Maximum-entropy and Padé-like approximations to atomic scattering factors

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Abstract. Three different methods, namely maximum entropy, combination of Dirac deltas and two-point Padé approximants, are used to construct tight model-independent approximations to the atomic form factor F(k) in terms of a few quantities related to its inverse Fourier trnsform, i.e. the one-particle density $\rho(r)$. The accuracy of these approximations is analyzed in a Hartree-Fock framework. These extrapolation techniques, being completely general and model-independent, can be applied to other kind of physical systems, such as solids, molecules or nuclei.

PACS: 02.30H; 02.30M

I Introduction

One of the most relevant magnitudes in the study of atomic and molecular systems is the electronic charge density $\rho(\mathbf{r})$. Its Fourier transform

$$F(\mathbf{k}) = \int \rho(\mathbf{r}) \exp\{i\,\mathbf{k}\cdot\mathbf{r}\}\,d\mathbf{r} \tag{1}$$

is the scattering factor (also called form factor or structure factor), which can be obtained from elastic X-ray and electron scattering experiments [1–3]. However, these experimental data can only be measured for a finite set of values of the momentum transferred $\mathbf{k}$ with a limited accuracy, due to the statistical errors. This means that, when computing the charge density from the inverse Fourier transform

$$\rho(\mathbf{r}) = \frac{1}{(2\pi)^3} \int F(\mathbf{k}) \exp\{-i\,\mathbf{k}\cdot\mathbf{r}\}\,d\mathbf{k} , \tag{2}$$

additional values of $F(\mathbf{k})$ beyond the limits of experimental possibilities are required and also the experimental errors should be taken into account. So, interpolation and extrapolation schemes, including the small and large k-behavior of the scattering factor, have to be devised (see e.g. [4]).

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For atomic systems it is interesting to work with spherical averages, i.e. the radial distribution function

$$D(r) = 4\pi r^2 \rho(r) ,$$

being $\rho(r) = \frac{1}{4\pi} \int \rho(\mathbf{r})d\Omega$, and the isotropic form factor

$$F(k) = \frac{1}{4\pi} \int F(\mathbf{k})d\Omega_k \tag{3}$$

where $d\Omega_k = \sin\theta_k d\theta_k d\phi_k$. Both quantities are connected by means of the Fourier-Bessel (or Hankel) transform

$$F(k) = \int_0^\infty D(r)j_0(kr)dr = 4\pi \int_0^\infty \rho(r)j_0(kr)r^2 dr \tag{4}$$

where $j_0(kr) = (kr)^{-1}\sin(kr)$ is the spherical Bessel function of order zero.

This later expression easily provides the small k-behavior of $F(k)$,

$$F(k) = N + \sum_{n=1}^\infty \frac{(-1)^n k^{2n}\langle r^{2n}\rangle}{(2n+1)!} \quad (k \to 0) \tag{5}$$

being $\langle r^m \rangle$ $(m = -2, -1, 0, 1, \ldots)$ the moments of the atomic charge distribution, i.e.

$$\langle r^m \rangle = \int r^m \rho(\mathbf{r})d\mathbf{r} = \int_0^\infty r^m D(r)dr$$
$$= 4\pi \int_0^\infty r^{m+2}\rho(r)dr \equiv 4\pi\mu_{m+2} \tag{6}$$

and $N = \langle r^0 \rangle$ the number of particles of the system. This behavior has been used, for example, to study scaling properties of the structure factor for some atoms [5]. Moreover, the asymptotic expansion of $F(k)$, given by [6, 7]

$$F(k) = 8\pi \sum_{n=1}^\infty (-1)^n n \frac{\rho^{(2n-1)}(0)}{k^{2n+2}} \quad (k \to \infty) \tag{7}$$

shows its strong influence on the central value of the charge density $\rho(0)$.

Thakkar and Smith [8] used the above expansions to obtain accurate expressions for the structure factors and total scattering intensities from explicitly correlated wavefunctions. The usefulness os such expansions is also shown in

the present work when constructing approximations to the atomic form factor. Additionally, the inverse Fourier transform gives the relation

$$\frac{1}{2\pi} \int_0^\infty k^2 F(k) dk = \pi \rho(0) \tag{8}$$

and other sum rules relating the derivatives of the structure function to the expectation values of the radial density $D(r)$ has been obtained [9].

It is also known that $F(k)$ is a non-negative function, i.e. $F(k) \geq 0$, and numerical evidence of its decreasing monotonicity (i.e. $F'(k) \leq 0$) has been recently shown [10]. Other interesting properties, including some lower bounds to $F(k)$, are studied in [11].

The knowledge of accurate form factors of atomic systems is important because they serve as reference for experimental techniques. Recently, the total inelastic and elastic intensities for X-ray and high energy electron scattering for a few ten electron molecules have been calculated by using configuration interaction wavefunctions. The results are compared with experiment, and chemical binding and correlation effects are also studied [12].

Generally speaking, due to the complexity of N-electron systems, no single approach to the study of form factors gives a satisfactory answer to several questions. Then, it is interesting to have tight approximations to these structure functions because of the relevant role which play in the connection between momentum and position spaces.

In this paper, three different methods are used to build up model-independent approximations to the atomic form factor: maximum-entropy, linear combinations of Dirac deltas and two-point Padé approximations (Sect. II). All of them use as basic ingredients to construct the approximations some quantities related to the one-particle density $\rho(\mathbf{r})$, namely some local values (e.g. $\rho^{(n)}(0)$, $n = 0, 1, \ldots$) and/or some radial expectation values $\langle r^n \rangle$. We show here that this kind of information in the position space is sufficient to have a good description of a quantity (like $F(k)$) in the whole range of the momentum space. The accuracy of those approximations is analyzed in Sect. III within a Hartree-Fock framework, and the appropriate conclusions are discussed in the final section.

II Description of the mathematical methods

A Maximum entropy (ME)

Consider the whole set of density functions $f(r)$ defined on the interval $[0, \infty)$ with the same first $M + 1$ moments $\{\mu_j\}_{j=0}^M$. The ME method provides, among all of these densities, the one which maximizes the entropy functional

$$S[f] = -\int_0^\infty f(r) \ln f(r) dr . \tag{9}$$

In doing so, one has to solve the variational problem

$$\delta \left[-\int_0^\infty f(r) \ln f(r) dr + \sum_{j=0}^M \lambda_j \left(\mu_j - \int_0^\infty r^j f(r) dr \right) \right] = 0 \tag{10}$$

which solution, to be called ME density, is

$$f_M^{ME}(r) = \exp \left(-\sum_{j=0}^M (\lambda_j r^j + \delta_{j,0}) \right) , \tag{11}$$

where $\delta_{j,0}$ stands for the Kronecker delta. Here the Lagrange multipliers $\{\lambda_j\}_{j=0}^M$ have to be computed from the following non linear system of equations:

$$\int_0^\infty r^j f_M^{ME}(r) dr = \mu_j , \quad j = 0, 1, \ldots, M . \tag{12}$$

Existence conditions for the ME density have been studied in [13–15]. On the other hand, due to the tightness of the ME approximations, this method has been widely used in the literature in a great variety of fields (see e.g. [16–27]). It is worthy to remark that analytical ME solutions are only known for the case $M = 1$, namely

$$f_1^{ME}(r) = \frac{(\mu_0)^2}{\mu_1} \exp \left\{ -\frac{\mu_0}{\mu_1} r \right\} \tag{13}$$

where a simple change of variable can be made in order to replace μ_1 by a moment of arbitrary order μ_α ($\alpha > 0$).

B Linear combinations of Dirac deltas (CDD)

Given a density function $f(r)$ and a sequence $\{\mu_j\}_{j=0}^M$ of its moments, this method provides approximations constructed by considering certain linear combinations of Dirac deltas [28]. To obtain them explicitly, two different cases have to be considered:

- The number $M + 1$ of moments is even ($M + 1 = 2m$). Then, the approximation is given by

$$f_m^e(r) = \sum_{i=1}^m w_i \delta(r - r_i) \tag{14}$$

where the weigths w_i and the poles r_i are obtained by impossing that the first $M + 1$ moments of $f_m^e(r)$ and the ones of $f(r)$ coincide, i.e.

$$\sum_{i=1}^m w_i r_i^j = \mu_j \quad (j = 0, 1, \ldots, M) . \tag{15}$$

- The number $M + 1$ of moments is odd ($M + 1 = 2m + 1$). Now, the approximation is

$$f_m^o(r) = \sum_{i=0}^m w_i \delta(r - r_i) \tag{16}$$

where $r_0 = 0$ and the weigths w_i and the poles r_i ($i > 0$) are obtained by solving the system of equations

$$\sum_{i=0}^m w_i r_i^j = \mu_j \quad (j = 0, 1, \ldots, M) . \tag{17}$$

In spite of the strong non linearity of the systems (15) and (17), Wheeler and Gordon [29] have developed an efficient algorithm to compute the weights and positions of the CDD approximations.

These authors [29] have considered these functions $f_m^e(r)$ and $f_m^o(r)$ to approximate integral transforms of $f(r)$

$$R(k) = \int_0^\infty G(r,k)f(r)dr \qquad (18)$$

by performing the same integral transform on $f_m^e(r)$ and $f_m^o(r)$. They also studied convergence properties of the approximations when m increases, and showed that the kernel $G(r,k)$ of the transformation strongly determines the characteristics and properties of the resulting function $R(k)$. For instance, it is known that kernels $G(r,k)$ having derivatives with respect to r (for any fixed k) of constant sign provides rigorous bounds on $R(k)$.

In fact, the above mentioned convergence and bounding properties are closely related to those of the generalized Padé approximants (see e.g. [30]). On the other hand, the approximations (14) and (16) are connected with the so-called Stieltjes-Chebyshev methods [28] which allows to obtain bounds on other kind of integrals involving the density function $f(r)$ (e.g. the cumulative density [28, 31–33]).

C Two-point Padé approximants (TPP)

Padé approximants is one of the widely used mathematical tools in a great variety of fields, ranging from Physics and Chemistry to Mathematics and other subjects. Because of that, many convergence and bounding properties of them have been considered in detail [30].

Different generalizations of this technique have been carried out with the aim of improving its powerfulness. Among them, multipoint Padé [34] and Padé-type [35] approximants are specially remarkable. The first one considers information of the function at several points, while the second allows one to play with the position of the poles of the approximants. Recently both generalizations have been joint giving rise to an extension which algebraic and convergence properties are studied in [36, 37].

The idea of this last method consists of constructing a subdiagonal Padé approximant to a given function $f(x)$

$$P_{LM}(x) = \frac{p_{M-1}(x)}{q_M(x)} \qquad (19)$$

where $p_{M-1}(x)$ and $q_M(x)$ are polynomials of degree at most $M-1$ and M respectively, such that $P_{LM}(x)$ satisfies L constraints at $x=0$ and $2M-L$ at $x=\infty$. The coefficients of $p_{M-1}(x)$ and $q_M(x)$ are determined from the conditions

$$P_{LM}(x) - f(x) = O(x^L) \quad \text{for} \quad x \to 0 \qquad (20)$$

$$P_{LM}(x) - f(x) = O(x^{L-2M-1}) \quad \text{for} \quad x \to \infty \qquad (21)$$

in such a way that these unknown coefficients are obtained in terms of the power series of $f(x)$ around 0 and ∞. Detailed properties of these approximations (e.g. existence, uniqueness, convergence, error bounds...) can be found in [36–38].
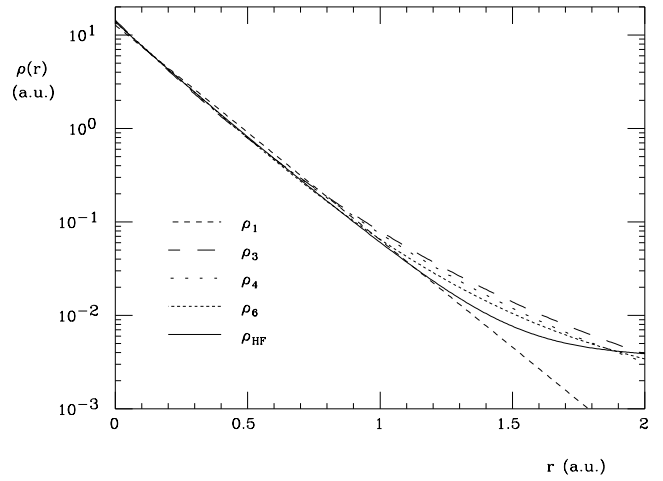

Fig. 1. Hartree-Fock charge density (ρ_{HF}). and ME approximations $\rho_1(r)$, $\rho_3(r)$, $\rho_4(r)$ and $\rho_6(r)$ for the Lithium atom ($Z = 3$). Atomic units (a.u.) are used

III Application to atomic form factors

In this section, the three methods of approximation previously described are jointly applied to study atomic form factors in terms of local and/or global quantities of the charge density, namely derivatives at the origin and radial expectation values, respectively.

To have an idea of the accuracy of the results given by those techniques, we construct the one-particle density $\rho(\mathbf{r})$ of Lithium (nuclear charge $Z = 3$), the corresponding form factor (i.e. the Fourier transform of the density) and the above mentioned derivatives and expectation values by using the Near-Hartree-Fock atomic wavefunctions of Clementi and Roetti [39]. Nevertheless, similar calculations can be performed not only for other atomic systems, but also for molecules and nuclei, due to the universality of the methods here involved.

Let us start by applying the ME method to the spherical average $\rho(r)$. Its moments μ_j are related to the radial expectation values $\langle r^{j-2} \rangle$ as given by (6). We have computed the ME density ρ_M compatible with the constraints $\{\mu_j\}_{j=0}^M$ for the Lithium atom.

In Fig. 1, the ME approximations ρ_1, ρ_3, ρ_4 and ρ_6 are compared with the Hartree-Fock density $\rho(r)$. In obtaining ρ_1, the analytical solution given by (13) has been considered. It is observed that (i) solutions depending on a very small number of moments are accurate for a wide range of electron-nucleus distances r, and (ii) increasing the number of moments one obtains a great improvement in the accuracy of the approximations. Specially remarkable is the well-behavior of the six-moment approximation ρ_6.

For the sake of completeness, we have computed the entropy and the central value of these ME approximations together with the corresponding Hartree-Fock ones. Their values are: $S_1 = -3.709$, $S_3 = -3.756$, $S_4 = -3.757$, $S_6 = -3.759$, $S_{HF} = -3.799$; $\rho_1(0) = 12.71$, $\rho_3(0) = 14.39$, $\rho_4(0) = 14.13$, $\rho_6(0) = 13.61$, $\rho_{HF}(0) = 13.83$.

We can obtain approximations to $F(k)$ by computing the Fourier transform of the aforementioned ME approximations to $\rho(r)$. Such transforms are compared in Fig. 2, where F_M
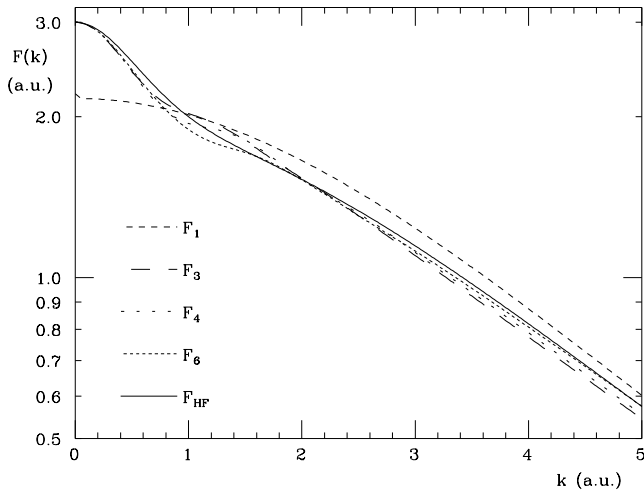
Fig. 2. Hartree-Fock form factor (F_{HF}). and ME approximations $F_1(k)$, $F_3(k)$, $F_4(k)$ and $F_6(k)$ for the Lithium atom ($Z = 3$). Atomic units (a.u.) are used

Fig. 3. Hartree-Fock form factor (F_{HF}). and even CDD approximations $d_6(k)$, $d_8(k)$, $d_{10}(k)$ and $d_{12}(k)$ for the Lithium atom ($Z = 3$). Atomic units (a.u.) are used

Fig. 4. Hartree-Fock form factor (F_{HF}). and odd CDD approximations $d_7(k)$, $d_9(k)$, $d_{11}(k)$ and $d_{13}(k)$ for the Lithium atom ($Z = 3$). Atomic units (a.u.) are used

denotes the Fourier transform of the ME density ρ_M. Let us notice that the function F_1 is not very accurate, specially for low values of k. This is, mainly, due to the fact that the information considered when constructing the approximate charge density $\rho_1^{ME}(r)$ does not include the number of particles $N = \langle r^0 \rangle$. However, the approximations F_3, F_4 and F_6 are much more accurate for the whole range of k here considered.

In using the second method (CDD) to study the atomic form factor $F(k)$, we first realize that this function is the integral transform of $\rho(r)$ through the kernel $G(r, k) = 4\pi r^2 j_0(kr)$ as pointed out in (4). In this case, the above mentioned monotonicity properties of the kernel do not hold, so the resulting transforms are not rigorous bounds but approximations on $F(k)$. Let us denote by d_{M+1} the approximation computed in terms of the sequence $\{\mu_j\}_{j=0}^M$. Then, it is easy to show that

$$d_{M+1}(k) = \sum_{i=1}^m w_i^e G(r_i^e, k) \tag{22}$$

if $M + 1 = 2m$ (i.e. $M + 1$ even), and

$$d_{M+1}(k) = \sum_{i=0}^m w_i^o G(r_i^o, k) \tag{23}$$

if $M + 1 = 2m + 1$ (i.e. $M + 1$ odd), taking into account (14)–(16).

In Fig. 3, a comparison between $F(k)$ for Lithium and the *even* approximations d_6, d_8, d_{10} and d_{12} is made. All the approximations oscillate around the Hartree-Fock $F(k)$, but the amplitude of such oscillations decreases when increasing the number of moments involved M. A similar conclusion can be extracted from Fig. 4, where the plotted approximations are the *odd* ones, i.e. d_7, d_9, d_{11} and d_{13}, for the same atomic system.

The two previous methods make use of the radial expectation values of the density as basic information for building up the approximations. In this sense, it is worthy to mention that direct and inverse Hankel transforms have been
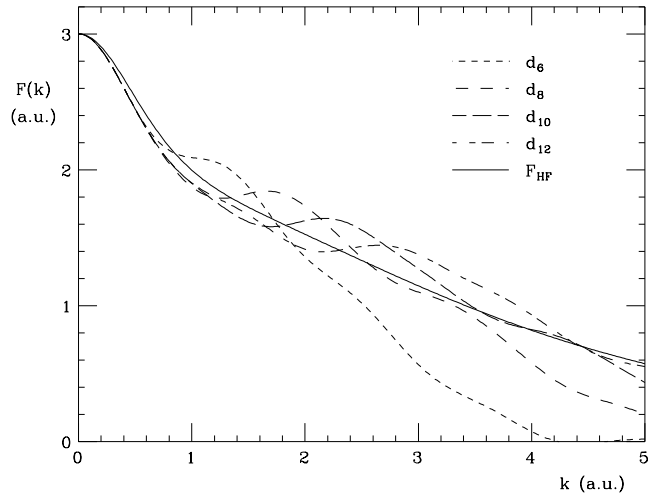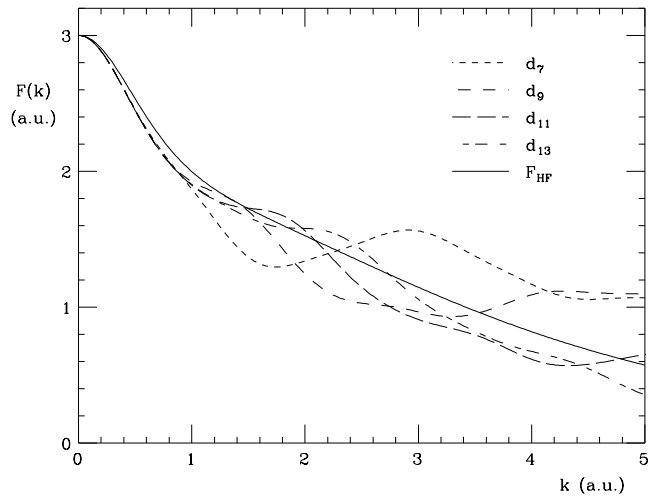
also used to find a solution for the reduced moment problem [40].

The third method (TPP) involves, as basic data, not only the aforementioned expectation values but also some of the first derivatives at the origin of the density. This is so because the coefficients of the small and large k-expansions of the form factor are expressed in terms of those quantites, as shown by (5) and (7).

We have considered here TPP approximants to $F(k)$ of the form $P_{MM}(k^2)$ (see (19)) which make use of the same number of constraints (i.e. M) at $k = 0$ and $k = \infty$, in such a way that the conditions to be fulfilled are

$$P_{MM}(k^2) - F(k) = O(k^{2M}) \quad (k \to 0) \tag{24}$$

$$P_{MM}(k^2) - F(k) = O(k^{-2(M+1)}) \quad (k \to \infty) \tag{25}$$

In Fig. 5, the approximations P_{22}, P_{33}, P_{44} and P_{55} to the form factor $F(k)$ for Lithium are compared with the Hartree-Fock one. It is apparent that the more information is used
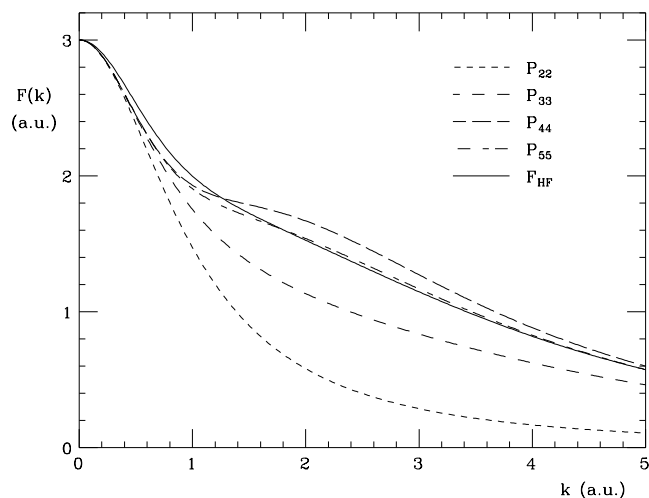
Fig. 5. Hartree-Fock form factor (F_{HF}). and TPP approximations $P_{22}(k^2)$, $P_{33}(k^2)$, $P_{44}(k^2)$ and $P_{55}(k^2)$ for the Lithium atom ($Z = 3$). Atomic units (a.u.) are used

the more tight the approximations are. In particular, P_{44} and specially P_{55} are very accurate.

As compared with the ME densities, the TPP ones use much more information for giving a similar accuracy.

Previous works with the Padé approximants applied to the study of form factors and other density functions are: [8], where the authors show the improvement of the Padé approximant [1/1] to $F(k)$ with respect to the truncated series of (5) and [41] where the studied functions are the Fourier transform of the one-particle density in momentum space and the atomic Compton profile.

IV Conclusions

In this work we have presented different approximations to an experimentally accesible quantity in momentum space, namely the form factor $F(k)$, in terms of a very limited number of magnitudes of ordinary space (local and radial expectation values of the charge density). The procedures here employed are model independent and give approximations to $F(k)$ for any value of k, allowing to compare the results with the predictions of any model or even with the experimental data. Other remarkable characteristic of these approximations, used for the first time in the atomic context, is the property of convergence when the amount of information considered increases.

Among the three methods, the ME one stands out from the rest because it produces very tight approximations in terms of a very scarce information. Conversely, the CDD needs a great amount of constraints to avoid the oscillating character of the produced density functions, and so is the worst one. In spite of this, it should be mentioned that it provides [28, 31–33] upper and lower bounds on other integral transforms of the density. The TPP method gives quantitatively good results for the whole range of k (specially for large k), contrary to the conventional Padé approximants used in previous works. The use of other generalizations of Padé approximants could be interesting whithin this type of problems although they would need more information.

Finally, it is clear that the methods here used are completely general and, then, they can be applied to other kind of systems, such as solids, molecules or nuclei, where similar relations between space and momentum magnitudes hold.

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