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Electron-spin polarization in the Thomas-Fermi and Thomas-Fermi-Dirac atoms

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The Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) statistical models are extended by the electron-spin interaction with an external uniform magnetic field B. The statistical atom, which is spherical, is then described with the aid of two distributions: the electron density $n(r)$ and the relative magnetization $\zeta(r)$. In the TF atom the magnetic field polarizes the electron spins totally ($\zeta=1$) in a region near the atomic boundary, while the rest of the TF atom is only partially polarized; however, $\zeta(r)$ and $n(r)$ are continuous. A convenient description of this atom is done with the aid of a suitably defined reduced potential $f(x)$ to which $n(r)$ and $\zeta(r)$ are related. At $B>0$ the neutral TF atom remains infinite. Its magnetic moment shows unphysical $B^{3/4}$ proportionality for small B. The inclusion of the exchange in the TFD model for $B>0$ results in two possible types of atom: the atom of the type I—which exists only for $B \leq 1.3\times10^7$ G—has continuous $n(r)$ and $\zeta(r)$; in the type-II atom there is a discontinuity in both $n(r)$ and $\zeta(r)$ that makes this atom unusable in physical applications. The type-I atoms have finite radii and are assumed to represent approximately the crystal atomic cells. The appropriate differential equation and boundary conditions for $\zeta(r)$, together with the relationship between $\zeta(r)$ and $n(r)$, have been derived for this atom. The solutions of the equations and the atomic radii have been obtained for a wide range of atomic numbers and magnetic fields. On the basis of these solutions, the coefficients for the volume magnetostriction, the spin susceptibilities, and the ionization energies have been calculated for elements of the whole periodic table. Qualitatively, the experimental tendencies are found to be represented well by the type-I TFD atoms. A modified virial theorem for the spin-polarized TF and TFD atoms has been proved.

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I. INTRODUCTION

The statistical approach to physical problems usually leads to approximate solutions. Although some of the system properties are then described only qualitatively, the statistical method is still a widely used tool in the calculation of the properties of matter [1–13]. The advantage of the method lies in its great simplicity in comparison with the other more sophisticated quantum-mechanical approaches. In fact, in the statistical method the solution is usually obtained from an ordinary (one-dimensional) differential equation. Nevertheless, the method gives a physically clear and usually a qualitatively correct description of the system.

As our system we assume a single atom built up from a point nucleus of charge Z and a spherical cloud of N electrons (we use throughout the paper the atomic units in which $|e|=\hbar=m_e=1$). In the absence of external fields the energy functional is the sum of kinetic and Coulomb parts giving the well-known Thomas-Fermi (TF) statistical model; when the exchange energy is included the Thomas-Fermi-Dirac (TFD) model is obtained [14–17]. The purpose of the paper is to raise the question of what happens to the TF atom and, especially, to the TFD atom when these atoms are placed in uniform magnetic field $\mathbf{B}=(0,0,B)$; the problem of the TF atom put in an external electric field was examined recently [12]. If the field B is very strong, it completely governs the transverse (i.e., perpendicular to $\mathbf{B}$) motion of electrons. On the other hand, the Coulomb forces influence only the longitudinal motion, which was the case analyzed in detail within the framework of the statistical method by Banerjee, Constantinescu, and Rehak [18]; an improved treatment of exchange was presented recently [19]. These authors considered both the TF and TFD models. The magnetic fields were within the range 10^{12}–10^{14} G, but the TFD atom remained spherical even in such strong fields; however, its radius (r_0) shrank proportionally to $B^{-2/5}$, which was found to be an accurate relation. In such strong fields all electron spins were assumed to be antiparallel to the field and played no role in the problem. In the present paper the electron-spin distribution is included in the original TF and TFD models. A detailed solution of the resulting equations is done for the whole range of the strength of the magnetic field beginning with very weak fields. The orbital effects are neglected similarly to their absence in the local-spin-density approximation of the density-functional theory [20]. We neglect these effects because we assume they are either quenched by the crystal field, or they can be roughly separated from the spin effects, so that we may concentrate on the latter ones.

In this paper we obtain a simple *ab initio* theory of an atom in a magnetic field. The simplicity of the approach, and especially the little amount of numerical labor involved in it, allows us to examine the atomic properties over large ranges of Z and B. Because we find that the TFD atom has a finite radius also in the case of an external magnetic field, this atom can be thought to be a single Wigner-Seitz cell of a perfect solid approximated by a sphere cell. In this case most of the properties of the solid state can be interpreted in terms of the properties obtained for atoms.

II. MODEL

A. Formulation

Similarly to the original TF and TFD models, the electron cloud around the atomic nucleus is described by the non-negative electron density $n(r)$ dependent on the distance r from the nucleus. The integral of $n(r)$ over the whole space gives the total number N of electrons:

$$\int n(r)d\mathbf{r}=N \ . \tag{1}$$

We assume that the magnetic field polarizes the density $n(r)$ into

$$n(r)=n_{\downarrow}(r)+n_{\uparrow}(r) \ , \tag{2}$$

where $n_{\uparrow}(r)$ and $n_{\downarrow}(r)$ are, respectively, spin-up and spin-down electron densities, the spin-quantization axis being in the direction of the field $\mathbf{B}$. The magnetic state of the statistical atom is then characterized by the relative magnetization $\zeta(r)$ defined as

$$\zeta(r)=\frac{n_{\downarrow}(r)-n_{\uparrow}(r)}{n_{\uparrow}(r)+n_{\downarrow}(r)} \ . \tag{3}$$

It is evident that $\zeta(r)$ is the ratio of the actual magnetization density

$$m(r)=-\mu_B[n_{\uparrow}(r)-n_{\downarrow}(r)]=\mu_B n(r)\zeta(r) \tag{4}$$

to the maximum value of the magnetization density at the point r equal to $\mu_B n(r)$. Since $n_{\downarrow}(r)$ and $n_{\uparrow}(r)$ are non-negative densities, $\zeta(r)$ fulfills the relation

$$-1\le\zeta(r)\le 1 \ . \tag{5}$$

The energy functional depends on both $n(r)$ and $\zeta(r)$:

$$\begin{aligned}E[n,\zeta]&=\int \kappa_k(\zeta(r))n^{5/3}(r)d\mathbf{r}-\int \kappa_a(\zeta(r))n^{4/3}(r)d\mathbf{r}+\tfrac{1}{2}\int\int \frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'-\int \frac{Z}{r}n(r)d\mathbf{r}-\int \mu_B B n(r)\zeta(r)d\mathbf{r}\\&=E_{\text{kin}}+E_x+E_{ee}+E_{en}+E_B \ .\end{aligned} \tag{6}$$

The first two terms of the functional are, respectively, the kinetic energy E_{kin} and the exchange energy E_x; the later term is absent in the TF case. Their densities are assumed to depend locally on $n(r)$ and $\zeta(r)$ in the same way as for the homogeneous electron gas. The dependence on $\zeta(r)$ is defined by [21]

$$\kappa_k(\zeta)=\tfrac{1}{2}[(1+\zeta)^{5/3}+(1-\zeta)^{5/3}]\kappa_{k0} \ , \tag{7}$$

$$\kappa_a(\zeta)=\tfrac{1}{2}[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}]\kappa_{a0} \ , \tag{8}$$

where $\kappa_{k0}=\frac{3}{10}(3\pi^2)^{2/3}=\kappa_k(0)$ are $\kappa_{a0}=\frac{3}{4}(3/\pi)^{1/3}=\kappa_a(0)$. The next terms in the functional (6) are the classical Coulomb interaction energies E_{ee} and E_{en} and the energy E_B associated with the magnetic interaction of the electron spins with the field B. As was mentioned above, we neglect the direct influence of the field on the electron motion, i.e., the orbital effects: We assume them to be either very small or separable from the spin effects. In the nonmagnetic state, i.e., for $\zeta(r)=0$, the energy functional (6) coincides with the original TFD (or TF for $E_x=0$) functional [17].

Following the density-functional theory, our task is to minimize the energy functional (6) with respect to both $n(r)$ and $\zeta(r)$ subjected to the constraints (1) and (5). We assume that both $n(r)$ and $\zeta(r)$ depend solely on $r=|\mathbf{r}|$, which means that the external magnetic field B does not change the spherical symmetry of the original TFD atom. This is an immediate consequence of the rotational invariance of the energy functional (6) on the condition that the minimizing distributions $n(r)$ and $\zeta(r)$ are unique.

B. General considerations

At the first step we rewrite Eq. (6):

$$E[n,\zeta]=\int F(n(r),\zeta(r))d\mathbf{r}+\tfrac{1}{2}\int\int \frac{n(r)n(r')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'-\int \frac{Z}{r}n(r)d\mathbf{r} \ , \tag{9}$$

where

$$F(n,\zeta)\equiv\kappa_k(\zeta)n^{5/3}-\kappa_a(\zeta)n^{4/3}-\mu_B Bn\zeta \ ; \tag{10}$$

the term $-\kappa_a(\zeta)n^{4/3}$ is absent in the TF case.

The functional $E[n,\zeta]$ depends on $\zeta(r)$ only through the volume integral of the function $F(n(r),\zeta(r))$. Therefore the distribution $\zeta(r)$ that minimizes $E[n,\zeta]$ must correspond—at any r—to the minimum of the function $F(n(r),\zeta)$

$$F(n(r),\zeta(r))=\min_{-1\le\zeta\le 1}F(n(r),\zeta) \ , \tag{11}$$

obtained for the correct, although not yet known, electron density $n(r)$ minimizing $E[n,\zeta]$. In general, depending on the form of the function F and the value of $n(r)$, this minimum can be attained either at the edges of the interval of ζ, i.e., at the points $\zeta(r)=\zeta=\mp 1$, or inside the interval $(-1,+1)$. If $|\zeta(r)|<1$, the extremum condition

$$\frac{\partial F}{\partial\zeta}(n(r),\zeta(r))=0 \tag{12}$$

must be fulfilled.

The minimization of $E[n,\zeta]$ with respect to $n(r)$ subjected to the normalization condition (1) yields the equation

$$\frac{\partial F}{\partial n}(n(r),\zeta(r))-V(r)-\mu=0 \; . \tag{13}$$

Here μ is the chemical potential, which is the Lagrange multiplier associated with the condition (1), and $V(r)$ denotes the classical electrostatic potential:

$$V(r)\equiv\frac{Z}{r}-\int\frac{n(r')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\equiv\frac{Z}{r}+V_e(r) \; , \tag{14}$$

$V_e(r)$ being a part due to electron interaction.

The solution of the minimization problem is done with the aid of the Poisson equation:

$$\Delta V(r)=\frac{d^2V(r)}{dr^2}+\frac{2}{r}\frac{dV(r)}{dr}=4\pi n(r) \; , \tag{15}$$

which holds for $r>0$ and follows from Eq. (14). Its right-hand side can be expressed in terms of $V(r)+\mu$ with the aid of Eqs. (13) and (12), where the latter formula is useful in the region(s) where $|\zeta(r)|<1$. Thus we obtain a differential equation for the potential $V(r)$. The values of the potential and its derivative are known at the edge of our spherical atom:

$$V(r_0)=\frac{Z-N}{r_0}, \quad \frac{dV}{dr}(r_0)=-\frac{Z-N}{r_0^2} \; . \tag{16}$$

Moreover, $V(r)$ fulfills another condition at $r=0$, viz.,

$$rV(r)|_{r=0}=Z \tag{17}$$

[cf. Eq. (14)].

In the case where $|\zeta(r)|<1$ in the whole atom [Eq. (12) holds there], we are able to solve Eq. (15) for a given atomic radius r_0, simultaneously finding μ and the distribution $V(r)$. At the next step we can obtain $n(r)$ and $\zeta(r)$, which allows us to calculate the corresponding atomic energy $E[n,\zeta]$ denoted as $E(Z,N,B,r_0)$. The atomic radius r_0 has to be chosen in such a way that the atomic energy $E(Z,N,B,r_0)$ is minimal. The necessary condition is

$$\frac{\partial E(Z,N,B,r_0)}{\partial r_0}=0 \; . \tag{18}$$

The derivative $\delta E(Z,N,B,r_0)/\partial r_0$ can be calculated in the same way as in the original TF and TFD models [17]. We differentiate Eq. (9) with respect to r_0, remembering that the value of r_0 affects the distributions $n(r)$, $\zeta(r)$ not only by restricting their argument to the interval $0\le r\le r_0$, but also by influencing their shapes (which leads to nonzero $\partial n/\partial r_0$ and $\partial\zeta/\partial r_0$). Next, Eqs. (12) and (13) are employed together with the normalization condition (1) differentiated with respect to r_0. Finally, we arrive at the result

$$\frac{1}{4\pi r_0^2}\frac{\partial E(Z,N,B,r_0)}{\partial r_0}=-n^2\frac{\partial}{\partial n}\left[\frac{F(n,\zeta)}{n}\right]\Bigg|_{r_0}=0 \; . \tag{19}$$

Physically, this equation is equivalent to the statement that the external pressure equal to

$$-(4\pi r_0^2)^{-1}\partial E(Z,N,B,r_0)/\partial r_0$$

vanishes. The expression (19) is the same as for the pressure in the homogeneous electron gas. From Eqs. (19) and (12) one can find both $n(r_0)$ and $\zeta(r_0)$. These, combined with Eqs. (13) and (16), give the value of the chemical potential:

$$\mu=-\frac{Z-N}{r_0}+F(n(r_0),\zeta(r_0)) \tag{20}$$

depending on r_0. Then, solving Eqs. (15) with the boundary conditions (16) and (17), one obtains r_0 and $V(r)$ corresponding to the minimum of the energy functional.

If $\zeta(r)$ changes its character at some internal boundary point $r=r_1$ $(r_1<r_0)$, e.g., $|\zeta(r)|<1$ for $r<r_1$ and $\zeta(r)=1$ for $r>r_1$, we need the matching conditions at this point:

$$V(r_1^-)=V(r_1^+), \quad \frac{dV}{dr}(r_1^-)=\frac{dV}{dr}(r_1^+) \; ; \tag{21}$$

they express the continuity of the potential and the electric field. To find the value of r_1 that corresponds to the minimum of the atomic energy, we demand that $\partial E/\partial r_1$ vanish. This finally leads to the equation

$$n^2\frac{\partial}{\partial n}\left[\frac{F(n,\zeta)}{n}\right]\Bigg|_{n=n(r_1^-),\zeta=\zeta(r_1^-)} =n^2\frac{\partial}{\partial n}\left[\frac{F(n,\zeta)}{n}\right]\Bigg|_{n=n(r_1^+),\zeta=\zeta(r_1^+)} \; , \tag{22}$$

which is derived in a way similar to Eq. (19). Equation (22) can be interpreted as the condition of equal pressure on both sides of the surface $r=r_1$. Employing this equation, together with Eq. (12) and another condition

$$\frac{\partial F}{\partial n}(n(r_1^-),\zeta(r_1^-))=\frac{\partial F}{\partial n}(n(r_1^+),\zeta(r_1^+)) \tag{23}$$

implied by the first of Eqs. (21) and Eq. (13), we can find all the values $n(r_1^-)$, $\zeta(r_1^-)$ and $n(r_1^+)$, $\zeta(r_1^+)$. Then, since Eq. (19) holds also for the presently considered type of atom [thus $n(r_0)$ and $\zeta(r_0)$ are known], both the radii r_0 and r_1 can be determined by solving Eq. (15) with the associated boundary and matching conditions; simultaneously we find $V(r)$, and, consequently, also $n(r)$ and $\zeta(r)$.

III. MAGNETIC THOMAS-FERMI ATOM

This atom, considered as a preliminary case in our model, is obtained by setting $\kappa_a=0$ in Eq. (10) in order to neglect exchange. The TF atom cannot magnetize spontaneously (i.e., it has $\zeta=0$ at $B=0$), since in the absence of exchange the energy functional $E[n,\zeta]$ for $B=0$ depends on ζ only through $\kappa_k(\zeta)$, which is a monotonically increasing function of ζ. For $B>0$, with the TF function

$$F(n,\zeta)=\kappa_k(\zeta)n^{5/3}-\mu_B Bn\zeta \; , \tag{24}$$

[cf. Eq. (10)] we find from the condition (11) that

$$\zeta(r)=1 \quad \text{if } y(r)\le y_m \equiv \left[\frac{\mu_B B}{\kappa_k'(1)}\right]^{1/2} , \tag{25}$$

where $y \equiv n^{1/3}$ and the prime denotes the derivative with respect to ζ. On the other hand, Eq. (19) yields

$$y(r_0)=0 . \tag{26}$$

Thus we conclude that in the magnetic TF atom there exists a fully spin-polarized ($\zeta=1$) region near the atomic edge ($r=r_0$). The region spreads from r_0 to some r_1 ($<r_0$); for $r<r_1$ the value of $y(r)$ becomes greater than y_m, so $\zeta(r)$ becomes less than 1. At the boundary point $r=r_1$, we have Eqs. (22) and (23), which, for the TF atom, implies that

$$\begin{aligned} &\zeta(r_1^-)=\zeta(r_1^+)=1 , \\ &y(r_1^-)=y(r_1^+)=y_m , \end{aligned} \tag{27}$$

so both $\zeta(r)$ and $n(r)$ are continuous at this point.

In the considered model it is convenient to introduce new, suitably scaled, variables:

$$x=\frac{b^{1/4}r}{a} , \tag{28}$$

$$f(x)=b^{1/4}r\left[\frac{V(r)+\mu}{b}+1\right] ; \tag{29}$$

we call them the reduced radius and the reduced potential, correspondingly. The parameters b and a are

$$b=\mu_B B , \tag{30}$$

$$a=\tfrac{5}{3}(4\pi)^{-2/3}\kappa_k(1) . \tag{31}$$

In the outer atomic region, $x_1<x<x_0$ ($x_0 \equiv b^{1/4}r_0/a$, $x_1 \equiv b^{1/4}r_1/a$), where $\zeta(x)=1$, Eq. (13) allows us to express y in terms of f (and x):

$$y=b^{1/2}[\tfrac{5}{3}\kappa_k(1)a]^{-1/2}\left[\frac{f}{x}\right]^{1/2} . \tag{32}$$

Thus the Poisson equation (15) takes the form of the standard Thomas-Fermi equation:

$$\frac{d^2f(x)}{dx^2}=\frac{f^{3/2}(x)}{x^{1/2}} ; \tag{33}$$

let us note that both x and $f(x)$ are defined somewhat differently than their original TF counterparts. For $0<x<x_1$, y is related to ζ through Eq. (12) yielding

$$y=b^{1/2}[\kappa_k'(\zeta)]^{-1/2} . \tag{34}$$

Then Eq. (15) gives the differential equation for $f(x)$:

$$\frac{d^2f(x)}{dx^2}=4\pi a^3x[\kappa_k'(\zeta)]^{-3/2} , \tag{35}$$

where ζ is determined from the relation

$$\frac{f}{ax}=\frac{5\kappa_k(\zeta)}{3\kappa_k'(\zeta)}-\zeta+1 , \tag{36}$$

which emerges from Eq. (13). It is not convenient to replace Eqs. (35) and (36) with the resulting differential equation for $\zeta(x)$ itself, since this equation is divergent at $x=x_1^-$, where $\zeta(x)=1$ [cf. Eq. (42)]; however, an equation for $\zeta(r)$ will be suitable in the TFD case (see Sec. IV B).

The boundary conditions are provided by Eqs. (16), (17), and (26), which in terms of $f(x)$ can be rewritten as follows:

$$f(x_0)=0, \quad x_0\frac{df}{dx}(x_0)=-\frac{q}{w} , \tag{37}$$

$$f(0)=\frac{1}{w} , \tag{38}$$

where $q=(Z-N)/Z$ is the degree of the atomic ionization and

$$w=\frac{b^{3/4}}{Z} . \tag{39}$$

After adding to them the matching conditions at $x=x_1$

$$\begin{aligned} &f(x_1^-)=f(x_1^+)=2ax_1 , \\ &\frac{df}{dx}(x_1^-)=\frac{df}{dx}(x_1^+) \end{aligned} \tag{40}$$

obtained from Eqs. (21), (27), (29), and (32), we are able to integrate Eqs. (33) and (35) (backwards, starting at $x=x_0$), and, in effect, find x_0, x_1, and the distribution $f(x)$. This solution depends on the three model parameters Z, N, and B only through their two combinations, q and w.

For neutral atoms ($Z=N$), we conclude from Eqs. (37) and (33) that $x_0=\infty$, just as in the original TF model; moreover, the expansion of $f(x)$ for large x emerging from Eq. (33) has the original TF form

$$f(x)=\frac{144}{x^3}(1+u+f_2u^2+f_3u^3+\dots) , \tag{41}$$

where $u=f_1x^{-\beta}$, $\beta=(-7+\sqrt{73})/2$, and $f_2, f_3, \dots$ are known numbers (cf. e.g., Ref. [5]). This expansion is then employed to start the integration of Eq. (33) at some large x. Thus, in the $Z=N$ case we look for f_1 and x_1 that lead to the distribution $f(x)$ satisfying the conditions (38) and (40).

Once the reduced potential $f(x)$ is determined, one can calculate $n=y^3$ and ζ, as functions of x, from Eqs. (32), (34), and (36). The plot of $\zeta(x)$ in the neutral TF atom is presented for several values of w in Fig. 1. The function $\zeta(x)$ and its derivative $d\zeta(x)/dx$ are continuous, also at $x=x_1$, as is seen in the enlarged part of Fig. 1; cf. also Eq. (27). One can prove that for $x \lesssim x_1$

$$\zeta(x)=1-\left[\left[2a-\frac{df}{dx}(x_1)\right]\Big/(2^{1/3}ax_1)\right]^{3/2}(x_1-x)^{3/2} + O((x_1-x)^{5/2}) . \tag{42}$$

This expansion implies that the higher derivatives $d^2\zeta(x)/dx^2, \dots$ diverge at $x=x_1^-$; for $x=x_1^+$ they all vanish. Near the atomic nucleus ($x=0$) ζ depends

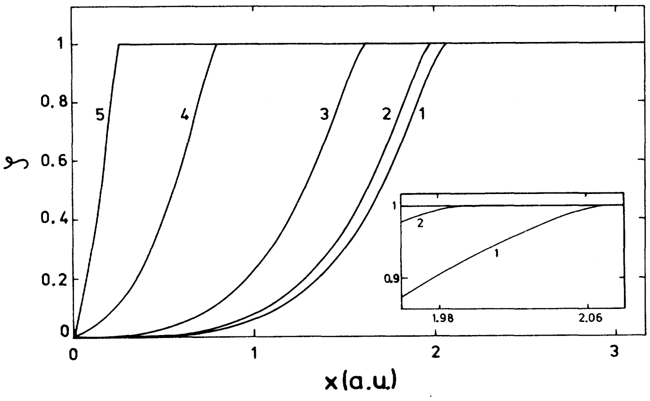

FIG. 1. The relative magnetization ζ as a function of x in the neutral TF atom for $w=0$ (curve 1), $w=10^{-6}$ (curve 2), $w=10^{-3}$ (curve 3), $w=10^{-1}$ (curve 4), and $w=1$ (curve 5); $Z=N=20$. The enlarged part shows the behavior of $\zeta(x)$ in the neighborhood of the boundary point x_1 $[=x_1(w)]$ for curves 1 and 2.

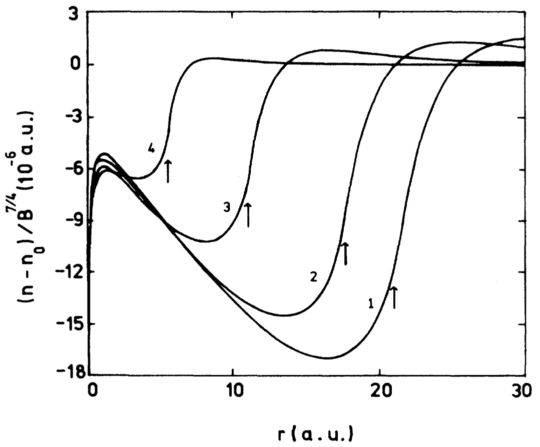

FIG. 2. The change of the electron density $n(r)-n_0(r)$ related to $B^{7/4}$, due to the magnetic field B in the neutral TF atom $[n_0(r)$ is the corresponding TF electron density at $B=0]$; $B=10^6$ G (curve 1), $B=2\times10^6$ G (curve 2), $B=10^7$ G (curve 3), $B=10^8$ G (curve 4); $Z=N=20$. The vertical arrows show the positions of r_1. The atomic unit (a.u.) of the distance r is the Bohr radius $a_0=0.529$ Å; the atomic unit (a.u.) of the electron density is $a_0^{-3}\approx 6.75$ Å^{-3}.

linearly on x (and also on r), although this is not evident in Fig. 1 because of the figure's scale [see also Eq. (57) and Fig. 7 referring to the magnetic TFD atom in Sec. IV where this linear dependence of $\zeta(r)$ is preserved when the exchange is switched on]. For $Z=N$ the distribution $\zeta(x)$ tends to some boundary form as w approaches 0; simultaneously, f_1 and x_1 attain the following limits:

$$\begin{aligned} f_1(w=0)&=-2.050\,786\,278\,009\ , \\ x_1(w=0)&=2.070\,608\,230\,048 \end{aligned} \tag{43}$$

[it should be noted that to solve the problem for $q=0$, $w=0$ we have to replace Eq. (38) by the condition $f(x)\to\frac{125}{3}\pi^{-2}a^{-3}\kappa_{k0}^{3}x^{-3}$ for $x\to0$, derived from Eqs. (35) and (36) for this case]. This implies that in the limit of small B we have

$$r_1\approx x_1(w=0)ab^{-1/4}\ . \tag{44}$$

On the other hand, in the $Z>N$ case, when $r_0(B=0)$ is finite, r_1 is close to r_0 at small B: $r_0-r_1\approx 2br_0^2(Z-N)^{-1}$.

If the electron density n is considered as a function of r, it differs from the original ($B=0$) TF electron density $n_0(r)$ only very slightly, even at fields B of millions of G. The difference between these densities is found to be of the order of $B^{7/4}$; the proportionality $n(r)-n_0(r)\propto B^{7/4}$ holds especially well at small r, where $\zeta(r)$ is small; cf. Fig. 2. At very small r the density difference diverges as $r^{-1/2}$, but it is still a very small fraction of $n_0(r)$, which, in turn, is proportional to $r^{-3/2}$. For a more detailed discussion of this unphysical behavior, see Sec. IV D 2 treating the TFD atom.

The obtained distributions $n(r)$ and $\zeta(r)$ can be used to calculate the magnetic moment of the atom

$$M=\int m(r)d\mathbf{r}=4\pi\int_0^{r_0}\mu_B n(r)\zeta(r)r^2dr\ . \tag{45}$$

The distribution of the radial magnetization density $4\pi r^2 m(r)$ in the neutral TF atom is shown in Fig. 3. The introduction of x instead of r as an integration variable in Eq. (45) and employment of the relations (32) and (34) allow us to express M as follows:

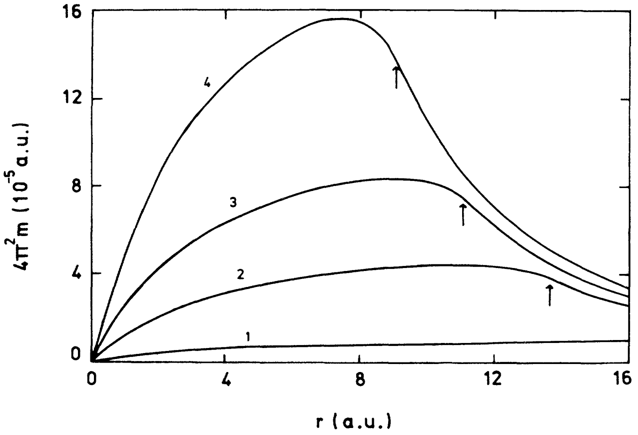

FIG. 3. The radial magnetization density $4\pi r^2 m(r)$ in the neutral TF atom plotted as a function of r for several magnetic fields: $B=10^6$ G (curve 1), $B=5\times10^6$ G (curve 2), $B=10^7$ G (curve 3), $B=2\times10^7$ G (curve 4); $Z=N=20$. The vertical arrows show the positions of r_1. The atomic unit (a.u.) of the radial magnetization density is $(2/\alpha)\mu_B a_0^{-1}\approx 518\mu_B$ Å^{-1}; α is the fine-structure constant.

$$M=b^{3/4}4\pi\mu_B a^3\int_0^{x_1}\zeta(x)[\kappa_k'(\zeta(x))]^{-3/2}x^2dx + b^{3/4}\mu_B\int_{x_1}^{x_0}x^{1/2}f^{3/2}(x)dx \ . \tag{46}$$

Thus, for the neutral magnetic TF atom, where $x_0=\infty$, we obtain M proportional to $B^{3/4}$ at small B, since x_1 and the distributions $\zeta(x)$ and $f(x)$, appearing in the above two integrals, have finite $w=0$ limits. This unphysical dependence of M on B, giving infinite susceptibility at $B=0$, is connected with the incorrect behavior of the TF potential $V(r)$ at large r, where $V(r)\propto r^{-4}$ [cf. Eq. (41)], which leads to $r_1\propto B^{-1/4}$. Some other features of the magnetic TF atom will be mentioned below in the discussion of the TFD case.

IV. MAGNETIC THOMAS-FERMI-DIRAC ATOM

A. Problem of spontaneous magnetization

This problem can be specified for the TFD atom assuming $F(n,\zeta)$ equal to (10). We find that there is no spontaneous magnetization of the TFD atom, i.e., $\zeta=0$ if $B=0$. To prove this let us first notice that $F(n,\zeta)$ for $B=0$ is a symmetric function of ζ, which allows us to limit our considerations to non-negative ζ. It can be shown that $F(n,\zeta)|_{B=0}$ attains its *absolute* minimum only either at $\zeta=0$ or $\zeta=1$ depending on the value of n. The latter case is realized at low densities n for

$$F(n,1)<F(n,0), \quad \text{if } n^{1/3}<\frac{\kappa_{a0}}{(2^{1/3}+1)\kappa_{k0}} \ . \tag{47}$$

A fully magnetic atom can be excluded at once, since the condition (47) is not fulfilled in the neighborhood of the atomic nucleus where $n(r)$ is large; it is implied by Eqs. (13) and (14). Another possibility is that the TFD atom in zero magnetic field is built up from two regions: $0<r<r_1$, where $\zeta=0$; and $r_1<r<r_0$, where $\zeta=1$, so that $\zeta(r)$ is a discontinuous function. To analyze this rather unphysical case, we solve Eqs. (19), (22), and (23) in order to find $n(r_0)$, $n(r_1^-)$, and $n(r_1^+)$. These values fulfill the inequality

$$n(r_1^+)\le n(r_0) \ . \tag{48}$$

It also holds in case we allow for more $\zeta=0$ and 1 regions placed in an alternating order in the atom (then r_1 is the internal boundary point nearest $r=r_0$). But $n(r)$ is found to be, at least in the interval $r_1<r<r_0$, a monotonically decreasing function with the increase of r for any $Z\ge N$, so the inequality (48) cannot be satisfied unless $r_1=r_0$. [The monotonic behavior of $n(r)$ comes from the fact that $V(r)$ decreases with the increase of r in the atom, while $n(r)$ found from Eq. (13)—and having the correct value $n(r_0)$ obtained from Eq. (19)—is a monotonically increasing function of the potential $V(r)$.] This means that $\zeta=0$ and 1 regions cannot coexist inside the atom for $B=0$ and $Z\ge N$. Thus $\zeta(r)=0$ remains a solely acceptable solution in the whole atom.

Let us note that the condition $Z\ge N$ agrees with the well-known fact that no negative ions (with $Z-N=-1,-2,\cdots$) are present in the original TFD atom.

B. TFD atom perturbed by an external magnetic field

The onset of the magnetic field $B>0$ implies that the function $F(n,\zeta)$ given in Eq. (21) is no longer symmetric and attains its absolute minimum somewhere within the interval $0<\zeta\le 1$. A local minimum inside this interval may exist, provided that $y\equiv n^{1/3}$ is large enough to satisfy the equation

$$y=y(\zeta)\equiv\frac{\kappa_a'+[(\kappa_a')^2+4\mu_B B\kappa_k']^{1/2}}{2\kappa_k'} \tag{49}$$

for some ζ. Equation (49) follows directly from Eq. (12) for $B>0$ and $y\ge 0$.

Since $\min_{0<\zeta\le 1}Y(\zeta)\equiv Y_{\min}$ is positive, the minimum of $F(n,\zeta)$ for $y<Y_{\min}$ is at $\zeta=1$. However, even for $y>Y_{\min}$ the *absolute* minimum is still at $\zeta=1$ until y achieves some critical value y_c ($>Y_{\min}$). For $y>y_c$ the local minimum $\zeta(y)$, obtained from Eq. (49), becomes the absolute minimum of $F(n,\zeta)$. The critical density $n_c\equiv y_c^3$ fulfills the following equation:

$$F(n_c,\zeta(y_c))=F(n_c,\zeta=1) \ . \tag{50}$$

We solve Eq. (50) for $\zeta_c\equiv\zeta(y_c)$ by substituting $Y^3(\zeta_c)$ for n_c; then we find $n_c=Y^3(\zeta_c)$ (cf. curve 2 in Fig. 4). It should be noticed that for $Y_{\min}<y<Y(\zeta=1)$ there are two solutions $\zeta(y)$ satisfying Eq. (49). Since one can prove that

$$\mathrm{sgn}[\partial^2F/\partial\zeta^2(n,\zeta(y))]=-\mathrm{sgn}[Y'(\zeta(y))] \ ,$$

we always choose the smaller $\zeta(y)$ for which $Y'(\zeta(y))$ is negative, so the minimum condition $\partial^2F/\partial\zeta^2(n,\zeta(y))>0$ is fulfilled.

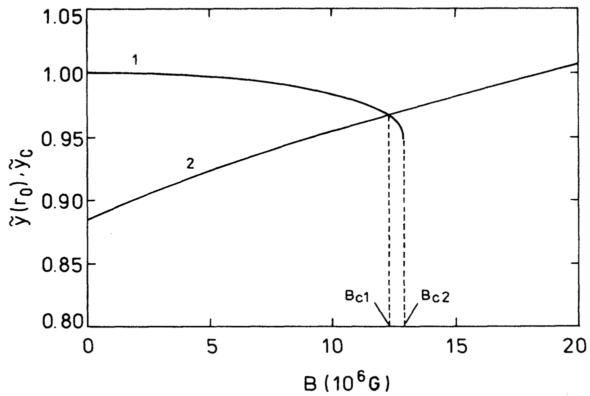

FIG. 4. The boundary value $\tilde{y}(r_0)\equiv y(r_0)/y_{00}$ (curve 1) for the type-I TFD atom compared with the critical value $\tilde{y}_c\equiv y_c/y_{00}$ (curve 2); $\tilde{y}(r_0)$ and $\tilde{y}_c$ depend only on B; the critical fields B_{c1} and B_{c2} are given in Eqs. (59) and (60); $y_{00}=\frac{1}{2}\kappa_{a0}/\kappa_{k0}$.

At small distances r the TFD density $n(r)$ becomes large because of $V(r)\approx Z/r$ appearing in Eq. (13). This implies $0<\zeta(r)<1$ for small r. Thus, as the simplest case, we consider an atom with $0<\zeta(r)<1$ everywhere inside the atom; both Eqs. (12) and (13) are then satisfied. We call it the *type-I atom*.

According to the relation (49), Eq. (13) leads to the following dependence:

$$V(r)+\mu=G(\zeta(r)) \ , \tag{51}$$

where

$$G(\zeta)=\tfrac{5}{3}\kappa_k(\zeta)Y^2(\zeta)-\tfrac{4}{3}\kappa_a(\zeta)Y(\zeta)-\mu_B B\zeta \ . \tag{52}$$

Equations (49) and (51) combined with the Poisson equation (15) give the second-order differential equation for $\zeta(r)$:

$$G'(\zeta(r))\left[\frac{d^2\zeta(r)}{dr^2}+\frac{2}{r}\frac{d\zeta(r)}{dr}\right]+G''(\zeta(r))\left[\frac{d\zeta(r)}{dr}\right]^2=4\pi Y^3(\zeta(r)) \ , \tag{53}$$

where the derivatives $G'(\zeta)$ and $G''(\zeta)$ are known analytical expressions because of Eqs. (52) and (49). The boundary value $\zeta(r_0)=\zeta_0(B)$ depends only on B and can be determined by combining Eq. (49) with the dependence of $y(r_0)$ on ζ_0 obtained from Eq. (19):

$$Y(\zeta_0)=y(r_0)=\frac{\kappa_a(\zeta_0)}{2\kappa_k(\zeta_0)} \ . \tag{54}$$

The other boundary condition at $r=r_0$ is obtained from the second equation (16) which, in view of Eq. (51), becomes

$$\frac{d\zeta}{dr}(r_0)=-[G'(\zeta_0)]^{-1}\frac{Z-N}{r_0^2} \ . \tag{55}$$

Since $G'(\zeta)$ is less than zero for $0<\zeta\le\zeta_0$, Eq. (51)—along with the negative value of $dV(r)/dr$ for $Z\ge N$—implies the monotonic increase of $\zeta(r)$ with r within the whole atom. To find the unknown atomic radius r_0 we need the third boundary condition

$$\lim_{r\to 0}\frac{\zeta(r)}{r}=\frac{3\mu_B B}{2Z} \tag{56}$$

equivalent to Eq. (17). Equation (56) is readily obtained from Eq. (12) provided that we use the expansion $\kappa_k'(\zeta)=\frac{10}{9}\kappa_{k0}\zeta+O(\zeta^3)$ and simultaneously put $y(r)=[3Z/(5\kappa_{k0})]^{1/2}r^{-1/2}$. The latter relation, valid for very small r, follows from Eq. (13), where $V(r)\approx Z/r$. [We assumed $\zeta(r)\approx 0$ at $r\to 0$, which, in fact, is a result obtained from Eq. (12) when $y(r)$ increases infinitely as $r\to 0$.]

Starting at $r=r_0$ and then integrating Eq. (53) backwards to $r=0$ we can find such r_0 that the condition (56) will be fulfilled. Equation (56) provides the leading term of the small-r expansion

$$\begin{aligned}\zeta(r)&=\sum_{i=2}^{\infty}\zeta_i r^{i/2}\\&=\frac{3\mu_B B}{2Z}r-\left[\frac{3\kappa_{a0}^2}{5\kappa_{k0}Z^3}\right]^{1/2}\mu_B B r^{3/2}+\zeta_4 r^2\\&\quad+\left[\left[-\frac{24\pi}{5}+\frac{2\kappa_{a0}^3}{15Z^2}\right]\left[\frac{3}{5\kappa_{k0}^3 Z}\right]^{1/2}\mu_B B\right.\\&\quad\left.+\left[\frac{3\kappa_{a0}^2}{5\kappa_{k0}Z}\right]^{1/2}\zeta_4\right]r^{5/2}\ \cdots \ ;\end{aligned} \tag{57}$$

further terms can be found from Eq. (53) when the small-ζ expansions of $Y(\zeta)$ and $G(\zeta)$ are employed. The coefficients ζ_2 and ζ_3 are fully defined by Z and B, while ζ_5 as well as higher coefficients depend also on ζ_4. The value of ζ_4 can be determined only after the full problem of the differential equation with its boundary conditions is solved. This situation is similar to that for the coefficient ψ_2 entering the expansion

$$\psi(x)=1+\psi_2 x+\psi_3 x^{3/2}+\cdots \tag{58}$$

of the reduced potential $\psi(x)$ in the original TF and TFD model [5,17]. Note that the expansion (57) holds also in the TF case, provided κ_{a0} entering ζ_i's is set equal to 0.

Equation (54) has two solutions for ζ_0. The larger of them cannot be accepted because the boundary value $y(r_0)=Y(\zeta_0)$ is then less than y_c. On the other hand, the smaller ζ_0 satisfies the required condition $y(r_0)=Y(\zeta_0)>y_c$, provided that B is less than

$$B_{c1}=1.232\,038\,295\times 10^7 \text{ G} \tag{59}$$

(cf. Fig. 4). In some interval of $B>B_{c1}$ we still have the solution for the type-I atom, but then certainly it does not correspond to the absolute minimum of the energy functional $E[n,\zeta]$. For B exceeding the critical value

$$B_{c2}=1.296\,057\,327\times 10^7 \text{ G} \ , \tag{60}$$

Eq. (54) has no solution for ζ_0, so the type-I atom ceases to exist. Therefore, we are led to the concept of the atoms other than those of the type I that have some region(s) with constant $\zeta=1$.

The simplest atom of this kind, discussed generally in Sec. II B, is the *type-II atom* for which we assume $\zeta(r)=1$ in some region $r_1<r<r_0$ near the atomic boundary, while $0<\zeta(r)<1$ is in the remaining part of the atom $(0<r<r_1)$. It resembles the magnetic TF atom presented in Sec. III. However, in the present atom, unlike in the TF atom, $\zeta(r)$ is not continuous at $r=r_1$ for $B>0$, as it follows from Eqs. (22), (23), and (12) yielding $\zeta(r_1^-)<1$. Also the electron density $n(r)$ shows the discontinuity at this point. This is the combined effect of the local-density approximations adopted for the kinetic and exchange energies in the TFD model. For the same reason the TFD density is discontinuous at $r=r_0$. The finite boundary density may be, however, a desirable feature if we treat the TFD atom as a part of a solid (cf. Sec. IV D). But even in this case, the discontinuity of the density inside the type-II atom (at $r=r_1$) is hardly acceptable from the physical point of view. Therefore, we will discuss this unphysical type of atom only briefly. Now, let us mention that the type-II model can be solved following the general lines presented in Sec. II B. Similarly, as in the type-I case, it is convenient to replace for $0<r<r_1$ [where $\zeta(r)<1$] Eq. (15) for $V(r)$ by the corresponding equation (53) for $\zeta(r)$.

There exist no other atomic types than I and II in our model. If they existed, the atom would contain some region $r_s<r<r_f$, where $\zeta(r)=1$, which would be surrounded by two other regions with $0<\zeta(r)<1$. Then, one could find from Eqs. (22), (23), and (12), applied at $r=r_s$ and $r=r_f$, that the values of $y(r_s^+)$ and $y(r_f^-)$ are equal. This, however, contradicts the monotonicity of $y(r)$ in the interval $r_s<r<r_f$. The latter property is a consequence of the monotonic decrease of the potential $V(r)$ within an atom (for $Z\geq N$) and the monotonic dependence of $y(r)$ on $V(r)$ obtained from Eq. (13) with $\zeta(r)=1$.

C. Expansion for small *B*

Now we would like to determine the response of the TFD atom to a weak magnetic field B. For such a field, ζ is small in the whole volume of the type-I atom and depends linearly on B:

$$\zeta(r)=[\tfrac{10}{9}\kappa_{k0}y_0^2-\tfrac{4}{9}\kappa_{a0}y_0(r)]^{-1}\mu_B B \equiv\lambda_\zeta(r)B \ , \tag{61}$$

as it follows from Eq. (12). Here $y_0(r)$ denotes the cubic root of the unperturbed density $n_0(r)$ in the original TFD model ($B=0$). Other quantities, viz., $y(r)$, $V(r)$, μ, and r_0, also show a simple dependence on B. Since they do not change when B changes its sign, these quantities should depend quadratically on B:

$$\begin{aligned} y(r)&=y_0(r)+\lambda_y(r)B^2 \ ,\\ V(r)&=V_0(r)+\lambda_V(r)B^2 \ ,\\ r_0&=r_{00}+\lambda_{r_0}B^2 \ ,\\ \mu&=\mu_0+\lambda_\mu B^2 \ , \end{aligned} \tag{62}$$

provided that they are analytical functions of B; the symbols $V_0(r)$, r_{00}, and μ_0 denote the corresponding quantities in the original TFD model. For the type-I atom the relations (62) can be rigorously proved with the aid of Eqs. (61), (13), and (15). These equations lead to the following relation between the coefficient functions $\lambda_y(r)$ and $\lambda_V(r)$:

$$\begin{aligned} \lambda_y(r)={}&A_0^{-1}(r)[\lambda_V(r)+\lambda_\mu]\\ &+\mu_B^2y_0^{-2}(r)A_0^{-3}(r)\\ &\times[\tfrac{5}{3}\kappa_{k0}y_0^2(r)-\tfrac{4}{3}\kappa_{a0}y_0(r)] \ , \end{aligned} \tag{63}$$

where $A_0(r)=\frac{10}{3}\kappa_{k0}y_0(r)-\frac{4}{3}\kappa_{a0}$. From the Poisson equation (15) it follows that

$$\Delta\lambda_V(r)=12\pi y_0^2(r)\lambda_y(r) \ , \tag{64}$$

which leads to the second-order differential equation for

$$\Gamma(r)\equiv r[\lambda_V(r)+\lambda_\mu] \ , \tag{65}$$

viz.,

$$\begin{aligned} \frac{d^2\Gamma(r)}{dr^2}={}&12\pi y_0^2(r)A_0^{-1}(r)\Gamma(r)\\ &+12\pi\mu_B^2rA_0^{-3}(r)\\ &\times[\tfrac{5}{3}\kappa_{k0}y_0^2(r)-\tfrac{4}{3}\kappa_{a0}y_0(r)] \ . \end{aligned} \tag{66}$$

The quantity $\Gamma(r)$ fulfills the boundary conditions:

$$\begin{aligned} &\Gamma(r=0)=0 \ ,\\ &\Gamma(r_{00})=-\frac{9\kappa_{k0}}{\kappa_{a0}^2}\mu_B^2r_{00}+\frac{Z-N}{r_{00}}\lambda_{r_0} \ ,\\ &r_{00}\frac{d\Gamma}{dr}(r_{00})-\Gamma(r_{00})=-4\pi\left[\frac{\kappa_{a0}}{2\kappa_{k0}}\right]^3r_{00}^2\lambda_{r_0} \ , \end{aligned} \tag{67}$$

which can be found on the basis of Eqs. (17), (63), (54), and (16). Together with Eq. (66), the three boundary conditions (67) allow us to find the distribution $\Gamma(r)$ and the coefficient λ_{r_0}. Then we can calculate $\lambda_y(r)$ with the help of Eq. (63), and also obtain $\lambda_V(r)=\Gamma(r)/r-\lambda_\mu$, since λ_μ can be expressed in terms of λ_{r_0} and Z, N, and B.

The range of fields B, where the approximation of a weak magnetic field can be applied, may be estimated from the requirement that $\zeta(r)$ should be small. Since $\zeta(r)$ has its largest value at the atomic boundary $r=r_0$ we calculate $\zeta(r_0)\approx\zeta(r_{00})$ with the help of Eq. (61) and $y_0(r_{00})=\frac{1}{2}\kappa_{a0}/\kappa_{k0}$ [cf. Eq. (54)]. To satisfy the requirement that $\zeta(r_0)\approx 18\kappa_{k0}\kappa_{a0}^{-2}\mu_B B$ should be less than 0.1, it is sufficient for B not to exceed 4.8×10^6 G, which is a very large value from the experimental point of view.

The type-II atom is qualitatively different from the type-I atom. The essence of the difference is that a certain boundary region having a totally spin-polarized electron density ($\zeta=1$) exists even for very weak B. This leads to a different behavior of physical quantities than in the type-I atom. The relations (62) are, in general, not fulfilled. Especially, for small B the increase of the atomic radius r_0-r_{00} (approximately equal to $r_{00}-r_1$) is found to be proportional to $B^{1/2}$ for $Z=N$ and to B for $Z>N$. This is in contradiction with the quadratic dependence $v_0(B)-v_0(B=0)\propto B^2$ obtained experimentally [22,23] for the atomic volume $v_0=\frac{4}{3}\pi r_0^3$. This provides further evidence that the type-II atom cannot be applied to represent real atoms. For this purpose we will use only the type-I atom, also because the interval of B for which the type-I atom exists covers the region of the presently experimentally accessible magnetic fields—at least the static ones.

D. Results and applications

The model TFD atom can be interpreted as a part of a metal. This assumption emerges naturally when the energy functional of the form given in Eq. (6) is applied to the whole of the metal; Z/r is then replaced by the sum of the potentials $Z/|\mathbf{r}-\mathbf{R}_j|$ produced by the nuclei located at points $\mathbf{R}_j$. In fact, with the spherical-cell approximation the total metal energy falls down into the sum of the energies of the spherical cells, since, being electrically neutral ($Z=N$), these cells do not interact. Then we can deal with a single atomic cell described by the energy functional (6). Such a cell has a finite radius and the vanishing density gradient $\nabla n(r)$ at its boundary ($r=r_0$), as it should. A theoretical positive ion ($Z>N$) can be thought to describe a single metal cell just after the ionization act, i.e., before the neighboring cells polarize their densities according to the potential created by the ion.

1. Atomic radius

The radius r_0 of the type-I atom increases with B in the whole allowed region: $0 \le B \le B_{c2}$ (cf. Fig. 5). The maximum value of $r_0 - r_{00}$ does not exceed 1.5% of r_{00}, which is the atomic radius for $B=0$. For a given B and neutral atoms ($Z=N$), the value of r_0-r_{00} is almost independent of Z: it changes by less than 3% in the interval $10 \le Z \le 100$. On the other hand, for positive ions ($Z>N$) this dependence on Z is much stronger. In Fig. 5 the exact r_0 is compared with the approximate $r_0 \approx r_{00} + \lambda_{r_0} B^2$ obtained from the expansion for small B [cf. Eq. (62)]. We see that the approximation is valid with a good accuracy for B less than 5×10^6 G. From the experimental point of view this is a very strong field, so the results of the approximate theory can be compared with experiment. In particular, we obtain the following coefficient for the volume magnetostriction:

$$\frac{v_0 - v_{00}}{v_{00}B^2} = \frac{3\lambda_{r_0}}{r_{00}}\ , \tag{68}$$

where $v_{00} \equiv v_0(B=0) = \frac{4}{3}\pi r_{00}^3$. The theoretical coefficient (68) slowly decreases with the increase of Z. A similar decrease is observed for the experimental data when they are compared within the subgroups of the periodic table (cf. Fig. 6). The comparison within the subgroups seems to be realistic because the model does not describe the atomic shell structure, but this structure does not change essentially for elements belonging to the same subgroup. The shell structure is of importance, however, when the *absolute* values of the atomic properties are considered. This may be the case for the magnetostriction coefficient whose theoretical values are generally not satisfactory (cf. Fig. 6).

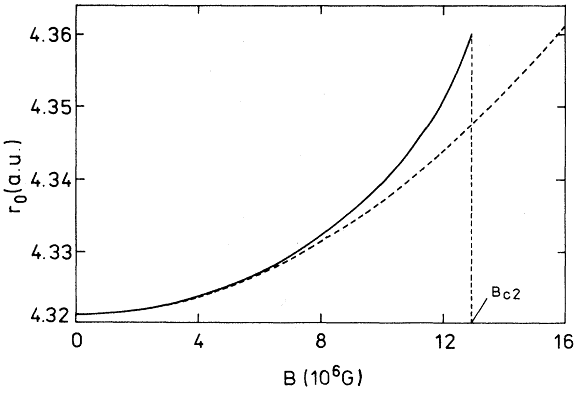

FIG. 5. The radius r_0 [in atomic units (a.u.)] of the type-I TFD atom plotted in the interval of allowed B [$0 \le B \le B_{c2}$; cf. Eq. (60)]; $Z=N=20$. Solid line, exact calculations; dashed line, the results of the quadratic approximation of the theory developed for small B; cf. Eq. (62). The atomic unit (a.u.) is the Bohr radius $a_0 \approx 0.529$ Å.

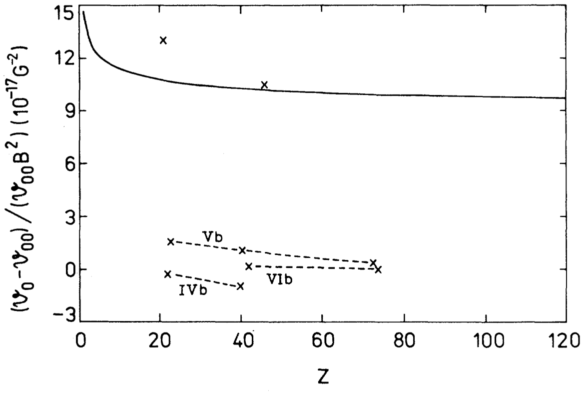

FIG. 6. The coefficient for the volume magnetostriction $(v_0-v_{00})/(v_{00}B^2)$ [cf. Eq. (68)] vs the atomic number Z calculated in the type-I TFD-atom model ($Z=N$) and compared with the experimental data [22,23] (cross points). The dashed line IVb links the experimental points corresponding to the elements from the subgroup IVb of the periodic table [Ti ($Z=22$) and Zr ($Z=40$)], the line Vb, from the subgroup Vb [V ($Z=23$), Nb ($Z=41$), and Ta ($Z=73$)] and the line VIb, from the subgroup VIb [Mo (42), W (74)]. The unlinked cross points correspond to Sc ($Z=21$) and Pd ($Z=46$).

The type-II model gives an unphysical dependence of $r_0 - r_{00} \approx r_{00} - r_1$ on the weak field B; cf. Sec. IV C. For very strong B, the type-II atom tends to the totally magnetic state ($\zeta=1$), which means that r_1 approaches zero. In this case r_0 tends to the finite value $r_0(\tilde{\zeta}=1)$, which is the radius of the atom having $\zeta(r)=\tilde{\zeta}=1$ everywhere constant [the TFD atom with constant $\zeta(r)$ is discussed in Refs. [24 and 25]].

2. Distribution of spin-polarized density: Spin susceptibility

Here we examine the influence of the magnetic field B on the distributions $\zeta(r)$ and $n(r)$. The dependences of $\zeta(r)$ in a neutral type-I atom for several values of B are presented in Fig. 7. As was proved before, for any B we have a monotonic increase of $\zeta(r)$ in the whole atom ($0 \le r \le r_0$). The increase of $\zeta(r)$ is larger, the closer r is to the atomic edge. For very small r the quantity $\zeta(r)$ falls down linearly to zero [cf. Eq. (56)], as is seen in the enlarged part of Fig. 7. To the first approximation, $\zeta(r)$ depends linearly on B at any r [cf. Eq. (61)]; the ratio $\zeta(r)/B$ tends then to the distribution $\lambda_\zeta(r)$ [cf. Eq. (61)].

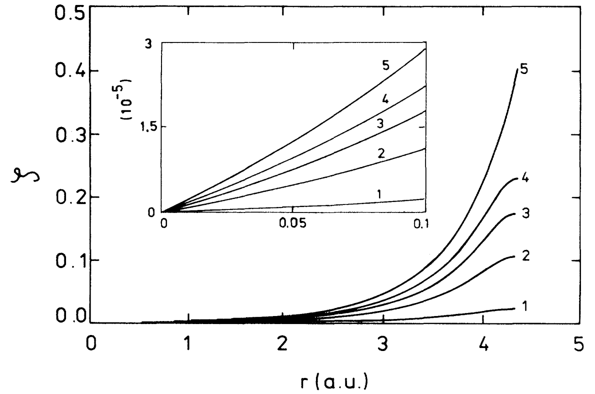

FIG. 7. The dependence of ζ on r in the type-I TFD atom for several magnetic fields: $B=10^6$ G (curve 1), $B=5\times10^6$ G (curve 2), $B=8\times10^6$ G (curve 3), $B=10^7$ G (curve 4), $B=B_{c2}$ (curve 5); $Z=20$; r is given in a.u. equal to the Bohr radius a_0. The enlarged part shows the behavior of $\zeta(r)$ near the atomic nucleus, where $\zeta(r)$ is proportional to Br; cf. Eq. (57).

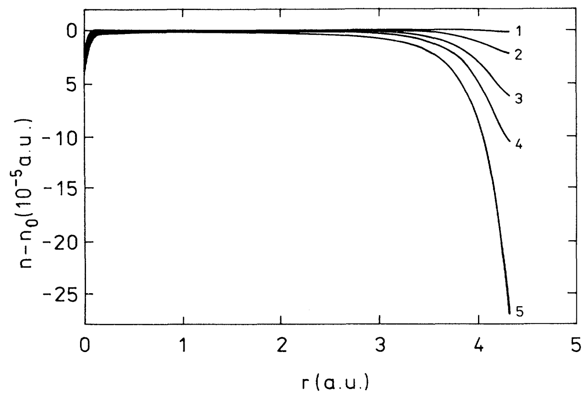

FIG. 8. The decrease of the electron density $n(r)-n_0(r)$ due to the magnetic field B in the type-I TFD atom. $B=2\times10^6$ G (curve 1), $B=5\times10^6$ G (curve 2), $B=8\times10^6$ G (curve 3), $B=10^7$ G (curve 4), $B=B_{c2}$ (curve 5); $Z=N=20$. The atomic unit (a.u.) of the electron density is $a_0^{-3}\approx6.75$ Å^{-3}.

For $0\leq B\leq5\times10^6$ G the difference $\zeta(r)/B-\lambda_\zeta(r)$ is less than 3% of $\lambda_\zeta(r)$ in the whole atomic volume. This presents another premise for the use of the theory for small B in applications. The dependence $\zeta(r)$ is similar for different Z. It is simply pushed to the right with little distortion when Z increases. This is so because the boundary value $\zeta(r_0)$ is independent of Z, while the atomic radius r_0 increases with Z. In positive ions $(Z>N)$ the distributions $\zeta(r)$ are, in general, similar to those obtained in the $Z=N$ case, but the region of large $\zeta(r)$ occurring near the atomic edge $(r=r_0)$ is narrower, which makes the distribution steeper in this region.

The expansion of an atom due to magnetic field implies some decrease of the electron density inside the atom. In fact, in the whole volume of the type-I atom $n(r)$ calculated for $B>0$ is less than the original density $n_0(r)$ (see Fig. 8); more precisely, this is true for $0\leq r\leq r_{00}$, where $n_0(r)>0$. The absolute value of the difference $n(r)-n_0(r)$ is the largest in the immediate neighborhood of the nucleus and it diverges at $r=0$. This is an unphysical effect caused by the unphysical divergences of $n(r)$ and $n_0(r)$. For small r both the densities behave, in the first approximation, like the term $r^{-3/2}$ multiplied by the same coefficient, and their difference is

$$\begin{aligned} n(r)-n_0(r)&=3\left[\frac{3Z}{5\kappa_{k0}}\right]^{3/2}\left[\frac{2\kappa_{a0}^2}{15\kappa_{k0}Z}-\frac{Z}{3\mu_B B}\zeta_4-\frac{3(4\pi)^{2/3}Z^{1/3}}{10\kappa_{k0}}\psi_2\right]r^{-1/2}\\ &\approx\left[\frac{9}{10}\left[\frac{3Z}{5\kappa_{k0}^3}\right]^{1/2}\frac{d\Gamma}{dr}(r=0)B^2\right]r^{-1/2}\;. \end{aligned} \tag{69}$$

The result at the first step is attained from the expansion of $n(r)$ for small r done with the aid of Eqs. (49) and (57); the expansion of $n_0(r)$ is obtained from the expansion (58) of the reduced potential in the original TFD model [the first equality in Eq. (69) also holds in the TF atom considered in Sec. III if we set $\kappa_{a0}=0$]. The second step in Eq. (69) is derived from the approximations of the theory for small B. Although the difference $n(r)-n_0(r)$ is large near the nucleus, it is negligible in comparison with $n_0(r)$ or $n(r)$. In consequence, the magnitude of the relative density difference $[n(r)-n_0(r)]/n_0(r)$ is the largest at the atomic edge $(r=r_0)$ and decreases rapidly for $r<r_0$, attaining zero at $r=0$. However, for any B admitted for the type-I atom, the difference $n(r)-n_0(r)$ is everywhere a very small fraction of the original density $n_0(r)$, so the general shape of the electron distribution remains unchanged under the influence of a magnetic field. Similarly to the case of $\zeta(r)$, the approximation of small B reproduces very well the exact $n(r)-n_0(r)$ in the whole atomic volume for fields $0\leq B\leq5\times10^6$ G. The distributions $n(r)-n_0(r)$ do not change qualitatively with Z. They are also similar to those obtained in the case of the positive type-I ions $(Z>N)$, though the boundary region where the difference is large is, as for $\zeta(r)$, much narrower for ions than for neutral atoms.

In Fig. 9 we present the distributions of $4\pi r^2 m(r)$, where $m(r)$ is the magnetization density [cf. Eq. (4)]. The largest contribution to the magnetic moment M,

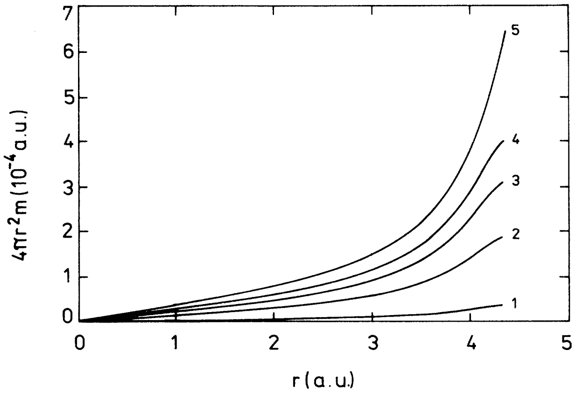

FIG. 9. The radial magnetization density $4\pi r^2 m(r)$ in the type-I TFD atom plotted as a function of r for several magnetic fields: $B=10^6$ G (curve 1), $B=5\times10^6$ G (curve 2), $B=8\times10^6$ G (curve 3), $B=10^7$ G (curve 4), $B=B_{c2}$ (curve 5); $Z=N=20$. The atomic unit (a.u.) of the radial magnetization density is $(2/\alpha)\mu_B a_0^{-1}\approx 518\mu_B$ Å^{-1}; α is the fine-structure constant.

defined in Eq. (45), comes from the outer regions of the atom, i.e., from the least-bound electrons. The substitution of $\lambda_\zeta(r)B$ for $\zeta(r)$, $n_0(r)$ for $n(r)$, and r_{00} for r_0 in Eq. (45) gives the linear dependence of $M(B)$, viz.,

$$M(B)=\chi_{\mathrm{at}}^{\mathrm{sp}}B \ , \tag{70}$$

its coefficient being

$$\chi_{\mathrm{at}}^{\mathrm{sp}}=36\pi\mu_B^2\int_0^{r_{00}}\frac{n_0^{2/3}(r)}{10\kappa_{k0}n_0^{1/3}(r)-4\kappa_{a0}}r^2dr \ . \tag{71}$$

Again, the approximation of small B turns out to be quite accurate.

The quantity $\chi_{\mathrm{at}}^{\mathrm{sp}}$ is a theoretical magnetic susceptibility coming from the electron spins of a single atom. For the molar spin susceptibility $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ of a metal we take $N_A\chi_{\mathrm{at}}^{\mathrm{sp}}$, where N_A is the Avogadro number. The calculated $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ is always positive and increases monotonically with the atomic number Z. This agrees with the behavior of the experimental values of the spin susceptibility obtained for the subgroup of the alkali metals (cf. Fig. 10); on average the theory overestimates $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ by about 30% of the experimental value.

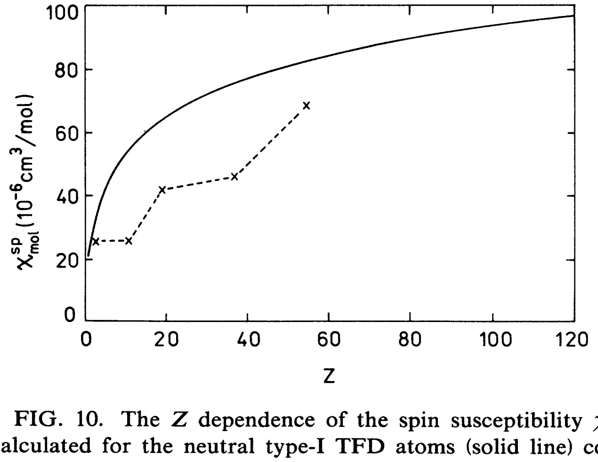

FIG. 10. The Z dependence of the spin susceptibility $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ calculated for the neutral type-I TFD atoms (solid line) compared with the experimental data [31] for alkali metals: Li ($Z=3$), Na ($Z=11$), K ($Z=19$), Rb ($Z=37$), Cs ($Z=55$) (cross points linked with a dashed line).

In the case of the neutral type-II atom, its magnetic moment M is proportional to $B^{1/2}$ at weak B, since the same dependence holds for the width of the interval $r_1<r<r_0$, where $\zeta(r)=1$. Thus the spin susceptibility of this atom diverges at $B\to0$, which is another unphysical feature. For large fields B the magnetic moment M tends to its maximum value $\mu_B N$. In fact, the atom becomes almost magnetically saturated only for B of the order of 10^{12} G: For such a strong field M attains 99% of its maximum value.

E. Energy relations

There exist relations among the components of the total energy appearing in Eq. (6). First, the equation

$$E_{ee}=-\tfrac{5}{6}E_{\mathrm{kin}}-\tfrac{2}{3}E_x-\tfrac{1}{2}E_{en}-\tfrac{1}{2}E_B+\tfrac{1}{2}\mu N \ , \tag{72}$$

is obtained by expressing the electronic potential $V_e(r)=-\int n(r')|\mathbf{r}-\mathbf{r}'|^{-1}d\mathbf{r}'$ with the help of the variational equation (13). The other energy relation is the so-called *virial theorem:*

$$E=-E_{\mathrm{kin}}+E_B \ . \tag{73}$$

Its present form differs from that obtained originally for the TFD atom by the term E_B. On the other hand, we can define the *internal* energy $E^0\equiv E-E_B$, which is the total energy apart from the component representing the direct interaction of the spin-polarized electron density with the external field. Then the virial theorem in the form of the equation $E^0=-E_{\mathrm{kin}}$ holds equally for $B=0$ and $\neq0$. The proof of Eq. (73) can be carried out with the standard procedure [17] first introduced by Fock [26]. Thus we consider the distributions

$$n_\lambda(r)=\lambda^3 n(\lambda r), \quad \zeta_\lambda(r)=\zeta(\lambda r) \ , \tag{74}$$

obtained by scaling of $n(r)$ and $\zeta(r)$ with the help of the parameter $\lambda>0$. Consequently, the atomic radius is equally scaled to $r_{0\lambda}=r_0/\lambda$. Nevertheless, the scaled atom has the unchanged electron number N, and $\zeta_\lambda(r)$ fulfills the condition (5). Therefore we can use $n_\lambda(r)$ and $\zeta_\lambda(r)$ as the trial distributions in the energy functional (6). If n and ζ correspond to the minimum of the functional (6), then the energy $E(\lambda)\equiv E[n_\lambda,\zeta_\lambda]$ attains its minimum at $\lambda=1$. Since

$$E(\lambda)=\lambda^2E_{\mathrm{kin}}+\lambda E_x+\lambda E_{en}+\lambda E_{ee}+E_B \ , \tag{75}$$

where all the energy components on the right-hand side are calculated for $\lambda=1$, the necessary minimum condition $dE/d\lambda(\lambda=1)=0$ immediately leads to Eq. (73). The virial theorem (73) is valid for the TFD atoms of both types I and II. This is so because the trial distributions

$n_\lambda(r)$, $\zeta_\lambda(r)$ represent the same type of atom as the original $n(r)$, $\zeta(r)$; therefore we can apply the variational principle for each atomic type separately. The virial theorem applies also to the magnetic TF atom discussed in Sec. III; to prove this, it is enough to omit E_x in the above discussion.

Let us note that the value of $E(B)-E(B=0)$ for weak B can be obtained from the well-known relation

$$\frac{dE(B)}{dB}=-M(B)\ , \tag{76}$$

which is an example of the Hellmann-Feynman theorem [27,28]. In order to prove Eq. (76) within our density-functional theory, let us consider as trial distributions in the energy functional $E[n,\zeta;B]$ for field B the distributions $n(r;B')$, $\zeta(r;B')$ corresponding to the minimum of the energy functional $E[n,\zeta,B']$ for a different value B' of the magnetic field than the field B. The energy

$$E(B',B)\equiv E[n(r;B'),\zeta(r;B');B]$$

attains its minimum, with respect to B', at $B'=B$, and $E(B'=B,B)=E(B)$. Therefore we have

$$\begin{aligned}\frac{dE(B)}{dB}&=\frac{\partial E}{\partial B'}(B'=B,B)+\frac{\partial E}{\partial B}(B'=B,B)\\&=\frac{\partial E}{\partial B}(B'=B,B)=\frac{\partial E[n,\zeta;B]}{\partial B}\ .\end{aligned} \tag{77}$$

This relation is true for any parameter B appearing in an energy functional. In our case, B is the magnetic field, and the derivative of the energy functional (6) with respect to B gives $-M$ defined in Eq. (45). Equation (76) is valid for each type of TFD atom separately on the grounds of arguments similar to those applied in the case of the virial theorem (75); it is also valid for the TF atom.

Since for the type-I atom M is proportional to B at weak magnetic fields, the integration of Eq. (76) yields the total energy decrease in the usual form

$$E(B)-E(B=0)\approx-\tfrac{1}{2}BM=\tfrac{1}{2}E_B\ . \tag{78}$$

It should be noticed that Eq. (78), combined with the virial theorem (73), also implies a decrease of the electron kinetic energy approximately equal to the term $\frac{1}{2}E_B$. At the same time, an increase of the internal energy E^0 by the term $-\frac{1}{2}E_B$ is observed. In the case of the neutral type-II atom the coefficient $\frac{1}{2}$ in Eq. (78) is replaced by $\frac{2}{3}$, since then $M\propto B^{1/2}$. For the neutral TF atom having $M\propto B^{3/4}$, it is equal to $\frac{4}{7}$.

From the theoretical point of view, a basic question may be, which type of atom, I or II, has a lower energy in the interval $0<B\leq B_{c2}$ where both the atomic types exist? The atom with a lower energy corresponds to the true minimum of the energy functional (6), so according to the basic idea of the density-functional theory, we should choose the low-energy atom to represent a real atom. Unfortunately, it turns out in the numerical calculations that the type-II atom has a lower energy. For weak magnetic fields this result is also implied by the analytically obtained power dependences of $E(B)-E(B=0)$ on B. We explain the energy preference obtained in our model for the unphysical type-II atom by the local-density approximation used for both the kinetic and exchange energies in the energy functional (6). If we had taken a more accurate form of the functional, e.g., that including a Weizsäcker-Kirzhnitz gradient correction [29,30], the discontinuities of $n(r)$ and $\zeta(r)$ occurring at the surface $r=r_1$ of the type-II atom would vanish. Then, we would have only one type of atom, that with continuous distributions $n(r)$ and $\zeta(r)$, which at weak magnetic fields is qualitatively closer to the type-I atom. The discontinuity of $n(r)$ obtained at $r=r_0$ in the type-I atom (similar to that present in the nonmagnetic TFD atom) is only spurious, on condition that this atom is assumed to represent a metal cell, since then the electron density of one cell joins smoothly with that of the neighboring cells.

V. SUMMARY AND DISCUSSION

In this paper we have introduced the electron-spin polarization into the statistical, TF or TFD, atom submitted to an external magnetic field. This extended statistical atom is described with the aid of two distributions: the electron density $n(r)$ and the relative magnetization $\zeta(r)$, which enter the energy functional $E[n,\zeta]$. The minimization of this functional at the zero magnetic field shows that no spontaneous magnetization can occur in the statistical atoms.

At the first step of the calculations, we dealt with the TF atom where exchange phenomena are neglected. This atom contains a totally spin-polarized ($\zeta=1$) region $r_1<r<r_0$ near the atomic edge $r=r_0$ (for the neutral TF atom r_0 is infinite), while for $r<r_1$ the polarization is only partial: $0<\zeta(r)<1$. However, $\zeta(r)$ as well as $n(r)$ are continuous on the internal boundary surface $r=r_1$ and the same applies to the derivatives $d\zeta(r)/dr$, $dn(r)/dr$. The variational equations are most conveniently expressed in terms of reduced variables: x and $f(x)$ with the aid of which r, $n(r)$, and $\zeta(r)$ can be easily calculated. The second-order differential equation for the reduced potential $f(x)$ and the corresponding boundary and matching conditions are obtained. In this description of the model the three parameters Z, N, and B enter in the form of the two combinations q and w. The magnetic moment of the neutral TF atom is found to be proportional to $B^{3/4}$ at weak B; this unphysical prediction is related to the incorrect behavior of the TF potential: $V(r)\propto r^{-4}$ at large r where $\zeta(r)=1$.

At the next step, the exchange energy given by the spin-extended TFD formula is included in $E[n,\zeta]$. Two types of atoms, I and II, emerge then in the model. The atom of type I is represented by smooth distributions of $n(r)$ and $\zeta(r)$. The second-order differential equation for $\zeta(r)$ and three boundary conditions are derived from the variational principle. They allow us to find the atomic radius r_0 and the distribution $\zeta(r)$; we also obtain the relation between $n(r)$ and $\zeta(r)$, which enables us to calculate $n(r)$. In the atom of type II there are unphysical discontinuities of $n(r)$ and $\zeta(r)$ on an internal surface $r=r_1$; also other properties of this atom show unphysical behavior. This type of the magnetic TFD atom evolves from the magnetic TF atom if the exchange is smoothly switched on at some fixed $B > 0$. However, the crude way in which the exchange is treated in the TFD model combined with the TF expression for the kinetic energy, which seems to be an even more drastic approximation, makes the resulting type-II TFD atom, with discontinuous $n(r)$, $\zeta(r)$, even more unphysical than the original magnetic TF atom. However, a positive exchange coefficient κ_{a0} gives, in our model, an alternate, much more physical, solution: the type-I atom. It exists for $0 < B < B_{c2}$; the maximum field B_{c2} is small at small κ_{a0}, but its value for the actual κ_{a0} [cf. Eq. (60)] is very large from the experimental point of view. The duality of the TFD solution would not be present in the case of the better treatment of the atomic energy functional, especially, the treatment of its kinetic part. In fact, $n(r)$ and $\zeta(r)$ become continuous, if a Weizsäcker-Kirzhnitz correction is included. Nevertheless, on the level of local-density energy functional adopted in this paper, the inclusion of the exchange term was crucial for obtaining a physically acceptable solution (i.e., the type-I, TFD-like solution) for a spin-polarized atom in a magnetic field.

For weak fields B the dominant terms in the expansions of r_0 and $n(r)$ with respect to B can be determined in the case of the type-I atom, through a solution of a B-independent differential equation. In this way the coefficient for the volume magnetostriction is obtained. Simultaneously, the relative magnetization $\zeta(r)$ for weak B can be expressed analytically with the aid of the unperturbed TFD density $n_0(r)$. Then the spin susceptibility $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ can be easily calculated through a single integration done for every atomic number Z. Our model predicts in the correct way the tendency of $\chi_{\mathrm{mol}}^{\mathrm{sp}}$ to increase with the increase of Z for elements within the subgroups of the periodic table; the numerical values, however, at least for alkali metals, are not in such good agreement with experiment as the results obtained with the use of the variational principle for the magnetic susceptibility in the method proposed by Vosko, Perdew, and MacDonald [31]. Let us note here that the latter treatment requires the solution of the Kohn-Sham equations, which makes it incomparably more laborious than the present calculation.

The type-II solutions, although their physical meaning is questionable (especially at small B), show that a very strong field, practically of the order of 10^{12} G, is required to polarize almost fully the electron spins in a TFD atom; for weaker B this polarization is considerably smaller. These calculations suggest that the assumption of exactly full spin polarization of the TFD atom in the fields $\sim 10^{12}$ G, made by Banerjee, Constantinescu, and Rehak [18] in their treatment of the orbital effects in the TFD atom, is not obvious. The orbital effects, neglected in our paper, lead to a TFD atomic volume that is much shrunken at very strong magnetic fields, which implies a large increase of the electron density. This density increase should act, as we may expect from our model, towards a considerable decrease of the spin polarization $\zeta(r)$. Therefore, the validity of the full polarization assumed in Banerjee's model can be checked only after the electron spins are included in this model and a full solution of the problem is obtained.

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