in Fig. 4 where, for this very reason, the abscissa is linear in $r^{1/3}$. It is also clear that only for systems with an enormous number of electrons can $y(r)$ be sufficiently large and negative for the asymptotic forms of Airy's function to be valid. From this point of view, one would not expect the TF limit to be particularly accurate for real atoms; but it is. (Look again at Fig. 1 of I.)

Now we come to various plots of the Rb$^+$ density, which all use an abscissa that is linear in the square root of $r$—a standard tool to stretch the structure at small distances. Figure 5 shows the radial density

$$D(r)=4\pi r^2 n(r) \tag{76}$$

with the low-density tail amplified by a factor of 10. The first, and most important, observation is that the density is positive everywhere, which is by no means obvious from Eqs. (152)–(154) of I. There are two main peaks and a very small third one beyond the edge of the ion, reminiscent of some kind of shell structure. The "fine structure" of the first peak and the following minimum should not be taken too seriously. It may well be spurious in view of Fig. 6, where $D(r)$ is decomposed into its two contributions from $n_{\text{strong}}$ and $\tilde{n}$. These are much smoother, and only the rapid decrease of $D_{\text{strong}}$ on top of the equally rapid increase of $\tilde{D}$ produces the wiggles. Another decomposition of $D(r)$ is shown in Fig. 7, where we see the graphical presentation of Eq. (1),

$$D(r)=(-r^2\nabla^2 V)-(-r^2\nabla^2 V_{\text{ex}})\equiv D_V - D_{V_{\text{ex}}}\ . \tag{77}$$

TABLE I. Experimental data for $\overline{r^2}$.

| $N$ | $Z=N$ | $Z=N+1$ | $Z=N+2$ |
|---|---|---|---|
| 18 | 1.373 | 1.023 | 0.750 |
| 36 | 1.010 | 0.772 | 0.632 |
| 54 | 1.027 | 0.821 | 0.678 |

TABLE II. Hartree-Fock predictions for $\overline{r^2}$.

| $N$ | $Z=N$ | $Z=N+1$ | $Z=N+2$ |
|---|---|---|---|
| 18 | 1.447 | 1.087 | 0.857 |
| 36 | 1.097 | 0.884 | 0.742 |
| 54 | 1.160 | 0.973 | 0.842 |

Again we observe that the fine structure of $D$ is made by the interplay of two smoother, though strongly oscillating, curves. Also remarkable is the fact that, beyond the edge of the ion, $D_V$ and $D_{V_{\text{ex}}}$ are of almost equal magnitude. This is a manifestation of the attractive nature of the exchange potential: the electron density in the exterior of the ion is reduced to the benefit of the interior.

As illustrated in Fig. 8, the new theory yields a variety of shapes for the electronic densities of systems with different $N$ and $Z$. While original TF gave a uniform look, there is now a lot of individuality. The potassium ion ($Z=19$, $N=18$) has an almost structureless density spread out over a large volume. The density of $\text{Rb}^+$ is much more localized and has much more structure, as we already know. For the cesium ion ($Z=55$, $N=54$) we see a smooth, well-concentrated main peak accompanied by a smaller one which is farther away from the nucleus. The obvious question now is: How do these densities compare with those obtained by Hartree-Fock calculations?

For the comparison of a new statistical density with a HF density, we once again pick out the $\text{Rb}^+$ ion—it is the most striking example. Figure 9 shows the differences.[5] The two densities agree only in the domain of the strongly bound electrons. We observe quite different peak structures and notice that at large distances the HF density is significantly larger. Unfortunately, there is no simple way of telling which one is closer to reality because electron densities cannot be measured directly. However, one can, of course, compare derived quantities. We chose the expectation value of the squared distance,

$$\overline{r^2}=\frac{1}{N}\int(d\vec{r})r^2n(\vec{r}) \tag{78}$$

since it provides a sensitive test of the density at large $r$.[6] Experimental data are obtained from measurements of the molar diamagnetic susceptibility

$$-\chi_m=\left[\frac{1}{\text{“}137\text{”}}\right]^2 N_A a_0^3 I=4.752\times10^{-6}I\ , \tag{79}$$

where, expressed in atomic units,

$$I=\tfrac{1}{6}\int(d\vec{r})r^2n(\vec{r})=\frac{N}{6}\overline{r^2}\ . \tag{80}$$

TABLE III. Predictions for $\overline{r^2}$ by the present, new theory.

| $N$ | $Z=N$ | $Z=N+1$ | $Z=N+2$ |
|---|---|---|---|
| 18 | 1.46 | 1.036 | 0.786 |
| 36 | 1.03 | 0.812 | 0.664 |
| 54 | 1.01 | 0.831 | 0.704 |

TABLE IV. Previous statistical prediction for $\overline{r^2}$.

| $N$ | $Z=N$ | $Z=N+1$ | $Z=N+2$ |
|---|---|---|---|
| 18 | 1.413 | 1.013 | 0.767 |
| 36 | 1.152 | 0.903 | 0.737 |
| 54 | 1.001 | 0.819 | 0.691 |

Let us first look at the experimental numbers,[7] Table I. Besides the expected decrease of $\overline{r^2}$ for increasing $Z$ and fixed $N$, we notice that from $N=18$ to 36 the systems shrink while growing by a smaller amount from $N=36$ to 54. This qualitative behavior—we anticipated it when describing the curves of Fig. 8—is reproduced by the HF numbers[8] of Table II. But quantitatively the HF performance is suprisingly poor. All HF predictions exceed the experimental numbers by 5–24%. In the case of $N=54$, the HF result for $Z=56$ is even larger than the one measured for $Z=55$. Obviously, HF densities are significantly in error at large distances.

On the other hand, our new statistical calculation, presented in Table III, is in quite good agreement with experiment, both qualitatively and quantitatively. For the ions with $Z=N+1$ and $N+2$ the deviations are between 1.2% and 5.3% which is of the magnitude of the experimental errors (the numbers reported for ions are extracted from measurements of the susceptibility of crystals). The predictions for the neutral atoms are off by 6.3%, 2.0%, and $-1.7\%$, which would seem to be worse in the view of the high experimental accuracy for these inert gases. Since the calculated $\overline{r^2}$ for $Z=N=54$ is actually a little bit smaller than the one for $Z=N=36$, one might say that the new theory gives a wrong qualitative prediction for neutral atoms. This remark would, however, ignore the fact that for $N=Z$ all numbers are obtained by the extrapolation described in the preceding section and are therefore less precise. That is also indicated in Table III by the smaller number of decimals for $N=Z$. For the same reason one should not be disappointed by the argon ($Z=N=18$) atom where HF, for once, is better than the new statistical calculation.[9]

We summarize by stating that the new theory doubtlessly outperforms HF as far as electronic densities at large distances are concerned. For electrons closer to the nucleus the two approaches are competitive—here a sensitive quantity is the total binding energy for which we made the comparison in Fig. 1 of I.[10]

For the sake of completeness, we also compare with the best previous statistical calculation,[2] the one that was based on Eq. (176) of I. It produced the numbers of Table IV. While they are not really worse than the new ones for $N=18$ and 54, the $N=36$ systems are described badly—only within HF accuracy. The obvious reason for this flaw is the absence of the 18-36-54 oscillation, which was not obtainable then; this previous approach was simply an extrapolation of the leading exchange and kinetic-energy

TABLE V. Values of the parameters $\zeta$, $\zeta_{1,2}$, $Q_{1,2}$, and of $-f'(0)$ for the various systems.

| $N$ | $Z$ | $\zeta$ | $\zeta_1$ | $\zeta_2$ | $Q_1$ | $Q_2$ | $-f'(0)$ |
|---|---|---|---|---|---|---|---|
| 18 | 18 | 0.0094 | 106.2 | 7.02 | 0.542 | 3.06 | 0.2238 |
| | 19 | 0.35021 | 120.52 | 8.861 | 0.5485 | 3.126 | 0.21517 |
| | 20 | 0.82382 | 135.84 | 10.981 | 0.5542 | 3.188 | 0.20708 |
| 36 | 36 | 0.0092 | 495.9 | 58.61 | 0.611 | 3.94 | 0.1439 |
| | 37 | 0.32989 | 526.57 | 63.425 | 0.6132 | 3.971 | 0.14120 |
| | 38 | 0.75722 | 558.28 | 68.521 | 0.6154 | 4.004 | 0.13856 |
| 54 | 54 | 0.0090 | 148.1 | 11.73 | 4.30 | 10.4 | 0.1184 |
| | 55 | 0.30991 | 155.96 | 13.482 | 4.316 | 10.45 | 0.11682 |
| | 56 | 0.69778 | 164.13 | 15.383 | 4.340 | 10.54 | 0.11530 |

quantum correction into the outer regions.

It is worth mentioning that apparently all models have the tendency to ascribe too large a size to atomic systems.

We close this section by reporting, in Table V, the parameters $\zeta$, $\zeta_{1,2}$, and $Q_{1,2}$ as well as the initial slope of $f(x)$ for the nine $Z$-$N$ pairs dealt with. While we do not intend to comment on all the numbers, we do want to emphasize that one should keep in mind the fact that numbers referring to neutral atoms have been obtained by an extrapolation and are therefore less reliable.

## ACKNOWLEDGMENTS

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[1] B.-G. Englert and J. Schwinger, preceding paper, Phys. Rev. A 29, 2339 (1984), referred to as I.

[2] B.-G. Englert and J. Schwinger, Phys. Rev. A 26, 2322 (1982).

[3] B.-G. Englert and J. Schwinger, this issue, Phys. Rev. A 29, 2331 (1984).

[4] One could, of course, include a constant in the definition of $x$, which is convenient for the original TF theory; it is not useful here, however.

[5] The HF density is compiled from D. R. Hartree, Proc. R. Soc. London, Ser. A 151, 96 (1935).

[6] One could also calculate the Fourier transform of the density in order to obtain predictions for elastic electron scattering cross sections. At large electron momenta this would be a good test of the interior of the atom. However, since we are mainly interested in the outer reaches, we are content with the diamagnetic susceptibilities.

[7] Diamagnetic susceptibilities for atoms, see *Handbook for Chemistry and Physics* (Chemical Rubber Co., Cleveland, Ohio, 1979/1980); for ions, see F. Hoare and G. Bridley, Proc. R. Soc. London, Ser. A 159, 395 (1937).

[8] S. Fraga, J. Karwowski, and K. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[9] A graphical presentation of Tables I—III is given in Fig. 4 of Ref. 1.

[10] As already mentioned in Ref. 1, it is likely that even the oscillations of Fig. 2 of Ref. 1 can be derived from a statistical calculation.