Z. Phys. D 28, 269–273 (1993)

ZEITSCHRIFT
FÜR PHYSIK D

Compton profiles and momentum space inequalities

J.C. Angulo[1], **J. Antolín**[2,*], **A. Zarzo**[3]

[1] Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain
[2] Departamento de Física Teórica, Facultad de Ciencias, Universidad de Zaragoza, E-50009 Zaragoza, Spain
[3] Departamento de Matemática Aplicada, E.T.S. Ingenieros Industriales, Universidad Politécnica de Madrid, E-28006 Madrid, Spain

Received: 19 April 1993 / Final version: 5 August 1993

Abstract. Rigorous upper and lower bounds to the atomic Compton profile $J(q)$ are obtained for any value of the momentum transferred q in terms of radial expectation values $\langle p^n \rangle$ of the atomic momentum density $\gamma(\mathbf{p})$. In doing so, a procedure based on moment-theoretic techniques and Chebyshev inequalities has been used. This type of results can be employed to study the compatibility of diverse information obtained by using different models, techniques, numerical calculations or experimental data. The same method allows also to obtain approximations to the Compton profile and to bound other relevant characteristics of $J(q)$. A comparison of the approximations with some previously known Maximum Entropy Approximations is done. In order to test the accuracy of the bounds, a numerical study of the results is carried out in a Hartree-Fock framework for atomic systems.

PACS: 31.10.+z; 31.15.+q

The one-electron densities of a N-electron system in position and momentum spaces, $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ respectively, are basic ingredients in the study of many physical properties from a Density Functional Theory perspective, which is nowadays one of the fundamental theories of matter [1].

Much attention has been paid to the relevant role played by the position-space density $\rho(\mathbf{r})$ in the description of many-electron systems. However, a similar study in terms of the electronic distribution in momentum space has still to be much more worked out. Moreover, in the last decade the electron momentum distribution of atomic and molecular systems has been shown to be experimentally accessible [2–4]. Let us just remark here that the atomic Compton profiles can be obtained by means of photon-photon or photon-electron coincidence measurements [5–7], high resolution Compton scattering [8], angular correlation of positron annihilation radiation [9], $(e, 2e)$ coincidence spectroscopy [10] and magnetic Compton scattering experiments [11].

It is worthy to point out that the height of the peak of the Compton profile may be the most accurately measured quantity in atomic and molecular physics [2]. However, the same accuracy does not occur when Compton experiments require high values of the momentum transferred. In spite of the experimental improvements, the relation between the measured cross sections and Compton profiles is not straightforward, specially at high energies. This is mainly due to the fact that the Compton profile $J(q)$ can only be measured up to some finite value of the momentum transferred $q_{\max}$, which depends on the type of experiment. So, the computation of quantities such as expectation values of the momentum density $\gamma(\mathbf{p})$ from experimental Compton profiles involves extrapolation techniques or the use of analytical models. In Ref. [12], a careful analysis of the expectation values of the momentum density predicted from statistically simulated Compton profiles is carried out. The numerical tests performed in this work indicate that the accuracy in the obtention of the higher order expectation values from $J(q)$ strongly depends on $q_{\max}$. An asymptotic constraint (calculated in a Hartree-Fock framework) had to be used to reduce drastically the admissible range for these moments and therefore to stabilize the extrapolation.

The reciprocal form factor or characteristic function [13–17], quantum-mechanical calculations [18–19] and information theory with momentum and energy constraints [20–22] have been also used to obtain Compton profile approximations. But results on this subject other than approximations are very scarce in the literature, particularly for the momentum density $\gamma(\mathbf{p})$ [23–25]. Therefore, it is useful and interesting to have rigorous relationships between Compton profiles and momentum expectation values in order to test theoretical approximations or experimental measurements.

In this work it is shown that the knowledge (from any source) of the first few moments of the momentum den-

* *Permanent address:* Departamento Física Aplicada, E.U.I.T.I.Z., Universidad de Zaragoza, E-50009 Zaragoza, Spain

sity $\langle p^n \rangle$ imposses serious restrictions on the values of the Compton profile at any point. In this sense, theoretical calculations of expectation values (based on electronic structure computations within a concrete model) can be used to check their compatibility with Compton profiles constructed by using experimental data, other models or techniques. To be more precise we rigorously bound from above and from below the Compton profile $J(q)$ for any value of the momentum transferred q in terms of the radial expectation values $\langle p^n \rangle$ of the electron momentum density $\gamma(\mathbf{p})$.

These type of results can also be used to obtain an allowed corridor for future Compton profiles values, as well as to study the consistency of different sets or sources of experimental data. Specifically, a filtration procedure of experimental points or error bars can be outlined: those experimental points whose error bars lie completely outside the allowed corridor are not compatible with the moments (and therefore with the model or the hypothesis used to calculate the moments).

The isotropic Compton profile $J(q)$ and the spherically averaged momentum density $\gamma(p)$ are related in the impulse approximation as follows [26-27]

$$J(q) = 2\pi \int_{|q|}^{\infty} p\gamma(p)\,\mathrm{d}p$$

where q is the projection of the initial momentum of the electron onto the scattering vector. Notice that the quantum-mechanical non-negativity of the density $\gamma(p)$ implies the monotonic decreasing of the function $J(q)$, i.e. that $J'(q) \leqq 0$. On the other hand, the momentum density $\gamma(p)$ can be obtained from the Compton profile $J(q)$ by differentiation:

$$\gamma(p) = -\frac{1}{2\pi p}\frac{\mathrm{d}J(p)}{\mathrm{d}p}$$

The above relations allow to express the radial expectation values of the momentum density

$$\langle p^n \rangle = \int p^n \gamma(\mathbf{p})\,\mathrm{d}\mathbf{p}$$

by means of the one-dimensional moments of the Compton profile, namely

$$\mu_n = \int_0^{\infty} q^n J(q)\,\mathrm{d}q$$

in the form

$$\langle p^n \rangle = \begin{cases} 2J(0), & n = -1 \\ 2(n+1)\mu_n, & 0 \leqq n < 5 \end{cases} \qquad (1)$$

where the upper limit on n is imposed by the high-momentum asymptotic behavior of the momentum density as $\gamma(p) \rightsquigarrow p^{-8}$ [26, 28-29]. Here, the normalization used is $\langle p^0 \rangle = N$, i.e. to the number of electrons of the system. Some of these expectation values have an intrinsic physical meaning. For instance, the kinetic energy of the N-electron system and its relativistic correction due to the mass variation are proportional to $\langle p^2 \rangle$ and $\langle p^4 \rangle$, respectively [30]. There are valuable, but limited, information on these expectation values, either from experimental data, or by using different models or rigorous relations. The results obtained in this work suggest that a greater effort in the model-independent knowledge of expectation values would be desirable.

The non-negativity of the function $-J'(q)$ allows to bound the quantity $J(q)$ in terms of the moments $\langle p^n \rangle$. In doing so, we will use moment theory and Chebyshev inequalities [31-33]. The same technique has been successfully applied in a variety of fields such as particle physics [34-35], solid state physics [36-37] and atomic physics [38-39]. Chebyshev inequalities provide upper and lower bounds for distributions of the type

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

with $g(q) \geqq 0$, in terms of the first $2n$ moments

$$\xi_k = \int_0^{\infty} q^k g(q)\,\mathrm{d}q \quad (k = 0, 1, \ldots, 2n-1)$$

The bounds are built up by computing the quadrature parameters $\delta_i^{(n)} > 0$, $q_i^{(n)} \in [0, \infty)$ which satisfy the moment equations [40]

$$\xi_k = \sum_{i=1}^{n} \delta_i^{(n)} [q_i^{(n)}]^k \quad (k = 0, 1, \ldots, 2n-1) \qquad (2)$$

The solution yields bounds on $\Psi(q)$ at the points $q_i^{(n)}$ in terms of $\delta_i^{(n)}$:

$$\sum_{j=1}^{i-1} \delta_j^{(n)} \leqq \Psi(q_i^{(n)}) \leqq \sum_{j=1}^{i} \delta_j^{(n)} \quad (\mathrm{i} = 1, 2, \ldots, n)$$

It is possible to obtain bounds at any point $q \geqq 0$ by reducing the order of the moment equations (2) in the form

$$\xi_k = \sum_{i=1}^{n} \delta_i^{(n)}(q) [q_i^{(n)}(q)]^k \quad (k = 0, 1, \ldots, 2n-2) \qquad (3)$$

where $q \equiv q_i^{(n)}$ for some value of i [32-33].

Now, let us consider the non-negative function $g(q) = -J'(q)$. Then, taking into account (1) we get

$$\xi_n = -\int_0^{\infty} q^n J'(q)\,\mathrm{d}q$$

$$= \begin{cases} J(0) = \dfrac{\langle p^{-1} \rangle}{2}, & n = 0 \\ \dfrac{\langle p^{n-1} \rangle}{2}, & 1 \leqq n < 6 \end{cases}$$

The use of these values in (3) provides upper and lower bounds on $\Psi(q) = J(0) - J(q)$ or, equivalently, we bound $J(q)$ in terms of radial expectation values $\langle p^n \rangle$ at any point q. The same method allows one to obtain rigorous bounds on the half-width $q_{0.5}$ of $J(q)$, which is a relevant parameter on the characterization of the Compton profile.

It is worthwhile to point out that, due to the procedure used, the arithmetic mean of the upper and the lower bounds to $J(q)$ would be convergent to this function by increasing the number of moments involved [32]. However, we should remember that the finite moments $\langle p^n \rangle$ are limited to the range $-3 < n < 5$ for atomic systems [28–29], being impossible to increase arbitrarily the number of them.

We have studied the accuracy of the upper and lower bounds to $J(q)$ by means of the near Hartree-Fock atomic wavefunctions of Clementi and Roetti [41] for several ground-state neutral atoms of the periodic table. We have observed that (i) in general, the accuracy of both upper and lower bounds decreases when increasing the number of electrons N, (ii) the best upper bounds correspond to the case of inert gases (iii) the halogens show up the more accurate lower bounds, and (iv) the worst upper and lower bounds (in accuracy) are those of the alkaline metals. It is also observed that the 6-moment bounds are only slightly better than the 4-moment bounds, being the improvement more apparent for the upper bounds. For illustration, the lower and upper bounds on $J(q)$ obtaining by using either 4 or 6 moments are shown for the Helium ($N=2$), Lithium ($N=3$), Neon ($N=10$) and Chlorine ($N=17$) atoms, in Figs. 1, 2, 3 and 4 respectively.

To the best of our knowledge, these are the first rigorous bounds provided for the Compton profile $J(q)$. However, some approximations obtained by means of information-theorectic methods are known [20–22]. Here, we will only remember the Maximum Entropy Approximations built up with the momentum and energy constraints [20–22]:

$$J_1(q) = \frac{N^2}{\langle p \rangle} e^{-\frac{2N}{\langle p \rangle} q} \tag{4}$$

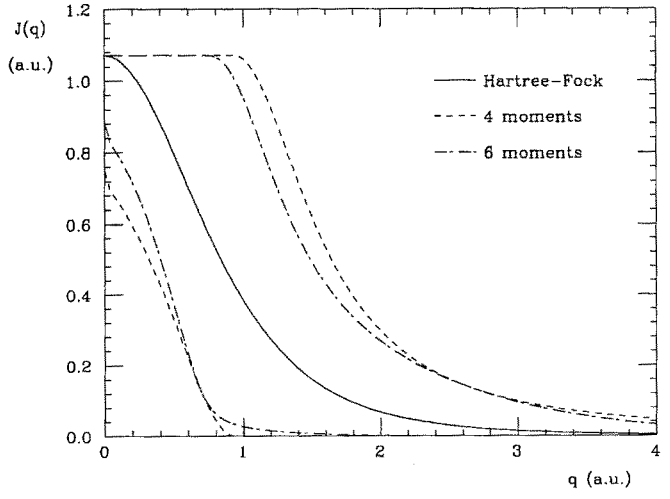

Fig. 1. Upper and lower bounds to the Compton profile $J(q)$ of the Helium ground state atom, obtained by using 4 and 6 moments. Numerical calculations were performed in the Hartree-Fock framework of Clementi and Roetti [41]. Atomic units are used

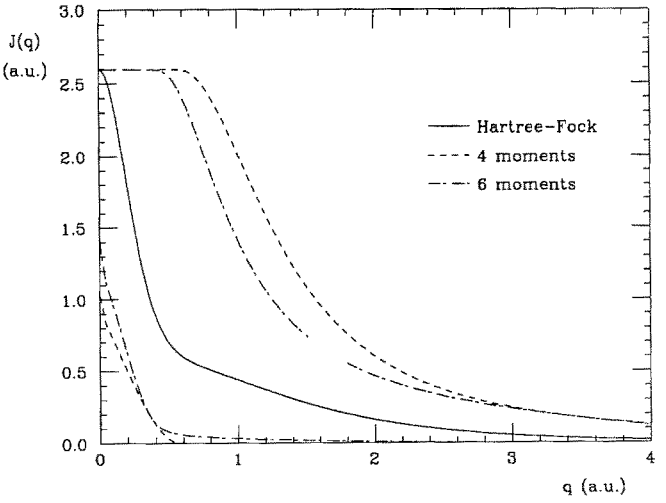

Fig. 2. Upper and lower bounds to the Compton profile $J(q)$ of the Lithium ground state atom, obtained by using 4 and 6 moments. Numerical calculations were performed in the Hartree-Fock framework of Clementi and Roetti [41]. Atomic units are used

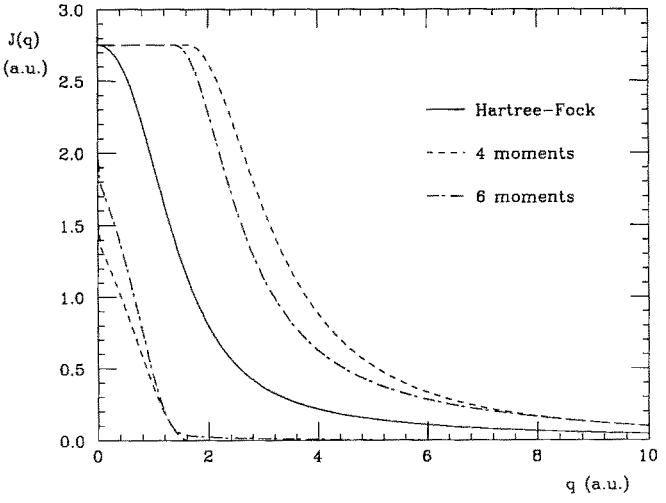

Fig. 3. Upper and lower bounds to the Compton profile $J(q)$ of the Neon ground state atom, obtained by using 4 and 6 moments. Numerical calculations were performed in the Hartree-Fock framework of Clementi and Roetti [41]. Atomic units are used

and [20, 21]

$$J_2(q) = \left(\frac{3N^3}{2\pi \langle p^2 \rangle} \right)^{1/2} e^{-\frac{3N}{2\pi \langle p^2 \rangle} q^2} \tag{5}$$

respectively. It is interesting to remark that Maximum Entropy Approximations and our Chebyshev bounds can be used as complementary methods in the study of Compton profiles by means of radial momentum expectation values, since the Chebyshev method provides rigorous upper and lower bounds on the profile and the Maximum Entropy Approximations choose, among all admissible functions (which satisfy the bounds), the one most reasonable in the sense that is the least-biased profile compatible with the information we actually have.

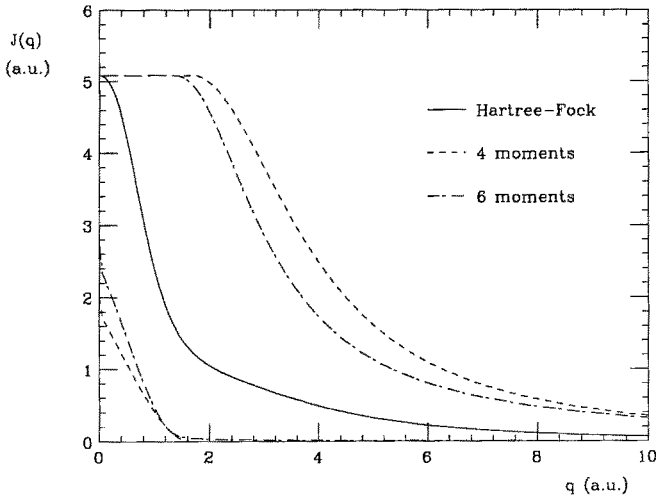

Fig. 4. Upper and lower bounds to the Compton profile $J(q)$ of the Chlorine ground state atom, obtained by using 4 and 6 moments. Numerical calculations were performed in the Hartree-Fock framework of Clementi and Roetti [41]. Atomic units are used

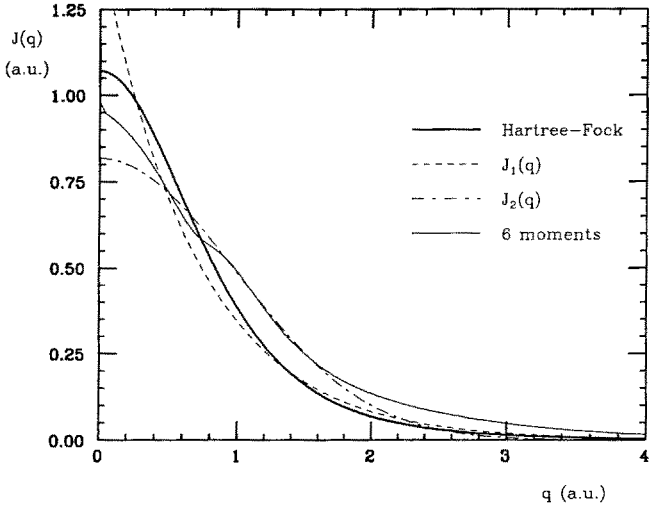

Fig. 5. Comparison between the Maximum Entropy Approximations [20–22] given by (4) and (5), and our 6-moment approximation to the Compton profile $J(q)$ of the Helium ground state atom. Numerical calculations were performed in the Hartree-Fock framework of Clementi and Roetti [41]. Atomic units are used

In Fig. 5 we compare the Maximum Entropy Approximations $J_1(q)$ and $J_2(q)$ with our 6-moment approximation for the Helium ground state atom in the above mentioned numerical framework. Notice that the relative quality of the three approximations depends largely on the region of q-values considered.

In summary, rigorous upper and lower bounds for the Compton profile $J(q)$ in terms of radial expectation values $\langle p^n \rangle$ have been obtained by means of moment-theoretic methods and Chebyshev inequalities. Moreover, an approximation to $J(q)$ in terms of the same expectation values has been obtained, being comparable to other ones obtained by using different information and techniques. The above results can be used to study the consistency and compatibility of different models (in which the moments are calculated) with experimental data or other kind of techniques or numerical approximations which indirectly lead to Compton profiles.

We are grateful to Prof. 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. Antoín and J.C. Angulo) wish to acknowledge partial finantial support from DGICYT under different contracts.

References

1. Parr, R.G, Yang, W.: Density-functional theory of atoms and molecules. Oxford: Oxford University Press 1989
2. Williams, B.G. (ed.): Compton scattering: The investigation of electron momentum distributions. New York: McGraw Hill 1977
3. Cooper, M.J.: Rep. Prog. Phys. **48**, 415 (1985)
4. McCarthy, I.E., Weigold, E.: Phys. Rep. C**27**, 275 (1976)
5. Manninen, S.: Phys. Rev. Lett. **57**, 1500 (1986)
6. Marchetti, V., Frank, C.: Phys. Rev. Lett. **59**, 1557 (1987)
7. European Synchrotron Radiation Facility, Foundation Phase Report, Chap. V (1987)
8. Manninen, S., Etelaniemi V., Suortti, P.: Phys. Rev. Lett. **61**, 2815 (1988)
9. Genoud, P., Singh, A.K., Manuel, A.A., Jarlborg, T., Walker, E., Peter, M., Weller, M.: J. Phys. F**18**, 1933 (1988)
10. Cook, J.P.D., Mitroy, J., Weigold, E.: Phys. Rev. Lett. **52**, 1116 (1984)
11. Cooper, M.J., Laundy, D., Cardwell, D.A., Timms, D.N., Holt, R.S., Clark, G.: Phys. Rev. B**34**, 5984 (1986)
12. Thakkar, A.J., Simas, A.M., Smith Jr., V.H.: Mol. Phys. **41**, 1153 (1980)
13. Gadre, S.R., Chakravorty, S.J.: Proc. Indian Acad. Sci. (Chem. Scie.) **96**, 241 (1986)
14. Koga, T., Morita, M.: J. Chem. Phys. **77**, 6345 (1982)
15. Benesch, R., Singh, S.R., Smith Jr., V.H.: Chem. Phys. Lett. **10**, 151 (1971)
16. Weyrich, W., Pattison, P., Williams, B.G.: Chem. Phys. **41**, 271 (1979)
17. Thakkar, A.J., Simas, A.M., Smith Jr., V.H.: Chem. Phys. **63**, 175 (1981)
18. Kryachko, E.S., Koga, T.: J. Chem. Phys. **91**, 1108 (1989)
19. Thakkar, A.J., Simas, A.M., Smith Jr., V.H.: J. Chem. Phys. **81**, 2953 (1984)
20. Gadre, S.R., Sears, S.B.: J. Chem. Phys. **71**, 4321 (1979)
21. Sears, S.B., Gadre, S.R.: J. Chem. Phys. **75**, 4626 (1981)
22. Koga, T.: Theor. Chim. Acta **64**, 249 (1984)
23. Gadre, S.R., Chakravorty, S.J.: Chem. Phys. Lett. **120**, 101 (1985)
24. Westgate, W.M., Simas, A.M., Smith Jr., V.H.: J. Chem. Phys. **83**, 4054 (1985)
25. Yue, W., Janmin, L.: Phys. Scr. **30**, 414 (1984)
26. Benesch, R., Smith Jr., V.H.: Wave mechanics: the first fifty years. Price, W.C., Chissick, S.S., Ravensdale, T. (eds.), pp. 357–377). London: Butterworth 1973
27. Dumond, J.W.M.: Phys. Rev. **35**, 643 (1929)
28. Kimball, J.C.: J. Phys. A**8**, 1513 (1975)
29. Thakkar, A.J.: J. Chem. Phys. **86**, 5060 (1987)
30. Epstein, I.R.: Phys. Rev. A**8**, 160 (1973)
31. Shohat, J., Tamarkin, A.J.: The problem of moments. New York: American Mathematical Society 1943
32. Corcoran, C.T., Langhoff, P.W.: J. Math. Phys. **18**, 651 (1977)
33. Baker Jr., G.A., Graves-Morris, P.: Padé approximants. In: Encyclopedia of Mathematics and its Applications. Vol. 14, pp. 132–138. London: Addison-Wesley 1981

34. Antolín, J. Cruz, A.: J. Phys. G**12**, 947 (1986)
35. Antolín, J.: J. Math. Phys. **31**, 791 (1990)
36. Gaspard, J.P., Cyrot-Lackmann, F.: J. Phys. C**6**, 3077 (1973)
37. López, C., Yndurain, F., Yndurain, F.J.: J. Phys. C**7**, 61 (1974)
38. Antolín, J., Zarzo, A., Angulo, J.C.: Phys. Rev. A**48**, December 1993
39. Zarzo, A., Angulo, J.C., Antolín,J.: J. Phys. B (1993) (in press)
40. Gilewicz, J.: Approximants de Padé. In: Lecture Notes in Mathematics. Vol. 667. Berlin, Heidelberg, New York: Springer 1978
41. Clementi, E., Roetti, C.: At. Data Nucl. Data Tables **14**, 177 (1974)