Atomic charge density at the nucleus and inequalities among radial expectation values

F. J. Gálvez and I. Porras
Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain
(Received 26 December 1990)

A self-consistent study of the function $f(r)=\rho(r)+\rho'(r)/(2Z)$, where $\rho(r)$ is the spherically averaged electron density of the ground state of an atom, shows that $f(r)\geq 0$ everywhere. This allows us to obtain several inequalities relating the atomic electronic density at the nucleus $\rho(0)$ and atomic radial expectation values $\langle r^\alpha\rangle$. In particular, we generalize upper bound found by Hoffmann-Ostenhof, Hoffmann-Ostenhof, and Thirring [J. Phys. B **11**, L571 (1978)] to $\rho(0)$. We also obtain accurate inequalities between the radial expectation values $\langle r^\alpha\rangle$ of atomic systems.

The electron density $\rho(\mathbf{r})$ of an N-electron atom, defined by

$$\rho(\mathbf{r})=N\sum_{\sigma_i}\int|\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)|^2 \times d\mathbf{r}_2\cdots d\mathbf{r}_N\ , \tag{1}$$

where $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)$ is the normalized electronic wave function—antisymmetric in the pairs of $(\mathbf{r}_i,\sigma_i)$ of position-spin electron coordinates—or the spherically averaged electron density, $\rho(r)$, defined by

$$\rho(r)=\frac{1}{4\pi}\int\rho(\mathbf{r})d\Omega\ , \tag{2}$$

is one of the most useful quantum-mechanical concepts of atomic physics, not only because it allows a more convenient and transparent interpretation of physical and chemical phenomena, but also because it is the cornerstone of modern atomic density-functional theories.[1,2]

It is hard to prove mathematical properties of this quantity in a rigorous way. One of the properties is its behavior at the origin, Kato's cusp condition[3,4] $\rho'(0)=-2Z\rho(0)$. (Atomic units are used throughout.) However, some other properties have been suggested by self-consistent numerical calculations. One of them is that the spherically averaged electron density of the ground state of neutral atoms is a monotonically decreasing function.[5,6] In addition, the positivity of the second derivative has been also studied both analytically[7] and numerically.[8]

A lot of work with these properties has been done. One manner of work leads to the description of the atomic density at the origin, $\rho(0)$, by means of bounds[9–11] in terms of atomic radial expectation values $\langle r^\alpha\rangle$, defined by

$$\langle r^\alpha\rangle=\int_{\mathbb{R}^3}r^\alpha\rho(\mathbf{r})d\mathbf{r}=4\pi\int_0^\infty r^{\alpha+2}\rho(r)dr\ . \tag{3}$$

In this work we obtain, based on the positivity of the function $f(r)$ defined by Eq. (4), one set of bounds to $\rho(0)$, which will improve the others mentioned above. Also, the use of this property will allow us to obtain several sets of accurate inequalities among radial expectation values $\langle r^\alpha\rangle$ of different orders.

The main objective of our study is to verify that the function

$$f(r)=\rho(r)+\frac{\rho'(r)}{2Z}\ , \tag{4}$$

for atoms in their ground state, has the property

$$f(r)\geq 0\ , \tag{5}$$

which can be considered as a spatial generalization of Kato's theorem as defined by March.[12]

The only atomic systems for which we know the exact form of $f(r)$ are the one-electron atoms. For these systems $f(r)=0$. For the other atoms we have the following information about $f(r)$.

(i) The Kato's cusp-condition states that

$$f(0)=0\ . \tag{6}$$

(ii) For large values of r it is already known[13] that

$$\rho(r)\propto\exp(-\sqrt{8I}\,r)\ , \tag{7}$$

where I is the first ionization potential. Equation (7) leads to

$$f(r)\propto\left[1-\frac{\sqrt{2I}}{Z}\right]\exp(-\sqrt{8I}\,r)\geq 0 \tag{8}$$

because of $2I\leq Z^2$.

In addition to this, the inequality (5) is formally correct if we use for $\rho(r)$ the total electron density of an arbitrary number of closed shells for a bare Coulomb potential energy $V(r)=-Ze^2/r$, as was proved by March.[12]

A numerical study of this function in the Hartree-Fock framework, using Clementi and Roetti's data[14] for atoms in their ground state between $Z=2$ and 54 shows that $f(r)$ is a positive function, which is illustrated in Fig. 1 where it has been plotted for the krypton atom, the behavior of the other atoms being similar to this one.

In addition to this, a comparison between this function and the atomic density $\rho(r)$ is shown in Fig. 2 for the same atom, where we can see how $\rho(r)$ is much greater than $f(r)$ for small values of r, where they are more significant.

Now we will use the positivity property of $f(r)$ in or-

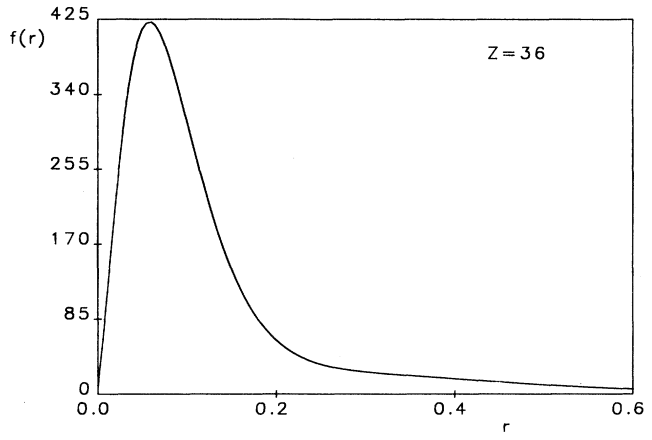

FIG. 1. Plot of the function $f(r)$, defined by Eq. (4), evaluated with the Hartree-Fock wave functions of Clementi and Roetti (Ref. 14) for the krypton atom ($Z=36$). Atomic units are used.

der to find inequalities among moments of this function. These moments are related to those of $\rho(r)$ by

$$\nu_n=\int_0^\infty r^n f(r)dr=\begin{cases}\dfrac{\langle r^{-2}\rangle}{4\pi}-\dfrac{\rho(0)}{2Z}, & n=0\\ \dfrac{1}{4\pi}\left[\langle r^{n-2}\rangle-\dfrac{n}{2Z}\langle r^{n-3}\rangle\right], & n>0\,.\end{cases} \tag{9}$$

For our purpose, we will use the following Stieljes theorem.[15]

If $f(r)$ is a density function (i.e., non-negative and integrable in its domain), then its moments ν_m satisfy the following determinant inequalities:

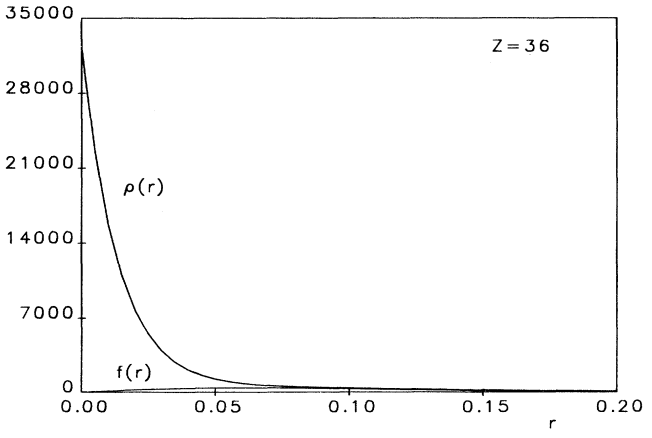

FIG. 2. Plot of the function $f(r)$, defined by Eq. (4), compared to the spherically averaged electron density $\rho(r)$ for the krypton atom ($Z=36$), both calculated with the Hartree-Fock data of Ref. 14. Atomic units are used.

$$\Delta_m^{(0)}\geq 0,\quad \Delta_m^{(1)}\geq 0,\quad m=0,1,\ldots, \tag{10}$$

where these symbols denote the Hadamard determinants, given by

$$\Delta_m^{(k)}=\begin{vmatrix}\nu_k & \nu_{k+1} & \cdots & \nu_{k+m}\\ \nu_{k+1} & \nu_{k+2} & \cdots & \nu_{k+m+1}\\ & & \ddots & \\ \nu_{k+m} & \nu_{k+m+1} & \cdots & \nu_{k+2m}\end{vmatrix} \tag{11}$$

if $m>0$, and

$$\Delta_0^{(k)}=\nu_k \quad \text{if } m=0\,.$$

The application of this theorem to the function $r^k f(r)$ will lead to the positivity of all the determinants $\Delta_m^{(k)}$ for any $k\geq 0$, $m\geq 0$.

From the positivity of $\nu_k(\Delta_0^{(k)})$ we obtain the following relations.

(a) For $k=0$,

$$\rho(0)\leq\frac{Z\langle r^{-2}\rangle}{2\pi}\equiv U_0^0\,. \tag{12}$$

This is the Hoffmann-Ostenhof upper bound[9] to $\rho(0)$.

(b) For $k>0$ we obtain

$$\langle r^{k-3}\rangle\leq\frac{2Z}{k}\langle r^{k-2}\rangle\equiv U_0^k\,. \tag{13}$$

Particular cases of Eq. (13) are

$$\langle r^{-2}\rangle\leq 2Z\langle r^{-1}\rangle\equiv U_0^1\,, \tag{14}$$

$$\langle r^{-1}\rangle\leq Z^2\equiv U_0^2\,, \tag{15}$$

$$\langle r\rangle\geq\tfrac{3}{2}\,, \tag{16}$$

where we make use of $\langle r^0\rangle=Z$ for a neutral atom.

From the positivity of $\Delta_m^{(0)}$ we can improve the Hoffmann-Ostenhof upper bound to $\rho(0)$ [Eq. (12)] by including more expectation values (increasing the value of m). If we denote by $\mathrm{adj}(\nu_j)$ the determinant of the adjoint matrix in Eq. (11) corresponding to the jth element of the first row, when $k=0$, we can write

$$\rho(0)\leq\frac{Z}{2\pi}\left[\langle r^{-2}\rangle+4\pi\frac{\sum_{j=1}^{m}\nu_j\mathrm{adj}(\nu_j)}{\mathrm{adj}(\nu_0)}\right]\equiv U_m^0\,. \tag{17}$$

Note that $\mathrm{adj}(\nu_0)=\Delta_m^{(1)}$. The second term in the right-hand side of Eq. (17) is a quantity smaller than zero for every m, and it depends on expectation values from $\langle r^{-2}\rangle$ up to $\langle r^{2m-2}\rangle$. For every value of $m>0$, Eq. (17) gives an upper bound sharper than the one given by Eq. (12). For the sake of clarity, let us write the lowest-order particular case:

$$\rho(0)\leq\frac{Z}{2\pi}\left[\langle r^{-2}\rangle-\frac{[\langle r^{-1}\rangle-\langle r^{-2}\rangle/(2Z)]^2}{N-\langle r^{-1}\rangle/Z}\right]\equiv U_1^0\,. \tag{18}$$

In Table I we study the accuracy of the upper bounds

TABLE I. Test of the upper bounds U_m^0 to the atomic density at the nucleus $\rho(0)$, given by Eq. (17), for some values of m, by means of the ratios $R_m=\rho(0)/U_m^0$. See details in text.

Z	$\rho(0)$	R_0	R_1	R_2	R_3	R_4	R_5	R_6
2	3.60	0.942	0.979	0.989	0.994	0.996	0.997	0.998
3	13.83	0.959	0.972	0.982	0.988	0.991	0.993	0.994
4	35.43	0.966	0.979	0.985	0.990	0.992	0.994	0.995
6	127.56	0.963	0.982	0.988	0.991	0.993	0.995	0.996
8	311.97	0.952	0.980	0.988	0.991	0.994	0.995	0.996
10	620.15	0.939	0.976	0.986	0.990	0.993	0.994	0.995
14	1765.71	0.926	0.963	0.976	0.982	0.985	0.988	0.990
18	3840.22	0.915	0.954	0.973	0.980	0.984	0.987	0.989
23	8178.33	0.906	0.945	0.959	0.959	0.975	0.979	0.982
29	16 626.73	0.897	0.940	0.953	0.964	0.970	0.975	0.979
36	32 228.20	0.889	0.931	0.949	0.960	0.968	0.975	0.979
44	59 490.87	0.880	0.923	0.939	0.949	0.956	0.961	0.966
54	111 163.94	0.873	0.915	0.933	0.945	0.954	0.960	0.965

given by Eq. (17), for some m values, in the near-Hartree-Fock framework mentioned above, by means of the ratios $R_m=\rho(0)/U_m^0$ for some illustrative atoms. The values R_0 corresponds to the bound of Hoffmann-Ostenhof, Hoffman-Ostenhof, and Thirring[9] of Eq. (12). We can see that the values of U_m^0 approximate rapidly to $\rho(0)$ when m increases.

We can notice how the simple expression in Eq. (18) improves the accurate upper bound of Hoffmann-Ostenhof, Hoffman-Ostenhof, and Thirring[9] increasing their ratios in 1.3–5 % range for atoms in the range $Z=2$–54, when tested with Hartree-Fock data.

The use of $\Delta_m^{(k)}\geq 0$, for a fixed value of $k>0$, allows us to obtain upper bounds to $\langle r^{k-3}\rangle$ in terms of other radial expectation values of higher orders. This condition leads to

$$\langle r^{k-3}\rangle \leq \frac{2Z}{k}\left[\langle r^{k-2}\rangle + \frac{4\pi\sum_{j=1}^{m}\nu_{j+k}\,\mathrm{adj}(\nu_{j+k})}{\mathrm{adj}(\nu_k)}\right]\equiv U_m^k \ . \tag{19}$$

Again, the second term in the right-hand side is a negative term, improving the bounds U_0^k. It depends on all the radial expectation values with orders between $k-2$ and $k+2m-2$.

For the simplest case, $m=1$, we have

$$\langle r^{k-3}\rangle \leq \frac{2Z}{k}\left[\langle r^{k-2}\rangle - \frac{\left[\langle r^{k-1}\rangle - \frac{k+1}{2Z}\langle r^{k-2}\rangle\right]^2}{\langle r^{k}\rangle - \frac{k+2}{2Z}\langle r^{k-1}\rangle}\right] . \tag{20}$$

Particular cases of Eq. (20) give the following upper bounds to the atomic moments $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$:

$$\langle r^{-2}\rangle \leq 2Z\left[\langle r^{-1}\rangle - \frac{(Z-\langle r^{-1}\rangle/Z)^2}{\langle r\rangle - \frac{3}{2}}\right]\equiv U_1^1 \tag{21}$$

and

$$\langle r^{-1}\rangle \leq Z\left[Z - \frac{(\langle r\rangle - \frac{3}{2})^2}{\langle r^2\rangle - 2\langle r\rangle/Z}\right]\equiv U_1^2 \ . \tag{22}$$

A test of the upper bounds U_m^k given by Eq. (19) to $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$ ($k=1$ and 2, respectively) is shown in Tables II and III, for some values of m, and Hartree-

TABLE II. Test of the upper bounds $U_m^{(1)}$ to the expectation value $\langle r^{-2}\rangle$, given by Eq. (19), for some values of m, by means of the ratios $R'_m=\langle r^{-2}\rangle/U_m^1$. See details in text.

Z	$\langle r^{-2}\rangle$	R'_0	R'_1	R'_2	R'_3	R'_4	R'_5
2	11.992	0.888	0.967	0.986	0.993	0.996	0.997
3	30.217	0.881	0.937	0.958	0.972	0.981	0.986
4	57.624	0.857	0.944	0.966	0.977	0.983	0.988
6	138.773	0.787	0.929	0.964	0.977	0.984	0.988
8	257.257	0.722	0.903	0.953	0.972	0.981	0.986
10	414.900	0.667	0.876	0.939	0.964	0.976	0.983
14	856.227	0.621	0.750	0.847	0.898	0.924	0.941
18	1465.009	0.584	0.726	0.824	0.885	0.917	0.936
23	2465.486	0.551	0.672	0.742	0.790	0.832	0.865
29	4014.377	0.511	0.658	0.720	0.765	0.805	0.838
36	6330.530	0.481	0.610	0.706	0.764	0.805	0.841
44	9648.752	0.456	0.570	0.636	0.691	0.735	0.768
54	14 818.051	0.432	0.535	0.616	0.673	0.722	0.763

TABLE III. Test of the upper bounds U_m^2 to the expectation value $\langle r^{-1}\rangle$, given by Eq. (19), for some values of m, by means of the ratios $R_m''=\langle r^{-1}\rangle/U_m^2$. See details in text.

Z	$\langle r^{-1}\rangle$	R_0''	R_1''	R_2''	R_3''	R_4''
2	3.3747	0.844	0.961	0.986	0.993	0.997
3	5.7156	0.635	0.870	0.931	0.956	0.970
4	8.4087	0.526	0.842	0.932	0.962	0.975
6	14.6893	0.408	0.763	0.898	0.948	0.969
8	22.2595	0.348	0.700	0.860	0.927	0.957
10	31.1132	0.311	0.654	0.829	0.908	0.946
14	49.2434	0.251	0.418	0.553	0.672	0.763
18	69.7248	0.215	0.419	0.559	0.668	0.754
23	97.2730	0.184	0.300	0.421	0.512	0.579
29	135.4781	0.161	0.282	0.394	0.480	0.549
36	182.8480	0.141	0.255	0.374	0.488	0.577
44	240.4579	0.124	0.212	0.285	0.351	0.418
54	317.8706	0.109	0.190	0.276	0.354	0.422

Fock values of the radial expectation values. These bounds include those given by Eqs. (14) and (21) ($m=0,1$) for $\langle r^{-2}\rangle$ and by Eqs. (15) and (22) ($m=0,1$) for $\langle r^{-1}\rangle$. We can see the large improvement in some cases when we increase the values of m, which are shown by the ratios $R_m'=\langle r^{-2}\rangle/U_m^1$ and $R_m''=\langle r^{-1}\rangle/U_m^2$.

By means of Eq. (19) we could find many inequalities among radial expectation values. We have only written explicitly and tested the simplest and the most accurate of them. We have noted here the bounds to $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$, not only because of their special tightness but also because they are upper bounds to radial expectation values of negative order in terms of higher-order moments, while in the literature only lower bounds were known, to the best of the author's knowledge, except for an upper bound to $\langle r^{-1}\rangle$ obtained by Thirring.[16] For example, using the monotonic decrease of $\rho(r)$, it has been found[17] that

$$\langle r^{-2}\rangle \geq \frac{4\langle r^{-1}\rangle}{3N} .$$

Using Eq. (14) in addition to this bound, and setting $N=Z$ for neutral atoms, the following interesting result is obtained:

$$2Z\langle r^{-1}\rangle \geq \langle r^{-2}\rangle \geq \frac{4\langle r^{-1}\rangle}{3Z} .$$

For $\langle r^{-1}\rangle$, Thirring found the upper bound

$$\langle r^{-1}\rangle \leq 2.289N^{4/3}$$

and, if we compare to the upper bounds given by Eq. (22), only for low Z atoms ($Z\leq 10$) is Thirring's bound improved.

This is a general feature of all these inequalities; they are more accurate for the low-Z atoms. We should keep in mind that all of them written here become equalities in the case of one-electron atoms because $f(r)=0$.

In conclusion, the assumption of non-negativity, for the ground state of the atoms, of the function $f(r)=\rho(r)+\rho'(r)/2Z$, which is verified for the Hartree-Fock wave functions of Clementi and Roetti, allows us to obtain inequalities between $\rho(0)$ and several expectation values $\langle r^k\rangle$, improving previous results. In addition, relationships among $\langle r^k\rangle$ values themselves are also obtained. Let us note that some of these values are experimentally measurable quantities or have a special physical interest.

We are very grateful for partial financial support from the Spanish Comisión Interministerial de Ciencia y Tecnología (CICyT).

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