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Reciprocal form factors from momentum density magnitudes

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Abstract. Tight model-independent approximations to the reciprocal form factor $B(\boldsymbol{r})$ are obtained in terms of a few quantities related to the one-particle momentum density $\gamma(\boldsymbol{p})$ with no use of any position quantity. In doing so, two different and complementary methods (maximum entropy and two-point Padé approximants) are used. The accuracy of the approximations is analysed in a Hartree–Fock framework.

The Fourier transform $B(\boldsymbol{r})$ of the electron momentum density $\gamma(\boldsymbol{p})$

$$B(\boldsymbol{r}) = \int \exp\{-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r}\}\gamma(\boldsymbol{p})\,\mathrm{d}\boldsymbol{p} \tag{1}$$

is known to be the autocorrelation function of the wavefunction in position space and is used to facilitate the study and interpretation of experimental Compton profiles and fundamental chemical concepts such as hybridization and bonding (Weyrich *et al* 1979, Thakkar *et al* 1981).

This important function, also called reciprocal form factor, characteristic function or internal folded density, was considered as a convenient bridge between the coordinate and momentum spaces and, consequently, a number of theoretical results and properties satisfied by this quantity have been studied (Weyrich *et al* 1979, Thakkar *et al* 1981).

There is an equivalence between the 'position space form factor' $B(\boldsymbol{r})$ and the momentum density on the one hand, and between the momentum space form factor $F(\boldsymbol{p})$ and the charge density on the other. Expansions and sum rules involving $B(\boldsymbol{r})$ (Koga and Morita 1982, Koga 1983) and $F(\boldsymbol{p})$ (Thakkar and Smith 1978, Thakkar and Koga 1985) reflect this equivalence and have been used to check the accuracy of experimental and theoretical results on the reliability of Compton profile fits to several functional forms (Thakkar *et al* 1980, Gadre and Chakravorty 1986).

In this work we obtain tight and simple approximations to the spherically averaged characteristic function

$$B(r) = \frac{1}{4\pi}\int B(\boldsymbol{r})\,\mathrm{d}\Omega = 4\pi\int_0^\infty p^2\gamma(p)\,j_0(pr)\,\mathrm{d}p \tag{2}$$

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which is related to the spherically averaged momentum density $\gamma(p) = (1/4\pi)\int \gamma(\boldsymbol{p})\,\mathrm{d}\Omega$ by means of a Hankel or Fourier–Bessel transform.

The approximations are constructed without referring to any coordinate-space magnitudes and in terms of very limited information in the momentum space. More precisely, we use the asymptotic expansion of the electron momentum density (Thakkar 1987, Thakkar *et al* 1987) and two kinds of important quantities, namely the expectation values of the momentum density (Thakkar *et al* 1981, Kryachko and Koga 1987)

$$\langle p^n \rangle = 4\pi \int_0^\infty p^{n+2}\gamma(p)\,\mathrm{d}p, \qquad n = -2, -1, \ldots, 4, \tag{3}$$

and values of derivatives of $\gamma(p)$ at the origin (i.e. $\gamma^{(n)}(0)$).

Some of these expectation values have an intrinsic physical meaning. For instance, the kinetic energy of an 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. These quantities appear in the small-r behaviour of $B(r)$

$$B(r) = N - \frac{\langle p^2 \rangle}{3!}r^2 + \frac{\langle p^4 \rangle}{5!}r^4 + \mathrm{O}(r^5) \qquad (r \to 0). \tag{4}$$

The central value of $\gamma(p)$ is related to the number of slow electrons and is also related to important physical observables (see e.g. Gálvez and Dehesa 1988, Angulo *et al* 1991).

Thakkar (1987) and Thakkar *et al* (1987) have computed the asymptotic expansion of the atomic momentum densities from hydrogen ($N = 1$) to lawrencium ($N = 103$) atoms. This asymptotic behaviour is of special interest because it plays a crucial role in the computation of moments from experimental isotropic Compton profiles.

This kind of information is sufficient to apply two complementary methods, the Padé and the maximum entropy methods, to build up tight estimations of $B(r)$ for the entire range of r.

1. Maximum entropy (ME) reconstruction of $B(r)$

First, maximum entropy approximations to $\gamma(p)$ are constructed in terms of its moments

$$\mu_n = \int_0^\infty p^n \gamma(p)\,\mathrm{d}p = \frac{\langle p^{n-2} \rangle}{4\pi}, \qquad n = 0, 1, \ldots, 6 \tag{5}$$

and then we insert these approximations in (2), obtaining (Leaseburg and Mead 1993) convergent approximations to $B(r)$.

The ME momentum densities are computed by maximizing the entropy functional constrained by the moments considered and so one has to solve the variational problem

$$\delta\left[-\int_0^\infty \gamma(p)\ln\gamma(p)\,\mathrm{d}p + \sum_{n=0}^{M}\lambda_n\left(\mu_n - \int_0^\infty p^n\gamma(p)\,\mathrm{d}p\right)\right] = 0. \tag{6}$$

Foundations, properties and applications of this powerful method can be found elsewhere (see e.g. Leaseburg and Mead 1993, Mead and Papanicolau 1983, Antolín *et al* 1994).

The solution of (6), to be called ME momentum density, has the form

$$\gamma_M^{ME}(p) = A\exp\left\{-\sum_{j=1}^{M}\lambda_j p^j\right\}, \tag{7}$$

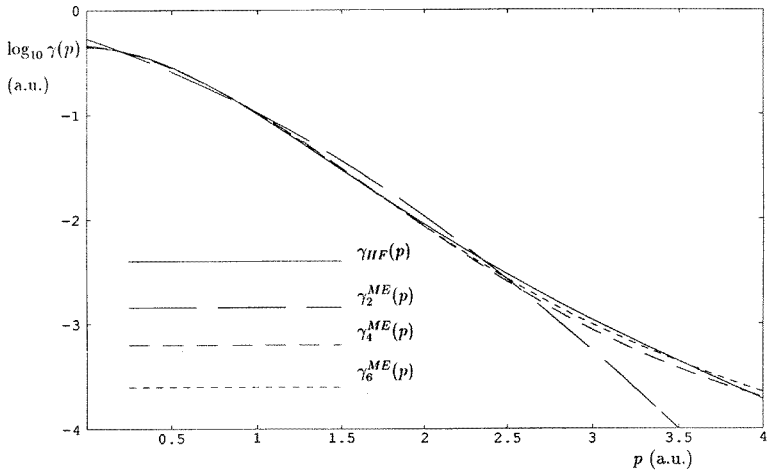

Figure 1. Hartree–Fock momentum density ($\gamma_{HF}(p)$) and ME approximations $\gamma_2^{ME}(p)$, $\gamma_4^{ME}(p)$ and $\gamma_6^{ME}(p)$ for the helium atom ($N = 2$). Atomic units (au) are used.

where $A = \exp\{-1 - \lambda_0\}$ and the Lagrange multipliers λ_j, $j = 1, \ldots, M$, have to be computed numerically from the extremely nonlinear system of constraints

$$\int_0^\infty p^n \gamma_M^{ME}(p)\,\mathrm{d}p = \frac{\langle p^{n-2}\rangle}{4\pi}, \qquad n = 0, 1, \ldots, M. \tag{8}$$

The power of this technique is apparent in figure 1, where some approximations to $\gamma(p)$ for the helium ($N = 2$) atom are shown (in logarithmic scale), together with the Hartree–Fock momentum density $\gamma_{HF}(p)$, for comparison. Clementi and Roetti (1974) wavefunctions have been used to construct these functions. It is worth remarking how the successive values of $\gamma(0)$ and of the entropy S_γ corresponding to these approximations, $\gamma_2(0) = 0.53$, $\gamma_4(0) = 0.46$, $\gamma_6(0) = 0.45$ and $S_2 = 0.4851$, $S_4 = 0.4753$, $S_6 = 0.4751$, converge to the exact values of these quantities, $\gamma_{HF}(0) = 0.44$, $S_{HF} = 0.4750$.

The ME approximations $\gamma_M^{ME}(p)$ to $\gamma(p)$ can be now inserted in (2) to obtain convergent (Leaseburg and Mead 1993) approximations $B_M^{ME}(p)$ to $B(r)$. These approximations are shown in figure 2, where the ME reciprocal form factors $B_2^{ME}(r)$, $B_4^{ME}(r)$ and $B_6^{ME}(r)$ are drawn (also in logarithmic scale) together with the exact Hartree–Fock characteristic function $B_{HF}(r)$ of helium ($N = 2$) computed from the Clementi and Roetti (1974) atomic data.

Such approximations can also be computed for any other atom since the technique employed here is completely general.

It is also possible to obtain 'direct' ME approximations to $B(r)$ by using the only existing moments of this magnitude, which are known to be (Thakkar *et al* 1980, Kryachko and Koga 1987)

$$\nu_0 = \int_0^\infty B(r)\,\mathrm{d}r = \frac{\pi\langle p^{-1}\rangle}{2} \tag{9}$$

$$\nu_1 = \int_0^\infty r B(r)\,\mathrm{d}r = \langle p^{-2}\rangle \tag{10}$$

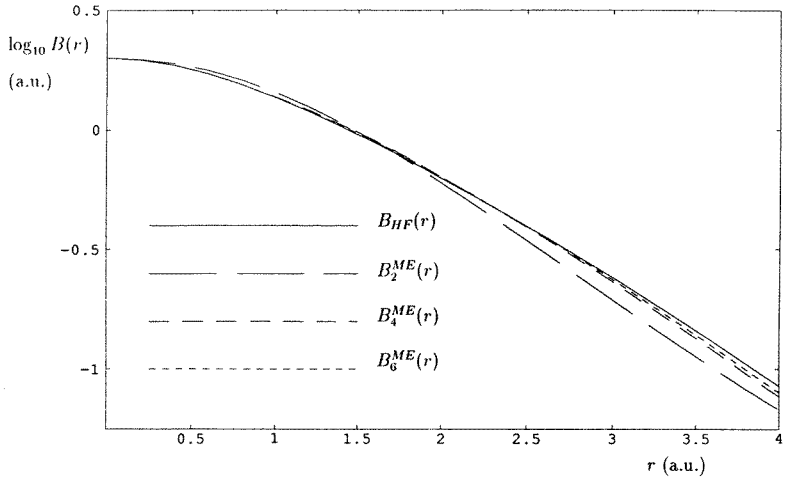

Figure 2. Hartree–Fock reciprocal form factor ($B_{HF}(r)$) and ME approximations $B_2^{ME}(r)$, $B_4^{ME}(r)$ and $B_6^{ME}(r)$ for the helium atom ($N = 2$). Atomic units (au) are used.

$$\nu_2 = \int_0^\infty r^2 B(r)\,\mathrm{d}r = 2\pi^2\gamma(0). \tag{11}$$

The approximants built up from $\{\nu_0, \nu_1\}$ and from $\{\nu_0, \nu_2\}$ are analytic (Angulo *et al* 1995), and have the form

$$B_k^{DME}(r) = \frac{\nu_0 k}{\Gamma(1/k)}\left(\frac{\nu_0}{k\nu_k}\right)^{1/k}\exp\left\{-\frac{\nu_0}{k\nu_k}r^k\right\}, \qquad k = 1, 2. \tag{12}$$

The approximation $B_{12}^{DME}(r)$ which takes into account all the existing moments of $B(r)$ (i.e. ν_0, ν_1 and ν_2) is of the form given by (7) and must be numerically computed. In spite of the small amount of information used, the latter is a good approximation to $B(r)$. This is shown in figure 3, where the aforementioned 'direct' approximations are plotted together with the corresponding Hartree–Fock one, $B_{HF}(r)$, for the helium atom (Clementi and Roetti 1974).

2. Two point Padé (TPP) reconstruction of $B(r)$

In this method we construct Padé approximants to $\gamma(p)$ taking into account the information provided by the first coefficients in its small-p behaviour, i.e.

$$\gamma(p) = \sum_{n=0}^{\infty}\frac{\gamma^{(n)}(0)}{n!}p^n \tag{13}$$

and considering simultaneously the corresponding large-p behaviour (Thakkar 1987). General expressions for the large- and small-p behaviour of electronic momentum densities, corresponding to atomic orbitals with arbitrary angular momentum quantum number l, have been derived (Thakkar 1987). These expansions were used to calculate the first three coefficients in each of the small-p Maclaurin and large-p asymptotic expansions of the total electronic momentum densities of all neutral atoms from hydrogen ($N = 1$) to lawrencium ($N = 103$) (Thakkar *et al* 1987).

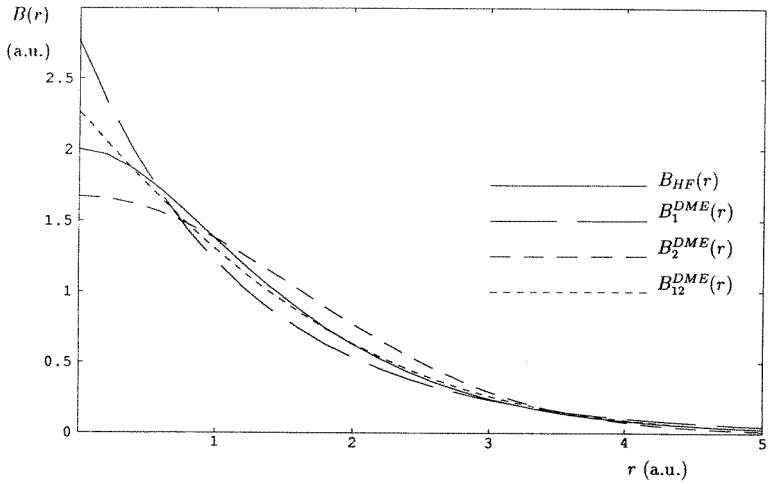

Figure 3. Hartree–Fock reciprocal form factor ($B_{HF}(r)$) and 'direct' ME approximations $B_1^{DME}(r)$, $B_2^{DME}(r)$ and $B_{12}^{ME}(r)$ for the helium atom ($N = 2$). Atomic units (au) are used.

This information is sufficient to construct TPP approximants $\gamma_{LM}(p)$ to $\gamma(p)$ in the whole range of p. These approximants are special cases of the so-called multipoint Padé approximants (Baker and Graves-Morris 1981) for which many results on algebraic properties, recurrence relations, bounds and convergence are known (see e.g. González-Vera and Casasús 1985, Draux 1987, González-Vera and Njåstad 1990).

We consider here subdiagonal TPP approximants of type

$$\gamma_{LM}^{TPP}(p) = \frac{P_{M-1}(p)}{Q_M(p)}, \qquad 0 \leqslant L \leqslant 2M \tag{14}$$

where L and $2M - L$ are the number of pieces of information at $p = 0$ and at infinity, respectively, and P_{M-1} and Q_M are polynomials at most of degree $M - 1$ and M in the variable p. These approximations are constructed in such a way that they fulfil the following conditions:

$$\gamma_{LM}^{TPP}(p) - \gamma(p) = \mathrm{O}(p^L) \qquad (p \to 0) \tag{15}$$

$$\gamma_{LM}^{TPP}(p) - \gamma(p) = \mathrm{O}(p^{(-2M-1+L)}) \qquad (p \to \infty). \tag{16}$$

Then, the coefficients of P_{M-1} and Q_M are computed by expanding (14) in power series of p and p^{-1} and imposing the constraints given by (15) and (16). In doing so, one has to consider the aforementioned small- and large-p behaviour of $\gamma(p)$.

It is clear that (14) gives approximations to $\gamma(p)$ in the whole range of p. Then, they can be inserted into (2) to obtain the corresponding TPP approximations to the reciprocal form factor $B(r)$ (to be denoted by $B_{LM}^{TPP}(r)$).

As an illustration (see figure 4), we show here TPP approximations of the form $\gamma_{34}^{TPP}(p)$, $\gamma_{44}^{TPP}(p)$ and $\gamma_{54}^{TPP}(p)$, i.e. those that make use of eight ($2M = 8$ in (14)) constraints: three, four and five at $p = 0$ and five, four and three at infinity, respectively. Previous two-point Padé approximants of lower order (e.g. $\gamma_{33}^{TPP}(p)$ or $\gamma_{22}^{TPP}(p)$) provide bad approximations in the neighbourhood of its poles because they lie in the positive real axis, while (as it might be expected) TPP approximants of higher order (like $\gamma_{55}^{TPP}(p)$) lead to approximations to $\gamma(p)$ as good as the ones plotted in figure 4. Finally, table 1 includes a comparison between

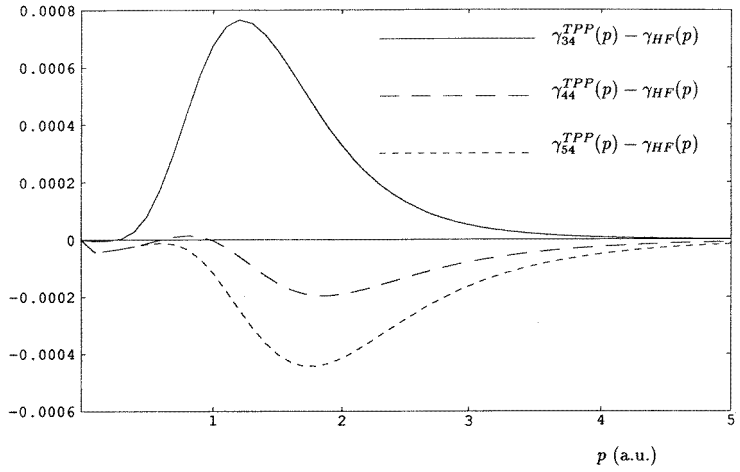

Figure 4. Differences $\gamma_{34}^{TPP} - \gamma_{HF}$, $\gamma_{44}^{TPP} - \gamma_{HF}$ and $\gamma_{54}^{TPP} - \gamma_{HF}$ between the Hartree–Fock momentum density ($\gamma_{HF}(p)$) and the TPP approximations $\gamma_{34}^{TPP}(p)$, $\gamma_{44}^{TPP}(p)$ and $\gamma_{54}^{TPP}(p)$ for the helium atom ($N = 2$). Atomic units (au) are used.

Table 1. Comparison among the reciprocal form factor $B(r)$ and different two-point Padé approximations in a Hartree–Fock framework for the helium atom. Atomic units are used.

r	B_{34}^{TPP}	B_{44}^{TPP}	B_{54}^{TPP}	Hartree–Fock
0.0	2.000 00	2.000 00	2.000 00	2.000 00
0.2	1.994 93	1.960 35	1.957 34	1.963 00
0.4	1.890 91	1.859 97	1.857 59	1.862 02
0.6	1.741 82	1.715 93	1.714 27	1.717 31
0.8	1.568 06	1.547 75	1.546 71	1.548 54
1.0	1.385 88	1.370 94	1.370 38	1.371 30
1.2	1.206 78	1.196 55	1.196 32	1.196 64
1.4	1.038 11	1.031 74	1.031 70	1.031 67
1.6	0.884 10	0.880 65	0.880 73	0.880 52
1.8	0.746 58	0.745 28	0.745 40	0.745 13
2.0	0.625 98	0.626 11	0.626 24	0.625 95
3.0	0.240 09	0.241 57	0.241 60	0.241 56
4.0	0.084 64	0.085 10	0.085 09	0.085 11
5.0	0.028 29	0.028 28	0.028 27	0.028 28
6.0	0.009 09	0.009 01	0.009 01	0.009 01
7.0	0.002 83	0.002 78	0.002 78	0.002 78
8.0	0.000 85	0.000 84	0.000 84	0.000 84

the corresponding Padé approximants to $B(r)$, i.e. $B_{34}^{TPP}(r)$, $B_{44}^{TPP}(r)$, $B_{54}^{TPP}(r)$, and the Hartree–Fock quantity $B_{HF}(r)$ (Clementi and Roetti 1974).

Summarizing, in this work we have presented two different tight approximations to an important quantity in the coordinate space such as the reciprocal form factor $B(r)$, in terms of a very limited amount of information related to the momentum space. These approximations are constructed by using two complementary methods (maximum entropy and two-point Padé approximants) having two relevant characteristics in common: the approximations provided by both of them are model independent, and also they are completely general, i.e. they can be applied to other atomic magnitudes (e.g. form factors (Zarzo *et al* 1996)) and

also to other kinds of systems, such as molecules, solids or nuclei (see e.g. Antolín *et al* 1996).

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