Characteristic function of momentum density distribution. II

Characteristic function of momentum density distribution. II

Toshikatsu Koga

Department of Applied Chemistry and Department of Applied Science for Energy, Muroran Institute of Technology, Muroran, Hokkaido, 050 Japan
(Received 3 March 1983; accepted 14 April 1983)

Rigorous relations between the moments $\langle p_x^l p_y^m p_z^n\rangle$ and $\langle p^n\rangle$ and the characteristic function $B(r)$ of the momentum density distribution $\rho(p)$ are here generalized to the case of negative l, m, and n. A simple application is given which illustrates that the present results enable us to obtain the moments of momenta without referring to any momentum-space quantity.

I. INTRODUCTION

The characteristic function $B(\mathbf{r})$ $[=\int d\mathbf{p}\exp(-i\mathbf{pr})\rho(\mathbf{p})]$ of the electron momentum density $\rho(\mathbf{p})$ is used to facilitate the analysis of experimental Compton profiles[1] and its fundamental properties have been discussed in detail by Weyrich *et al.*[2] and Thakkar *et al.*[3] In a previous paper,[4] we have shown that $B(\mathbf{r})$ and its spherical average

$$b(r)\left[=(4\pi)^{-1}\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\sin\theta B(\mathbf{r})\right]$$

are useful for the calculation of the moments $\langle p_x^l p_y^m p_z^n\rangle$ and $\langle p^n\rangle$ where $p=|\mathbf{p}|=(p_x^2+p_y^2+p_z^2)^{1/2}$. The resultant relations are

$$\langle p_x^l p_y^m p_z^n\rangle = i^{l+m+n}B^{(l,m,n)}(0)\ , \tag{1}$$

$$\langle p^n\rangle=\begin{cases}(-1)^{3n/2}(n+1)b^{(n)}(0) & \text{for even } n\ ,\\ (-1)^{(n+1)/2}[2(n+1)/\pi]\int_0^\infty dr\, r^{-1}b^{(n)}(r) & \text{for odd } n\ ,\end{cases} \tag{2}$$

where $B^{(l,m,n)}(\mathbf{r})$ and $b^{(n)}(r)$ denote, respectively, $\partial^{l+m+n}B(\mathbf{r})/\partial x^l\partial y^m\partial z^n$ and $d^nb(r)/dr^n$, and l, m, and n are nonnegative integers.

In this paper, we discuss the corresponding formulas for negative integers l, m, and n, in order to complete a general relation between the characteristic function and the moments of momenta. The results are illustrated by the calculation of the moments $\langle p^n\rangle$ for several Slater-type orbitals.

II. $B(\mathbf{r})$ AND $\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle$

We assume l, m, and n are positive integers. By definition,

$$\begin{aligned}\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle &= \int d\mathbf{p}\,p_x^{-l}p_y^{-m}p_z^{-n}\rho(\mathbf{p})\\ &=(2\pi)^{-3}\int d\mathbf{r}\,B(\mathbf{r})\left[\int d\mathbf{p}\,p_x^{-l}p_y^{-m}p_z^{-n}\exp(+i\mathbf{pr})\right]\ .\end{aligned} \tag{3}$$

Since the Fourier transform of p_x^{-l} is $i^l\operatorname{sgn}(x)(\pi/2)^{1/2}\times[(l-1)!]^{-1}x^{l-1}$ (Ref. 5), Eq. (3) is rewritten as

$$\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle = 2^{-3}i^{l+m+n}[(l-1)!\,(m-1)!\,(n-1)!]^{-1}\times\int d\mathbf{r}\,B(\mathbf{r})[\operatorname{sgn}(x)x^{l-1}][\operatorname{sgn}(y)y^{m-1}][\operatorname{sgn}(z)z^{n-1}]\ . \tag{4}$$

It is then clear that $\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle$ vanishes if one of l, m, and n is odd, because $B(\mathbf{r})$ is an even function. For even l, m, and n, we finally obtain

$$\langle p_x^{-l}p_y^{-m}p_z^{-n}\rangle = i^{l+m+n}[(l-1)!\,(m-1)!\,(n-1)!]^{-1}\times\int_0^\infty\int_0^\infty\int_0^\infty dx\,dy\,dz\,x^{l-1}y^{m-1}z^{n-1}B(\mathbf{r})\ . \tag{5}$$

When only one or two components are concerned, Eq. (5) is reduced to

$$\langle p_x^{-l}\rangle = i^l[(l-1)!]^{-1}\int_0^\infty dx\,x^{l-1}B(x,0,0)\ , \tag{6a}$$

$$\langle p_x^{-l}p_y^{-m}\rangle = i^{l+m}[(l-1)!\,(m-1)!]^{-1}\times\int_0^\infty\int_0^\infty dx\,dy\,x^{l-1}y^{m-1}B(x,y,0)\ , \tag{6b}$$

and their analogs.

When positive and negative l, m, and n are mixed, equations with mixed form of Eqs. (1) and (5) are obtained. For example,

$$\langle p_x^{+l}p_y^{-m}p_z^{-n}\rangle = i^{-l+m+n}[(m-1)!\,(n-1)!]^{-1}\times\int_0^\infty\int_0^\infty dy\,dz\,y^{m-1}z^{n-1}B^{(l,0,0)}(0,y,z)\ , \tag{7a}$$

$$\langle p_x^{+l}p_y^{+m}p_z^{-n}\rangle = i^{-l-m+n}[(n-1)!]^{-1}\int_0^\infty dz\,z^{n-1}B^{(l,m,0)}(0,0,z)\ , \tag{7b}$$

where all of l, m, and n are assumed to be even.

III. $b(r)$ AND $\langle p^{-n}\rangle$

Since $b(r)$ is related to the radial momentum density

$$I(p)\left[=\int_0^{2\pi}d\phi_p\int_0^{\pi}d\theta_p\,p^2\sin\theta_p\,\rho(\mathbf{p})\right]$$

through

$$rb(r)=\int_0^\infty dp\sin(pr)[I(p)/p]\ ,$$

$$\begin{aligned}\langle p^{-n}\rangle &= \int_0^\infty dp\,p^{-n}I(p)\\ &=(2/\pi)\int_0^\infty dr\,rb(r)\left[\int_0^\infty dp\,p^{-n+1}\sin(pr)\right]\ .\end{aligned} \tag{8}$$

For a special case of $n=1$, we obtain

$$\langle p^{-1}\rangle=(2/\pi)\int_0^\infty dr\,b(r)\ , \tag{9}$$

since $\int_0^\infty dp\sin(pr)=1/r$ in the sense of hyperfunctions.[6] For $n\geq 2$, the integral in the square brackets of Eq. (8) is a special case of a more general integral $\int_0^\infty dp\sin(pr)/p^a$ $(a,r>0)$. By taking its finite part (*partie finie*), the latter integral is found to be[7]

 0021-9606/83/151384-03$02.10

TABLE I. Existing moments $\langle p^n \rangle$ for the first six Slater-type orbitals with exponent ζ.

	$\langle p^n \rangle / \zeta^n$														
Orbital	$n=-6$	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	7	8
1s	...	...	...	...	5	$\frac{16}{3\pi}$	1	$\frac{8}{3\pi}$	1	$\frac{16}{3\pi}$	5	...	...	...	...
2s	...	...	...	...	11	$\frac{368}{45\pi}$	1	$\frac{8}{5\pi}$	$\frac{1}{3}$	$\frac{16}{15\pi}$	1	...	...	...	...
2p	...	...	21	$\frac{256}{15\pi}$	$\frac{7}{3}$	$\frac{64}{15\pi}$	1	$\frac{128}{45\pi}$	1	$\frac{64}{15\pi}$	$\frac{7}{3}$	$\frac{256}{15\pi}$	21	...	...
3s	...	...	...	...	$\frac{93}{5}$	$\frac{5632}{525\pi}$	1	$\frac{128}{105\pi}$	$\frac{1}{5}$	$\frac{256}{525\pi}$	$\frac{1}{5}$	$\frac{128}{105\pi}$	1	$\frac{5632}{525\pi}$	$\frac{93}{5}$
3p	...	...	$\frac{289}{5}$	$\frac{6656}{175\pi}$	$\frac{37}{9}$	$\frac{9088}{1575\pi}$	1	$\frac{9472}{4725\pi}$	$\frac{7}{15}$	$\frac{128}{105\pi}$	$\frac{17}{45}$	$\frac{512}{315\pi}$	$\frac{9}{5}$	...	...
3d	$\frac{429}{5}$	$\frac{2048}{35\pi}$	$\frac{33}{5}$	$\frac{1024}{105\pi}$	$\frac{9}{5}$	$\frac{2048}{525\pi}$	1	$\frac{512}{175\pi}$	1	$\frac{2048}{525\pi}$	$\frac{9}{5}$	$\frac{1024}{105\pi}$	$\frac{33}{5}$	$\frac{2048}{35\pi}$	$\frac{429}{5}$

$$\int_0^\infty dp \sin(pr)/p^a = \begin{cases} \pi r^{a-1}/[2\Gamma(a)\sin(\pi a/2)] & \text{for } a \neq \text{even integer} , \\ (-1)^{a/2} r^{a-1}[(a-1)!]^{-1}[\ln(r) - \psi(a)] & \text{for } a = \text{even integer} , \end{cases} \tag{10}$$

where $\psi(a)[=-\gamma+\sum_{n=1}^{\infty}(a-1)/\{n(a-1+n)\}]$ is the digamma function with γ being the Euler constant. We therefore obtain

$$\langle p^{-n} \rangle = \begin{cases} (-1)^{n/2-1}[(n-2)!]^{-1}\int_0^\infty dr\, r^{n-1} b(r) & \text{for even } n , \\ (-1)^{(n-1)/2}(2/\pi)[(n-2)!]^{-1}\int_0^\infty dr\, r^{n-1} b(r)[\ln(r) - \psi(n-1)] & \text{for odd } n . \end{cases} \tag{11}$$

Note that for a positive integer n, $\psi(n)$ is simplified to the finite sum $-\gamma+1+1/2+1/3+\cdots+1/(n-1)$. The results for $\langle p^{-1} \rangle$ and $\langle p^{-2} \rangle$ agree with those given by Thakkar *et al.*[3]

IV. A SIMPLE APPLICATION

An important aspect of the characteristic function $B(\mathbf{r})$ is that for one-electron orbitals (e.g., independent-particle model and natural orbital expansion), $B(\mathbf{r})$ is equivalent to the overlap integral $S(\mathbf{r})$.[2] Therefore we can evaluate the moments $\langle p_x^{\pm l} p_y^{\pm m} p_z^{\pm n} \rangle$ and $\langle p^{\pm n} \rangle$ directly in position space based on the table of overlap integrals (see, e.g., Refs. 8–10) without invoking the momentum-space concepts such as momentum density (cf. Ref. 11). As a simple application of this method, we have examined the moments $\langle p^{\pm n} \rangle$ for the first six Slater-type orbitals with exponent ζ. The $b(r)$ functions are obtained as

$$b_{1s}(r) = S_{1s} = \exp(-t)(1+t+t^2/3) ,$$

$$b_{2s}(r) = S_{2s} = \exp(-t)(1+t+4t^2/9+t^3/9+t^4/45) ,$$

$$b_{2p}(r) = \tfrac{1}{3}S_{2p\sigma} + \tfrac{2}{3}S_{2p\pi} = \exp(-t)(1+t+t^2/3-t^4/45) ,$$

$$b_{3s}(r) = S_{3s} = \exp(-t)(1+t+7t^2/15+2t^3/15 +2t^4/75+t^5/225+t^6/1575) ,$$

$$b_{3p}(r) = \tfrac{1}{3}S_{3p\sigma} + \tfrac{2}{3}S_{3p\pi} = \exp(-t)(1+t+19t^2/45 +4t^3/45+4t^4/675-t^5/675-t^6/1575) ,$$

$$b_{3d}(r) = \tfrac{1}{5}S_{3d\sigma} + \tfrac{2}{5}S_{3d\pi} + \tfrac{2}{5}S_{3d\delta} = \exp(-t)(1+t+t^2/3-2t^4/75-t^5/225+t^6/1575) ,$$

where $t=\zeta r$. Then applying Eqs. (2) and (11), we have calculated $\langle p^{\pm n} \rangle$ for various n. The existing moments are summarized in Table I, which of course agree with the results from the momentum-space calculation. Interestingly, we see some regularity for the coefficients $\langle p^n \rangle / \zeta^n$. For 1s, 2p, and 3d orbitals, the coefficients are symmetric with respect to $n=1$, and for 3s orbital they are symmetric with respect to $n=3$. However, there seems to be no regularity for the 2s and 3p orbitals.

ACKNOWLEDGMENTS

I acknowledge Mr. Takeshi Miyahara for his assistance in checking the results of Table I. Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

[1]P. Pattison, N. K. Hansen, and J. R. Schneider, Chem. Phys. **59**, 231 (1981), and the references cited therein.
[2]W. Weyrich, P. Pattison, and B. G. Williams, Chem. Phys. **41**, 271 (1979).
[3]A. J. Thakkar, A. M. Simas, and V. H. Smith, Jr., Chem. Phys. **63**, 175 (1981).
[4]T. Koga and M. Morita, J. Chem. Phys. **77**, 6345 (1982).
[5]I. N. Sneddon, *The Use of Integral Transforms* (McGraw–Hill, New York, 1972), p. 506.
[6]A. Papoulis, *The Fourier Integral and Its Applications* (McGraw–Hill, New York, 1962), p. 278.
[7]I. Imai, *Applied Theory of Hyperfunctions*. I. (in Japanese) (Science, Tokyo, 1981), p. 119.
[8]R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, J. Chem. Phys. **17**, 1248 (1949).
[9]C. C. J. Roothaan, J. Chem. Phys. **19**, 1445 (1951).
[10]M. Kotani, A. Amemya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals*, second ed. (Maruzen, Tokyo, 1963).
[11]I. R. Epstein, Chem. Phys. Lett. **9**, 9 (1971).