Minimum-cross-entropy estimation of atomic charge densities from scattering factors

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J Antolín†§, J C Cuchí‡ and J C Angulo†‖

† Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, 18071-Granada, Spain
‡ Departament d'Enginyeria Agroforestal, ETSEA, Universitat de Lleida, 25006-Lleida, Spain

Abstract. Tight model-independent approximations to the one-particle atomic density $\rho(r)$, derived from very few values of the form factor $F(k)$, are obtained by means of the minimum-cross-entropy technique. For completeness, the accuracy of the approximations is analysed within a Hartree–Fock framework.

1. Introduction

The one-particle density $\rho(r)$ of a many-fermion system is the fundamental variable in the description of its physical and chemical properties, as shown up by the density functional theory and its successive extensions (Parr and Yang 1989). However, a direct experimental measurement of such density is a very difficult task, even for many-electron systems such as atoms or molecules.

Usually, the determination of the density $\rho(r)$ comes through the inverse Fourier transform of the elastic scattering factor (or form factor) $F(k)$ (Coppens 1982) as

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

The atomic form factor, or its spherical average $F(k)$, can be experimentally obtained from x-ray elastic scattering or high-energy electron scattering (Nishikawa and Iijima 1987, Barbieri and Bonham 1991). However, these experimental data are only accessible for a finite and discrete set of values of the momentum transferred $k = |k|$, as well as up to a maximum value k_{max} which depends on the type of experiment involved. Consequently, non-trivial interpolation and extrapolation schemes, including the small and large k behaviour of $F(k)$, have to be devised (Goscinski and Linder 1970, Fink *et al* 1976).

The important role played by the elastic and inelastic components of the total scattering intensity in the analysis of chemical binding and correlation effects in those systems has enforced the separate measurements of its components (Duguet *et al* 1983, McClelland and Fink 1985) as well as the obtention of highly accurate computations of scattering factors (Wang *et al* 1993, 1995). In this sense, the authors have obtained tight approximations to $F(k)$ in

§ Permanent address: Departamento de Física Aplicada, EUITIZ, Universidad de Zaragoza, 50009-Zaragoza, Spain.
‖ Permanent address: Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, 18071-Granada, Spain.

atoms by means of few local values of the density $\rho(r)$ and/or some radial expectation values (Zarzo *et al* 1997)

$$\langle r^n \rangle \equiv \int r^n \rho(r) \, \mathrm{d}r = 4\pi \int_0^\infty r^{n+2} \rho(r) \, \mathrm{d}r \qquad (n > -3). \qquad (2)$$

Several other properties of form factors have been considered in the opposite problem, i.e. using information on $F(k)$ (i.e. in momentum space) to estimate the density $\rho(r)$ in position space. Frissberg and Massa used x-ray structure-form factor data to obtain an idempotent density matrix corresponding to a single-determinant wavefunction (Frisberg and Massa 1981). Moreover, the topological properties of $\nabla^2 F(k)$ are related to shell structure (Schmider *et al* 1991), and sum rules involving form factors, radial expectation values $\langle r^n \rangle$ and the derivatives of the charge density at the nucleus have also been derived (Thakkar 1985).

2. Minimum cross-entropy

In this paper we deal with the problem of obtaining a model-independent approximation to the charge density $\rho(r)$ in terms of a very limited set of values $\{F(k_i)\}$ ($i = 0, \ldots, n$) of the form factor $F(k)$. In doing so, we employ Kullback's principle of minimum cross-entropy (MCE) (Kullback 1959), related to the maximum-entropy (ME) principle (Jaynes 1978), that applies when, apart from the constraints, additional information on the density is known.

The MCE principle is based on the concept of *cross-entropy* or *relative entropy* $S[D, D_0]$ between two distributions $D(r)$ and $D_0(r)$ with the same normalization over X, defined by (Shore and Johnson 1980)

$$S[D, D_0] \equiv \int_X D(r) \ln \frac{D(r)}{D_0(r)} \, \mathrm{d}r. \qquad (3)$$

Among the properties of the functional $S[D, D_0]$ let us remark that it is always non-negative, convex and equals zero only when $D(r) = D_0(r)$. For a given *prior* density $D_0(r)$, the distribution $D(r)$ that satisfies some given constraints and minimizes the relative entropy is the closest one to $D_0(r)$ among all those that fulfil the constraints. When the prior distribution is a uniform one, the minimization of the cross-entropy is equivalent to the maximization of the Shannon entropy functional

$$S_D \equiv - \int_X D(r) \ln D(r) \, \mathrm{d}r \qquad (4)$$

which provides the least-biased charge density compatible with the given constraints, as predicted by the Jaynes entropy concentration theorem (Jaynes 1978). Different rigorous results concerning convergence of the approximations to the exact density when increasing the number of considered constraints are known (Borwein and Lewis 1993), not only for the relative entropy $S[D, D_0]$ but also for other entropy functionals. In this sense, weak-star convergence (or entropy convergence) holds almost unconditionally (Mead and Papanicolau 1984), and weak convergence is guaranteed if the level sets of the objective function are weakly compact (Borwein and Lewis 1991a). In order to obtain norm convergence, additional assumptions are required, such as strict convexity (Borwein and Lewis 1991b), and uniform convergence theorems concerning the entropy functional considered in the present work were also proved (Borwein and Lewis 1991b). Different properties (Buck and Macaulay 1991, Kapur and Kesavan 1992, Ihara 1993) and applications (Skilling and Bryan 1984, Nakahigasi *et al* 1993, Antolín *et al* 1994, Tanata *et al* 1994, Zarzo *et al* 1996) of these methods can be found elsewhere.

For the case of atomic systems, it is sufficient to deal with the spherically averaged density $\rho(r)$ or, equivalently, with the radial charge density $D(r) \equiv 4\pi r^2 \rho(r)$, related to the form factor $F(k)$ by means of a Hankel (or Fourier–Bessel) transform as

$$F(k) = \int_0^\infty D(r) j_0(kr) \, dr \tag{5}$$

where $j_0(kr) = \sin(kr)/(kr)$ is the spherical Bessel function of order zero.

Let us calculate the radial charge density $D_n(r)$ that, constrained by the knowledge of the form factor at $n + 1$ values of the momentum transferred, namely

$$\mu_i \equiv F(k_i) = \int_0^\infty D(r) j_0(k_i r) \, dr \qquad i = 0, 1, \ldots, n, \tag{6}$$

minimizes the *relative entropy* functional

$$S[D, D_0] \equiv \int_0^\infty D(r) \ln \left[\frac{D(r)}{D_0(r)} \right] dr \tag{7}$$

where $D_0(r) = 4\pi r^2 \rho_0(r)$ is an *a priori* radial distribution, with the same normalization as $D(r)$, which indicates the previous degree of knowledge on the density we are estimating, and where the normalization of the density to the total number of electrons N of the system is taken into account by choosing $k_0 = 0$, so that

$$\mu_0 = F(0) = \int_0^\infty D(r) \, dr = N. \tag{8}$$

The null functional variation of $S[D, D_0]$ constrained by equation (6) leads to the MCE solution

$$D_n(r) = D_0(r) \exp \left(-1 - \sum_{i=0}^n \lambda_i j_0(k_i r) \right) \tag{9}$$

where the multiplier λ_0 can be expressed in terms of the normalization given by equation (8) as

$$e^{-1-\lambda_0} = \frac{F(0)}{Z} = \frac{N}{Z} \tag{10}$$

where Z is the partition function

$$Z = \int_0^\infty D_0(r) \exp \left(-\sum_{i=1}^n \lambda_i j_0(k_i r) \right) dr. \tag{11}$$

Then, the MCE solution is given by

$$D_n(r) = D_0(r) \frac{N}{Z} \exp \left(-\sum_{i=1}^n \lambda_i j_0(k_i r) \right) \tag{12}$$

containing n Lagrange multipliers $\lambda_1, \lambda_2, \ldots, \lambda_n$ which values must be numerically determined from the nonlinear set of equations

$$\int_0^\infty D_n(r) j_0(k_i r) \, dr = F(k_i) \qquad i = 1, \ldots, n \tag{13}$$

The necessary and sufficient existence conditions that the set of constraints must fulfil in order to have an MCE solution are not known. However, the numerical results of the present work show that such a minimum is always reached, independently of the number of constraints as well as of the *a priori* density used.

In this paper, four different *a priori* functions $D_0^{(i)}(r)$ ($i = 1, 2, 3, 4$) are considered in order to estimate $\rho(r)$ from $F(k)$. These choices are based on justified properties of the one-particle density $\rho(r)$. For every $\rho_0^{(i)}(r)$, one constructs the function $4\pi r^2 \rho_0^{(i)}(r)$ and normalizes it to the number of particles N (i.e. the same normalization as $D(r)$), giving rise to $D_0^{(i)}(r)$.

First, the distribution

$$\rho_0^{(1)}(r) = \rho(0)e^{-2Nr} \tag{14}$$

is a known rigorous lower bound for the one-particle density for any value of the position r (Hoffmann-Ostenhof *et al* 1978).

Second, the function

$$\rho_0^{(2)}(r) = \frac{N\langle r^{-2}\rangle}{2\pi}e^{-\sqrt{8\varepsilon}r} \tag{15}$$

behaves asymptotically as the exact density (through the ionization potential ϵ) and takes at $r = 0$ the value of a well known (Thirring *et al* 1981) lower bound on $\rho(0)$.

Third, an upper bound on $\rho(r)$ which also depends on the ionization potential ϵ (Thirring *et al* 1981) suggests the use of the density

$$\rho_0^{(3)}(r) = \frac{N\langle r^{-2}\rangle}{2\pi}(1+r)^\beta e^{-\sqrt{8\varepsilon}r} \qquad \beta = \frac{1}{\sqrt{2\varepsilon}} - 1. \tag{16}$$

Four, the analytical ME approximation to the density $\rho(r)$ constrained by the radial expectation values $\langle r^{-2}\rangle$ and $\langle r^{-1}\rangle$ (closely related to relevant quantities) is given by (Zarzo *et al* 1996)

$$\rho_0^{(4)}(r) = \frac{\langle r^{-2}\rangle^2}{\langle r^{-1}\rangle}\exp\left(-\frac{\langle r^{-2}\rangle}{\langle r^{-1}\rangle}r\right). \tag{17}$$

3. Numerical results

To study the accuracy of this estimation method, we compare the approximations, obtained from the above set of *a priori* densities, to HF one-particle densities calculated with the Clementi and Roetti wavefunctions (Clementi and Roetti 1974). In computing the approximations, tabulated values of the form factors from correlated wavefunctions (Wang *et al* 1993, 1995) and from NHF wavefunctions (Clementi and Roetti 1974) have been used.

In figure 1, the power of the method is shown in a simple case, which is the estimation of the charge density of the helium atom ($N = 2$). The *a priori* function $\rho_0^{(1)}(r)$ is quite far from the HF density we are trying to estimate. However, the inclusion of just a pair of values of the form factor (Wang *et al* 1995) corresponding to $k = 1$ and 2 au leads to a significant improvement of the accuracy for low and medium r, such improvement being much smaller for higher r due to the asymptotic behaviour of the *a priori* function.

To avoid the previous effect we use the *a priori* function $\rho_0^{(2)}(r)$ which, being also far from the exact HF density, behaves asymptotically as the exact density. Imposing the same pair of constraints, the result is a much more accurate approximation to the density.

Additional constraints on the values of the form factor $F(k)$ consequently improve the approximations. In order to illustrate the effect of the inclusion of such constraints, we have restricted ourselves to a small number of them. In figure 2, different approximations for the charge density of the helium atom are shown, corresponding to the four different *a priori* functions, by using a fixed set of five constraints on the form factor (Wang *et al* 1995), namely $k = 1, 2, 3, 4$ and 5.3 au. It is observed that the inclusion of the asymptotic behaviour of the density plays a relevant role in the goodness of the approximations: $\rho_0^{(2)}(r)$ and $\rho_0^{(3)}(r)$ are
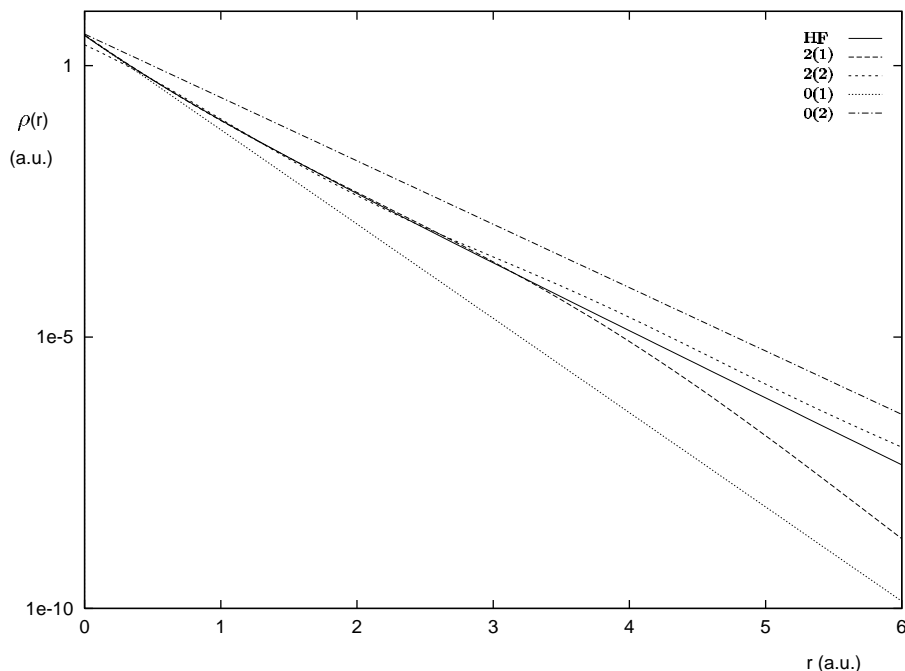
Figure 1. HF density $\rho(r)$ and MCE approximations $\rho_2^{(1)}$ and $\rho_2^{(2)}$ to $\rho(r)$ for helium ($N = 2$), in terms of two values of the form factor $F(k)$ and using as *a priori* densities $\rho_0^{(1)}(r)$ and $\rho_0^{(2)}(r)$, respectively. Atomic units are used.

Table 1. Radial expectation values $\langle r^k \rangle$ ($k = -1, \ldots, 3$) of the ME approximations $D_5^{(i)}(r)$ ($i = 1, 2, 3, 4$) constrained by five values of the form factor $F(k)$ and using as *a priori* density $D_0^{(i)}$, respectively, compared with the Hartree–Fock (HF) ones for the helium atom ($N = 2$). Atomic units are used.

k	$i = 1$	$i = 2$	$i = 3$	$i = 4$	HF
-1	3.3724	3.3446	3.3552	3.3627	3.3747
0	2.0000	2.0000	2.0000	2.0000	2.0000
1	1.8581	1.8594	1.8591	1.8585	1.8545
2	2.3818	2.3878	2.3872	2.3833	2.3693
3	3.9010	3.9390	3.9356	3.9097	3.8796

clearly more accurate than $\rho_0^{(1)}(r)$ and $\rho_0^{(4)}(r)$. This is the reason why we will use $\rho_0^{(2)}(r)$ as an *a priori* function for cobalt (table 2 and figure 3).

In tables 1 and 2, it is also shown how the above approximations allow us to accurately estimate the values of relevant quantities, such as the radial expectation values $\langle r^m \rangle$. In table 1 is observed, for the helium atom ($N = 2$), the weak dependence of the predicted values on the *a priori* radial density for a fixed number of constraints, because the high value of the ionization potential for that system makes its density decrease very quickly and, consequently, the main contribution to the expectation values comes from the low-r region, being less conditioned by the asymptotic behaviour.

From table 2, corresponding to cobalt ($N = 27$), one can see the relevant role played by the number of constraints n involved in computing the ME approximation. Let us consider the constraints given by the form factor $F(k)$ at $k = 1, 2, \ldots, n$ au. The predicted values of
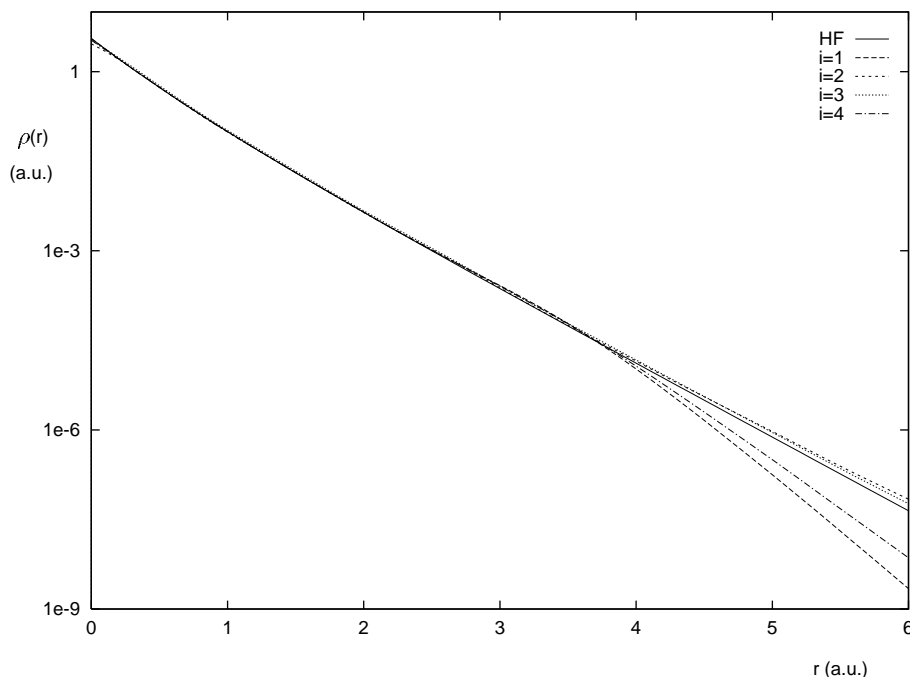
Figure 2. HF density $\rho(r)$ and MCE approximations $\rho_5^{(i)}$ ($i = 1, 2, 3, 4$) to $\rho(r)$ for helium ($N = 2$), in terms of five values ($k = 1, 2, 3, 4, 5.3$) of the form factor $F(k)$ and using as *a priori* densities $\rho_0^{(i)}(r)$ ($i = 1, 2, 3, 4$), respectively. Atomic units are used.

Table 2. Radial expectation values $\langle r^k \rangle$ ($k = -1, \ldots, 3$) of the ME approximations $D_n^{(2)}(r)$ ($n = 5, 10, 15, 20, 25$) constrained by n values of the form factor $F(k)$ and using as *a priori* density $D_0^{(2)}$, compared with the Hartree–Fock (HF) ones for the cobalt atom ($N = 27$). Atomic units are used.

k	$n = 5$	$n = 10$	$n = 15$	$n = 20$	$n = 25$	HF
-1	70.578	91.031	96.569	100.481	105.157	122.047
0	27.000	27.000	27.000	27.000	27.000	27.000
1	22.013	21.710	21.681	21.669	21.660	21.910
2	36.709	36.817	36.836	36.833	36.833	39.409
3	101.076	101.926	102.068	102.046	102.047	121.497

$\langle r^m \rangle$ converge to the exact ones when increasing n. However, such a convergence is more apparent for radial expectation values of low order. The reason is that, for low m, the quantity $\langle r^m \rangle$ strongly depends on the density $\rho(r)$ around $r = 0$, which is connected via the Fourier transform (1) with the form factor $F(k)$ at high values of the momentum transferred k. In order to better estimate quantities like $\langle r^2 \rangle$ or $\langle r^3 \rangle$, one should considered constraints $F(k_i)$ corresponding to lower values of k_i.

In figure 3, the successive approximations to the radial charge density $D(r)$ of cobalt ($N = 27$) when the number of constraints is increased are shown. We have chosen equidistant values of k, in such a way that the approximation $\rho_n^{(2)}(r)$ is constrained by the n form factors (Clementi and Roetti 1974) corresponding to $1, 2, \ldots, n$ au.

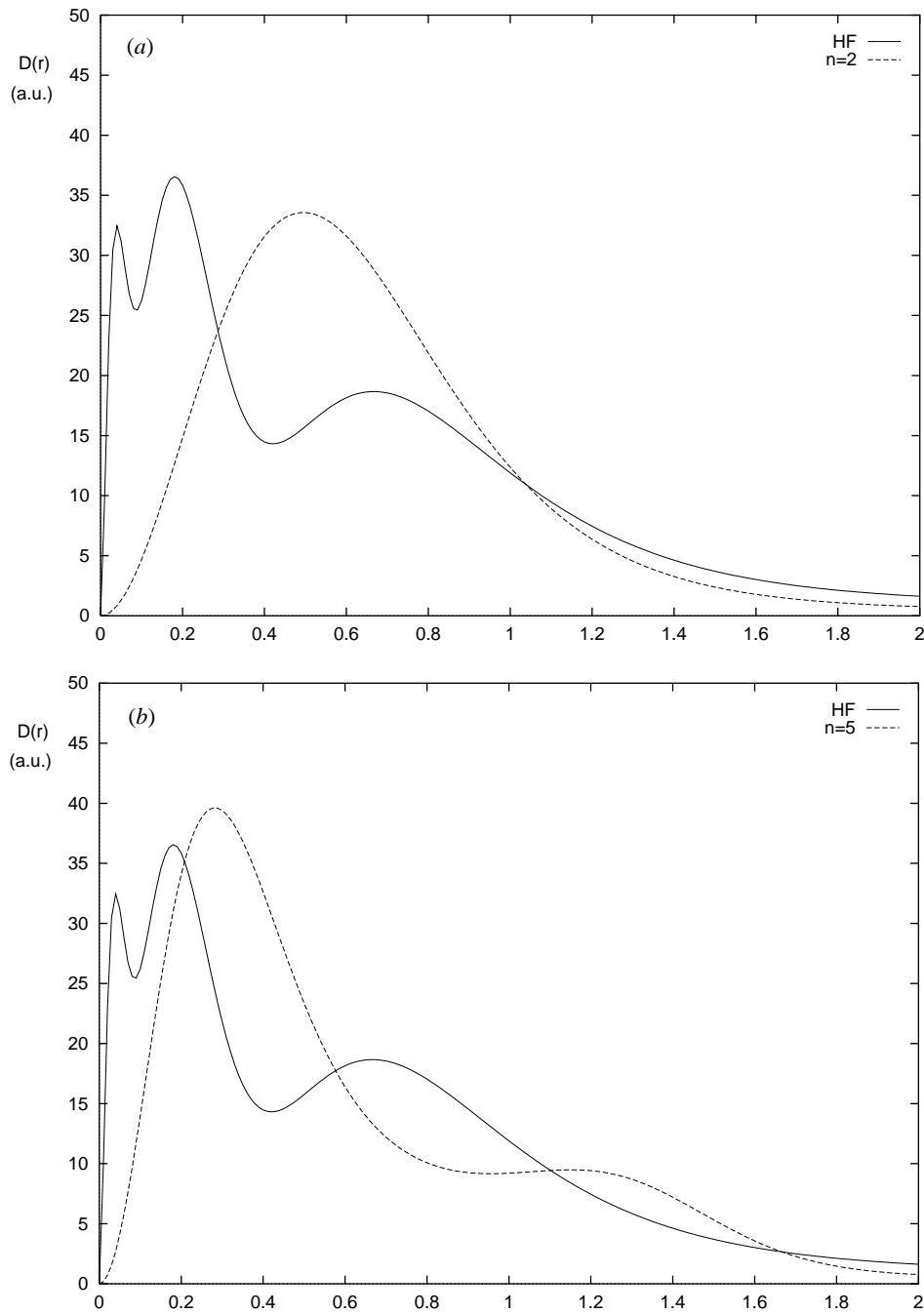In spite of the initial distance between the *a priori* function and the exact one, a significant

Figure 3. HF radial density $D(r)$ and MCE approximations $D_n^{(2)}$ ($n = 2, 5, 10, 15$) to $D(r)$ for cobalt ($N = 27$), in terms of n values of the form factor $F(k)$ and using as *a priori* density $\rho_0^{(2)}(r)$. Atomic units are used.

improvement in the approximations is observed when increasing the number of constraints. This fact is especially relevant to the study of the atomic shell structure. The approximation
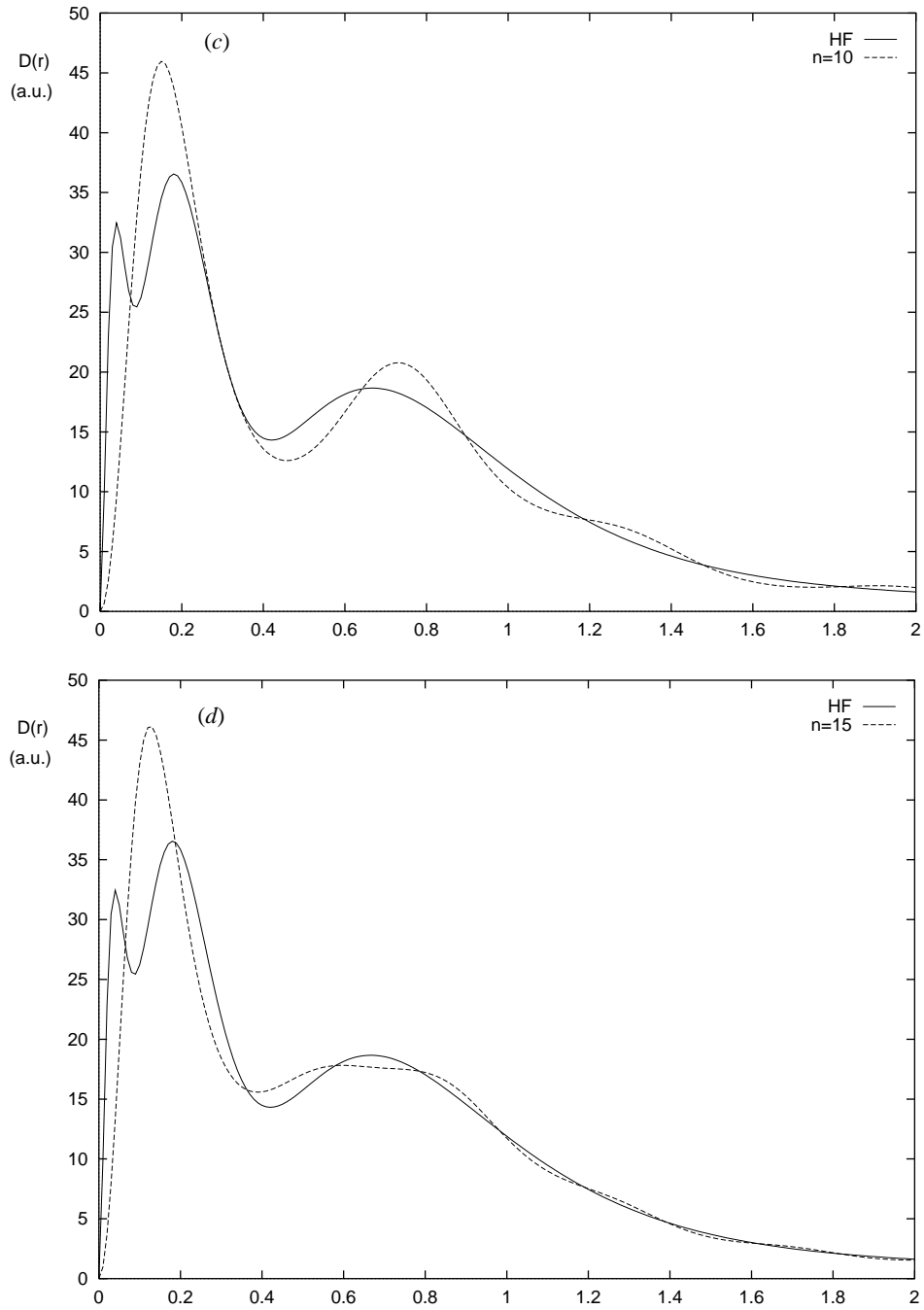
Figure 3. (Continued)

calculated from only two constraints displays a single *peak* at a medium position among the ones displayed by the exact density. When increasing the number of constraints ($n = 5, 10, 15$), such a peak progressively approaches an intermediate position between the first and the second

maxima. Additionally, for $n \geqslant 5$ a new maximum appears, which becomes closer to the third peak of the exact $D(r)$ with increasing n.

The accuracy of the approximations can be evaluated by comparing the values of their relative entropies with respect to $D_0^{(2)}(r)$ in the cobalt atom: $S(n = 2) = 27.930$, $S(n = 5) = 32.548$, $S(n = 10) = 36.471$, $S(n = 15) = 36.793$, $S(n = 20) = 36.979$, $S(n = 25) = 37.257$. The relative entropy of the HF density and $D_0^{(2)}(r)$ for this atom is $S_{HF} = 37.819$. It is observed that (i) the entropies $S(n)$ increase with increasing n, but (ii) the difference between $S(n)$ and S_{HF} decreases with increasing n. This is because the corresponding approximations become closer to the *exact* one, while the distance to the *a priori* distribution (not very close to the HF one) increases.

Results for other atoms are similar to those shown in this paper. We have also studied the dependence of the results with different choices of the values of the momentum transferred k, showing (as previously observed in the cobalt atom) that high values of k lead to tight approximations for r low and vice versa.

In summary, we have shown how the MCE technique, together with a small number of values of the form factor, are enough to tightly approximate the electronic densities in atomic systems. The universality of the method allows one also to deal with densities of different multifermionic systems, such as nuclei or molecules, when discrete values of the corresponding form factors are known.

Acknowledgments

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