Minimum Cross-Entropy Estimation of Internally Folded Densities from Compton Profiles

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ABSTRACT: The internally folded density or reciprocal form factor $B(\mathbf{r})$ of many-electron systems is tightly estimated from the knowledge of a small discrete set of values of the Compton profile $J(\mathbf{q})$. In doing so, the minimum cross-entropy technique is employed. A numerical analysis of the approximations is carried out for the Helium atom.

Key words: reciprocal form factor; Compton profile; momentum density; minimum cross-entropy

Introduction

The Fourier transform

$$B(\mathbf{r}) = \int \exp\{-i\mathbf{p}\cdot\mathbf{r}\}\gamma(\mathbf{p})\,d\mathbf{p} \qquad (1)$$

of the electron momentum density $\gamma(\mathbf{p})$ is used in the study and interpretation of fundamental chemical concepts, such as hybridization and bonding. This relevant function, called *reciprocal form factor* or *internally folded density*, was considered as an appropriate bridge between the position and momentum spaces and, consequently, many properties and theoretical results concerning this quantity have been investigated [1].

In particular, the connection of $B(\mathbf{r})$ to overlap integrals and, more generally, to other electron-density functionals was studied, as well as the chance of extracting accurate bond lengths from it [2].

Expansions and sum rules involving $B(\mathbf{r})$ have been used to check the accuracy of both experimental and theoretical results on the reliability of Compton profile fits to several functional forms [3, 4]. More recently, tight model-independent approximations to $B(\mathbf{r})$ were also obtained in terms of a few quantities related to the one-particle momentum density $\gamma(\mathbf{p})$ with no use of any position quantity. In doing so, two different but comple-

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mentary methods, based on maximum-entropy and two-point Padé approximants techniques, were employed [5].

The aim of this work is to obtain simple, tight and model-independent approximations to the spherically averaged characteristic function,

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

(j_0 being the spherical Bessel function of the first kind of order zero) in terms of experimentally accessible quantities, namely a limited set of values of the isotropic Compton profile [6],

$$J(q) = 2\pi \int_q^\infty p\gamma(p)\, dp. \quad (3)$$

Differentiation of the previous equation gives

$$\frac{dJ(q)}{dq} = -2\pi q\gamma(q), \quad (4)$$

which may be substituted in Eq. (2) to yield (after an integration by parts) the well-known fact that $B(r)$ and $J(q)$ are a pair of Fourier cosine transforms [1]:

$$B(r) = 2\int_0^\infty \cos(qr) J(q)\, dq, \quad (5)$$

$$J(q) = \frac{1}{\pi}\int_0^\infty \cos(qr) B(r)\, dr. \quad (6)$$

The obtention of $B(r)$ from the Compton profile by means of Eq. (5) would demand the complete knowledge of $J(q)$. However, the experimental access to this quantity is usually limited to a finite and discrete set of values $\{q_i\}$ $(i = 1, 2, \ldots, n)$ of the momentum transferred, up to a maximum value $q_{\max}$ which depends on the type of experiment carried out. Consequently, both interpolation and extrapolation on the experimental data are required before performing the Fourier transform.

Instead of using such a procedure, let us regard the values of $J(q)$ in Eq. (6) as *generalized moments* μ_i of the function $B(r)$, namely,

$$\mu_i = J(q_i) = \frac{1}{\pi}\int_0^\infty \cos(q_i r) B(r)\, dr, \qquad i = 0, 1, \ldots, n, \quad (7)$$

where $q_0 \equiv 0$. Then we face such a moment problem by using a generalization of the maximum-entropy method, namely the minimum cross-entropy method [7].

Following the steps given in Ref. [8], let us minimize the cross-entropy functional

$$S[B, B_0] \equiv \int_0^\infty B(r) \ln \frac{B(r)}{B_0(r)}\, dr, \quad (8)$$

taking into account the knowledge of the set of values $\{J(q_i)\}$ $(i = 0, \ldots, n)$, where $B_0(r)$ is an a priori reciprocal form factor, which can be regarded as a first estimation to the *exact* $B(r)$. The solution $B_n(r)$ to this variational problem is given by

$$B_n(r) = B_0(r) \exp\left\{-1 - \frac{1}{\pi}\sum_{i=0}^{n} \lambda_i \cos(q_i r)\right\}. \quad (9)$$

The Lagrange multipliers $\{\lambda_i\}$ are determined by imposing on $B_n(r)$ the given constraints.

Although the existence of such a solution is not guaranteed, we have always been able to locate the absolute minimum for any of the a priori densities and constraints considered in this work.

In what follows, three different kinds of problems (each one associated to a different choice of a priori density and constraints) will be discussed: maximum-entropy a priori functions, overlap a priori functions and *mixed constraints*. All them can be applied to the study of any many-particle system. For illustration, the accuracy of the approximations is analyzed within a Hartree–Fock framework [9] for the helium atom ($N = 2$).

Maximum-Entropy (ME) (a prior) Functions

The starting approximation to the reciprocal form factor is the maximum-entropy one [5] constrained by the first moments [1],

$$\nu_0 \equiv \int_0^\infty B(r)\, dr = \frac{\pi \langle p^{-1}\rangle}{2} = \pi J(0) = \mu_0 \pi,$$

$$\nu_1 \equiv \int_0^\infty B(r) r\, dr = \langle p^{-2}\rangle,$$

$$\nu_2 \equiv \int_0^\infty B(r) r^2\, dr = 2\pi^2 \gamma(0).$$

It is worth mentioning that the central value $\gamma(0)$ of the momentum density, which plays a relevant role in the description and interpretation of different physical phenomena [10], is not usually accessible with much reliability from a Compton profile experiment. However, many numerical calculations and estimations [4, 11] on $\gamma(0)$ have been carried out. Among them, let us notice

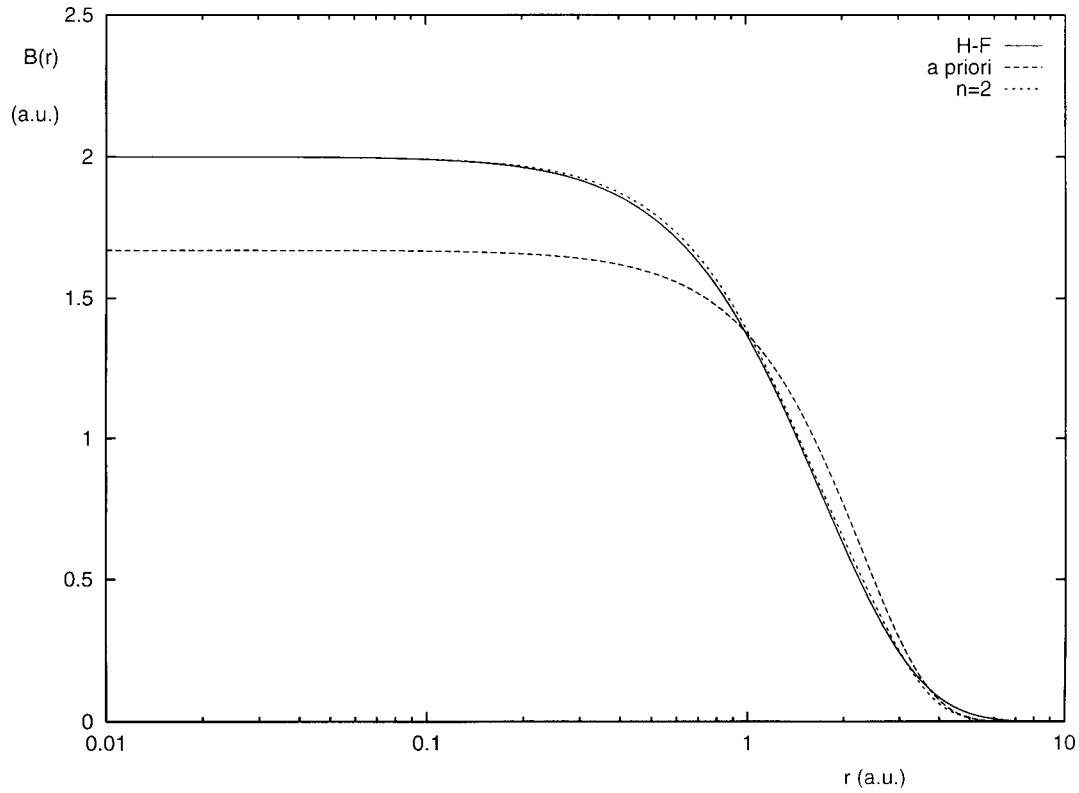

FIGURE 1. Hartree–Fock reciprocal form factor $B(r)$ and two-constraints approximation with ME a priori density function $B_{02}(r)$ for the helium atom. Atomic units (a.u.) are used.

those based on maximum-entropy approximations on $\gamma(p)$ [5, 12]. Additionally, different lower bounds to $\gamma(0)$ in terms of radial expectation values are also known [13, 14].

In this work the a priori ME distributions $B_{01}(r)$, $B_{02}(r)$, and $B_{012}(r)$ are used, the indexes denoting the moments ν_i used as constraints.

For the numerical comparison, we will consider the atomic wavefunctions of Ref. [9] for the helium atom $N = 2$. Concerning the constraints, we will consider equidistant values q_i ranging from 0 up to 4 a.u. (i.e., $0, 4/n, 8/n, \ldots, 4$ a.u. for the n-constraints approximation), except for the case $n = 2$ for which $q = 0, 1, 2$ a.u.

The approximations built from different values of the Compton profile and involving $B_{01}(r)$ and $B_{02}(r)$ as a priori functions have been compared to the Hartree–Fock (HF) ones, obtained by means of the analytical wavefunctions of Ref. [9]. Two main comments are in order: first, the improvement in the accuracy of the estimations when increasing the number of constraints is clearly observed. Such accuracy can be measured in terms of the relative entropy S_n between the n-constraints approximation and the a priori density. For the case of the a priori function $B_{01}(r)$, the values are $S_2 = 0.0257$, $S_4 = 0.0297$, $S_8 = 0.0481$, and $S_{16} = 0.0484$, to be compared to the Hartree–Fock value $S_{\mathrm{HF}} = 0.0487$.

A similar comparison can be done when considering the a priori function $B_{02}(r)$. This is carried out in Figure 1, where only the $n = 2$-constraints approximation is compared to the HF and the a priori ones, because the estimations built from a higher number of constraints are almost indistinguishable from the $n = 2$ one, which is very close to the Hartee–Fock $B(r)$ within the whole range of r here considered. Concerning the relative entropies S_n between the different approximations and the a priori density, the values converge to the Hartree–Fock one $S_{\mathrm{HF}} = 0.06361$ as $S_2 = 0.02967$, $S_4 = 0.02969$, $S_8 = 0.05260$, and $S_{16} = 0.06017$.

Second, it is observed that the approximations based on $B_{02}(r)$ (which depends on the momentum density at the origin) are more accurate than those involving $B_{01}(r)$ (constructed from the expectation value $\langle p^{-2} \rangle$).

Overlap A Priori Functions

It is based on the low-r expansion [1],

$$B(r) = N - \frac{\langle p^2 \rangle}{6} r^2 + O(r^4)$$

in terms of the number of electrons N and the kinetic energy (which is twice the expectation value $\langle p^2 \rangle$). The *overlap* a priori function $B_{\mathrm{ov}}(r)$ is given by the parametrization

$$B_{\mathrm{ov}}(r) = (a_0 + a_1 r + a_2 r^2) e^{-\xi r},$$

where the involved parameters are determined by imposing that the low-r expansion of $B_{\mathrm{ov}}(r)$ and $B(r)$ be identical up to order r^3. Then, the above parameters are given by

$$a_0 = N, \qquad a_1 = \left(N \langle p^2 \rangle\right)^{1/2},$$
$$a_2 = \frac{\langle p^2 \rangle}{3}, \qquad \xi = \left(\frac{\langle p^2 \rangle}{N}\right)^{1/2}.$$

In Figure 2, the $n = 2$ approximation is compared to the a priori and the Hartree–Fock ones. As happened with the a priori function $B_{02}(r)$, two constraints are quite enough to tightly approximate the density $B(r)$ for the whole range of r considered. Nevertheless, and for the sake of completeness, the aforementioned relative entropies S_n converge to $S_{\mathrm{HF}} = 0.007400$ as $S_2 = 0.003509$, $S_4 = 0.003514$, $S_8 = 0.007217$, and $S_{16} = 0.007392$.

Mixed Constraints

Consider now the problem of estimating $B(r)$ from the simultaneous knowledge of the first few moments ν_i and some values of the Compton profile $J(q)$. In doing so, we employ the maximum-entropy procedure [15] with two different kinds of Lagrange multipliers, γ_i and λ, associated to the aforementioned constraints, respectively. The re-

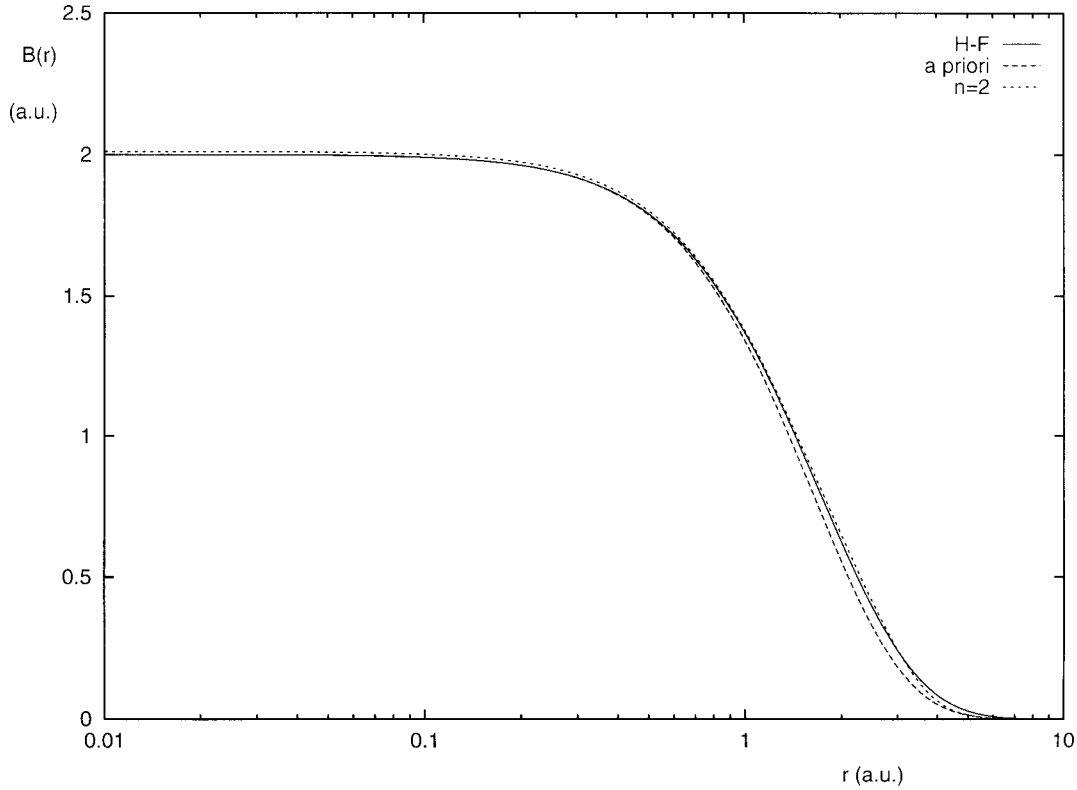

FIGURE 2. Hartree–Fock reciprocal form factor $B(r)$ and two-constraints approximation based on overlap a priori density function $B_{\mathrm{ov}}(r)$ for the helium atom. Atomic units (a.u.) are used.

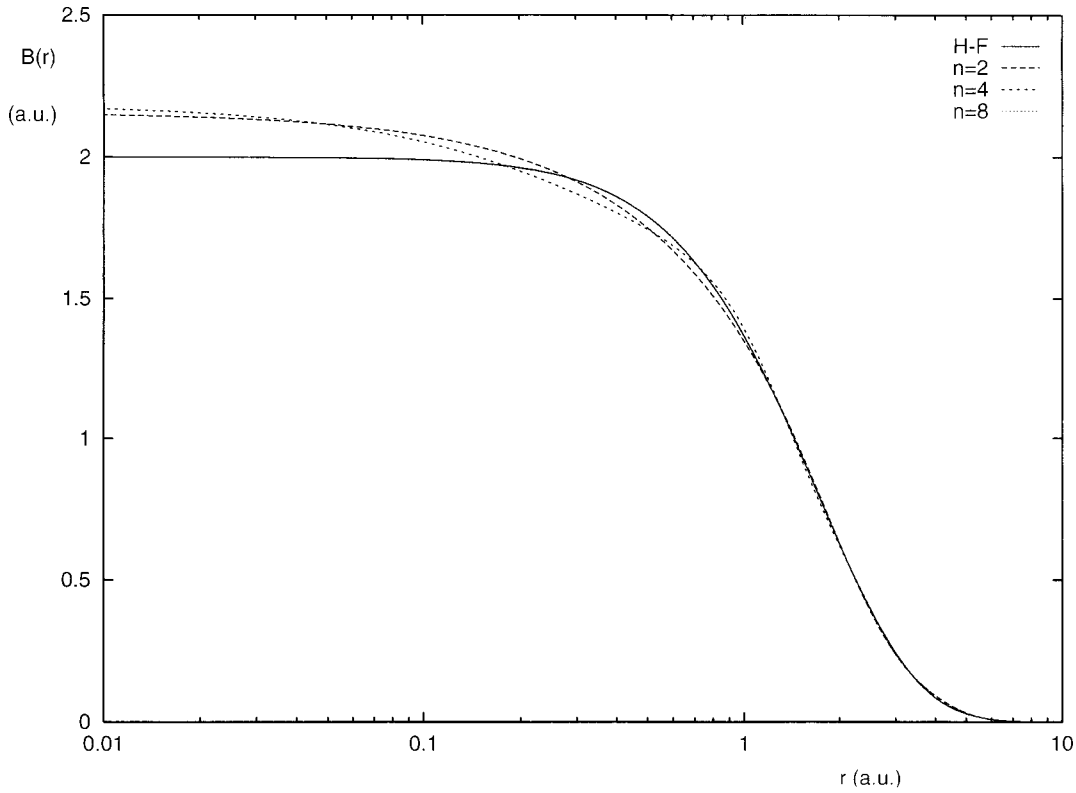

FIGURE 3. Hartree–Fock reciprocal form factor $B(r)$ and approximation involving mixed constraints with $m = 2$, $n = 2, 4, 8$ for the helium atom. Atomic units (a.u.) are used.

sulting approximation is

$$B_{n,m}(r) = A \exp\left\{-\sum_{i=1}^{m} \gamma_i r^i\right\} \exp\left\{-\sum_{j=1}^{n} \lambda_j \cos(q_j r)\right\}, \tag{10}$$

where Eq. (6) has been taken into account.

For the numerical study, we will consider in the present work the case $m = 2$ for $n = 2, 4, 8$. A comparison between such approximations to the Hartree–Fock (HF) function is carried out in Figure 3. The accuracy greatly improves when increasing the number of constraints, making the $n = 8$ estimation indistinguishable from the HF one.

The information entropy of the different densities involved in the figure, defined as

$$S[B] \equiv -\int_0^\infty B(r) \ln B(r)\, dr \tag{11}$$

provides a measure of the accuracy of the approximation. For the present case, the entropy S_n of the different estimations $B_{2,n}(r)$ decreases as follows: $S_2 = -0.103114$, $S_4 = -0.104368$, and $S_8 = -0.105742$, the last one very close to the information entropy of the Hartree–Fock reciprocal form factor, which is $S_{\mathrm{HF}} = -0.105752$.

For the sake of completeness, three different approximations corresponding to the above studied problems are compared to the HF one in Figure 4. The dashed curves correspond to: maximum-entropy (ME) $B_{012}(r)$ and overlap $B_{\mathrm{ov}}(r)$ a priori functions with four constraints, and mixed-constraints approximation for the case $m = 2$, $n = 1$. Note their great accuracy, especially relevant when considering the low-r expansion of $B(r)$ by means of the overlap a priori function.

Summarizing, the maximum-entropy and minimum cross-entropy techniques provide model-independent tight approximations to the reciprocal form factor of atomic systems. Due to the universality of these methods, they can also be employed in the study of different density functions associated to any many-particle system in terms of some expectation values of the involved density.

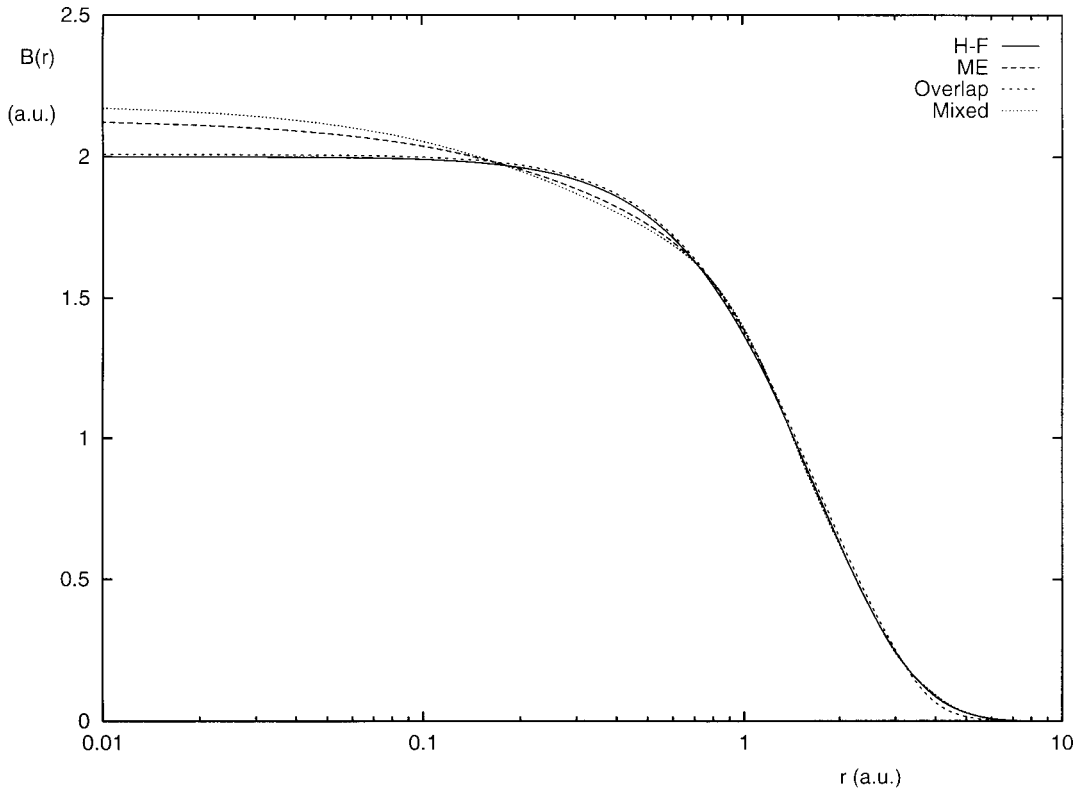

FIGURE 4. Hartree–Fock reciprocal form factor $B(r)$ and comparison among the approximation involving mixed constraints with $m = 2$ and $n = 4$ and the estimation based on B_{012} and overlap a priori density functions with four constraints for the helium atom. Atomic units (a.u.) are used.

References

1. Thakkar, A. J.; Simas, A. M.; Smith, Jr., V. H. Mol Phys 1980, 41, 1153.
2. Weyrich, W.; Pattison, P.; Williams, B. G. Chem Phys 1979, 41, 271.
3. Koga, T.; Morita, M. J Chem Phys 1982, 77, 6345.
4. Gadre, S. R.; Chakravorty, S. J. Proc Ind Acad Sci (Chem Sci) 1986, 96, 241.
5. Antolín, J.; Cuchí, J. C.; Zarzo, A.; Angulo, J. C. J Phys B 1996, 29, 5629.
6. Williams, B. G., Ed. Compton Scattering: The Investigation of Electron Momentum Distributions; McGraw-Hill: New York, 1977.
7. Kapur, J. N.; Kasevan, H. K. Entropy Optimization Principles with Applications; Oxford Univ. Press: New York, 1992.
8. Antolín, J.; Cuchí, J. C.; Angulo, J. C. J Phys B 1999, 32, 577.
9. Clementi, E.; Roetti, C. At Data Nucl Data Tables 1974, 14, 177.
10. Thakkar, A. J. J Chem Phys 1987, 86, 5060.
11. Gadre, S. R.; Gejji, S. P. J Chem Phys 1984, 80, 1175.
12. Zarzo, A.; Angulo, J. C.; Antolín, J.; Yáñez, R. J. Z Phys D 1996, 37, 295.
13. Angulo, J. C.; Dehesa, J. S.; Gálvez, F. J. Z Phys D 1991, 18, 127.
14. Gálvez, F. J. Phys Rev A 1989, 39, 501.
15. Mead, L. R.; Papanicolau, N. J Math Phys 1983, 25, 2404.