Momentum unimodality effects in atomic systems

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Starting from the known unimodal character of the momentum density $\gamma(p)$ of numerous ground-state atoms, two general inequalities relating the location of the maximum p_{max}, the value at the origin $\gamma(0)$, and the momentum expectation values $\langle p^\alpha \rangle$, $\alpha > -3$, are found. As a limiting case, an upper bound to p_{max} is given in terms of the number of electrons N and the mean logarithmic momentum $\langle \ln p \rangle$. Finally, the quality of these bounds is numerically analyzed.

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The electron momentum density $\gamma(\mathbf{p})$ of an N-electron system is defined by

$$\gamma(\mathbf{p}) = \sum_{\sigma_i=-1/2}^{+1/2} \int |\tilde{\Psi}(\mathbf{p},\mathbf{p}_2,\ldots,\mathbf{p}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)|^2 \times d\mathbf{p}_2 \cdots d\mathbf{p}_N ,$$

where $\tilde{\Psi}$ denotes the $3N$-dimensional Fourier transform of the position wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;\sigma_1,\sigma_2,\ldots,\sigma_N)$ of the system. This quantity has been intensively studied during the last two decades both experimentally and theoretically. Indeed (i) it is accessible by many techniques [1–4] including x-ray and γ-ray Compton scattering and positron annihilation [1] as well as high-energy electron-impact spectroscopy [2] and binary $(e,2e)$ spectroscopy [3]; (ii) it has been recently used as the basic variable to set up new density-functional methods to analyze physical and chemical properties of atomic and molecular systems [4].

In spite of this increasing interest, the knowledge of rigorous properties of the momentum density $\gamma(\mathbf{p})$ or of its spherical average

$$\gamma(p) = \frac{1}{4\pi} \int \gamma(\mathbf{p}) d\Omega_p$$

is very scarce. Apart from the quantum mechanical non-negativity, one knows [5] that it behaves asymptotically as p^{-8}. On the other hand, the radial expectation values $\langle p^\alpha \rangle$ given by

$$\langle p^\alpha \rangle = \int p^\alpha \gamma(\mathbf{p}) d\mathbf{p} = 4\pi \int_0^\infty p^{\alpha+2} \gamma(p) dp, \quad -3 < \alpha < 5$$

are known to have a relevant physical meaning and, even more, some of them are experimentally measurable [6]. For instance, $\langle p^{-1} \rangle$ is twice the height of the peak of the Compton profile in photon-electron interaction, $\langle p^0 \rangle$ is the number of electrons of the system, $\langle p^2 \rangle$ is twice the kinetic energy, and $\langle p^4 \rangle$ is proportional to the relativistic correction to the kinetic energy by effect of mass variation.

We have studied [7] the momentum density $\gamma(p)$ of all ground-state atoms of the Periodic Table, hydrogen through xenon, by means of the near Hartree-Fock wave functions of Clementi and Roetti [8]. We found that, except in nine cases where $\gamma(p)$ have two maxima, the atomic momentum density is of unimodal character; this corroborates previous observations of various authors [9]. Specifically, in the atomic region $1 \le Z \le 54$ the momentum density belongs to one of the three following types.

(i) In atoms with $Z = 1$–7, 11–13, 19–26, 31, 37–42, and 49–50 the density $\gamma(p)$ is monotonically decreasing, i.e., it is unimodal with maximum at the origin.

(ii) In atoms with $Z = 8$–10, 14–18, 32–36, 46, and 51–54 the momentum density is unimodal with the maximum located away from the origin.

(iii) There are a few atoms, those with $Z = 27$–30, 43–45, and 47–48, with a momentum density having two maxima, one of them at the origin.

For illustration, in Fig. 1 the momentum density of three atoms is shown, one of each of the types mentioned above.

In this paper we will use the unimodality property of the momentum density to directly connect the location of the maximum, p_{max}, with various atomic fundamental

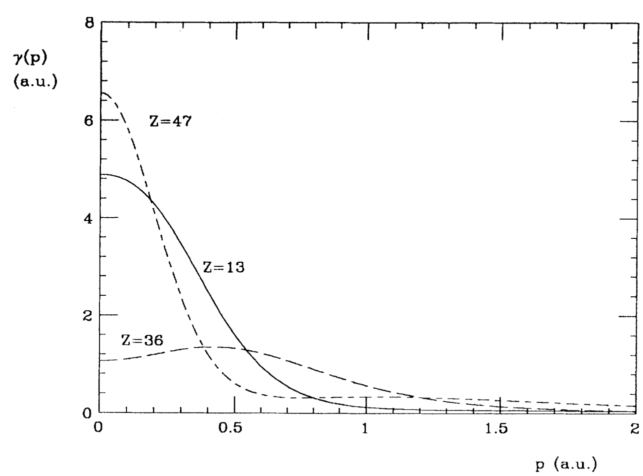

FIG. 1. Momentum density $\gamma(p)$ for the ground-state atoms with $Z = 13$, 36, 47 (types 1, 2, and 3, respectively; see text for further details). Calculations have been performed by means of the atomic wave functions of Clementi and Roetti [8]. Atomic units are used throughout.

quantities. Apart from its statistical meaning, i.e., the most probable value of the electron linear momentum, the location of the maximum of $\gamma(p)$, together with the well-known bounds and approximations on the value of $\gamma(0)$ [10] and the asymptotic behavior for $p\to\infty$ [5] would allow us to find rigorous information about the shape of the density $\gamma(p)$ from the knowledge of some of the above-mentioned fundamental quantities.

To start with, we realize that a straightforward consequence of the momentum unimodality is that the function

$$f(p)=(p_{\max}^x-p^x)\gamma'(p), \quad x>0$$

is non-negative. Then, its moments around the origin ξ_j, defined by

$$\xi_j=\int_0^\infty p^j f(p)dp, \quad j\ge 0 \tag{1}$$

are also non-negative. Since the ξ moments given by Eq. (1) have the values

$$\xi_j=\begin{cases}\frac{x}{4\pi}\langle p^{x-3}\rangle-p_{\max}^x\gamma(0), & j=0\\ \frac{j+x}{4\pi}\langle p^{j+x-3}\rangle-\frac{j}{4\pi}\langle p^{j-3}\rangle p_{\max}^x, & j>0\end{cases}$$

the condition $\xi_j\ge 0$ allows to find the following two sets of upper bounds to the location of the maximum $p_{\max}$:

$$p_{\max}\le\left[\frac{x\langle p^{x-3}\rangle}{4\pi\gamma(0)}\right]^{1/x}, \quad x>0$$

and

$$p_{\max}\le\left[\frac{(j+x)\langle p^{j+x-3}\rangle}{j\langle p^{j-3}\rangle}\right]^{1/x}, \quad j,x>0 .$$

In addition, the limiting case $x\to 0$ in the last inequality leads to another set of upper bounds given by

$$p_{\max}\le\exp\left\{\frac{1}{j}+\frac{\langle p^{j-3}\ln p\rangle}{\langle p^{j-3}\rangle}\right\}, \quad j>0 ,$$

where logarithmic expectation values are involved.

As interesting particular cases, we have some in terms of $\gamma(0)$ and one expectation value $\langle p^\alpha\rangle$, e.g.,

$$p_{\max}\le\left[\frac{\langle p^{-1}\rangle}{2\pi\gamma(0)}\right]^{1/2}=\left[\frac{J(0)}{\pi\gamma(0)}\right]^{1/2},$$

$$p_{\max}\le\left[\frac{3N}{4\pi\gamma(0)}\right]^{1/3},$$

$$p_{\max}\le\left[\frac{5\langle p^2\rangle}{4\pi\gamma(0)}\right]^{1/5}=\left[\frac{5E}{2\pi\gamma(0)}\right]^{1/5},$$

$$p_{\max}\le\left[\frac{7\langle p^4\rangle}{4\pi\gamma(0)}\right]^{1/7},$$

where $J(q)$ is the Compton profile and E is the absolute value of the total energy of the electronic system (equal to the kinetic energy, due to the virial theorem). Particular cases in terms of two radial expectation values are, e.g.

$$\begin{aligned}
p_{\max}&\le\frac{3N}{2\langle p^{-1}\rangle}=\frac{3N}{4J(0)}\equiv A ,\\
p_{\max}&\le\left[\frac{5\langle p^2\rangle}{2\langle p^{-1}\rangle}\right]^{1/3}=\left[\frac{5E}{2J(0)}\right]^{1/3},\\
p_{\max}&\le\left[\frac{7\langle p^4\rangle}{2\langle p^{-1}\rangle}\right]^{1/5}=\left[\frac{7\langle p^4\rangle}{4J(0)}\right]^{1/5},\\
p_{\max}&\le\left[\frac{5\langle p^2\rangle}{3N}\right]^{1/2}=\left[\frac{10E}{3N}\right]^{1/2},\\
p_{\max}&\le\left[\frac{7\langle p^4\rangle}{3N}\right]^{1/4},\\
p_{\max}&\le\left[\frac{7\langle p^4\rangle}{5\langle p^2\rangle}\right]^{1/2}=\left[\frac{7\langle p^4\rangle}{10E}\right]^{1/2},
\end{aligned} \tag{2}$$

and another one depending on the number of particles and the mean logarithmic momentum:

$$p_{\max}\le\exp\left\{\frac{1}{3}+\frac{\langle \ln p\rangle}{N}\right\}\equiv B . \tag{3}$$

Here, it is worth pointing out that the quantity $\langle \ln p\rangle$ (strongly related to the structure of the density in momentum space [7,11]) has been shown to provide tight upper bounds to the information entropy in momentum space, $S_\gamma\equiv-\int\gamma(\mathbf{p})\ln\gamma(\mathbf{p})d\mathbf{p}$ [7,11]. Moreover, the relation of $\langle \ln p\rangle$ with some other density functionals and radial expectation values is known [12].

All these bounds are valid for any atom having a unimodal $\gamma(p)$, i.e., of types 1 and 2. In principle, it is not

TABLE I. Values, for atoms of type 2 (see text for details), of the height of the Compton profile peak $J(0)$, the mean logarithmic momentum $\langle \ln p\rangle$, and the location $p_{\max}$ of the maximum of the momentum density $\gamma(p)$, as well as of the upper bounds given by Eqs. (2) and (3). Calculations have been performed by means of the atomic wave functions of Clementi and Roetti [8]. Atomic units are used throughout.

Z	$J(0)$	$\langle \ln p\rangle$	$p_{\max}$	A	B
8	2.78	0.701	0.30	2.16	1.52
9	2.75	0.809	0.44	2.45	1.53
10	2.73	0.908	0.55	2.75	1.53
14	5.11	0.916	0.08	2.05	1.49
15	5.07	0.957	0.19	2.22	1.49
16	5.11	1.014	0.30	2.35	1.49
17	5.08	1.032	0.37	2.51	1.48
18	5.07	1.071	0.43	2.66	1.48
32	7.00	1.463	0.12	3.43	1.46
33	7.05	1.476	0.21	3.51	1.46
34	7.15	1.487	0.30	3.57	1.46
35	7.20	1.500	0.36	3.65	1.46
36	7.24	1.513	0.42	3.73	1.46
46	7.04	1.678	0.92	4.90	1.45
51	9.61	1.677	0.16	3.98	1.44
52	9.74	1.682	0.26	4.00	1.44
53	9.82	1.688	0.31	4.05	1.44
54	9.88	1.695	0.36	4.10	1.44

possible to say which inequality provides the tightest bound. However, it is observed that, in general, the lower the order of the considered moments, the tighter the bound is. For illustration, let us study the accuracy of the bounds (2) and (3) in a numerical Hartree-Fock framework. Table I shows the accuracy of these bounds for all atoms of type 2 and up tp $Z=54$. It is observed that the bound depending on the experimentally measurable quantity $J(0)$ is always lower than 5 a.u., while the bound expressed by means of N and $\langle \ln p \rangle$, which goes from 1.44 to 1.53 a.u., clearly improves the aforementioned result in terms of $J(0)$.

Taking into account the quantity $\langle \ln p \rangle$ one improves clearly the bound. For all unimodal atoms studied, the bound to $p_{\max}$ goes from 1.44 to 1.53 a.u.

Summarizing, in the N-electron systems with a unimodal electronic momentum density it has been shown that the location of the maximum can be bounded from above by means of fundamental and/or experimentally measurable quantities such as, e.g., the atomic ground-state energy, the height of the Compton profile peak, the mean logarithmic momentum, the number of electrons, the relativistic correction to the kinetic energy, and the momentum density at the origin. The corresponding upper bounds are simple and transparent, although of a poor quality. Other upper bounds of much higher quality, as well as new lower bounds, can be easily obtained following the Stieltjes technique recently discussed and used in atomic and molecular physics [10]. This technique is based on the positivity of the so-called Hadamard determinants of the moments $\{\xi_j\}$, i.e.,

$$\Delta_j^n = \begin{vmatrix} \xi_j & \xi_{j+1} & \cdots & \xi_{j+n} \\ \xi_{j+1} & \xi_{j+2} & \cdots & \xi_{j+n+1} \\ \vdots & \vdots & \ddots & \vdots \\ \xi_{j+n} & \xi_{j+n+1} & \cdots & \xi_{j+2n} \end{vmatrix} > 0, \qquad n=0,1,2,\ldots .$$

The positivity of Δ_j^n for values of n other than zero produces more accurate but much more involved upper and lower bounds to $p_{\max}$.

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