Nonconvexity of the atomic charge density and shell structure

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The logarithmic derivative and the second derivative of the spherically averaged charge density $\rho(r)$, denoted as $\rho'(r)/\rho(r)$ and $\rho''(r)$, respectively, are numerically studied in a Hartree-Fock framework for all ground-state atoms from hydrogen ($Z=1$) through uranium ($Z=92$). It is observed that (i) the logarithmic derivative of $\rho(r)$ always attains its absolute minimum at the nucleus for $Z=1-92$, which extends a previous result for $Z\leq 54$, (ii) the second derivative of $\rho(r)$ presents pairs of local minima and maxima, the number of which never decreases with increasing nuclear charge, and (iii) the occurrence of new local maxima and minima in $\rho''(r)$ always corresponds to the addition of an electron in a new subshell. The regularity in the behavior of the local characteristics of $\rho''(r)$ not only suggests an alternative way of studying the atomic shell structure by means of the one-particle density, but also provides further evidence of the hierarchical arrangement of the atomic charge density.

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I. INTRODUCTION

Since the formulation of Hohenberg and Kohn's theorem [1] about the role played by the one-particle density $\rho(\mathbf{r})$ in the physical and chemical description of many-fermion systems, much attention has been paid to the effect which monotonicity properties of $\rho(\mathbf{r})$ have on the relevant quantities of such systems [2,3].

Only a few rigorous structural properties of the charge density $\rho(\mathbf{r})$ or its spherical average

$$\rho(r)\equiv\frac{1}{4\pi}\int\rho(\mathbf{r})d\Omega_{\mathbf{r}} \tag{1.1}$$

are known, apart from its quantum-mechanical nonnegativity. For atomic systems, we should mention the so-called Kato's cusp condition [4] for $\rho(r)$ [5].

$$\rho'(0)=-2Z\rho(0) \tag{1.2}$$

[where $\rho'(r)$ denotes the first derivative of $\rho(r)$ and Z is the nuclear charge], and the asymptotic behavior [6]

$$\rho(r)\sim Cr^{\beta}e^{-\alpha r}, \tag{1.3}$$

where

$$\alpha=(8\epsilon)^{1/2},$$

$$\beta=2\left[\frac{Z-N+1}{(2\epsilon)^{1/2}}-1\right],$$

ϵ being the first ionization potential, N the number of electrons of the system, and C a constant of proportionality. Moreover, it has been rigorously proven [7] that the charge density $\rho(r)$ is not only monotonically decreasing but also convex for $r\geq Z/\epsilon$. For the sake of completeness, let us also mention here the spatial generalization of Kato's theorem for the bare-Coulomb-field model [8] and the numerical extension [9] for $r>0$ for ground-state atomic systems with $Z\leq 54$, in the form

$$\rho'(r)\geq -2Z\rho(r) \tag{1.4}$$

by means of analytical Hartree-Fock wave functions [10]. Notice that the above-mentioned expression can be rewritten in the form

$$\frac{\rho'(r)}{\rho(r)}\geq -2Z=\frac{\rho'(0)}{\rho(0)}, \tag{1.5}$$

which means that the logarithmic derivative of $\rho(r)$ reaches its absolute minimum at the origin for all ground-state atoms with $1\leq Z\leq 54$. It is worthwhile to point out that small violations of this property for some atoms were reported in Ref. [9], due to the deviation from the cusp condition by the analytical wave functions employed [11].

Several other monotonicity properties have been shown to be physically relevant by means of many realistic atomic models. For ground-state atomic systems, it is well known [12,13] that the electron density $\rho(r)$ is a monotonically decreasing function of the distance from the nucleus or, equivalently, that $\rho(r)$ displays first-degree monotonicity [14,15].

However, the property of convexity (i.e., second-degree monotonicity) is *not* a general feature for all ground-state atoms with nuclear charge up to $Z=54$, as was shown in Ref. [16] in an analytical Hartree-Fock framework. Some atomic systems ($Z=1-2,7-15,33-44$) exhibit a convex $\rho(r)$, i.e., the second derivative $\rho''(r)$ is nonnegative everywhere. For others ($Z=3-6,16-32,45-54$), a small nonconvexity region appears close to the nucleus (always before 3 a.u.). However, such a region is usually narrow and $\rho''(r)$ possesses a small absolute value in this region as compared to the values around the nucleus.

This study [16] has recently been [17,18] corroborated and extended for ground-state atoms up to $Z=92$ [19], showing that the atomic systems with $55\leq Z\leq 92$ belong

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to the class of nonconvex atoms. The existence of nonconvexity for small atoms has also been verified with the use of highly accurate configuration-interaction (CI) wave functions [18]. The regularities observed in the occurrence, location, and width of such nonconvexity regions suggest that there exists a physical meaning in this effect, although the values of Z for which the phenomenon occurs permits us to state that it is not related to the contribution of new shells to the density $\rho(r)$. These results raise some interesting questions: should nonconvexity be viewed as a natural phenomenon particular to only certain atoms, or can it be viewed in a broader context as belonging to a hierarchical arrangement of the properties of all atomic charge densities? Such an arrangement was proposed in Ref. [18], where the strongest restriction that could be imposed on all atomic densities was that of *strict pseudoconvexity*. If we accept the former argument then we should limit our attention to the separate study of those systems possessing nonconvexities. However, acceptance of the latter would suggest that we look for global properties (periodic table) of the nonconvexities. One possibility would be to attempt to establish and study physical features (if any) in $\rho''(r)$ valid for the entire periodic table.

Other attempts to study the atomic shell structure by means of functions related to the charge density $\rho(r)$ have been made [e.g., the radial density $4\pi r^2\rho(r)$ [15,20], the logarithmic derivative $\rho'(r)/\rho(r)$ [21], the Laplacian $\rho''(r)+(2/r)\rho'(r)$ [22,23] and other related functionals [24]]. However, in all these studies, there is always at least one shell *missing* for some atoms, i.e., the structure of these functions is not enough to detect all the shells occupied in all of the atomic systems. Some recent results in this laboratory, based on a suggestion of Sen, Slamet, and Sahni [20], indicate that functionals connected with the second derivative of the radial density $D(r)$ exhibit the correct number of shells for all ground-state atoms [25].

Some of these structural features have allowed the derivation of numerous relationships among the density and its first derivative at the nucleus, $\rho(0)$ and $\rho'(0)$, respectively, as well as some radial expectation values $\langle r^\alpha\rangle \equiv \int r^\alpha \rho(\mathbf{r})d\mathbf{r}$ [9,16], increasing greatly the interest in the study of the monotonicity characteristics of the one-particle density $\rho(r)$.

In this work, we will show that (i) the study of the maxima and minima of $\rho''(r)$, independent of the sign of this function at these points, provides a different interpretation of the shell structure in terms of the one-particle density, and (ii) that the extended cusp inequality $\rho'(r)\geq -2Z\rho(r)$ also holds for the region $55\leq Z\leq 92$ of the periodic table. In doing so, we have used the Clementi and Roetti [10] ($1\leq Z\leq 54$) and McLean and McLean [19] ($55\leq Z\leq 92$) near-Hartree-Fock self-consistent field (SCF) atomic wave functions. Atomic units are used throughout this report.

II. RESULTS AND DISCUSSION

Firstly we have searched for the local maxima and minima of $\rho''(r)$, i.e., the zeros of the third derivative $\rho'''(r)$, for all ground-state atoms with $1\leq Z\leq 92$. The following cases are found:

(1) $Z=1-2$ display neither minima nor maxima.
(2) $Z=3-10$ display one pair of extrema.
(3) $Z=11-36$ display two pairs of extrema.
(4) $Z=37-80$ display three pairs of extrema.
(5) $Z=81-92$ display four pairs of extrema.

In Fig. 1 we present the location of the successive minima for all ground-state atoms up to $Z=92$, while in Fig. 2 the value of the second derivative at its maxima is shown.

Some comments are in order. First, it is observed that a new minimum-maximum pair in $\rho''(r)$ occurs only in the case in which the last electron occupies a new subshell. The opposite, however, it not true, i.e., only the cases $2s^1$, $3s^1$, $5s^1$, and $6p^1$ correspond to the occurrence of a new minimum-maximum pair. However, contrary to the number of nonconvexity regions, the total number of local maxima and minima never decreases for increasing nuclear charge Z. Second, the location of each minimum of $\rho''(r)$ behaves very regularly with Z, as may be seen from Fig. 1, *independent of the sign of the function.* Locations of the maxima of $\rho''(r)$ when plotted against Z yielded a similar behavior. In Fig. 2 we present the values of $\rho''(r)$ at its local maxima. Note that this plot is done on a logarithmic scale. An analogous analysis for the minima is hampered by the negativity of some minima and irregularities due to the greater sensitivity of details in $\rho''(r)$. Clearly, these facts suggest that there is a relationship that exists for all atoms independent of the nature of the classification, i.e., convex or nonconvex, of the particular atom. This result adds weight to the argument that there is a hierarchical arrangement of atomic charge densities. For completeness, we also show in Fig. 3 the width of the nonconvexity region for the atoms where such a region appears. The relation between this width and the atomic shell structure, if any, has still to be understood.

Third, we have shown that Kato's cusp condition in the form of the inequality (1.4) as given in Ref. [9] for

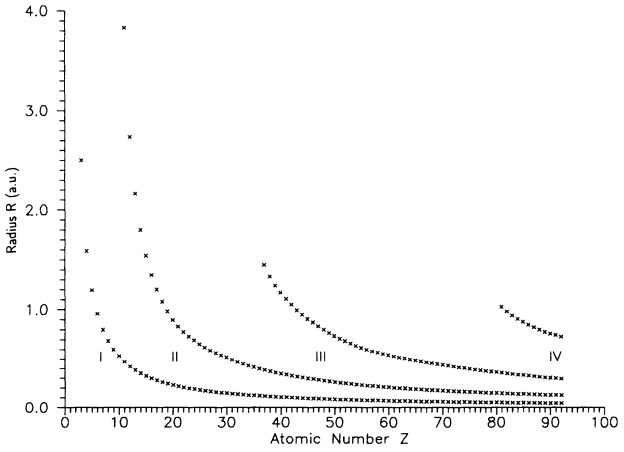

FIG. 1. Location of the first (I), second (II), third (III), and fourth (IV) minima of the second derivative $\rho''(r)$ of the atomic charge density $\rho(r)$ for all ground-state atoms with $1\leq Z\leq 92$. The calculations were performed by means of analytical Hartree-Fock wave functions [10,19].

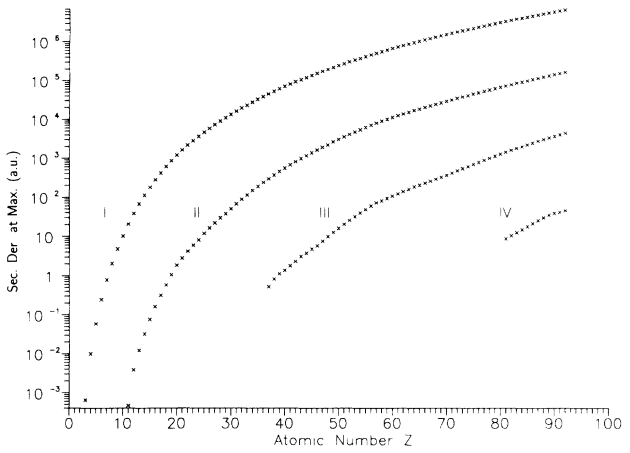

FIG. 2. Value of the second derivative $\rho''(r)$ of the atomic charge density $\rho(r)$ at its first (I), second (II), third (III), and fourth (IV) maxima for all ground-state atoms with $1 \leq Z \leq 92$. The calculations were performed by means of analytical Hartree-fock wave functions [10,19].

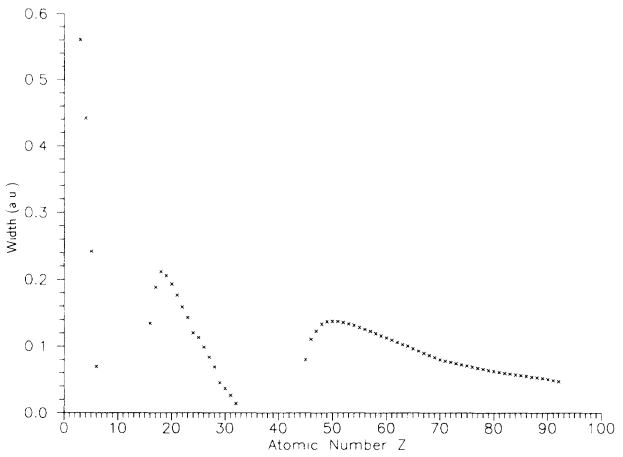

FIG. 3. Width of the nonconvexity region [in which the function $\rho''(r)$ is negative; see text for further details] for all ground-state nonconvex atoms with $1 \leq Z \leq 92$. The calculations were performed by means of analytical Hartree-Fock wave functions [10,19].

atomic systems up to $Z \leq 54$ also holds for the region of the periodic table beyond xenon up to $Z = 92$. Moreover, the small deviations reported in Ref. 9 for this condition in some atoms do not appear beyond $Z = 30$.

III. SUMMARY

In this work we have studied the atomic shell structure by means of the logarithmic derivative and the second derivative of the charge density $\rho(r)$. It is observed that, for all ground-state atoms from hydrogen ($Z = 1$) through uranium ($Z = 92$), (i) the logarithmic derivative of $\rho(r)$ attains its minimum value at the nucleus, (ii) the number of pairs of local minima and maxima of the second derivative $\rho''(r)$ of the charge density $\rho(r)$ never decreases when increasing the nuclear charge Z, and (iii) the location of the local minima and maxima, independent of the sign of $\rho''(r)$, and the intensity of the local maxima have a regular behavior in going through the periodic table from hydrogen to uranium. This result substantiates the argument that the nonconvexity of atomic systems should not be regarded as a physical property pertaining only to certain systems, but rather as a feature of the hierarchical arrangement of the atomic electron density of all atoms.

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