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Maximum-entropy analysis of one-particle densities in atoms

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Abstract. The Maximum-Entropy formalism is used to obtain approximations to the spherically averaged charge and momentum densities. The only information required is the first few radial expectation values. Analytical and numerical approximations to the central values of the densities are calculated. Moreover, the unused or unknown radial expectation values are estimated by means of the moments of these Maximum-Entropy densities. As illustration, the accuracy of these approximations are numerically studied in a Hartree-Fock framework. This method is complementary to the one which makes use of the Stieltjes-Chebyshev inequalities and leads to the least biased approximate densities compatible with the information we use.

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1. Introduction

The one-particle densities of a N-fermion system in position and momentum spaces, $\rho(\boldsymbol{r})$ and $\gamma(\boldsymbol{p})$ 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].

One of the most important ways of obtaining experimental information on such densities is the measurement of Compton profiles [2–4],

$$J(q) = \frac{1}{2} \int\limits_{p \geq q} \frac{\gamma(\boldsymbol{p})}{p} \, \mathrm{d}\boldsymbol{p} \; (p = |\boldsymbol{p}|) \tag{1}$$

specially by means of photon-photon or photon-electron coincidence experiments [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].

However, the main problem is 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 $\gamma(\boldsymbol{p})$ from experimental Compton profiles involves extrapolation techniques or the use of analytical models [12].

From a theoretical point of view, not so much rigorous information is known about $\rho(\boldsymbol{r})$, $\gamma(\boldsymbol{p})$ and $J(q)$, in spite of the efforts of many authors during the last few years. For atomic systems, some rigorous properties are well known [13–16]. Moreover, several other structural properties [17–22], numerical computations [23–25] and inequalities involving the expectation values [21, 26–31]

$$\mu_n = \int\limits_0^\infty r^n \rho(r) \, \mathrm{d}r = \frac{\langle r^{n-2} \rangle}{4\pi} \tag{2}$$

$$\nu_n = \int\limits_0^\infty p^n \gamma(p) \, \mathrm{d}p = \frac{\langle p^{n-2} \rangle}{4\pi} \tag{3}$$

(where $\rho(r) \equiv (1/4\pi) \int \rho(\boldsymbol{r}) \, \mathrm{d}\Omega$ and $\gamma(p) \equiv (1/4\pi) \int \gamma(\boldsymbol{p}) \, \mathrm{d}\Omega_p$ are the spherical averages) have been recently derived. The normalization $\langle r^0 \rangle = \langle p^0 \rangle = N$ is considered throughout.

In view of the aforementioned scarce information available on the one-electron densities $\rho(r)$ and $\gamma(p)$, and taking into account that some of the atomic expectation values are physically meaningful [14, 32–37] and/or experimentally measurable [3, 38–40], it turns out of great interest to obtain reliable (and simple) approximations to these densities by using the limited information coming from their expectation values.

In this work we use the Maximum-Entropy (ME) formalism to obtain approximations to $\rho(r)$ and $\gamma(p)$ in terms of their first few radial expectation values (2)–(3) respectively. It should be noticed that an increase of the

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amount of information leads to an improvement on the approximations. Moreover, these approximate densities allow to calculate several physical quantities of the system to be compared with different models or experimental data. In Sect. II, the ME mathematical technique is described. In Sect. III, the aforementioned approximations are obtained and numerically analyzed in a Hartree-Fock framework.

II. Maximum-entropy technique

If we know the first few radial expectation values of a density, how can we get information on the value of such density at any point? We are faced to an underdetermined moment problem, for which various alternative solutions can be devised (see e.g. [41–43]). Taking into account the limited known information (i.e. the first few moments of the density) it is clear that there is not a unique solution, i.e. there is an infinite number of densities which first moments are the known ones.

The ME method, based on information theory, chooses, among all the admissible densities, the least biased function compatible with the information we actually have [44]. Considering the density $\rho(r)$ as an statistical probability density, the choice is performed by maximizing the information entropy functional

$$S[\rho] \equiv -\int_0^\infty \rho(r)\ln\rho(r)\,\mathrm{d}r \tag{4}$$

under the constraints given by the knowledge of its first few moments.

Jaynes entropy concentration theorem [44] shows that, among all possible distributions compatible with a given incomplete information, the ME distribution is the one which occurs in the greatest number of ways, and that the majority of them have entropy very close to the maximum. It should be mentioned that this ME method has been also applied in a great variety of fields, including e.g. radioastronomy [45], parameter spectral estimation [46], particle physics [47] or atomic and many-fermion physics [25, 48–50]. On the other hand, let us remark that the ME technique provides complementary information to the one obtained from the Stieltjes-Chebyshev method, recently applied to the study of $\rho(r)$ [29], $\gamma(p)$ [31] and $J(q)$ [30]. From the latter, rigorous upper and lower bounds on the values of the density are obtained, while the ME method chooses, among all the admissible functions which are compatible with these bounds, the most plausible in the sense described above.

It should be also mentioned that different numerical methods have been used to solve the previous reduced moment problem, e.g. orthogonal expansions or reference density methods [51], recursion or continued fraction methods [52], the Stieltjes-Chebyshev method [41], moment preserving splines techniques [53] and Pollaczek polynomials [54]. Although the power of the ME method has been extensively checked and compared with other techniques [55–57], we are not claiming that the ME method leads to more approximate densities than other methods do. As a matter of fact, due to the nonunicity and unstability of the inference problem, each method has its own advantages and difficulties and then, they should be used not as competitors but as complementary techniques. In particular, this is the case of the Stieltjes-Chebyshev and ME methods.

From now on, we will center our attention in the atomic charge density $\rho(r)$, keeping in mind that all the results given below are also valid for the momentum density $\gamma(p)$ by only replacing the moments μ_n by ν_n.

The maximization of $S[\rho]$ subject to the constraints

$$\mu_n = \int_0^\infty r^n \rho(r)\,\mathrm{d}r \quad (n = 0, 1, \ldots, M)$$

give rise to the following Lagrange multiplier problem:

$$\delta\left[-\int_0^\infty \rho(r)\ln\rho(r)\,\mathrm{d}r + \sum_0^M \lambda_n\left(\mu_n - \int_0^\infty r^n\rho(r)\,\mathrm{d}r\right)\right] = 0 \tag{5}$$

where $\lambda_0, \ldots, \lambda_M$ are Lagrange multipliers. It is easy to show that the ME solution (if it exists) is

$$\rho^{ME}_{12\ldots M}(r) = A\exp\left(-\sum_{n=1}^M \lambda_n r^n\right) \tag{6}$$

where $A = \mathrm{e}^{1-\lambda_0}$ is the normalization constant and the remaining Lagrange multipliers $\lambda_1, \ldots, \lambda_n$ must be numerically calculated from the extremely nonlinear system of equations

$$\int_0^\infty r^n \rho^{ME}_{12\ldots M}(r)\,\mathrm{d}r = \mu_n \quad (n = 1, \ldots, M) \tag{7}$$

where the subscript $12\ldots M$ gives the list of moments included in the constraints. Only for $M = 1$ the corresponding Lagrange multiplier λ_1 can be obtained analytically.

Concerning the existence of ME solution, let us remind that it always exists when the moment problem is defined on a finite interval [57]. However, this important result can not be extended to the case of infinite or semiinfinite intervals. In such case, some analytical and numerical existence conditions are known, which depend on the number of moments involved. In the next section a detailed discussion of these conditions in the context of atomic systems is done.

III. Maximum-entropy solutions

A. Existence conditions

The elementary case $M = 1$ always provides an analytical ME solution, namely

$$\rho^{ME}_1(r) = \frac{\mu_0^2}{\mu_1}\exp\left\{-\frac{\mu_0}{\mu_1}r\right\}. \tag{8}$$

In a similar way, one obtains the more general ME solution

$$\rho_k^{ME}(r) = \frac{k\mu_0}{\Gamma(1/k)}\left(\frac{\mu_0}{k\mu_k}\right)^{1/k} \exp\left\{-\frac{\mu_0}{k\mu_k}\, r^k\right\} \quad (k > 0) \qquad (9)$$

subject to the constraints $\{\mu_0, \mu_k\}$.

For $M = 2$, the following condition for the existence of ME solution with the constraints $\{\mu_0, \mu_1, \mu_2\}$ is known [58]:

$$\mu_1^2 < \mu_0\mu_2 < 2\mu_1^2 .$$

The general existence condition with the constraints $\{\mu_0, \mu_k, \mu_{2k}\}$ $(k > 0)$ is also known [59]

$$\mu_k^2 < \mu_0\mu_{2k} < (k+1)\,\mu_k^2 .$$

We have checked, by using near Hartree-Fock wave functions [60, 61] that, for atomic systems, the Dowson and Wragg [58] existence condition is only satisfied by the Hydrogen atom (nuclear charge $Z = 1$) in the position space and by the atoms $Z = 1, 2, 8, 9, 10$ in the momentum space. So the ME approximation to the atomic charge density, $\rho_{12}^{ME}(r)$, does not exist except for the Hydrogen atom and the ME momentum density, $\gamma_{12}^{ME}(p)$, does exist only for the aforementioned atoms.

For $M = 3$ no analytical existence conditions are known. Kociszewski [62] and Tagliani [63] found numerically the allowed values of $\{\mu_0, \mu_1, \mu_2, \mu_3\}$ for which the ME solution exists. We have verified in the same framework that, for the atomic systems with $Z = 1 - 92$, the corresponding ME approximations $\rho_{123}^{ME}(r)$ and $\gamma_{123}^{ME}(p)$ exist for those atoms which do not have ME solution with $M = 2$.

Figures 1 and 2 show the allowed (I) and forbidden (II) Kociszewski regions for the existence of ME charge and momentum densities, respectively, having prescribed the first three moments. The figures are plotted in terms of the relative moments defined as

$$\bar{\mu}_n = \frac{\mu_0^{n-1}\,\mu_n}{\mu_1^n} \quad (n = 1, 2, 3).$$

Heavier atoms not included in these figures also belong to the allowed region I.

Finally, in [63] it has been shown that for $M \geq 4$ there always exists ME solution.

B. Maximum-entropy densities

In this section we apply the ME technique to the spherically averaged atomic densities $\rho(r)$ and $\gamma(p)$. This method provides model independent estimations on these functions from a few expectation values $\langle r^n\rangle$ and $\langle p^n\rangle$. Moreover, in order to have an idea of the accuracy of the approximations, some numerical computations are also carried out in a Hartree-Fock framework.

When the normalization and only one additional constraint (μ_k) are considered, the expression of the ME solution is given by (9) which can be expressed in terms of the radial expectation values by using (2). Some interesting examples are

$$\rho_1^{ME}(r) = \frac{\langle r^{-2}\rangle^2}{4\pi\langle r^{-1}\rangle} \exp\left\{-\frac{\langle r^{-2}\rangle}{\langle r^{-1}\rangle}\, r\right\}$$

$$\rho_2^{ME}(r) = \left(\frac{\langle r^{-2}\rangle^3}{8\pi^3 N}\right)^{1/2} \exp\left\{-\frac{\langle r^{-2}\rangle}{2N}\, r^2\right\}.$$

From these two ME solutions, approximations to the radial expectation values are obtained in terms of $\langle r^{-2}\rangle$,

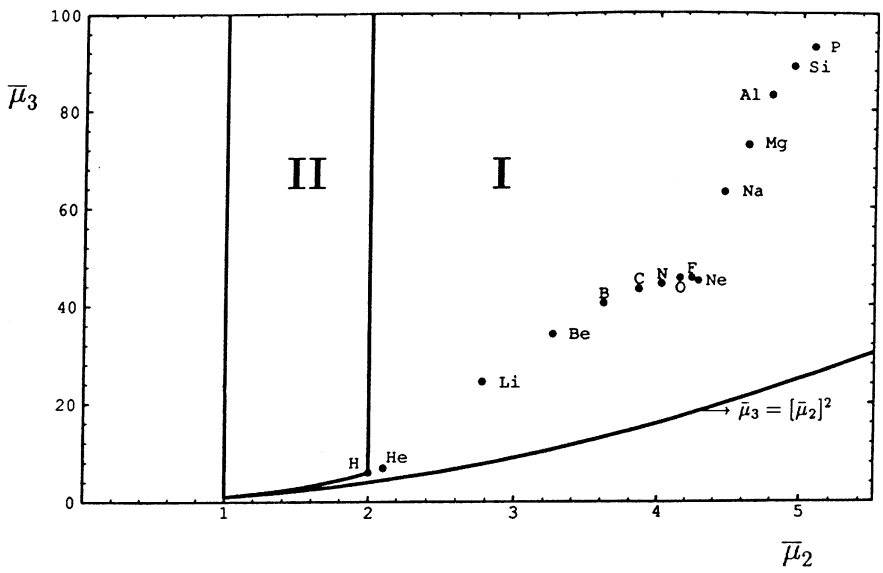

Fig. 1. Existence conditions for ME distributions in the position space having prescribed the first three moments in terms of relative moments $\bar{\mu}_2 = \mu_0\mu_2/\mu_1^2$ and $\bar{\mu}_3 = \mu_0^2\mu_3/\mu_1^3$. Regions I and II represent the positivity inequalities for these relative moments. Moreover, *region I* is alowed and *region II* is forbidden for the existence of a ME distribution in accordance with the Kociszewski [61] conditions. Atomic units (a.u.) are used

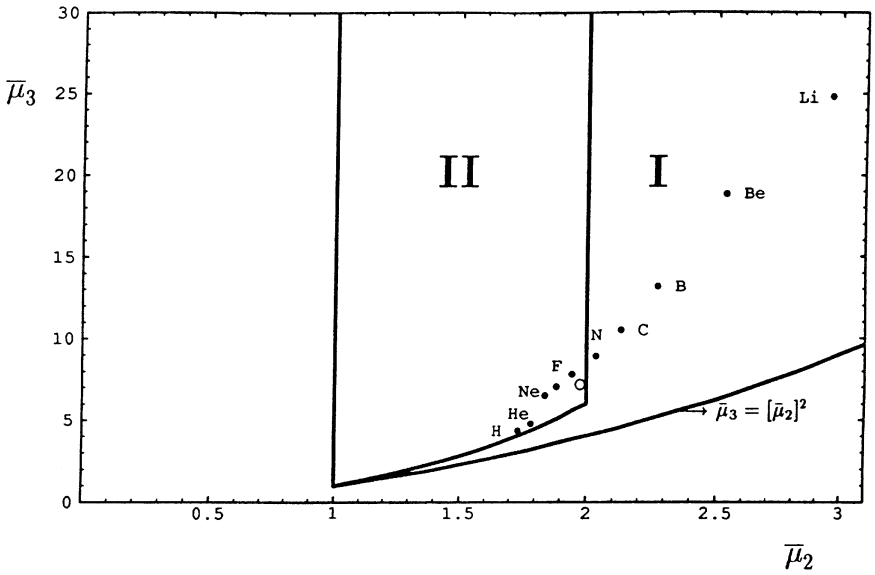

Fig. 2. Existence conditions for ME distributions in the momentum space having prescribed the first three moments in terms of relative moments $\bar{\mu}_2 = \mu_0\mu_2/\mu_1^2$ and $\bar{\mu}_3 = \mu_0^2\mu_3/\mu_1^3$. *Regions I* and *II* represent the positivity inequalities for these relative moments. Moreover, *region I* is allowed and *region II* is forbidden for the existence of a ME distribution in accordance with the Kociszewski [61] conditions. Atomic units (a.u.) are used

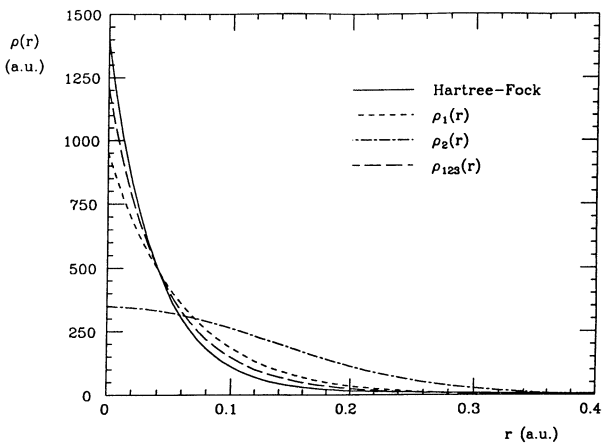

Fig. 3. Hartree-Fock charge density and ME approximations $\rho_1(r)$, $\rho_2(r)$ and $\rho_{123}(r)$ for the Aluminium atom ($Z = 13$). Atomic units (a.u.) are used

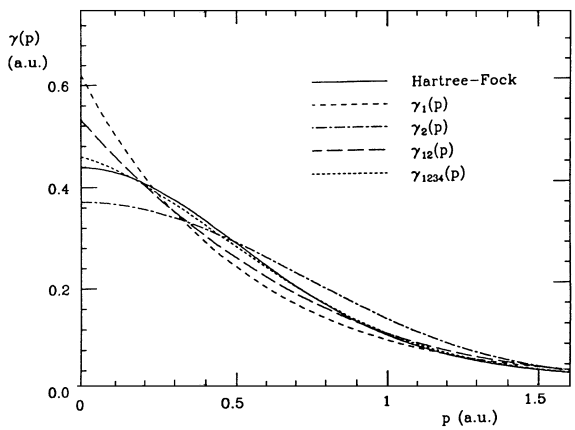

Fig. 4. Hartree-Fock momentum density and ME approximations $\gamma_1(p)$, $\gamma_2(p)$, $\gamma_{12}(p)$ and $\gamma_{1234}(p)$ for the Helium atom ($Z = 2$). Atomic units (a.u.) are used

$\langle r^{-1}\rangle$ and N:

$$\langle r^k\rangle_1^{ME} = \int_0^\infty r^k \rho_1^{ME}(r)\,\mathrm{d}r = \Gamma(k+3)\frac{\langle r^{-1}\rangle^{k+2}}{\langle r^{-2}\rangle^{k+1}} \quad (k > -3)$$

$$\langle r^k\rangle_2^{ME} = \int_0^\infty r^k \rho_2^{ME}(r)\,\mathrm{d}r$$

$$= \left[\frac{(2N)^{(k+2)}}{\pi}\right]^{1/2} \frac{\Gamma[(k+3)/2]}{\langle r^{-2}\rangle^{k/2}} \quad (k > -3).$$

Similar expressions can be obtained for the atomic momentum density by replacing ρ and r by γ and p respectively.

It is worthy to mention that the ME approximation $\rho_1^{ME}(r)$ for the Hydrogen atom gives the exact atomic charge density. This fact is related to the particular position of the Hydrogen atom in Fig. 1.

When more constraints are taken into account, the ME solutions must be numerically obtained. As illustration, we have calculated the approximate densities $\rho_1^{ME}(r)$, $\rho_2^{ME}(r)$, $\rho_{123}^{ME}(r)$ for Aluminium ($Z = 13$) and $\gamma_1^{ME}(p)$, $\gamma_2^{ME}(p)$, $\gamma_{12}^{ME}(p)$ and $\gamma_{1234}^{ME}(p)$ for Helium ($Z = 2$) using near Hartree-Fock wave functions [60]. These approximations are compared with the Hartree-Fock ones in Figs. 3 and 4. It is apparent that the more information is considered the more accurate are the ME approximations, being $\rho_{123}^{ME}(r)$ and $\gamma_{1234}^{ME}(p)$ very close to the exact densities.

On the other hand, in Table 1 we also compare the central values and some moments, predicted by the approximations to $\gamma(p)$, as well as the entropies associated to

Table 1. Comparison between the Hartree-Fock and the ME predictions for the central value $\gamma(0)$ and the expectation values $\langle p \rangle$, $\langle p^2 \rangle$ and $\langle p^3 \rangle$ of the Helium momentum density. Atomic units (a.u.) are used

	$\gamma(0)$	$\langle p \rangle$	$\langle p^2 \rangle$	$\langle p^3 \rangle$	S_γ
γ_1^{ME}	0.62	3.52	7.37	19.29	0.4801
γ_2^{ME}	0.37	2.23	2.93	4.37	0.4851
γ_{12}^{ME}	0.53	2.56	4.06	7.54	0.4774
γ_{1234}^{ME}	0.46	2.80	5.72	16.65	0.4753
γ_{HF}	0.44	2.80	5.72	17.99	0.4750

those approximations, with the corresponding Hartree-Fock values for Helium. Notice that the one-constraint approximations give accurate predictions in spite of the scarce information used. As it should be expected, the predictions obtained from $\gamma_{12}^{ME}(p)$ and $\gamma_{1234}^{ME}(p)$ substantially improve the values given by the one-constraint densities. Remark the decreasing and convergent [64] behavior of the entropies associated to the different approximations when considering a higher number of moments, being the corresponding to γ_{1234}^{ME} really close to the Hartree-Fock one.

Summarizing, the ME method provides a powerful tool to approximate unknown densities from very limited information. These model-independent approximations can be used to estimate not available properties of the densities which would be difficult to obtain by other means. In this work, the ME technique has been applied to the spherically averaged charge and momentum densities in atomic systems, where the aforementioned characteristics are especially relevant.

References

1. Parr, R.G., Yang, W.: Density-functional theory of atoms and molecules. New York: 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. Kato, T.: Commun. Pure Appl. Math. **10**, 151 (1957)
14. Benesch, R., Smith Jr., V.H.: In: Wave mechanics: the first fifty years. Price, W.C., Chissick, S.S., Ravensdale, T. (eds.). London: Butterworths 1973
15. Hoffman-Ostenhof, M., Hoffman-Ostenhof, T.: Phys. Rev. A **16**, 1782 (1977)
16. Thakkar, A.J.: J. Chem. Phys. **86**, 5060 (1987)
17. Sperber, G.: Int. J. Quantum Chem. **5**, 189 (1971)
18. Gadre, S.R., Gejji, S.P.: J. Chem. Phys. **80**, 1175 (1984)
19. Gadre, S.R., Chakravorty, S.J., Pathak, R.K.: J. Chem. Phys. **78**, 4581 (1983)
20. Gálvez, F.J.: Phys. Rev. A **39**, 501 (1989)
21. Angulo, J.C., Dehesa, J.S., Gálvez, F.J.: Phys. Rev. A **42**, 4069 (1990); erratum Phys. Rev. A **43**, 641 (1991)
22. Angulo, J.C., Dehesa, J.S.: Phys. Rev. A **44**, 1516 (1991)
23. Westgate, W.M., Simas, A.M., Smith Jr., V.H.: J. Chem. Phys. **83**, 4054 (1985)
24. Kryachko, E.S., Koga, T.: J. Chem. Phys. **91**, 1108 (1989)
25. Sears, S.B., Gadre, S.R.: J. Chem. Phys. **75**, 4626 (1981)
26. Sears, S.B., Matcha, R.L.: J. Chem. Phys. **74**, 589 (1981)
27. King, F.W.: J. Chem. Phys. **80**, 4371 (1984)
28. Yue, W., Janmin, L.: Phys. Scr. **30**, 414 (1984)
29. Antolín, J., Zarzo, A., Angulo, J.C.: Phys. Rev. A **48**, 4149 (1993)
30. Angulo, J.C., Antolín, J. Zarzo, A.: Z. Phys. D **28**, 269 (1993)
31. Zarzo, A., Angulo, J.C., Antolín, J.: J. Phys. B **26**, 4663 (1993)
32. Fraga, S., Malli, G.: Many electron systems: properties and interactions. Philadelphia: Saunders 1968
33. Bonham, R.A., Lee, J.S., Kennerly, R., St. John, W.: Adv. Quantum Chem. **11**, 1 (1978)
34. Pucci, R., March, N.H.: J. Chem. Phys. **76**, 4089 (1982)
35. King, F.W.: Phys. Rev. A **38**, 6017 (1988)
36. Porras, I., Gálvez, F.J.: Phys. Rev. A **41**, 4052 (1990)
37. Defranceschi, M., Berthier, G.: J. Phys. France **51**, 2791 (1990)
38. Epstein, I.R.: Phys. Rev. A **8**, 160 (1973)
39. Manninen, S.: Phys. Rev. Lett. **59**, 1557 (1987)
40. Angulo, J.C., Dehesa, J.S., Gálvez, F.J.: Z. Phys. D **18**, 127 (1991)
41. Corcoran, C.T., Langhoff, P.W.: J. Math. Phys. **18**, 651 (1977)
42. Landau, H.J.: Bull. Am. Math. Soc. **16**, 47 (1987)
43. Ciulli, S., Mounsif, M., Gorman, N., Spearman, T.D.: J. Math. Phys. **32**, 1717 (1991)
44. Jaynes, E.T.: Phys. Rev. **106**, 620 (1957) and **108**, 171 (1957)
45. Skilling, J., Bryan, R.K.: Mon. Not. R. Astr. Soc. **211**, 111 (1984)
46. Liu, D.M., Wong, E.K.: Phys. Rep. **193**, 41 (1990)
47. Antolín, J.: Phys. Rev. D **43**, 1532 (1991)
48. Koga, T.: Theor. Chim. Acta (Berlin) **64**, 249 (1984)
49. Antolín, J., Zarzo, A., Angulo, J.C.: Phys. Rev. A **50**, 240 (1994)
50. Angulo, J.C., Yáñez, R.J., Antolín, J., Zarzo, A.: Int. J. Quantum Chem. **56**, 747 (1995)
51. Corcoran, C.T., Langhoff, P.W.: Chem. Phys. Lett. **41**, 609 (1976)
52. Haydock, R. Heine, V., Kelly, M.: J. Phys. C **5**, 2845 (1972)
53. Frontini, M., Gautschi, V., Milovanovic, G.V.: Numer. Math. **50**, 503 (1987)
54. Escalas, E., Viano, G.A.: J. Math. Phys. **34**, 5781 (1993)
55. Antolín, J.: J. Math. Phys. **31**, 791 (1990)
56. Leasenburg, M.J., Mead, L.R.: J. Math. Phys. **34**, 6009 (1993)
57. Csiszar, I. Ann. Probab. **3**, 146 (1975)
58. Dowson, D.C., Wragg, A.: IEEE Trans. Inf. Theory **IT-19**, 689 (1973)
59. Tagliani, A., Frontini, M.: Private communication
60. Clementi, E., Roetti, C.: At. Data Nucl. Data Tables **14**, 177 (1974)
61. McLean, A.D., McLean, R.S.: At. Data Nucl. Data Tables **26**, 197 (1981)
62. Kociszewski, A.: J. Phys. A **19**, L823 (1986)
63. Tagliani, A.: J. Math. Phys. **34**, 326 (1993)
64. Frontini, M., Tagliani, A.: Entropy convergence in Stieltjes and Hamburger moment problem. Milano: Politecnico di Milano 1995 (Preprint)