A study of the atomic momentum density by means of radial expectation values

1993 J. Phys. B: At. Mol. Opt. Phys. 26 4663

(http://iopscience.iop.org/0953-4075/26/24/002)

J. Phys. B: At. Mol. Opt. Phys. 26 (1993) 4663–4669. Printed in the UK

A study of the atomic momentum density by means of radial expectation values

A Zarzo†, J C Angulo‡ and J Antolín§‖

† Departamento de Matemática Aplicada, ETS Ingenieros Industriales, Universidad Politécnica de Madrid, 28006-Madrid, Spain

‡ Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, 18071-Granada, Spain

§ Departamento de Física Teórica, Facultad de Ciencias, Universidad de Zaragoza, 50009-Zaragoza, Spain

Received 31 March 1993

Abstract. It is shown how knowledge of a few low-order radial momentum expectation values $\langle p^k \rangle$ and the central value $\gamma(0)$ of the electron momentum density in atomic systems allows us to bound from below and above the momentum density $\gamma(p)$ for any value of the linear momentum, as well as the cumulative density and the cumulative radial density of any atom. The bounds are obtained by using Chebyshev inequalities and moment-theoretic methods. Knowledge of a greater number of expectation values results in an improvement in the accuracy of the above mentioned bounds. A numerical study of this accuracy is carried out in a Hartree–Fock framework.

1. Introduction

The electron distribution of atomic systems in momentum space, described in terms of the monoparticular density $\gamma(\boldsymbol{p})$, allows an easy interpretation of numerous physical and chemical phenomena (Parr and Yang 1989). The study of this distribution by means of the radial expectation values $\langle p^k \rangle$ defined by

$$\langle p^k \rangle \equiv \int p^k \gamma(\boldsymbol{p})\, \mathrm{d}\boldsymbol{p} = 4\pi \int_0^\infty p^{k+2} \gamma(p)\, \mathrm{d}p \qquad (k > -3) \tag{1}$$

where $\gamma(p)$ denotes the spherically averaged electronic momentum density, i.e.

$$\gamma(p) \equiv \frac{1}{4\pi} \int \gamma(\boldsymbol{p})\, \mathrm{d}\Omega_{\boldsymbol{p}} \tag{2}$$

is particularly interesting. Some of the expectation values $\langle p^k \rangle$ can be indirectly calculated from measurements in x- or γ-ray Compton scattering processes, as well as from electron scattering experiments (Williams 1977, Thakkar *et al* 1981, Cooper 1985, Bonham and Fink 1986).

We should note the physical meaning (Epstein 1973) of quantities like $\langle p^2 \rangle$ (twice the electron kinetic energy), $\langle p^4 \rangle$ (proportional to the relativistic correction to the kinetic energy, due to the mass variation), $\langle p^{-1} \rangle$ (twice the height of the peak of the Compton profile) and

‖ Permanent address: Departamento Física Aplicada, EUITIZ, Universidad de Zaragoza, 50009-Zaragoza, Spain.

0953-4075/93/244663+07$07.50

$\langle p^0 \rangle$ (the number of electrons of the system). The semiclassical relation between $\langle p^3 \rangle$ and the mean charge density $\langle \rho \rangle$, as well as between $\langle p \rangle$ and the Dirac–Slater exchange energy K_0 is also known (Gadre and Pathak 1981). Many other rigorous relationships among these quantities have been recently proved (see, e.g., Porras and Gálvez 1990).

The well known asymptotic behaviour (Benesch and Smith 1973)

$$\gamma(p) \rightsquigarrow p^{-8}$$

valid for high p-values, is of great importance in determining the range of orders for which the expectation values $\langle p^\alpha \rangle$ exist. It is easy to show that only those with $-3 < \alpha < 5$ are finite.

Moreover, it is also known (Thakkar 1987) that the atomic momentum density at the origin, $\gamma(0)$, plays a significant role in describing the long-range behaviour of the atomic charge density $\rho(r)$. Some lower bounds to $\gamma(0)$ have been published (Gálvez 1989, Angulo *et al* 1991). They are usually expressed in terms of one or more radial expectation values $\langle p^\alpha \rangle$. Numerical approximations and calculations of $\gamma(0)$ have also been reported (Gadre and Gejji 1984, Gadre and Chakravorty 1986).

Not many other properties of $\gamma(p)$ are known. For atoms with nuclear charge Z up to $Z = 54$, it has been numerically shown (Westgate *et al* 1985) that monotonicity (i.e. the negativity of the first derivative) only occurs for $Z = 1$–7, 11–13, 19–26, 31, 37–42, 49–50. For the remaining atoms in this region of the periodic table, some of them ($Z = 27$–30, 43–45, 47–48) present their absolute maximum at the origin, i.e. $\gamma_{\max} = \gamma(0)$, while for those with $Z = 8$–10 ,14–18, 32–36, 46, 51–54 this maximum is located at positions $p \neq 0$.

The aim of this work is to obtain rigorous upper and lower bounds to the spherically averaged atomic momentum density $\gamma(p)$ in terms of the aforementioned quantities $\gamma(0)$ and $\langle p^\alpha \rangle$. So, we cover the range of intermediate values of p for which rigorous results are very scarce. This type of result allows one to check numerical approximations and theoretical computations on $\gamma(p)$ or related quantities.

The only existing result in this field is that of Yue and Janmin (1984), who extended a previous work by King and Dykema (1983). They obtained upper bounds on $\gamma(p)$ in terms of the momentum expectation values $\langle p^{-2} \rangle$ and $\langle p^{-1} \rangle$, and the quantity $\langle r^2 \rangle$ (related to the diamagnetic susceptibility (March 1975)).

Here, we are interested in obtaining rigorous upper and lower bounds to $\gamma(p)$ in terms of $\gamma(0)$ and the first few lowest-order expectation values $\langle p^\alpha \rangle$, using a procedure based on Chebyshev inequalities (Shohat and Tamarkin 1943, Corcoran and Langhoff 1977). The same procedure also allows us to obtain upper and lower bounds on (i) the integrated momentum density $\Psi(p) = \int_0^p \gamma(p)\,\mathrm{d}p$ and (ii) the number of electrons with linear momentum lower than p, $B(p) = 4\pi \int_0^p p^2 \gamma(p)\,\mathrm{d}p$.

This technique has also been applied to find (Antolín *et al* 1993) upper and lower bounds to the atomic charge density $\rho(r)$, its first derivative $\rho'(r)$, the integrated charge density $\Psi(r) = \int_0^r \rho(r)\,\mathrm{d}r$ and the number of electrons enclosed in a sphere of radius r, $Q(r) = 4\pi \int_0^r r^2 \rho(r)\,\mathrm{d}r$, as well as in a variety of fields such as particle physics (Antolín and Cruz 1986, Antolín 1990), thermodynamics (Gordon 1968) and solid state physics (Gaspard and Cyrot-Lackmann 1973, López *et al* 1974).

In section 2, a review of the technique used is given. In section 3, the results of the previous section are applied to the physical cases represented by the aforementioned atomic functions $\gamma(p)$, $\Psi(p)$ and $B(p)$ (i.e. momentum density, integrated momentum density and integrated radial momentum density, respectively). Finally, some concluding remarks are given in section 4.

2. Chebyshev upper and lower bounds

Let $g(p)$ be a non-negative function related to $\gamma(p)$, in which the moments around the origin can be expressed in terms of $\gamma(0)$ and the radial expectation values $\langle p^\alpha \rangle$. We construct the Stieltjes function

$$H(z) = \int_0^\infty \frac{g(p)}{1 - zp}\,\mathrm{d}p.$$

The non-negativity of the weight function $g(p)$ allows us to obtain, via moment theory, approximations or rigorous bounds on $H(z)$ by using the properties of the orthogonal polynomials associated with the weight $g(p)$.

A formal series expansion of $H(z)$ can be obtained in terms of the moments

$$\mu_k = \int_0^\infty p^k g(p)\,\mathrm{d}p \qquad (k = 0, 1, 2, \ldots)$$

in the form

$$H(z) = \sum_{i=0}^{\infty} \mu_i z^i.$$

The rigorous bounding properties of the Padé approximants for this type of function are the consequence (Corcoran and Langhoff 1977, Antolín *et al* 1993) of bounding the cumulative weight $G(p) \equiv \int_0^p g(p)\,\mathrm{d}p$. The residues and poles of the Padé approximants are easily related to the quadrature parameters $\delta_i^{(n)} > 0$, $p_i^{(n)} \in [0, \infty)$ which satisfy the extremely non-linear moment equations

$$\mu_k = \sum_{i=1}^{n} \delta_i^{(n)} [p_i^{(n)}]^k \qquad k = 0, 1, \ldots, 2n - 1 \tag{3}$$

and yield bounds on $G(p)$ at the points $p_i^{(n)}$ in terms of $\delta_i^{(n)}$ as follows

$$\sum_{j=1}^{i-1} \delta_j^{(n)} \leqslant G(p_i^{(n)}) \leqslant \sum_{j=1}^{i} \delta_j^{(n)} \qquad i = 1, 2, \ldots, n. \tag{4}$$

It is possible to obtain bounds at any point $p \in [0, \infty)$, and not only at the fixed points $p_i^{(n)}$, by reducing the order of the moment equations (3) in the form

$$\mu_k = \sum_{i=1}^{n} \delta_i^{(n)}(p) [p_i^{(n)}(p)]^k \qquad k = 0, 1, \ldots, 2n - 2 \tag{5}$$

where now we can impose a quadrature point at an arbitrary position $p \equiv p_i^{(n)}$ for some value of i (Corcoran and Langhoff 1977, Baker and Graves-Morris 1981, Antolín and Cruz 1986). A more detailed description of the method can be found in the above mentioned references, as well as in Antolín *et al* (1993). It should be pointed out that, due to the procedure used to obtain the bounds, the arithmetic mean of the upper and the lower bound obtained for a given number of moments is a convergent approximation to $\gamma(p)$. This type of approximation can be compared with other techniques which build up densities from moments (Antolín 1990).

3. Applications to atomic systems

In the previous section, a model-independent method to obtain lower and upper pointwise bounds to a given quantity $G(p)$ has been derived in terms of the moments of $g(p)$. Here this method can be applied in a straightforward manner to the following atomic quantities: the momentum density $\gamma(p)$; the integrated momentum density $\Psi(p)$, and the number of electrons with linear momentum lower than p, $B(p)$ taking into account the following observations.

(i) $g(p) = -\gamma'(p)$. The non-negativity of this function occurs for many atomic systems, as previously pointed out. We can bound the cumulative weight

$$\int_0^p g(p)\,\mathrm{d}p = \gamma(0) - \gamma(p)$$

in terms of the moments

$$\mu_k = \int_0^\infty p^k g(p)\,\mathrm{d}p = \begin{cases} \gamma(0) & k = 0 \\ k\langle p^{k-3}\rangle/4\pi & k = 1, 2, \ldots, 7 \end{cases}$$

which results in upper and lower bounds to $\gamma(p)$ in terms of $\gamma(0)$, $\langle p^{-2}\rangle$, $\langle p^{-1}\rangle$, ...

(ii) $g(p) = \gamma(p)$. The quantum-mechanical non-negativity of the electron momentum density allows us to bound the function

$$\Psi(p) = \int_0^p g(p)\,\mathrm{d}p$$

in terms of the moments

$$\nu_k = \int_0^\infty p^k g(p)\,\mathrm{d}p = \frac{\langle p^{k-2}\rangle}{4\pi} \qquad k = 0, 1, \ldots, 6.$$

(iii) $g(p) = 4\pi p^2 \gamma(p) \equiv I(p)$. The non-negativity of the radial momentum density makes it possible to bound the function

$$B(p) = \int_0^p I(p)\,\mathrm{d}p.$$

(which represents the number of electrons with linear momentum lower than p) in terms of the radial expectation values

$$\xi_k = \int_0^\infty p^k I(p)\,\mathrm{d}p = \langle p^k\rangle \qquad k = 0, 1, 2, 3, 4.$$

Then, the method provides rigorous pointwise lower and upper bounds to $\gamma(p)$, $\Psi(p)$ and $B(p)$ in the whole periodic table by means of $\gamma(0)$ and the momentum expectation values $\langle p^k\rangle$. To have an idea of the quality of these bounds, we have numerically analysed them in three different atoms (helium, potassium, rubidium) within the framework of a realistic model.

In figures 1(*a*), 2(*a*) and 3(*a*), we compare the bounds obtained by using four, six and eight moments with the Hartree–Fock (Clementi and Roetti 1974) momentum density $\gamma(p)$ of helium ($Z = 2$), potassium ($Z = 19$) and rubidium ($Z = 37$) atoms, respectively. It is

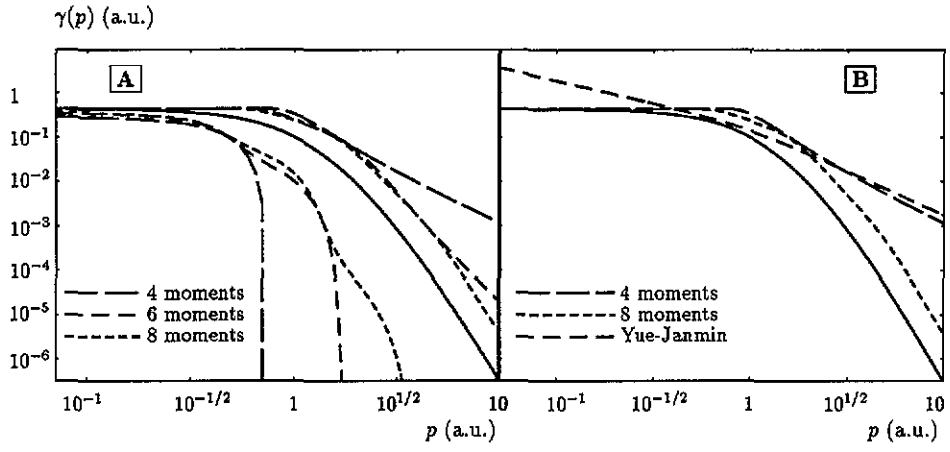

Figure 1. (*a*) Spherically averaged momentum density $\gamma(p)$ (full curve) and four, six and eight moment upper and lower bounds and (*b*) comparison between the four and eight moment upper bounds and the Yue and Janmin upper bound (see equation (1) of Yue and Janmin (1984)) for the helium ground-state atom. The full curve represents the spherically averaged momentum density. Atomic units are used.

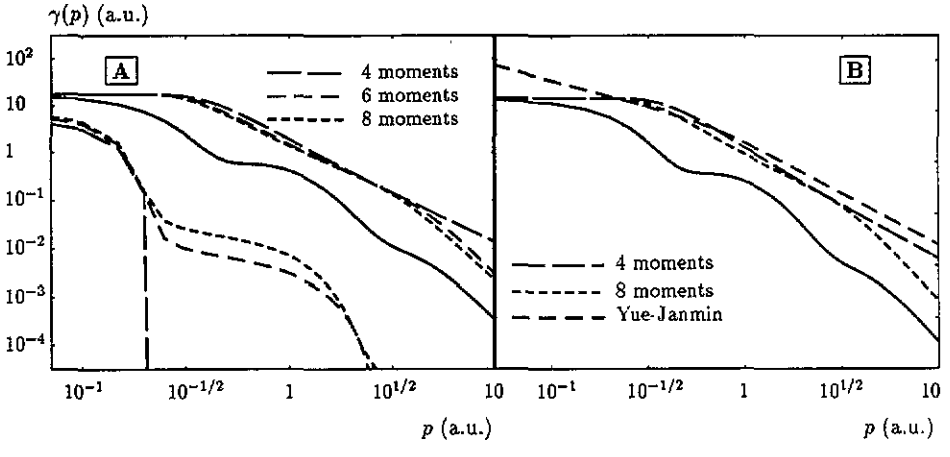

Figure 2. (*a*) Spherically averaged momentum density $\gamma(p)$ (full curve) and four, six and eight moment upper and lower bounds, and (*b*) comparison between the four and eight moment upper bounds and the Yue and Janmin upper bound (see equation (1) of Yue and Janmin (1984)) for the potassium ground-state atom. The full curve represents the spherically averaged momentum density. Atomic units are used.

observed that the accuracy of these bounds improves for the three atoms here studied, when the number of moments considered increases, as we expected. This improvement is more evident for the lower bounds, particularly in going from the four-moment to the six-moment case.

In figures 1(*b*), 2(*b*) and 3(*b*), our upper bounds are compared with the best (for intermediate and high momenta) upper bound of Yue and Janmin, i.e. equation (1) of Yue and Janmin (1984), for each of the above mentioned atoms. Notice that our results are

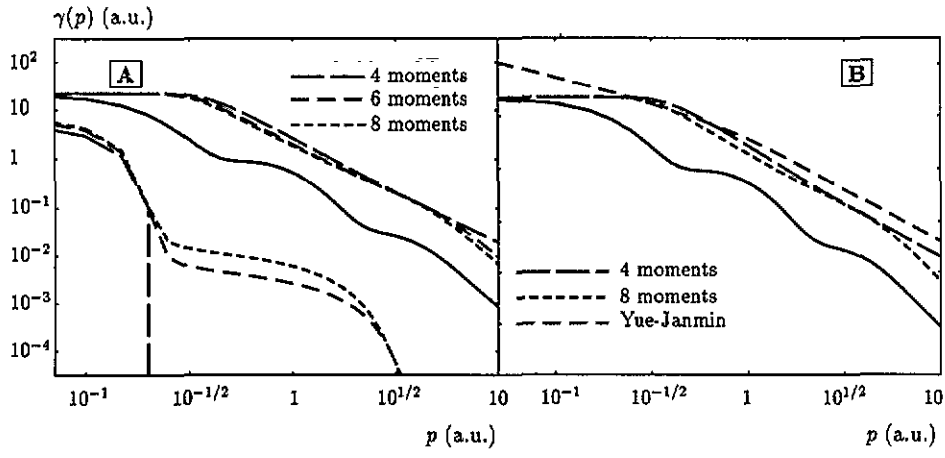

Figure 3. (*a*) Spherically averaged momentum density $\gamma(p)$ (full curve) and four, six and eight moment upper and lower bounds and (*b*) comparison between the four and eight moment upper bounds and the Yue and Janmin upper bound (see equation (1) of Yue and Janmin (1984)) for the rubidium ground-state atom. The full curve represents the spherically averaged momentum density. Atomic units are used.

considerably better than those of Yue and Janmin at low and high momenta (specially for the case of eight moments), while their upper bound is lower than ours for a narrow region around $p = 1$ au.

4. Concluding remarks

The knowledge of some radial momentum expectation values $\langle p^k \rangle$ and the central value of the electron momentum density $\gamma(0)$ allows us to obtain rigorous upper and lower bounds not only to the momentum density $\gamma(p)$ for those atoms having a $\gamma(p)$ monotonically decreasing, but also to the cumulative momentum density $\Psi(p)$ as well as the cumulative radial momentum density $B(p)$ for any atom. These bounds require knowledge of only the few lowest-order radial expectation values $\langle p^k \rangle$, as their accuracy improved when the number of moments considered is increased.

It is remarkable that the arithmetic mean of the upper and lower bound to $\gamma(p)$, $\Psi(p)$ and $B(p)$ for a given number of moments converges to the exact bounded function when this number increases.

Moreover, it should be pointed out that the procedure described here in order to obtain the bounds can be applied to many other interesting density functions.

Acknowledgments

We are grateful to Professor J S Dehesa of the Departamento de Física Moderna of the Universidad de Granada for helpful comments and for his kind interest in this work.

Two of the authors (J Antolín and J C Angulo) wish to acknowledge partial financial support from DGICYT under different contracts. Also, A Zarzo is grateful to the Universidad Politécnica de Madrid due to the 'acción concertada' No A92012.

References

Angulo J C, Dehesa J S and Gálvez F J 1991 *Z. Phys.* D **18** 127

Antolín J 1990 *J. Math. Phys.* **31** 791

Antolín J and Cruz A 1986 *J. Phys. G: Nucl. Phys.* **12** 947

Antolín J, Zarzo A and Angulo J C 1993 *Phys. Rev.* A **48** in press

Baker G A Jr and Graves-Morris P 1981 *Padé Approximants (Encyclopedia of Mathematics and its Applications 14)* (London: Addison-Wesley) pp 132–8

Benesch R and Smith Jr V H 1973 *Wave Mechanics: The First Fifty Years* ed W C Price, S S Chissick and T Ravensdale (London: Butterworths) pp 357–77

Bonham R A and Fink M 1986 *Phys. Rev.* A **33** 1569

Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 177

Cooper M J 1985 *Rep. Prog. Phys.* **48** 415

Corcoran C T and Langhoff P W 1977 *J. Math. Phys.* **18** 651

Epstein I R 1973 *Phys. Rev.* A **8** 160

Gadre S R and Chakravorty S J 1986 *Phys. Rev.* A **33** 1374

Gadre S R and Gejji S P 1984 *J. Chem. Phys.* **80** 1175

Gadre S R and Pathak R K 1981 *Phys. Rev.* A **24** 2906

Gálvez F J 1989 *Phys. Rev.* A **39** 501

Gaspard J P and Cyrot-Lackmann F 1973 *J. Phys. C: Solid State Phys.* **6** 3077

Gordon R G 1968 *J. Math. Phys.* **9** 655

King F and Dykema K J 1983 *J. Phys. B: At. Mol. Phys.* **16** 2071

López C, Yndurain F and Yndurain F J 1974 *J. Phys. C: Solid State Phys.* **7** 61

March N H 1975 *Self-Consistent Fields in Atoms* (Oxford: Pergamon)

Parr R G and Yang W 1989 *Density-Functional Theory of Atoms and Molecules* (New York: Oxford University Press)

Porras I and Gálvez F J 1990 *Phys. Rev.* A **41** 4052

Shohat J and Tamarkin A J 1943 *The Problem of Moments* (New York: American Mathematical Society)

Thakkar A J 1987 *J. Chem. Phys.* **86** 5060

Thakkar A J, Simas A M and Smith V H Jr 1981 *Chem. Phys.* **63** 175

Westgate W M, Simas A M and Smith V H Jr 1985 *J. Chem. Phys.* **83** 4054

Williams B G (ed) 1977 *Compton Scattering: The Investigation of Electron Momentum Distributions* (New York: McGraw-Hill)

Yue W and Janmin L 1984 *Phys. Scr.* **30** 414