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Some inferential Compton profiles based on the knowledge of energy

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Methods of constructing approximate Compton profiles $J(q)$ are proposed and compared, when only the energy E of a system is known. For the q-range of interest, the inferential Compton profiles are shown to be of the accuracy of the non-variational single STO (Slater-type orbital) description for atoms.

Key words: Compton profile – Momentum density – Characteristic function – Moments of momentum.

1. Introduction

The Doppler broadening of Compton lines due to moving electrons results in the familiar Compton profile which plays a fundamental role in momentum-space physics and chemistry, since it is directly related to the momentum distributions of electrons in atoms, molecules, and solids (see e.g. Ref. [1]). Under the impulse approximation (which assumes the scattering process by single electron with the neglect of electron binding energy and the condition of plane wave final electron state) [1], the isotropic Compton profile $J(q)$ is related to the radial momentum density $I(p)$ through

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

$$I(p)=-2p[dJ(p)/dp], \tag{1b}$$

where $I(p)$ is defined by $I(p)=\int_0^{2\pi} d\phi_p \int_0^{\pi} d\theta_p p^2 \sin\theta_p \rho(\boldsymbol{p})$ based on the three-dimensional momentum density $\rho(\boldsymbol{p})$. Therefore, various physical properties are derived from the Compton profile. For example, several moments of momentum

$\langle p^n \rangle [= \int_0^\infty dp\, p^n I(p)]$ are given by [2–5]

$$\langle p^n \rangle = 2(n+1) \int_0^\infty dq\, q^n J(q), \qquad (n \geq 0) \tag{2a}$$

and

$$\langle p^{-1} \rangle = 2J(0), \tag{2b}$$

$$\langle p^{-2} \rangle = 2 \int_0^\infty dq\, q^{-2}[J(0) - J(q)]. \tag{2c}$$

$\langle p \rangle$ is the average momentum and has been reported [6] to have a good correlation with the Hartree–Fock exchange energy for atoms. $\langle p^2 \rangle$ is just twice the kinetic energy T, which is the negative of the total energy E if the virial theorem holds in its simplest form $T+E=0$. The second moment $\langle p^2 \rangle$ has been also applied to the study of interatomic interactions, and the reorganizations in the momentum density and the Compton profile have been rigorously connected with the interaction energy ΔE and the interatomic force F [7–11]. $\langle p^4 \rangle$ appears in the approximate relativistic correction to the kinetic energy for the change of the electron mass with velocity [12].

Recently, Gadre and Sears [13, 14] have studied the inverse problem of estimating the Compton profile and its properties from the knowledge of the moments $\langle p^n \rangle$. Based on the maximum-entropy principle in information theory (see e.g. Refs. [15, 16]), they have constructed approximate Compton profiles and discussed the relations between the moments $\langle p^n \rangle$ and various Compton profile parameters such as the peak height $J(0)$ and the half width q_{hw} defined by $2J(q_{hw}) = J(0)$. The method of maximum-entropy inference has been also applied to the estimation of the momentum density reorganization during the process of interatomic interactions when the interaction energy is known [17].

In this paper, we examine alternative methods of constructing approximate Compton profiles $J(q)$ based on some functional approximations to the spherical average $b(r)$ of the characteristic function $B(\boldsymbol{r})$ of the momentum density. The functions $B(\boldsymbol{r})$ and $b(r)$ are defined by

$$B(\boldsymbol{r}) = \int d\boldsymbol{p} \exp(-i\boldsymbol{p} \cdot \boldsymbol{r}) \rho(\boldsymbol{p}), \tag{3a}$$

$$b(r) = (4\pi)^{-1} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta\, B(\boldsymbol{r}), \tag{3b}$$

and their properties have been studied in Refs. [18–21]. Since $J(q)$ and $b(r)$ are a pair of the Fourier cosine transforms,

$$J(q) = (1/\pi) \int_0^\infty dr \cos(qr) b(r), \tag{4a}$$

$$b(r) = 2 \int_0^\infty dq \cos(rq) J(q), \tag{4b}$$

we can obtain inferential $J(q)$ from the approximations to $b(r)$ and vice versa.

In the sense of information theory, the more information (or constraints) is given, the more the inference becomes reliable. In the following, however, we assume that only the second moment $\langle p^2 \rangle$ is known in advance. Because $\langle p^2 \rangle = -2E$ for atoms and molecules in their equilibrium conformations, the second moment is a readily available fundamental physical quantity of atoms and molecules. In the next section, three methods of constructing approximate $J(q)$ are shown including the maximum-entropy inference. In Sect. 3, the inferential Compton profiles are compared and their reliability is discussed. Atomic units are used throughout this paper.

2. Inferential Compton profiles *J*(*q*)

2.1. Maximum-entropy approximation to J(q)

Since $J(q)$ is an even function under the impulse approximation (see Eq. (1a)), the normalization condition is

$$\int_0^\infty dq\, J(q) = N/2, \tag{5a}$$

where N is the number of electrons. The second moment satisfies

$$\int_0^\infty dq\, q^2\, J(q) = \langle p^2 \rangle / 6 \tag{5b}$$

from Eq. (2a). As shown by Gadre and Sears [13], the Compton profile $J(q)$ which maximizes the information entropy

$$S_I = -\int_0^\infty dq\, J(q) \ln [J(q)] \tag{6}$$

under the constraints (5a) and (5b) is a normal (or Gaussian) distribution

$$J(q) = [3N^3/(2\pi \langle p^2 \rangle)]^{1/2} \exp[-(3N/2\langle p^2 \rangle) q^2]. \tag{7}$$

Information-theoretically, this is the most unbiased estimate of $J(q)$ when only the information (5) is given [15]. This inferential profile is correct for the 1*s* GTO (Gaussian-type orbital).

2.2. Padé approximation to b(r)

Instead of the direct estimation of $J(q)$, approximate $J(q)$ can also be derived from the estimation of $b(r)$ through Eq. (4a). General relations between $b(r)$ and the moments $\langle p^n \rangle$ have been shown in Refs. [20, 21]. The resultant equations imply that as far as the moments exist, the coefficients of odd powers of r are zero and those of even powers of r are proportional to the moments of the corresponding orders when $b(r)$ is expanded in the Maclaurin series. Namely, we can write

$$b(r) = N - (\langle p^2 \rangle / 6) r^2 + O(r^4), \tag{8}$$

since the moments $\langle p^n \rangle$ always exist for $0 \leq n \leq 4$. In Eq. (8) the expansion is specified up to the third order, and we know $b(r) \to 0$ as $r \to \infty$. Then we may construct [0/3] and [1/2] Padé approximants to $b(r)$ (see e.g. Ref. [22]). In both cases, the results are found to be

$$b(r) = N/[1 + (\langle p^2 \rangle / 6N) r^2] \tag{9}$$

which is also derived from the [0/2] approximant. Using Eq. (4a), we obtain the inferential profile

$$J(q) = (3N^3/2\langle p^2 \rangle)^{1/2} \exp[-(6N/\langle p^2 \rangle)^{1/2} q]. \tag{10}$$

However, this Compton profile has a cusp at the origin and is not physically acceptable (see Sect. 3 and Fig. 1a). By the analogy of Eq. (9), we may alternatively assume a function

$$b(r) = c_1/(1 + c_2 r^2)^m. \tag{11}$$

Then it is found that

$$c_1 = N, \qquad c_2 = \langle p^2 \rangle / (6mN) \tag{12}$$

from Eq. (8), and

$$J(q) = N 2^{1-2m} [(m-1)!]^{-1} c_2^{-1/2} \exp(-c_2^{-1/2} q) \times \sum_{k=0}^{m-1} [(2m-k-2)!(2c_2^{-1/2} q)^k] / [k!(m-k-1)!] \tag{13}$$

from Eq. (4a), but the positive integer m remains undetermined. For $m \geq 2$, Eq. (13) does not have the incorrect cusp. Interestingly, Eq. (13) monotonically converges to the maximum-entropy $J(q)$ (Eq. (7)) as m approaches infinity.

2.3. Overlap approximation to b(r)

An important property of the characteristic function is that it is reduced to the overlap integral for one-electron orbitals [18, 21]. We can therefore assign functions similar to overlap integrals for $b(r)$, instead of the Padé approximants.

Since four coefficients are given in the expansion (8), we first examine a function with four parameters

$$b(r) = \exp(-\zeta r)(a_0 + a_1 r + a_2 r^2) \tag{14}$$

which imitates the overlap integral between two STO's. Comparison of Eq. (8) with the Maclaurin expansion of Eq. (14) gives

$$\zeta = (\langle p^2 \rangle / N)^{1/2}, \qquad a_0 = N, \qquad a_1 = (N \langle p^2 \rangle)^{1/2}, \qquad a_2 = \langle p^2 \rangle / 3 \tag{15}$$

and hence

$$J(q) = (8/3\pi)(\langle p^2 \rangle^5 / N^3)^{1/2} (q^2 + \langle p^2 \rangle / N)^{-3}. \tag{16}$$

This inferential $J(q)$ is correct for the 1s STO. Indeed, Eq. (14) has the same form as the overlap integral between the 1s STO's. Consequently, Eq. (16) is expected to be a good approximation for He, H_2, and their analogs where the 1s character is predominant.

When we assume a function $b(r) = \exp(-\zeta r^2) \times$ (polynomial of r) from the analogy of the GTO overlaps, the result is identical to the maximum-entropy inference (Eq. (7)).

3. Reliability of inferential $J(q)$

In Fig. 1, the inferential Compton profiles, Eqs. (7), (10), (13), and (16), are shown and compared with the results from several STO's. All the parameters have been so adjusted that $N = \langle p^2 \rangle = 1$ is satisfied.

The Padé approximation (10) has an incorrect cusp at the origin. The overlap approximation (16) emphasizes the distribution around the origin, whereas the maximum-entropy distribution (7) emphasizes the profile around $q \simeq 0.8$ with the lowest peak $J(0)$. The approximation (13) shows an intermediate behaviour. Though the Compton profiles for atoms must have an asymptotic behaviour of q^{-6} for a large q value [2], the comparison of Figs. 1a and 1b shows that for the q-range of interest, the inferential $J(q)$'s are physically acceptable except for the approximation (10).

Table 1 summarizes several characteristic properties of the inferential Compton profiles, which entirely depend on N and $\langle p^2 \rangle$. The corresponding properties for the STO's are given in Table 2. For single STO's, these results (except for S_I) are independent of exponents and hence atoms, and constitute general relations. As the properties for the STO's vary from one orbital to another, the inferential properties given in Table 1 vary depending on the method of estimation. We cannot conclude which method is best for the construction of approximate Compton profiles. However, some of the inferential properties are quite constant

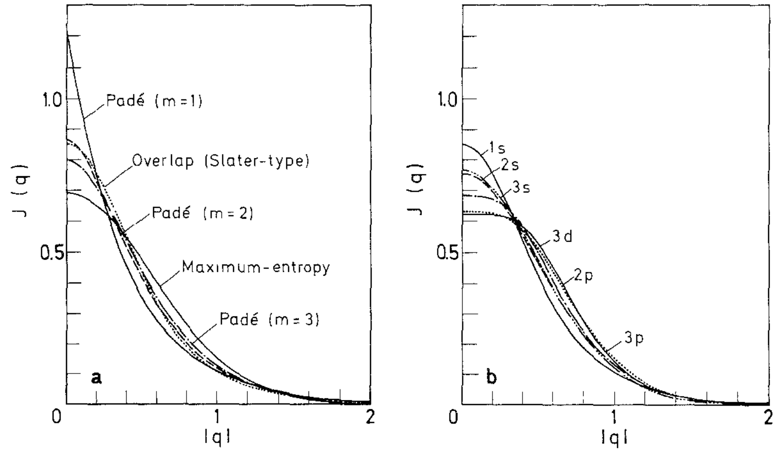

Fig. 1a. Inferential Compton profiles. **b** STO Compton profiles

Table 1. Comparison of several properties of the inferential Compton profiles $J(q)$

Property	$J(q)$ from maximum-entropy approximation	$J(q)$ from approximations to $b(r)$							
		Padé approximation						Overlap approximation	
		$m=1$	$m=2$	$m=3$	$m=4$	$m=5$	$m=\infty$	Slater-type	Gauss-type
$J(0)/[N^{3/2}\langle p^2\rangle^{-1/2}]$	0.6910	1.2247	0.8660	0.7955	0.7655	0.7488	Same as the results of maximum-entropy approximation	0.8488	Same as the results of maximum-entropy approximation
$q_{hw}/[N^{-1/2}\langle p^2\rangle^{1/2}]$	0.6798	0.2830	0.4845	0.5492	0.5817	0.6012		0.5098	
S_I[a]	0.4348	0.3986	0.4228	0.4287	0.4310	0.4322		0.4114	
$\langle p^{-2}\rangle/[N^2\langle p^2\rangle^{-1}]$	3.0	—	6.0	4.5	4.0	3.75		5.0	
$\langle p^{-1}\rangle/[N^{3/2}\langle p^2\rangle^{-1/2}]$	1.3820	2.4495	1.7321	1.5910	1.5309	1.4977		1.6977	
$\langle p\rangle/[N^{1/2}\langle p^2\rangle^{1/2}]$	0.9213	0.8165	0.8660	0.8839	0.8930	0.8986		0.8488	
$\langle p^3\rangle/[N^{-1/2}\langle p^2\rangle^{3/2}]$	1.2284	1.6330	1.4434	1.3749	1.3396	1.3180		1.6977	
$\langle p^4\rangle/[N^{-1}\langle p^2\rangle^2]$	1.6667	3.3333	2.5	2.2222	2.0833	2.0		5.0	

[a] Calculated under the condition of $N=\langle p^2\rangle=1$.

Table 2. Comparison of several properties of the STO Compton profiles $J(q)$

	Orbital					
Property[a]	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*
$J(0)/[N^{3/2}\langle p^2\rangle^{-1/2}]$	0.8488	0.7514	0.6791	0.7636	0.6274	0.6209
$q_{hw}/[N^{-1/2}\langle p^2\rangle^{1/2}]$	0.5098	0.6091	0.6763	0.6072	0.7561	0.7567
S_I[b]	0.4114	0.4197	0.4296	0.4098	0.4332	0.4320
$\langle p^{-2}\rangle/[N^2\langle p^2\rangle^{-1}]$	5.0	3.6667	2.3333	3.72	1.9185	1.8
$\langle p^{-1}\rangle/[N^{3/2}\langle p^2\rangle^{-1/2}]$	1.6977	1.5029	1.3581	1.5271	1.2547	1.2417
$\langle p\rangle/[N^{1/2}\langle p^2\rangle^{1/2}]$	0.8488	0.8821	0.9054	0.8677	0.9341	0.9313
$\langle p^3\rangle/[N^{-1/2}\langle p^2\rangle^{3/2}]$	1.6977	1.7643	1.3581	1.7353	1.2172	1.2417
$\langle p^4\rangle/[N^{-1}\langle p^2\rangle^2]$	5.0	9.0	2.3333	5.0	1.7347	1.8

[a] $N=1$.

[b] Calculated under the condition of $N=\langle p^2\rangle=1$.

except for the Padé approximation with $m=1$. For instance, we see

$$\langle p^{-1}\rangle/[N^{3/2}\langle p^2\rangle^{-1/2}]\sim 1.5, \tag{17a}$$

$$\langle p\rangle/[N^{1/2}\langle p^2\rangle^{1/2}]\sim 0.9, \tag{17b}$$

in Table 1. The inferential relation (17a) also applies to the 1s-3s STO's and the relation (17b) applies to all the STO's examined in Table 2. It may be important that Eq. (17b) is approximately valid for all kinds of STO's. This supports the semi-quantitative reliability of the inference for the intermediate q-range. It also suggests that a similar relation holds for the total atomic Compton profile, when the independent particle model is assumed. However, the results for $\langle p^{-2}\rangle$, $\langle p^3\rangle$, and $\langle p^4\rangle$ are dispersive in both Tables 1 and 2, and reflect the fact that the Compton profiles differ considerably in the small and large q-regions depending on the methods of inference and the types of orbitals. The energy information alone seems to be insufficient for the estimation of the distribution in these q-regions.

On the basis of the knowledge of the energy, semi-quantitative estimates seem to be possible for the intermediate q-range, when we consider the Compton profile of single STO's. However, the single STO description is not very accurate even for small atoms. For the orbitals represented by the linear combination of some basis functions, the properties summarized in Tables 1 and 2 are no longer constants but depend greatly on the exponents, coefficients of linear combination, and so on. For this reason, the results for actual atoms depend on individual atoms and deviate from the values in Tables 1 and 2 as shown in Table 3. Even the relations (17) do not hold except for H and He; though Eq. (17b) seems to be valid for Li–Ne if the constant 0.9 is replaced with 0.7.

In summary, the present methods of constructing approximate Compton profiles based only on the knowledge of $\langle p^2\rangle=-2E$ are not satisfactory for actual atoms

Table 3. Comparison of several properties of the atomic Compton profiles $J(q)$[a]

	Atom									
Property	H(^2S)	He(^1S)	Li(^2S)	Be(^1S)	B(^2P)	C(^3P)	N(^4P)	O(^3P)	F(^2P)	Ne(^1S)
N	1	2	3	4	5	6	7	8	9	10
$-E$[b]	0.5	2.8617	7.4326	14.573	24.529	37.688	54.400	74.808	99.408	128.54
$\langle p^2 \rangle$	1.0	5.7234	14.865	29.145	49.055	75.372	108.79	149.61	198.81	257.08
$\langle p^{-2} \rangle / [N^2 \langle p^2 \rangle^{-1}]$	5.0	5.8538	43.651	45.899	31.815	24.581	20.158	17.451	15.458	13.971
$\langle p^{-1} \rangle / [N^{3/2} \langle p^2 \rangle^{-1/2}]$	1.6977	1.8108	3.8441	4.2604	3.7442	3.3987	3.1512	2.9984	2.8691	2.7611
$\langle p \rangle / [N^{1/2} \langle p^2 \rangle^{1/2}]$	0.8488	0.8273	0.7346	0.6885	0.6800	0.6800	0.6835	0.6857	0.6895	0.6942
$\langle p^3 \rangle / [N^{-1/2} \langle p^2 \rangle^{3/2}]$	1.6977	1.8581	2.1439	2.3575	2.4957	2.5872	2.6479	2.6981	2.7298	2.7486
$\langle p^4 \rangle / [N^{-1} \langle p^2 \rangle^2]$	5.0	6.3597	8.2323	9.9137	11.238	12.258	13.037	13.713	14.212	14.602

[a] Atomic wave functions have been taken from Ref. [23] for He and from Ref. [24] for Li-Ne.

[b] Total energy E is included to show the accuracy of the wave function employed.

in a quantitative sense. The present results are of the accuracy of the (non-variational) single STO description for atoms. In addition to the knowledge of the energy, more information seems to be needed to improve the quantitative applicability.

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