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Approximate upper bounds to the momentum expectation value ratios $\langle p^2\rangle/\langle p^{-1}\rangle$ and $\langle p\rangle/\langle p^{-1}\rangle$ in atoms

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Within an isoelectronic series of atoms, reasonably tight upper bounds on the ratios of the momentum expectation values $\langle p^2\rangle/\langle p^{-1}\rangle$ and $\langle p\rangle/\langle p^{-1}\rangle$ respectively have been derived for the first time by using the Dresher's inequality.

Key words: Momentum density — Density functional

The nth moment of momentum, $\langle p^n\rangle$, represents a valuable parameter in the theory of electronic structure of atoms, molecules and solids. Through the radial momentum density, $I(p)$, the nth moment is related to the three dimensional momentum density, $\bar{\rho}(p)$, according to the following equations [1]

$$\langle p^n\rangle = \int_0^\infty dp\, p^n I(p) \tag{1}$$

$$I(p) = \int_0^{2\pi} d\phi_p \int_0^{\pi} d\theta_p\, p^2 \sin\theta_p \bar{\rho}(p) \tag{2}$$

It can be shown, using the definition of the isotropic Compton profile, $J(q)$,

$$J(q) = \tfrac{1}{2}\int_{|q|}^\infty dp\, p^{-1} I(p) \tag{3}$$

that $\langle p^{-1}\rangle$ is just twice the peak height, $J(0)$ of the Compton profile. The quantity $\langle p\rangle$ has been related [2] to the exchange energy of electrons in atoms within the free electron approximation. The electronic kinetic energy is well known to be given by $\langle p^2\rangle/2$ [3].

The purpose of this communication is to show that the representations of $\langle p^{-1}\rangle$, $\langle p\rangle$ and $\langle p^2\rangle$ in terms of the spherically symmetric single particle density $\rho(r)$ as given by

$$\langle p^{-1}\rangle=\frac{1}{2}\left(\frac{3}{\pi}\right)^{2/3}\int \rho(r)^{2/3}\,d\tau \tag{4}$$

$$\langle p\rangle=\pi\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \rho(r)^{4/3}\right]d\tau \tag{5}$$

and

$$\langle p^2\rangle=\frac{3}{5}(3\pi^2)^{2/3}\int \rho(r)^{5/3}\,d\tau \tag{6}$$

respectively, can be used to obtain the upper bounds to the ratios $\langle p^2\rangle/\langle p^{-1}\rangle$ and $\langle p\rangle/\langle p^{-1}\rangle$ within an isoelectronic series of atoms.

Denoting the three consecutive members in a given isoelectronic series with atomic numbers Z, $Z+1$, and $Z+2$ as A, B, and C respectively we propose that

$$\langle p^2\rangle_B/\langle p^{-1}\rangle_B\le\tfrac{1}{2}[\langle p^2\rangle_A/\langle p^{-1}\rangle_A+\langle p^2\rangle_C/\langle p^{-1}\rangle_C] \tag{7}$$

and

$$[\langle p\rangle_B/\langle p^{-1}\rangle_B]^{3/2}\le\tfrac{1}{2}[(\langle p\rangle_A/\langle p^{-1}\rangle_A)^{3/2}+(\langle p\rangle_C/\langle p^{-1}\rangle_C)^{3/2}] \tag{8}$$

The proposed bounds can be obtained from the Dreshers' inequality [4]

$$\left(\frac{\int |f+g|^p\,dT}{\int |f+g|^r\,dT}\right)^{1/(p-r)}\le\left(\frac{\int f^p\,dT}{\int f^r\,dT}\right)^{1/(p-r)}+\left(\frac{\int g^p\,dT}{\int g^r\,dT}\right)^{1/(p-r)} \tag{9}$$

valid for $p\ge 1\ge r\ge 0$, $f,\ g\ge 0$. The choice of $p=\frac{5}{3}$, $r=\frac{2}{3}$, $f=\rho_A$ and $g=\rho_C$ and the approximation [6] $\rho_A+\rho_C=2\rho_B$ in Eq. (9) leads to Eq. (7). Similarly, Eq. (8) can be obtained from Eq. (9) using the value of $p=\frac{4}{3}$ and the other quantities remaining the same as given above.

In Table 1 we have presented the results of the numerical tests of Eq. (7) and Eq. (8) on the Be-Ne, Ar and Kr isoelectronic series respectively. The momentum expectation values $\langle p^2\rangle$, $\langle p\rangle$ and $\langle p^{-1}\rangle$ have been taken from a recent compilation [5] based on the analytic Hartree-Fock wave functions [6]. It is remarkable to find that the quantities $\langle p^2\rangle/\langle p^{-1}\rangle$ and $[\langle p\rangle/\langle p^{-1}\rangle]^{3/2}$ respectively for a given member B within an isoelectronic series of atoms are bounded from above by the arithmatic mean of the same quantities corresponding to the two adjacent neighbours A and C respectively. Equations (7)-(8) can be used to obtain bounds on multinegative ions within a given iso-electronic series.

Table 1. Numerical tests of Eqs. (7) and (8) for the iso-electronic series of atoms containing 4, 6, 7, 8, 10, 18 and 36 electrons respectively

Atom	$[\langle p^2\rangle/\langle p^{-1}\rangle]$ HF	$\leq$ Eq. (7)	$[\langle p\rangle/\langle p^{-1}\rangle]^{3/2}$ HF	$\leq$ Eq. (8)
Li^-	1.047		0.210	
Be	4.61	6.19	1.28	1.85
B^+	11.342		3.48	
B^-	5.55		1.40	
C	15.06		3.98	4.78
N^+	24.57		8.16	
C^-	9.63		2.66	
N	19.44	21.64	6.19	7.13
O^+	33.65		11.60	
N^-	14.55		4.19	
O	26.95	29.31	8.83	9.88
F^+	44.07		15.5	
F^-	28.91	9.09		
Ne	47.12	49.84	16.39	17.68
Na^+	70.77		26.26	
Cl^-	76.40		17.61	
Ar	104.03	105.88	25.92	26.64
K^+	135.37		35.67	
Br^-	312.92		66.35	
Kr	380.14	380.62	85.73	86.09
Rb^+	448.33		105.86	

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