Maximum-Entropy Analysis of Atomic Compton Profiles

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Received June 13, 1994; revised manuscript received November 29, 1994; accepted December 2, 1994

ABSTRACT

The maximum-entropy formalism is used to obtain approximations to the atomic Compton profile, $J(q)$, in terms of the first few radial expectation values $\langle p^n \rangle$ of the momentum density $\gamma(\mathbf{p})$. This method leads to the least-biased results by the information not used. In particular, analytical and numerical approximations to the kinetic energy T and to the height of the peak $J(0)$ and the half-width $q_{0.5}$ of the Compton profile are obtained. Our results generalize and improve some approximations to $J(q)$ previously obtained by other authors. For illustration, the accuracy of these approximations are studied by means of near-Hartree–Fock wave functions.

Introduction

One of the most important theories of matter, namely, the density functional theory, has the one-body density in position space $\rho(\mathbf{r})$ as a basic variable [1, 2]. An alternative formulation of this theory in terms of the one-body density in momentum space $\gamma(\mathbf{p})$ has been also carried out [3, 4].

In the modern density functional theory, the structural properties of the variables $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ play a relevant role in the description of many-body systems. However, it is not easy to experimentally access these kinds of properties. Probably, the main way of obtaining experimental data on such one-particle densities is the measurement of isotropic Compton profiles [5–7]:

$$J(q) = \frac{1}{2} \int_{p \geq q} \frac{\gamma(\mathbf{p})}{p} \, d\mathbf{p}. \qquad (1)$$

International Journal of Quantum Chemistry, Vol. 56, 747–752 (1995)

CCC 0020-7608 / 95 / 060747-06

Inelastic photon scattering [8–10], high-resolution Compton scattering [11], angular correlation of position annihilation radiation [12], $(e,2e)$ coincidence spectroscopy [13], and magnetic Compton scattering [14] are some experiments which provide information of $J(q)$.

However, all these experiments allow one to measure the Compton profile $J(q)$ up to a maximum value q_{max} (which depends on the kind of experiment) of the momentum transferred. To calculate properties of the one-particle densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$, such as radial expectation values, one needs to extrapolate $J(q)$ beyond q_{max} or to assume an analytical model [15].

In this work, the maximum-entropy (ME) method is used to obtain approximations on $J(q)$ in terms of the first few radial expectation values $\langle p^n \rangle \equiv \int p^n \gamma(\mathbf{p})\, d\mathbf{p}$ of the momentum density $\gamma(\mathbf{p})$. Let us remark that some of these expectation values are physically meaningful [16–22] (e.g., $\langle p^2 \rangle$ is twice the kinetic energy and $\langle p^4 \rangle$ gives the relativistic correction to this energy) and/or experimentally accessible [6, 8, 23–25] (e.g., $\langle p^{-1} \rangle$ is twice the height of the peak of the Compton profile). In this article, we generalize some previous results concerning information theoretic analysis of Compton profiles [26–29]. In [27], ME approximations to a few atomic and molecular Compton profiles are obtained in terms of two expectation values, namely, $\langle p \rangle$ and $\langle p^n \rangle$ $(n = 2, 3, 4)$, which provide semiempirical relations among $J(0)$, N (the number of electrons), $\langle p \rangle$, and $\langle p^2 \rangle$. In [29], different ME approximations to the same quantity, when only the energy of the system is known, are constructed.

Here, we also analyze the existence conditions of the ME solution for a given set of moments for all neutral atoms with $N = 1 - 92$ in a Hartree–Fock framework. This ME technique has been also applied by the authors to the obtention of ME approximations to the one-particle atomic densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ [30] and to the electron-pair density $h(\mathbf{r}_{12})$ in atomic systems [31]. Other fields of application are molecular physics [32], radioastronomy [33], parameter spectral estimation [34], and particle physics [35].

In the following section, the ME technique is described. The approximations to the atomic Compton profile $J(q)$ and their predictions on the values of several unknown quantities such as radial expectation values $\langle p^n \rangle$ are obtained in the third section and, for some atomic systems, numerically analyzed in the fourth section within a near-Hartree–Fock framework. It is interesting to remark the complementarity of the ME method with the Stieltjes–Chebyshev [25] upper and lower bounds to $J(q)$ in terms of radial expectation values, recently obtained by the authors [36]. The appropriate conclusions are given in the last section.

Maximum-Entropy Technique

The knowledge of any radial expectation value $\langle p^n \rangle$ $(n \geq 0)$ of the momentum density $\gamma(\mathbf{p})$ allows us to calculate, by means of Eq. (1), the n-th moment μ_n of the Compton profile $J(q)$ as follows:

$$\mu_n \equiv \int_0^\infty q^n J(q)\, dq = \frac{\langle p^n \rangle}{2(n+1)} \quad (5 > n > -1), \tag{2}$$

where the upper limit in n is due to the asymptotic behavior $J(q) \sim q^{-6}$ for large q.

For a given finite set of moments $\{\mu_n\}$ containing the normalization constant $\mu_0 = N/2$ (N being the number of constituents of the system), there exists an infinite set of normalized-to-μ_0 functions $\{J_\alpha(q)\}$ whose corresponding moments coincide with the given set $\alpha \equiv \{\mu_n\}$. The choice of the least-biased function within the set $\{J_\alpha(q)\}$ compatible with the moments $\{\mu_n\}$ is a well-known problem in information theory, whose solution is provided by the ME method [31, 37–39]. The ME solution $J_{ME}(q) \in \{J_\alpha(q)\}$ is given by the maximization of the information entropy functional

$$S[J] \equiv -\int_0^\infty J(q) \ln J(q)\, dq, \tag{3}$$

subject to the constraints given by the moments $\{\mu_n\}$, i.e.:

$$\int_0^\infty q^n J_{ME}(q)\, dq = \mu_n. \tag{4}$$

Moreover, as it is shown in Jaynes entropy concentration theorem [40], the information entropy of the majority of the functions in $\{J_\alpha(q)\}$ is very close to the maximum.

The maximization process of $S[J]$ under the constraints (4) requires one to solve the Lagrange multipliers equation:

$$\delta\left[-\int_0^\infty J(q)\ln J(q)\,dq + \sum_n \lambda_n\left(\mu_n - \int_0^\infty q^n J(q)\,dq\right)\right] = 0, \quad (5)$$

where λ_n are Lagrange multipliers and the summation runs over the whole set $\{\mu_n\}$ of the moments considered as constraints. It is easy to show that the ME solution (if it exists) is

$$J_{ME}(q) = \exp\left(-1 - \sum_n \lambda_n q^n\right), \quad (6)$$

where the Lagrange multipliers λ_n must be calculated from the system of equations

$$\mu_n = \int_0^\infty q^n J_{ME}(q)\,dq. \quad (7)$$

The existence of an ME solution for a given set of moments $\{\mu_n\}$ depends on (i) the number of moments and (ii) the values of such moments. Let us denote by M the number of moments considered (excluding the normalization constraint given by $\mu_0 = \langle p^0\rangle/2 = N/2$). Then, (i) it is known that for $M = 1$ there always exists an analytical ME solution (see, e.g., [37, 41]). For the atomic Compton profiles, the following ME solutions $J_k(q)$ in terms of $\{\mu_0, \mu_k\}$ $(k > 0)$ are obtained:

$$J_k(q) = \frac{\mu_0 k}{\Gamma(1/k)}\left(\frac{\mu_0}{k\mu_k}\right)^{1/k} \times \exp\left\{-\frac{\mu_0}{k\mu_k}q^k\right\} \qquad (k > 0) \quad (8)$$

or, equivalently,

$$J_k(q) = \frac{Nk}{2\Gamma(1/k)}\left(\frac{(k+1)N}{k\langle p^k\rangle}\right)^{1/k} \times \exp\left\{-\frac{(k+1)N}{k\langle p^k\rangle}q^k\right\} \qquad (k > 0), \quad (9)$$

which generalizes some previously published results (see, e.g., [27]). The latter expression readily provides approximations to the height of the Compton peak $J(0)$ and to $q_{0.5}$, which is defined as the value of q for which $J(q) = \frac{1}{2}J(0)$, namely,

$$q_{0.5}^{(k)} = \left[\frac{k\ln 2}{(k+1)N}\langle p^k\rangle\right]^{1/k}. \quad (10)$$

(ii) For $M = 2$, the ME solution $J_{k,2k}(q)$ in terms of $\{\mu_0, \mu_k, \mu_{2k}\}$ $(k > 0)$ exists if and only if [42]

$$\mu_k^2 < \mu_0\,\mu_{2k} < 2\mu_k^2. \quad (11)$$

(iii) For $M = 3$, there are no analytical conditions. However, Kociszewski [43] and Tagliani [44] found numerically the allowed values of $\{\mu_0, \mu_1, \mu_2, \mu_3\}$ for which the ME solution $J_{123}(q)$ exists. (iv) For $M \geq 4$, there always exists an ME solution [44].

Maximum-Entropy Solutions

Let us consider the one-constraint solution given by Eq. (9): One can use the moments of the function $J_k(q)$ to estimate the unknown radial expectation values $\langle p^j\rangle$ $(j \neq 0, k)$ in the form

$$\langle p^j\rangle \approx \langle p^j\rangle^{(k)} \equiv N\frac{\Gamma\left(\frac{j+k+1}{k}\right)}{\Gamma\left(\frac{k+1}{k}\right)} \times \left(\frac{k}{(k+1)N}\langle p^k\rangle\right)^{j/k}. \quad (12)$$

Some interesting examples correspond to the cases $k = 1, 2$ for which the ME approximations to $J(q)$ are, respectively [27, 29],

$$J_1(q) = \frac{N^2}{\langle p\rangle}\exp\left\{-\frac{2N}{\langle p\rangle}q\right\} \quad (13a)$$

$$J_2(q) = \left(\frac{3N^3}{2\pi\langle p^2\rangle}\right)^{1/2}\exp\left\{-\frac{3N}{2\langle p^2\rangle}q^2\right\}, \quad (13b)$$

where Eq. (9) has been taken into account. The estimations on $\langle p^j\rangle$ are given, also respectively, by

$$\langle p^j\rangle^{(1)} = N\Gamma(j+2)\left(\frac{\langle p\rangle}{2N}\right)^j \quad (14a)$$

$$\langle p^j\rangle^{(2)} = \frac{2N\Gamma\left(\frac{j+3}{2}\right)}{\pi^{1/2}}\left(\frac{2\langle p^2\rangle}{3N}\right)^{j/2}. \quad (14b)$$

We analyzed the existence conditions of the two- and three-constraint approximations to $J(q)$, as given by [42] and [43, 44], respectively, for all neutral ground-state atoms from hydrogen ($N = 1$) through uranium ($N = 92$). In doing so, we used the atomic wave functions of [45] ($N = 1$–54) and [46] ($N = 55$–92). It was observed that the two-moment condition of Eq. (11) for $\{\mu_0, \mu_1, \mu_2\}$ is verified only by hydrogen and helium, while for $\{\mu_0, \mu_2, \mu_4\}$ the corresponding ME approximation $J_{24}(q)$ in the whole range $Z = 1$–92 does not exist. In Figure 1, it is shown that the three-moment approximation $J_{123}(q)$ exists for all atoms with $N = 3$–92.

In Figure 2, the ME approximations $J_{12}(q)$ and $J_{1234}(q)$ are compared with the Hartree–Fock value $J_{HF}(q)$ of the Compton profile helium ($Z = 2$). Improvement in the accuracy of the approximation when the number of constraints increases from two to four is observed. A similar behavior is shown in Figure 3, where the approximations $J_1(q)$ and $J_{123}(q)$ are compared with the Hartree–Fock value $J_{HF}(q)$ for carbon ($Z = 6$).

Let us point out here that one can also obtain ME approximations to the derivative $J'(q)$ of the Compton profile in terms of the quantities $\langle p^n \rangle$. In doing so, it is sufficient to take into account that $-J'(q) = 2\pi q\gamma(q)$, and then

$$\nu_n \equiv -\int_0^\infty q^n J'(q)\, dq = \frac{\langle p^{n-1} \rangle}{2} \quad (n > -2). \tag{15}$$

Due to the relationship between $J'(q)$ and $\gamma(q)$, the ME approximations to $-J'(q)$ in terms of $\{\nu_n\}$ can be considered as approximations to the momentum density $\gamma(p)$ in terms of its radial expectation values $\langle p^n \rangle$, different from those given by directly applying the ME technique to the function $\gamma(p)$ with the constraints $\{\langle p^n \rangle\}$ [30]. As in the case of $J(q)$, there always exists the M-constraint approximation to $-J'(q)$ with $M = 1$ and $M \geq 4$. The existence regions of the periodic table for the cases $M = 2, 3$ are, respectively, $Z = 1$–2, 9–10 and $Z = 3$–8, 11–92.

The asymptotic exponential behavior of the ME approximations strongly differs from the Hartree–Fock one as q^{-6}. Because of that, the predictions $\langle p^i \rangle^{(k)}$ on the unknown radial expectation values and other constructed from ME approximations

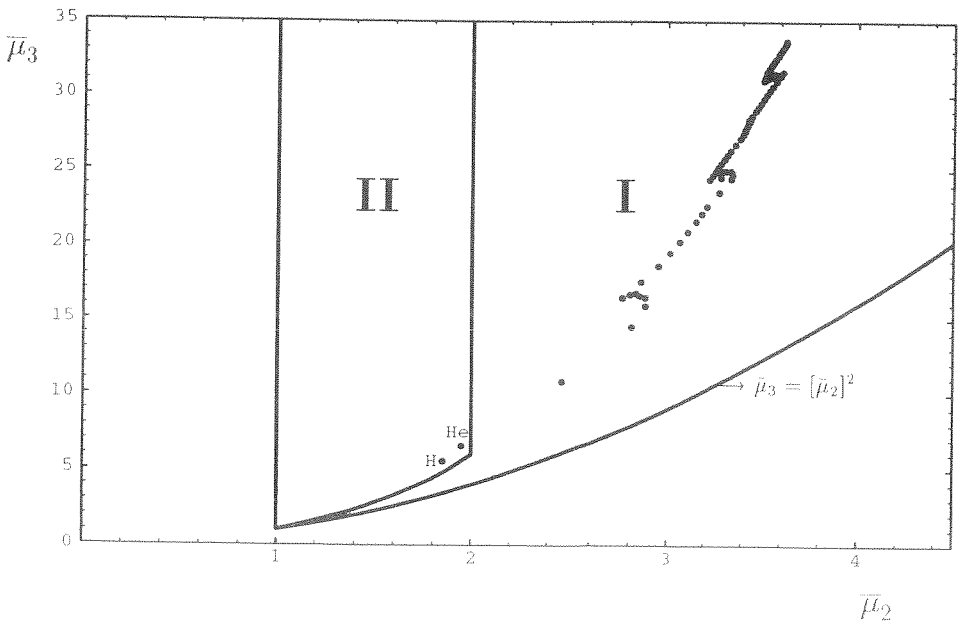

FIGURE 1. Existence conditions for ME distributions having prescribed the first three moments in terms of relative moments $\bar{\mu}_2 = \mu_0\mu_2/\mu_1^2$ and $\bar{\mu}_3 = \mu_0^2\mu_3/\mu_1^3$. Regions I and II represent the positivity inequalities for these relative moments. Moreover, region I is allowed and region II is forbidden for the existence of an ME distribution in accordance with the Kociszewski [43] conditions. Atomic units (au) are used.

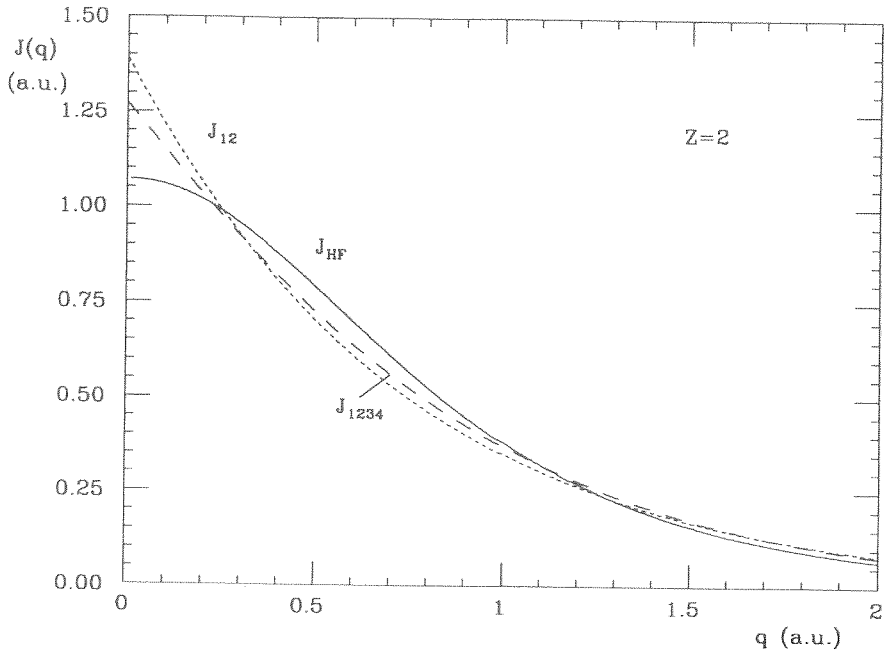

FIGURE 2. Hartree–Fock Compton profile $J_{HF}(q)$ and ME approximations $J_{12}(q)$ and $J_{1234}(q)$ for the helium atom ($Z = 2$). Atomic units (au) are used.

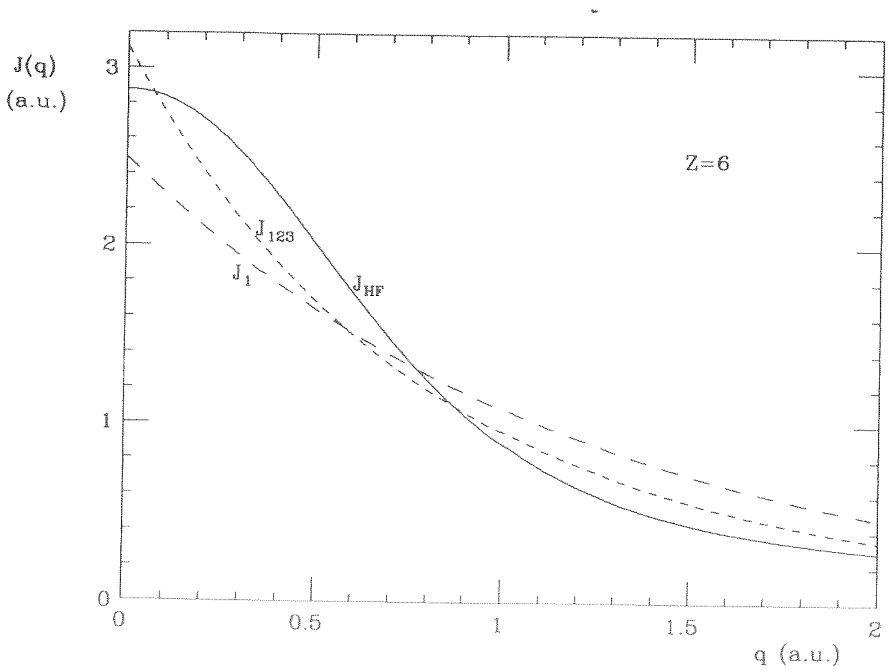

FIGURE 3. Hartree–Fock Compton profile $J_{HF}(q)$ and ME approximations $J_1(q)$ and $J_{123}(q)$ for the carbon atom ($Z = 6$). Atomic units (au) are used.

with a higher number of constraints are not very accurate, because the evaluation of such quantities involves values of $J(q)$ for large q. However, the predictions on the values of *local quantities* [e.g., $J(0)$ or $q_{0.5}$] are better. For illustration, we have (in atomic units) $J(0) = 2.8773$ for carbon ($Z = 6$), while $J_1(0) = 2.4893$, $J_2(0) = 1.1697$, and $J_{123}(0) = 3.2492$. Similarly, for helium, $J(0) = 1.0703$, $J_{12}(0) = 1.3891$, and $J_{1234}(0) = 1.2726$.

Conclusions

The ME method has been applied to obtain approximations to the atomic Compton profiles in terms of very limited information. The method chooses, among the infinite set of functions compatible with the constraints (i.e., a few radial expectation values $\langle p^n \rangle$), the unique function which is maximally noncommittal about the unknown moments.

The ME method is just complementary to the Padé-type method presented in some previous articles (see, e.g., [36]). The latter provides rigorous upper and lower bounds to the Compton profile and the ME method selects the most reasonable approximation in the sense described above.

Some analytical and numerical approximations to quantities related to the atomic Compton profiles are obtained by using the ME method. In particular, approximations to $J(0)$, $q_{0.5}$, and radial expectation values $\langle p^n \rangle$ are constructed and can be used to estimate many other related quantities. The same method can be also applied to the study of different many-particle systems (e.g., molecules and nuclei).

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