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On the non-convexity of charge densities in atoms and ions☆

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Abstract

For neutral atoms with the number of electrons $N \leq 103$ and singly charged cations and anions with $N \leq 54$, the second derivative $\rho''(r)$ of the spherically averaged one-particle density $\rho(r)$ is studied within the Hartree–Fock framework. In all the three series of neutrals, cations and anions, $\rho''(r)$ displays one or more pairs of local extrema, whose number never decreases when the nuclear charge Z and/or the number of electrons N increase. The existence of one or two *non-convexity* regions of r is observed for some species, where $\rho''(r)$ is negative. The location and width of non-convexity regions are examined, and their dependence on Z and N is discussed, as well as the properties of the other local extrema in $\rho''(r)$.

Keywords: Atoms and ions; Hartree–Fock electron density; Charge convexity 31.10. + z; 31.15. + q

1. Introduction

The one-particle density $\rho(\mathbf{r})$ of many-electron systems plays a fundamental role in the description of many important properties of the systems [1], as revealed by the Hohenberg–Kohn theorem [2]. However, our knowledge on the rigorous properties of the density $\rho(\mathbf{r})$ and its spherical average $\rho(r)$,

$$\rho(r) \equiv \frac{1}{4\pi} \int \rho(\mathbf{r})\, \mathrm{d}\Omega,$$

is very limited even for atoms. Apart from their non-negativity $\rho(\mathbf{r}), \rho(r) \geq 0$, we only know two rigorous relations: the so-called cusp condition [3,4], $\rho'(0) = -2Z\rho(0)$, in which Z is nuclear charge and the prime ($'$) means the differentiation with respect to r, and the long-range asymptotic behavior [5,6], $\rho(r) \sim r^{2(\gamma-1)}\, \mathrm{e}^{-\sqrt{8\varepsilon}r}$, in which ε is the first ionization potential and $\gamma = (Z - N + 1)/\sqrt{2\varepsilon}$ with N being the number of electrons.

In recent years, much effort has been made to elucidate additional rigorous properties of the spherically averaged charge density $\rho(r)$ of atomic systems, such as monotonicity [7–10], convexity [5,11] and others [12–14]. Among recent findings, it is worthy to remember that for ground-state neutral atoms with the number of electrons $N = 1$, 2, 7–15, 33–44, the monotonic character of $\rho(r)$ as well as its convexity (i.e. the non-negativity of the second derivative $\rho''(r)$ for any r) have allowed us to derive many rigorous inequalities between local and/or global characteristics of the density $\rho(r)$, such as its value at the nucleus $\rho(0)$ [11,13] and the radial moments $\langle r^k \rangle$ [12–14]. Studies on $\rho''(r)$ showed [10,11,15,16] that the convexity of $\rho(r)$ is very *weakly* violated for $N =$ 3–6, 16–32, 45–103 among the 103 neutral atoms from H ($N = 1$) to Lr ($N = 103$); the ratio $|\rho''_{\min}|/\rho''(0)$ between the minimum $\rho''_{\min}$ of $\rho''(r)$ and its value at the nucleus $\rho''(0)$ is only of the order of

☆ Dedicated to Professor R. Gáspár on the occasion of his 80th year.

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10^{-10}–10^{-5}. The extremely small violation of the convex property of the charge density suggests that the accuracy of the wave functions employed in constructing the density would be very important in studying the convex character of the charge density of atoms and ions. The same comment applies to some local characteristics (e.g. existence, location and sign of local extrema) of the second derivative $\rho''(r)$ of the charge density.

In this work, a few structural properties of the second derivative $\rho''(r)$ of the charge density $\rho(r)$ are studied for neutral atoms with $N \leq 103$ and singly charged cations and anions with $N \leq 54$, by using very accurate analytical Hartree–Fock wave functions (K98) developed very recently by Koga et al. [17,18]. The properties examined are the convexity of the charge density $\rho(r)$, the number of pairs of local extrema in $\rho''(r)$ and the sign of local minima. The present results concerning local extrema are compared with the previous ones [15] for neutral atoms with $N \leq 92$, obtained from less accurate wave functions of Clementi and Roetti (CR) [19] and of McLean and McLean (MM) [20]. Hartree atomic units are used throughout this paper.

2. Convexity of charge densities of atoms and ions

The atomic charge density $\rho(r)$ is said to be convex, if the condition

$$\rho''(r) \equiv \frac{d^2\rho(r)}{dr^2} \geq 0$$

is satisfied for any non-negative values of r. For all the 103 neutral atoms from H ($N = 1$) to Lr ($N = 103$), as well as for singly charged 54 cations and 43 anions with $N \leq 54$, in their experimental ground states, we have examined the convexity of $\rho(r)$ using very accurate recently developed Roothaan–Hartree–Fock wave functions (K98) [17,18]. Their wave functions [17] are considered to be particularly suited for the present purpose, because sufficiently large Slater-type basis sets are used, and all the linear and nonlinear parameters are variationally optimized under the constraints of the orbital-wise cusp condition [21,22] and correct long-range exponential decay condition [23–26] for all the species with $N \leq 54$. For the neutral atoms with $55 \leq N \leq 103$, the K98 wave functions [18] do not satisfy the cusp and long-range conditions, but are considerably more accurate than those of MM [20]. Especially, accurate analytical wave functions for the atoms with $93 \leq N \leq 103$ have not been available previously.

Our convexity examination of $\rho(r)$ for the atoms and ions based on the K98 functions can be summarized as follows:

1. Among the 103 neutral atoms, the 23 atoms with $N = Z = 1$, 2, 7–15, 33–44 have a convex charge density, while the 80 atoms with $N = Z = 3$–16, 16–32, 45–103 have a non-convex one.
2. Among the 54 cations ($N = Z - 1$), the 23 cations with $N = 1$, 2, 6–14, 32–43 (i.e. $Z = 2$, 3, 7–15, 33–44) have a convex density, while the 31 cations with $N = 3$–5, 15–31, 44–54 (i.e. $Z = 4$–6, 16–32, 45–55) have a non-convex one.
3. Among the 43 anions ($N = Z + 1$), the 19 anions with $N = 2$, 7–16, 34–45 (i.e. $Z = 1$, 6–15, 33–44) have a convex density, while the 24 anions with $N = 4$–16, 17–33, 46–54 (i.e. $Z = 3$–5, 16–32, 45–53) have a non-convex one.

For the neutral atoms, the present classification of the charge densities into convex and non-convex functions coincides with those reported in Refs. [11,15] for $N \leq 92$, based on the less accurate CR and MM wave functions and with those reported in Refs. [10,16] for $N \leq 103$, based on analytically fitted functions of numerical Hartree–Fock densities. The sole exception is the neutral Ge atom ($N = Z = 32$), which was found to be convex in Refs. [10,16] but non-convex in Refs. [11,15] and in the present work. This atom has an exceptionally narrow region ($0.469 < r < 0.477$) of non-convexity, and it is highly probable that the region was overlooked in Refs. [10,16].

For the cationic and anionic charge densities, the present classification is completely identical to that reported in Ref. [16]. It is interesting to observe that the convex character of neutral atoms and singly charged ions for $N = 1 - 54$ appears to depend mainly on the nuclear charge Z rather than on the number of electrons N, i.e. charge densities of isonuclear systems with the same Z belong to the same convex or non-convex category. The only exceptions are the cation Li^+ ($Z = 3$, $N = 2$) and the anion C^- ($Z = 6$, $N = 7$), which have convex densities as

Table 1
Location r_0 of the minimum of the second derivative $\rho''(r)$ and width Δ of the non-convexity region for some non-convex neutral atoms, calculated with the K98 wave functions and the CR ($N \leq 54$) and MM ($N \geq 55$) wave functions

N	K98		CR–MM	
	r_0 (bohr)	Δ (bohr)	r_0 (bohr)	Δ (bohr)
3	2.500	0.555	2.501	0.561
4	1.589	0.441	1.590	0.442
5	1.196	0.240	1.197	0.242
6	0.960	0.063	0.960	0.070
16	1.348	0.137	1.314	0.315
20	0.895	0.192	0.897	0.193
24	0.694	0.124	0.694	0.121
28	0.563	0.067	0.564	0.069
32	0.472	0.008	0.472	0.014
45	0.909	0.075	0.910	0.080
60	0.542	0.113	0.542	0.112
75	0.396	0.070	0.397	0.070
90	0.302	0.050	0.303	0.050

pointed out in Ref. [16], whereas the corresponding neutral atoms Li and C have non-convex densities.

For the species with a non-convex $\rho(r)$, we have computed the characteristics of the non-convexity region, i.e. the location r_0 of the negative minimum and the width Δ of r where $\rho''(r)$ is negative. For some selected neutral atoms with $N \leq 92$, the present results obtained from the K98 wave functions are compared in Table 1 with those obtained previously [15] from the CR and MM wave functions. Fortunately, the two sets of the values are found to be very similar. In Table 2, a comparison of the characteristics $\{r_0, \Delta\}$ is given for $N = Z - 1, Z, Z + 1$. It is observed that for $Z > 18$, the values are almost independent of N, and the non-negligible differences appear only for light atoms. Thus we may say that the characteristics $\{r_0, \Delta\}$ depend little on the number of electrons N for a fixed nuclear charge Z, especially for heavy atoms, supporting our previous argument that

Table 2
Location r_0 of the minimum of the second derivative $\rho''(r)$ and width Δ of the non-convexity region for some non-convex neutral atoms ($N = Z$), anions ($N = Z + 1$) and cations ($N = Z - 1$), calculated with the K98 wave functions

Z	r_0 (bohr)			Δ (bohr)		
	$N = Z + 1$	$N = Z$	$N = Z - 1$	$N = Z + 1$	$N = Z$	$N = Z - 1$
3	2.538	2.500		0.761	0.555	
5	1.215	1.196	1.168	0.219	0.240	0.304
16	1.354	1.348	1.345	0.165	0.137	0.020
17	1.204	1.200	1.198	0.209	0.190	0.149
19	0.979	0.979	0.980	0.205	0.204	0.205
21	0.837	0.832	0.833	0.173	0.176	0.176
22	0.783	0.779	0.779	0.156	0.159	0.160
24	0.694	0.694	0.695	0.124	0.124	0.122
25	0.656	0.654	0.654	0.108	0.112	0.112
26	0.623	0.620	0.621	0.093	0.098	0.096
28	0.566	0.563	0.566	0.062	0.067	0.060
29	0.541	0.541	0.541	0.045	0.045	0.042
31	0.493	0.493	0.493	0.021	0.021	0.021
32	0.472	0.472	0.472	0.007	0.008	0.006
45	0.909	0.909	0.910	0.075	0.075	0.082
46	0.871	0.873	0.871	0.105	0.110	0.109
47	0.835	0.835	0.836	0.124	0.125	0.127
49	0.769	0.769	0.769	0.135	0.135	0.135
50	0.740	0.740	0.740	0.136	0.136	0.136
51	0.712	0.712	0.712	0.136	0.136	0.136
52	0.687	0.687	0.687	0.135	0.135	0.135
53	0.663	0.663	0.663	0.133	0.133	0.133

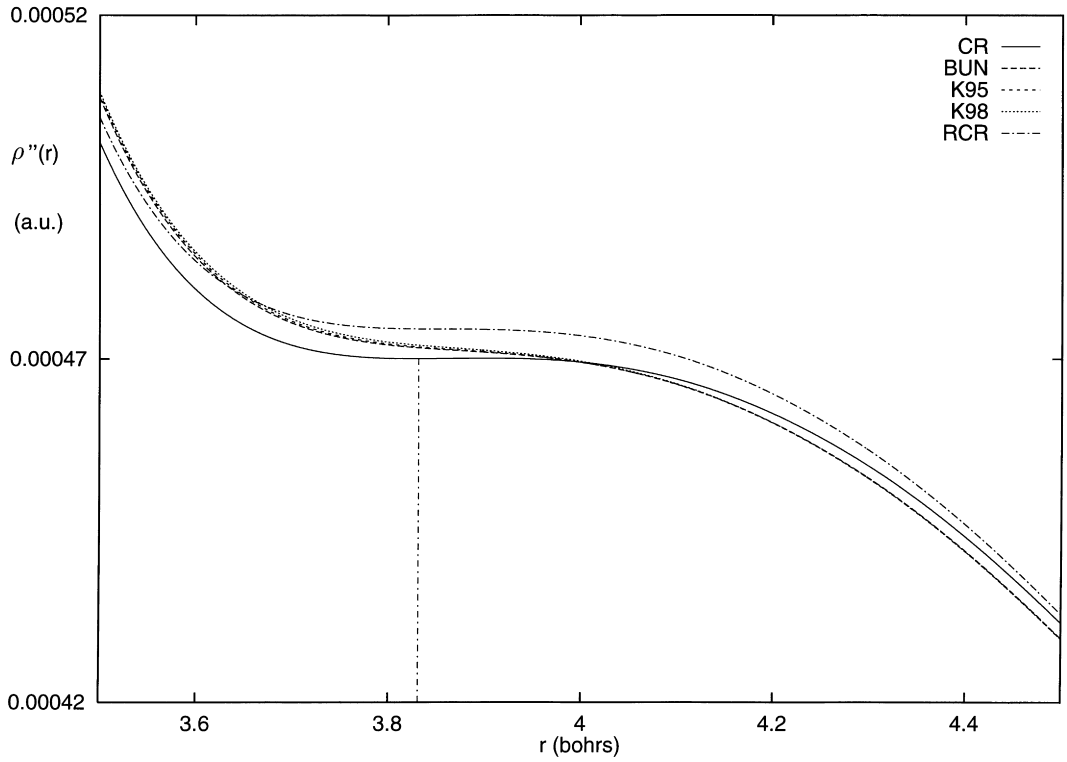

Fig. 1. Second derivative $\rho''(r)$ of the charge density for Na ($Z = N = 11$), computed by means of the CR, BUN, RCR, K95 and K98 wave functions.

the convexity of atomic charge densities depends mainly on Z rather than N.

3. Local extrema of the second derivative of charge densities

The appearance of a non-convexity region where $\rho''(r) < (0)$ in some atoms and ions implies the existence of, at least, a pair of local extrema (i.e. a minimum and a maximum) in $\rho''(r)$, the minimum being negative. However, the derivative $\rho''(r)$ may exhibit additional pairs of local extrema with *positive* values of $\rho''(r)$, which do not produce non-convexity regions. This question was discussed in Ref. [15] for the case of neutral atoms with $N \leq 92$ by using the CR and MM wave functions. In the present work, we have improved and extended such a study based on the more accurate K98 wave functions for the neutral atoms up to $N = 103$ and for the singly charged ions with $N \leq 54$.

The results of our analysis of the 103 neutral atoms, the 54 cations and the 43 anions in their experimental ground states are well classified based on the number of electrons N. The number N_p of pairs of extrema (independent of their signs) in $\rho''(r)$ is summarized as:

(i) No extrema for $N = 1$ and 2.
(ii) One pair for $N = 3$–11.
(iii) Two pairs for $N = 12$–36.
(iv) Three pairs for $N = 37$–80.
(v) Four pairs for $N = 81$–103.

There is one exception, however; the Rb^+ cation with $N = 36$ has three pairs of extrema instead of two. The number N_p of pairs of extrema appears to depend on the principal, n, and azimuthal, l, quantum numbers of the outermost subshell. We empirically find that the

Table 3
Sign of local minima of the second derivative $\rho''(r)$ for neutral atoms (nuclear charge $Z \leq 103$) and singly charged ions ($Z \leq 55$). Example of notation: $++-+$ denotes the existence of four local minima, the third one being negative and the other three positive

Sign of minima	Nuclear charge Z for		
	Anions	Neutrals	Cation
No minima	1	1–2	3
$-$	3–5	3–6	4–6
$+$	6–9	7–11	7–12
$++$	11–15	12–15	13–15
$+-$	16–32	16–32	16–32
$++$	33–35	33–36	33–36
$+++$	37–44	37–44	37–44
$++-$	45–53	45–80	45–55
$++-+$		81–96	
$++--$		97–103	

relation

$$N_p = n - 1 - \left[\frac{n-l}{3}\right]$$

holds for most cases, where $[x]$ denotes the greatest integer that does not exceed x. Exceptions are Na^-, Mg, Al^+ and Rb^+, for which the formula predicts one less pair than the observed. The above equation suggests that the extremum characteristics of $\rho''(r)$ reflects properties of the outermost or valence subshell of an atom.

A comparison of the present classification with that given in Ref. [15] for the first 92 neutral atoms shows that the 11 new atoms ($N = 93 - 103$) have four pairs of extrema as the preceding atoms with $N = 81 - 92$. Among the first 92 atoms, a difference between the present and previous classifications is found for the Na atom ($N = 11$), which exhibits a single pair of extrema in $\rho''(r)$ with the K98 wave function but two pairs with the CR wave function. In Ref. [15], the appearance of a new pair of extrema in $\rho''(r)$ was naturally interpreted in terms of the electronic occupation of a new shell in atoms. To solve the discrepancy between the K98 and CR wave functions that appeared for the Na atom, we have performed an additional examination of $\rho''(r)$ for this atom using three more different wave functions: a reoptimized version of CR wave function (RCR) [27], a wave function by Bunge et al. (BUN) [28] and a wave function by Koga et al. (K95) [29]. The variational accuracies of these wave functions generally increase in the order of CR, RCR, BUN, K95 and K98. We have found that all of the RCR, BUN, K95 wave functions exhibit only one pair of local extrema in the second derivative of the density, as the K98 function does. In Fig. 1, we explicitly compare the behavior of $\rho''(r)$ obtained from the five different wave functions, in the region where the CR function predicted the second local minimum. It is observed that the second minimum at $r = 3.831$ bohr associated with the CR function is *very weak*; the ratio between the $\rho''(r)$ values at the minimum and its associated maximum differs from unity only by about 10^{-7}. On the other hand, the second derivatives $\rho''(r)$ obtained from the RCR, BUN, K95 and K98 functions do not have the corresponding minimum. Thus the previous discussion [15] on the relation between a new pair of extrema in $\rho''(r)$ and a new shell occupation of atoms meets an exception. The result also implies that the use of sufficiently accurate wave functions is important in order to study finer structural properties of the charge density.

We finally focus our attention on the signs of the minima of $\rho''(r)$. A general rule deduced previously [15] from the neutral atoms with $N \leq 92$ is that the non-convexity of atomic charge densities discussed in the previous section is because of the existence of a *single* non-convexity region. The present study, extended to the neutral atoms with $N \leq 103$ and the singly charged atomic ions with $N \leq 54$, confirms that the rule is true for the first 96 neutral atoms and for all the singly charged ions. However, the rule is found to be invalid for very heavy neutral atoms: the seven atoms with $N = 97$–103 have *two* distinct non-convexity regions. For these atoms, the location r_0 of the first and second negative minima vary from 0.273 ($Z = 97$) to 0.252 bohr ($Z = 103$), and from 0.660 ($Z = 97$) to 0.592 bohr ($Z = 103$), respectively. Both values decrease almost linearly when Z increases. On the other hand, the corresponding two widths Δ of the non-convex regions show different Z-dependencies; the width of the first region decreases very slowly from 0.040 ($Z = 97$) to 0.031 bohr ($Z = 103$), whereas that of the second region increases, with increasing Z, from 0.038 ($Z = 97$) to 0.092 bohr ($Z = 103$). In Table 3, the above-mentioned five categories (i)–(v) are further

subdivided into nine classes according to the signs of the successive minima. For species with $N \leq 54$, it is observed from the table, that the majority of the systems are separated into different classes, again depending on the value of Z rather than N. Exceptions are the two cations (Li^+, Mg^+) and the two anions (C^-, Na^-). However, the physical meaning of the appearance of different arrays of successive signs remains unclear at present.

4. Summary

Using accurate Hartree–Fock wave functions, we have studied the convex properties of spherically averaged charge densities $\rho(r)$ for the neutral atoms with $N \leq 103$ and the singly charged cations and anions with $N \leq 54$ in their experimental ground states. The present results have improved and extended previous ones for the neutral atoms with $N \leq 92$, and have pointed out that the CR functions do not have sufficient accuracy for the study of detailed structural characteristics of the charge density. Our comparative study of the neutral and ionic atoms with $N \leq 54$ has clarified that, with very few exceptions, the convex character of the density is governed by the nuclear charge Z, whereas the number of local extrema in the second derivative $\rho''(r)$ depends on the number of electrons N. For heavy neutral atoms with $N \geq 97$, it has been found that the charge density exhibits two non-convexity regions, against a single region known before for the neutral atoms with $N \leq 92$.

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