Minimum-cross-entropy estimation of electron-pair densities from scattering intensities

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Abstract

Tight approximations to the electron-pair density $h(\mathbf{u})$ of atomic systems are obtained in terms of a very limited set of values of the total scattering intensity $K(\mathbf{k})$, by means of the minimum-cross-entropy technique. The accuracy of the approximations is analyzed for two- and four-electron systems. © 1999 Published by Elsevier Science B.V. All rights reserved.

The intracule or electron-pair density $h(\mathbf{u})$ in many-electron systems is the probability density associated to the interelectronic vector $\mathbf{u} \equiv \mathbf{r}_1 - \mathbf{r}_2$, i.e. $h(\mathbf{u})d\mathbf{u}$ gives the probability of finding a pair of electrons with $\mathbf{r}_1 - \mathbf{r}_2$ between $\mathbf{u}$ and $\mathbf{u} + d\mathbf{u}$. Such a density is a basic quantity in the $e^- - e^-$ correlation problem [1], as well as in the description of different energy functionals in a density-functional-theory framework [2]. The obtention of experimental data concerning $h(\mathbf{u})$ is based on the determination of X-ray [3] and high energy electron [4] scattering cross-sections.

For most purposes, it is sufficient to deal with the spherically averaged electron-pair density

$$H(u) \equiv \frac{1}{4\pi} \int h(\mathbf{u}) \, d\Omega_{\mathrm{u}} \qquad (1)$$

The major problem in the study of physical and chemical properties of many-electron systems (e.g., atoms, molecules) in terms of the electron-pair density is that not many rigorous properties of $h(u)$ are known, even for very simple systems such as two-electron ions. Moreover, numerical treatments based on realistic models are very scarce and difficult, especially when going beyond two-electron systems, for which it is usually necessary to work at a Hartree–Fock level.

Among the known rigorous properties of $h(u)$, it is worthy to remark the so-called *cusp condition* [5],

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i.e. $h'(0) = h(0)$. Numerical studies concerning the relation between $h(u)$ and its first derivative for arbitrary interelectronic distance u have also been carried out for two-electron ions, giving rise to the *extended cusp condition* [6], $h'(u) \leq h(u)$. Additional structural aspects are unimodality [6] and bounds to local values of $h(u)$ [7].

Other relevant physical and chemical properties of atomic and molecular systems are described in terms of the moments μ_n of $h(u)$, proportional to the radial expectation values $\langle u^{n-2} \rangle$ as

$$\langle u^{n-2} \rangle = 4\pi\mu_n = 4\pi \int_0^\infty u^n h(u)\, du \qquad (2)$$

It is worthy to mention that $\langle u^{-1} \rangle$ is the electron–electron repulsion energy, for which additional properties have been also reported [8]. The normalization to the number of pairs $\langle u^0 \rangle = N(N-1)/2$ will be considered throughout.

The obtention of accurate experimental data on the total scattering intensity I_{tot}, related to $h(u)$ by the Fourier transform

$$K(k) = 4\pi \int_0^\infty u^2 h(u) j_0(ku)\, du \qquad (3)$$

(with $K(k) = (I_{\text{tot}} - N)/2$ and $j_0(x)$ being the spherical Bessel function of order zero) has induced quantum-mechanical calculations of $K(k)$ of similar accuracy [9,10]. However, the determination of the electron-pair density $h(u)$ from the inverse relation

$$h(u) = \frac{1}{2\pi^3 u^2} \int_0^\infty ku \sin(ku) K(k)\, dk \qquad (4)$$

involves difficult interpolation and extrapolation techniques. For instance, an accurate determination of $h(u)$ around the origin requires the knowledge of $K(k)$ very accurately for high values of the momentum transferred k which are not easily accessible from scattering experiments. On the other hand, the behavior of $K(k)$ for low k is related to the radial expectation values $\langle u^n \rangle$ of $h(u)$ as [11]

$$K(k) = \frac{N(N-1)}{2}$$
$$+ \sum_{n=1}^\infty (-1)^n \frac{\langle u^{2n} \rangle}{(2n+1)!} k^{2n} (k \to 0) \qquad (5)$$

All of these properties involving quantities of the position and momentum spaces have been used to obtain sum rules for total scattering intensities [11] as well as accurate approximations to those intensities in terms of global and/or local properties of $h(u)$ [12].

The aim of this work is the opposite to that of Ref. [12], i.e. the model-independent estimation of the pair density $h(u)$ from a limited set of values $\{K(k_j, j = 0, 1, \ldots, m\}$ of the scattering function $K(k)$ (where the normalization constraint is included by choosing $k_0 = 0$) and, optionally, from the first few moments μ_j ($j = 0, 1, \ldots, n$) of $h(u)$. In doing so, we first consider an a priori density $h_0(u)$ (which takes into account known properties of the electron-pair density) and, then, we observe that the quantities $K(k_j)$ can be seen as *generalized moments* of the electron-pair density $h(u)$, namely

$$\nu_0 \equiv K(0) = \langle u^0 \rangle = \frac{N(N-1)}{2}$$

$$\nu_j \equiv K(k_j) = 4\pi \int_0^\infty u^2 h(u) j_0(k_j u)\, du$$
$$\times (j = 1, 2, \ldots, m) \qquad (6)$$

The above problem provides (for a finite number of constraints) many different solutions. Now, in order to *choose* one of them we use the minimum-cross-entropy [13–15] technique involving the constraints given by the above equation. Following the steps given in Ref. [12], let us first calculate the radial pair density $H_m(u) \equiv 4\pi u^2 h_m(u)$, constrained by the above $m+1$ values of $K(k)$, which minimizes the cross-entropy functional

$$S[H, H_0] \equiv \int_0^\infty H(u) \ln \frac{H(u)}{H_0(u)}\, du \qquad (7)$$

where $H_0(u) \equiv 4\pi u^2 h_0(u)$ is an a priori radial pair density, also normalized to the number of pairs $N(N-1)/2$, and which denotes the previous degree of knowledge on the function we are trying to estimate. The null variation of $S[H, H_0]$ constrained by Eq. (6) provides the minimum-cross-entropy solution

$$h_m(u) = h_0(u) \exp\left\{ -1 - \sum_{j=0}^m \lambda_j j_0(k_j u) \right\} \qquad (8)$$

where $\lambda_0, \ldots, \lambda_m$ are Lagrange multipliers to be determined from the given constraints. The necessary

and sufficient conditions on the existence of such a solution are not known. However, the numerical results provided in this work suggest that the minimum is always reached, independently of the involved a priori density and constraints.

In the present work, we will consider three different kinds of problems, associated to different choices of a priori densities and constraints: maximum-entropy a priori functions, overlap a priori functions and mixed constraints.

(A) Maximum-entropy a priori functions. Here we employ the maximum-entropy approximations constrained by $\langle u^{-2} \rangle$ and/or $\langle u^{-1} \rangle$ given in Ref. [16]. More precisely, let us consider the approximations

$$h_{02}(u) = \left(\frac{\langle u^{-2} \rangle^3}{4N(N-1)\pi^3} \right)^{1/2}$$
$$\times \exp\left\{ -\frac{\langle u^{-2} \rangle}{N(N-1)} u^2 \right\} \qquad (9)$$

and

$$h_{012}(u) = A \exp\{ -au - bu^2 \} \qquad (10)$$

where the parameters A, a and b are numerically determined from the set of constraints (N, $\langle u^{-2} \rangle$, $\langle u^{-1} \rangle$). The involved expectation values can be

estimated from the sum rules concerning the scattering intensity I_{tot} [11] as

$$\langle u^{-2} \rangle = \int_0^\infty kK(k)\,dk, \quad \langle u^{-1} \rangle = \frac{2}{\pi} \int_0^\infty K(k)\,dk \qquad (11)$$

In order to have an idea of the accuracy of the approximations on the electron-pair density $h(u)$ given by Eq. (8), let us consider two different systems, namely He ($N = 2$) and Be ($N = 4$) atoms. For the first one, the Hylleraas-type atomic wavefunctions of Ref. [17] have been used to calculate the involved quantities, while those corresponding to Be are given at a Hartree–Fock level [18].

Fig. 1 corresponds to He, for which we take the a priori density $h_{012}(u)$ of Eq. (10). The accuracy of the approximations obtained by considering different numbers of constraints (i.e., $m = 2, 5, 10$) is observed All of them are well-behaved close to the origin, and a significant improvement is observed for large interelectronic distance u when increasing the number of constraints. The level of accuracy can be measured by comparing the cross-entropy $S_m \equiv S[H_m, H_0]$ between the approximation $H_m(u)$ and the a priori radial pair density $H_0(u) = 4\pi u^2 h_{012}(u)$ to the Hylleraas pair density $H(u)$ and $H_0(u)$. For increas-
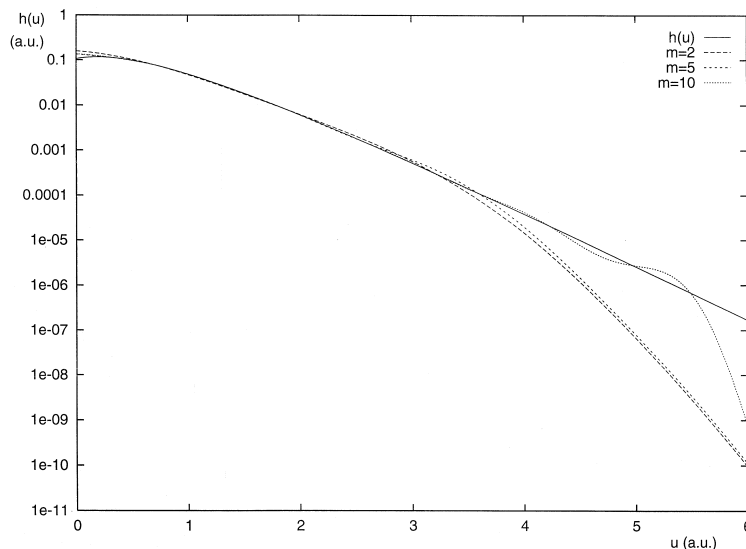

Fig. 1. Hylleraas-type electron-pair density $h(u)$ and approximations $h_m(u)$ ($m = 2, 5, 10$) with maximum-entropy a priori density function $h_{012}(u)$ for the helium atom. Atomic units (a.u.) are used.
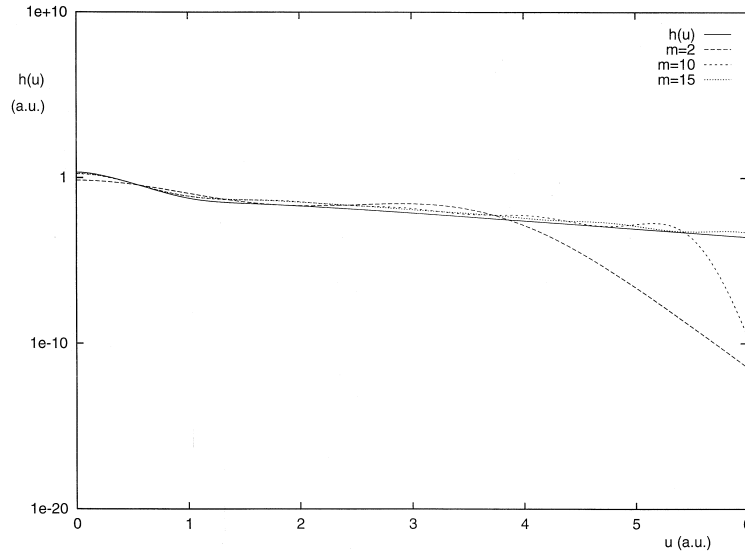
Fig. 2. Hartree-Fock electron-pair density $h(u)$ and approximations $h_m(u)$ ($m = 2, 10, 15$) with maximum-entropy a priori density function $h_{02}(u)$ for the beryllium atom. Atomic units (a.u.) are used.

ing number of constraints m, the cross-entropy S_m converges to $S[H, H_0] = 0.0229$ as $S_2 = 0.0164$, $S_5 = 0.0185$ and $S_{10} = 0.0224$.

A similar comparison is carried out in Fig. 2 for the Be atom, taking as a priori density $h_{02}(u)$ as given by Eq. (9), using a set of $m = 2, 5, 10, 15$ constraints, respectively. The more significant improvement again occurs for large values of the inter-electronic distance u. Moreover, the corresponding cross-entropies for the different approximations are $S_2 = 14.09$, $S_5 = 14.24$, $S_{10} = 18.70$ and $S_{15} = 22.34$, to be compared to $S[H, H_0] = 22.38$, $H(u)$ being the Hartree–Fock radial pair density of Be.

(B) Overlap a priori functions. The knowledge of $\langle u^2 \rangle$ allows to obtain an approximation to $K(k)$ by imposing that the expansion of the parametrization given in Ref. [19]

$$K_{ov}(k) = \left(a_0 + a_1 k + a_2 k^2 \right) e^{-\xi k} \qquad (12)$$

be the same as the one given by Eq. (5) up to order k^3. Then, the above parameters are expressed in terms of $\langle u^2 \rangle$ as follows:

$$a_0 = \frac{N(N-1)}{2}, \; a_1 = \left[\frac{N(N-1)}{2} \langle u^2 \rangle \right]^{1/2},$$

$$a_2 = \frac{\langle u^2 \rangle}{3}, \xi = \left[\frac{2 \langle u^2 \rangle}{N(N-1)} \right]^{1/2} \qquad (13)$$

Estimations on $\langle u^2 \rangle$ can be obtained from values of the scattering function $K(k)$ for low k by means of the expansion (5). Then, the inverse Fourier transform

$$h_{ov}(u) = \frac{1}{2\pi^2} \int_0^\infty k^2 j_0(ku) K_{ov}(k) \, dk \qquad (14)$$

provides the a priori electron-pair density involved in the cross-entropy functional, i.e. $H_0(u) = 4\pi u^2 h_{ov}(u)$.

Let us consider again the Be atom. A similar comparison to the one carried out in Fig. 2 for the case of maximum-entropy a priori density $h_{02}(u)$ is given in Fig. 3, now in terms of $h_{ov}(u)$. It is apparent that increasing the number of constraints from 5 to 10 provides a much more accurate approximation.

(C) Mixed constraints. An approximation to $h(u)$ involving simultaneously the first few radial expectation values $\langle u^{i-2} \rangle$ and some values of $K(k)$ can be also obtained. In doing so, two different kinds of Lagrange multipliers γ_i and λ_j are used, corresponding to the constraints $\langle u^{i-2} \rangle$ and $K(k_j)$ respectively, giving rise to the solutions

$$h_{n,m}(u) = A \exp\left\{ - \sum_{i=1}^n \gamma_i u^i \right\} \exp\left\{ - \sum_{j=1}^m \lambda_j j_0(k_j u) \right\} \qquad (15)$$
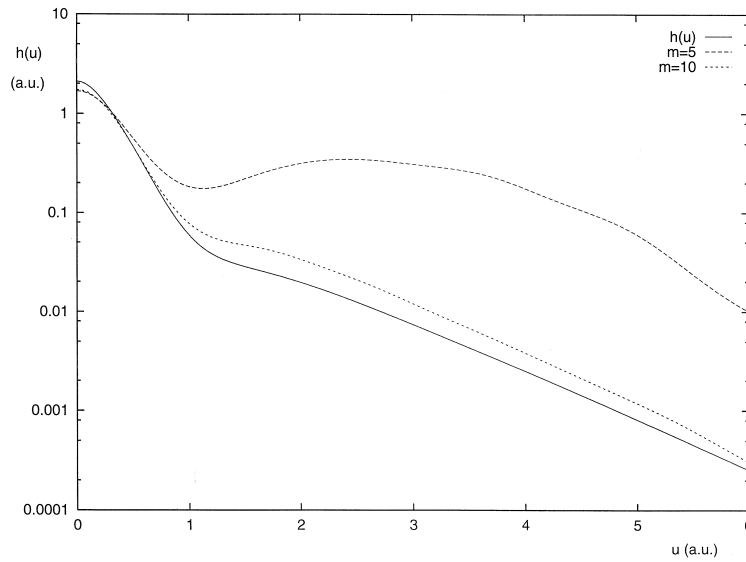
Fig. 3. Hartree–Fock electron-pair density $h(u)$ and approximations based on overlap a priori density function $h_{ov}(u)$ with m constraints ($m = 5, 10$) for the beryllium atom. Atomic units (a.u.) are used.

For a fixed number of $m = 5$ constraints in the He atom, we compare in Fig. 4 the accuracy of the different approximations obtained by using the three methods considered in this work of constructing an a priori density, i.e. maximum-entropy, overlap and mixed-constraints. More precisely, the densities $h_{012}(u)$, $h_{ov}(u)$ and $h_{5,5}(u)$ given by Eqs. (10), (14) and (15), respectively, are considered. It is observed that the three methods provide very accurate approximations, except for very small u, where the use of
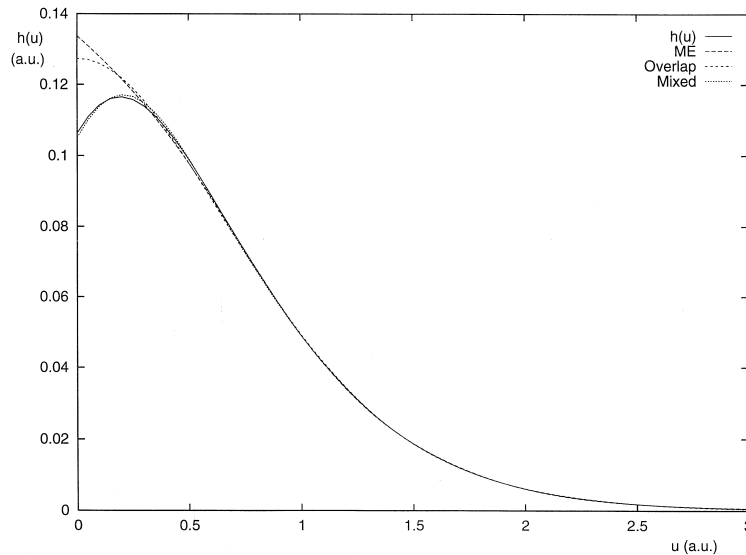

Fig. 4. Hylleraas-type electron-pair density $h(u)$ and comparison among the approximations based on maximum-entropy, overlap and mixed-constraints a priori density functions for the helium atom. Atomic units (a.u.) are used.

mixed constraints gives a pair density much closer to the *exact* one than the other two.

The technique employed here, being model-independent and completely general, can also be applied to estimate different density functions, physically relevant for atomic systems, in terms of a discrete set of values of their Fourier transform (e.g., the characteristic function $B(r)$ [20] in terms of the momentum density $\gamma(p)$), as well as to the study of different many-particle systems, not only atoms but also molecules, nuclei, etc.

References

[1] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

[2] E.S. Kryachko, E.V. Ludeña, Energy Functional Density Theory of Many-Electron Systems, Kluwer, Dordrecht, 1990.

[3] K. Nishikawa, T. Iijima, J. Chem. Phys. 87 (1987) 3753.

[4] R.S. Barbieri, R.A. Bonham, Phys. Rev. A 44 (1991) 7361.

[5] A.J. Thakkar, V.H. Smith Jr., Chem. Phys Lett. 42 (1976) 476.

[6] J.S. Dehesa, J.C. Angulo, T. Koga, K. Matsui, Z. Phys. D 25 (1992) 9.

[7] J.S. Dehesa, J.C. Angulo, T. Koga, K. Matsui, Phys. Rev. A 47 (1993) 5202.

[8] J.M. Ugalde, C. Sarasola, Phys. Rev. A 49 (1994) 3081.

[9] J. Wang, R.O. Esquivel, V.H. Smith Jr., C.S. Bunge, Phys. Rev. A 51 (1995) 3812.

[10] J. Wang, A.N. Tripathi, V.H. Smith Jr., J. Chem. Phys. 101 (1994) 4842.

[11] A.J. Thakkar, T. Koga, J. Chem. Phys. 83 (1985) 747.

[12] J.C. Cuchí, J. Antolín, A. Zarzo, J.C. Angulo, Phys. Lett. A 230 (1997) 321.

[13] E.T. Jaynes, in: R.D. Levine, M. Tribus (Eds.), The Maximum Entropy Formalism, MIT Press, Boston, 1978, pp. 15–118.

[14] S. Ihara, Information Theory for Continuous Systems, World Scientific, Singapore, 1993.

[15] J.N. Kapur, H.K. Kasevan, Entropy Optimization Principles with Applications, Oxford University Press, New York, 1992.

[16] J. Antolín, A. Zarzo, J.C. Angulo, Phys. Rev. A 50 (1994) 240.

[17] T. Koga, K. Matsui, Z. Phys. D 27 (1993) 97.

[18] A. Sarsa, F.J. Gálvez, E. Buendía, J. Chem. Phys. 109 (1998) 7075.

[19] T. Koga, Theor. Chim. Acta 64 (1984) 249.

[20] J. Antolín, J.C. Cuchí, A. Zarzo, J.C. Angulo, J. Phys. B 29 (1996) 5629.