

Structural properties of reciprocal form factor in neutral atoms and singly charged ions

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Structural characteristics of the spherically averaged internally folded density or reciprocal form factor $B(r)$ are studied within the Hartree–Fock framework for 103 neutral atoms, 54 singly charged cations, and 43 anions in their ground state. The function $B(r)$ is classified throughout the Periodic Table into three types: (i) monotonic decrease from the origin, (ii) maximum at $r=0$ and a negative minimum at $r>0$, and (iii) a local maximum at $r=0$ and a pair maximum–minimum out of the origin. A detailed study of the corresponding properties for individual subshells as well as their relative weight for the total $B(r)$ is also carried out. For completeness, the analytical $B(r)$ for hydrogenlike atoms in both ground and excited states is also analyzed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667467]

I. INTRODUCTION

The reciprocal form factor $B(\mathbf{r})$ of a many-particle system (e.g., atom, molecule) is defined in terms of the one-particle density in momentum space, $\Pi(\mathbf{p})$, as the Fourier transform^{1–3} (atomic units are used throughout)

$$B(\mathbf{r}) \equiv \int e^{-i\mathbf{p}\cdot\mathbf{r}} \Pi(\mathbf{p}) d\mathbf{p}. \quad (1)$$

For atomic systems, the main information of the three-dimensional reciprocal form factor may be condensed into its spherical average $B(r)$. Similarly, some relevant quantities in momentum space can be described by only considering the spherical average $\Pi(p)$ of the one-particle density, such as the radial expectation values

$$\langle p^n \rangle = \int p^n \Pi(\mathbf{p}) d\mathbf{p} = 4\pi \int_0^\infty p^{n+2} \Pi(p) dp \quad (2)$$

with the normalization given by $\langle p^0 \rangle = B(0) = 1$. For the particular cases $n = -2, -1$ it is verified that $\langle p^{-1} \rangle = (2/\pi) \int_0^\infty B(r) dr$ and $\langle p^{-2} \rangle = \int_0^\infty r B(r) dr$. The functions $B(r)$ and $\Pi(p)$ are each one the Fourier transform of the other, given by the one-dimensional integrals

$$B(r) = 4\pi \int_0^\infty p^2 \Pi(p) j_0(pr) dp \quad (3)$$

and

$$\Pi(p) = \frac{1}{2\pi^2} \int_0^\infty r^2 B(r) j_0(pr) dr, \quad (4)$$

$j_0(x)$ being the zeroth spherical Bessel function of the first kind. Consequently, $\int_0^\infty B(r) r^2 dr = 2\pi^2 \Pi(0)$.²

The interest in studying the reciprocal form factor of atomic systems is based not only on its equivalent role to the one played by the form factor $F(\mathbf{k})$ in connection to the

charge density, but also on its usefulness on checking the accuracy of different experimental measures, such as those involving Compton profiles of scattering processes.^{4,5}

From a theoretical point of view, not many rigorous results are known on the structural characteristics of $B(r)$, apart from the asymptotic behavior close to the origin:²

$$B(r) = 1 - \frac{\langle p^2 \rangle}{6} r^2 + \frac{\langle p^4 \rangle}{120} r^4 + O(r^5), \quad r \rightarrow 0. \quad (5)$$

Concerning the numerical studies of $B(r)$ within different models, let us mention not only the calculations (e.g., Ref. 6) but also the tight approximations in terms of moments of $B(r)$ and local values of the momentum density⁷ or the Compton profile.⁸

The aim of this work is to study the structural properties of the reciprocal form factor for some atomic systems. In Sec. II we show that for the ground-state atomic systems studied (103 neutral atoms, 43 single anions, and 53 single cations), using the Roothaan–Hartree–Fock wave functions of Koga *et al.*,⁹ the reciprocal form factor falls into three different categories attending to the number of its local maxima and minima. A study of the relative contributions of the different subshells to the total reciprocal form factor for the aforementioned systems is also carried out. Finally, in Sec. III, a detached study of the structural characteristics of $B(r)$ is analytically done for one-electron atoms in excited states.

II. CATEGORIES OF RECIPROCAL FORM FACTORS

In order to compute the reciprocal form factors of the systems considered in the present work, two different methods have been employed. In both cases, the starting point is an accurate Sater-type basis set from which the momentum density $\Pi(p)$ is analytically described. The results on $B(r)$ here discussed have been obtained by numerically performing the Fourier transform, employing the algorithm of R. Peissens *et al.* (see www.netlib.org/quadpack/readme for a

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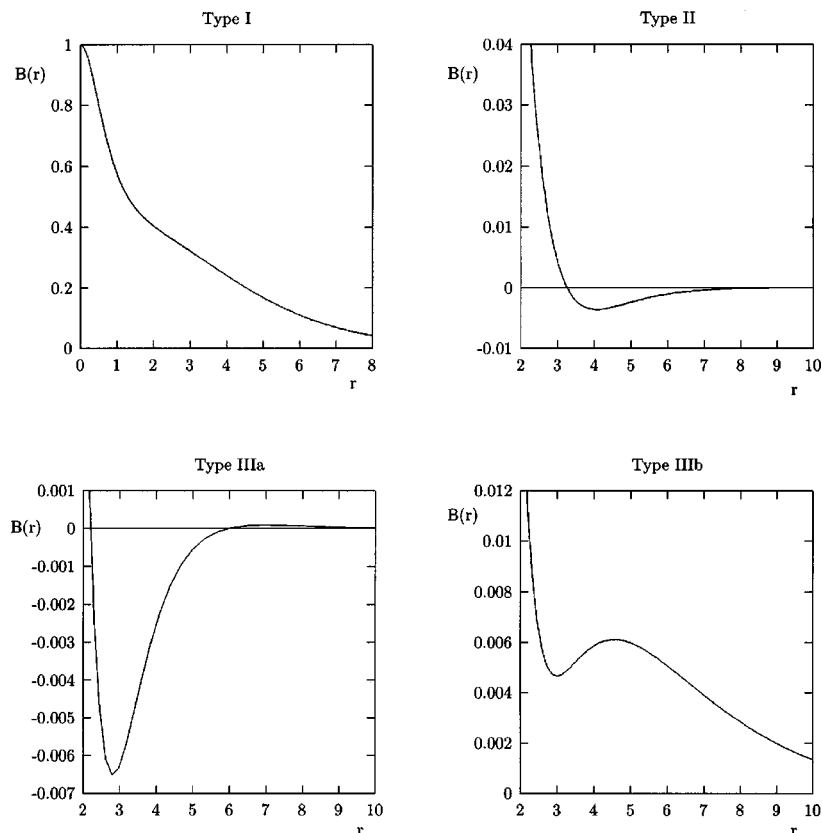


FIG. 1. Reciprocal form factor $B(r)$ for neutral atoms with nuclear charge $Z=4$ (type I), $Z=10$ (type II), $Z=46$ (type III-a), and $Z=79$ (type III-b). Atomic units are used.

detailed description). Nevertheless, we have successfully contrasted such results by carrying out the Fourier transform of the analytical expression of $\Pi(p)$ in terms of the basis set.

Examination of the spherically averaged reciprocal form factor $B(r)$ for neutral atoms with nuclear charge $1 \leq Z \leq 103$ by means of the accurate Roothan–Hartree–Fock wave functions of Koga and co-workers⁹ (of great accuracy, significantly high up to $Z=54$) shows that, attending to the number of local extrema, $B(r)$ is classified into three types:

- Type I. Monotonic decrease from the origin. The following 64 neutral atoms have a type-I $B(r)$: $Z=1-4, 11, 12, 19-30, 37-41, 43, 55-77$, and $87-103$. Figure 1(a) shows the reciprocal form factor of the Be atom ($Z=4$).

- Type II. A local maximum at $r=0$ and a negative minimum at $r>0$ for the following 30 neutral atoms: $Z=5-10, 13-18, 31-36, 49-54$, and $81-86$. Figure 1(b) shows the reciprocal form factor of the Ne atom ($Z=10$).

- Type III. A local maximum at $r=0$ and a pair minimum-maximum out of the origin for the 9 neutral atoms: $Z=42, 44-48$, and $78-80$. Attending to the sign of the minimum value B_{\min} of $B(r)$, we can distinguish (i) the type III-a when $B_{\min} < 0$ (for $Z=46$) and (ii) the type III-b when $B_{\min} > 0$ (for $Z=42, 44, 45, 47, 48$, and $78-80$). Figures 1(c) and (d) show the atoms Pd ($Z=46$) and Au ($Z=79$) which have a $B(r)$ of type III-a and III-b, respectively.

Reciprocal form factors of type I are found for atoms of groups 1–9 except Mo, Ru, and Rh, for all lanthanides and actinides, and for He, Ni, Cu, Zn. Type II is found for all the atoms of groups 13–18 except He. This second type occurs for all atoms with one or more electrons in p orbitals of the

outermost shell. Type-II atoms are the norm for groups 10–12 (except Ni, Cu, Zn) and for Mo, Ru, and Rh.

Analysis of the reciprocal form factor of singly charged atoms, 43 single anions and 53 single cations in their ground state, by means of the Roothan–Hartree–Fock wave functions, shows that the modalities of $B(r)$ fall into one of the three categories found above for the neutral atoms.

- Type I: the 20 anions with $Z=1, 3, 11, 19, 21-29, 37$, and $39-44$, and the 14 cations with $Z=3-5, 12, 13, 20-22, 25, 26, 31$, and $38-40$ have a $B(r)$ that belongs to this type.

- Type II: the 20 anions with $Z=5-9, 13-17, 31-35$, and $49-53$, and the 24 cations with $Z=6-11, 14-19, 32-37$, and $50-55$ have a $B(r)$ of this type.

- Type III: The 3 anions with $Z=45-47$ have a $B(r)$ of type III-b. No anions are with a $B(r)$ of type III-a. The 11 cations with $Z=23, 24, 27-29, 41, 42$, and $44-47$ have a $B(r)$ of type III-a and the 4 cations with $Z=30, 43, 48$, and 49 have a $B(r)$ of type III-b.

The extremum characteristics of the type-II and type-III reciprocal form factor are summarized in Tables I and II. First should be noticed the small height of the local peaks compared to the absolute maximum value $B(0)=1$; then, a high accuracy on computing the function $B(r)$ is a basic requirement for the subsequent analysis and interpretation of such local characteristics. On the other hand, some details of the classification could be an artifact of the basis set.

For type-II atoms, in all the cases the values of location of the minimum r_{\min} increase when the number of outermost p or d electrons increases. Moreover, the location of the minimum in neutral and singly charged atoms shows up a

TABLE I. Extremum characteristics of type-II reciprocal form factors for atoms. $A(\pm n)$ means $A \times 10^{\pm n}$.

Z	Anions		Neutral atoms		Cations	
	r_{\min}	B_{\min}	r_{\min}	B_{\min}	r_{\min}	B_{\min}
5	1.48(1)	-1.875(-3)	1.23(1)	-1.323(-4)		
6	9.99	-2.204(-3)	8.63	-5.193(-4)	1.10(1)	-2.978(-6)
7	8.25	-2.646(-3)	6.68	-1.028(-3)	7.25	-9.109(-5)
8	6.87	-2.954(-3)	5.42	-2.205(-3)	5.49	-4.026(-4)
9	5.82	-3.246(-3)	4.64	-3.017(-3)	4.37	-1.377(-3)
10			4.07	-3.601(-3)	3.74	-2.310(-3)
11					3.30	-3.089(-3)
13	1.73(1)	-1.246(-3)	1.29(1)	-3.951(-4)		
14	1.16(1)	-1.826(-3)	9.74	-9.387(-4)	1.04(1)	-9.946(-5)
15	9.76	-2.271(-3)	7.91	-1.518(-3)	7.83	-4.973(-4)
16	8.24	-2.724(-3)	6.79	-2.429(-3)	6.43	-1.091(-3)
17	7.07	-3.191(-3)	5.96	-3.153(-3)	5.54	-2.079(-3)
18			5.31	-3.784(-3)	4.91	-2.963(-3)
19					4.42	-3.745(-3)
31	1.76(1)	-5.380(-4)	1.22(1)	-2.262(-4)		
32	1.16(1)	-9.242(-4)	9.65	-5.112(-4)	1.00(1)	-7.389(-5)
33	9.97	-1.200(-3)	8.05	-8.701(-4)	7.87	-3.275(-4)
34	8.58	-1.525(-3)	7.12	-1.395(-3)	6.68	-6.984(-4)
35	7.49	-1.879(-3)	6.38	-1.864(-3)	5.93	-1.284(-3)
36			5.78	-2.317(-3)	5.37	-1.845(-3)
37					4.92	-2.385(-3)
49	1.73(1)	-3.830(-4)	1.34(1)	-1.205(-4)		
50	1.24(1)	-6.096(-4)	1.07(1)	-3.108(-4)	1.12(1)	-4.232(-5)
51	1.08(1)	-8.432(-4)	8.99	-5.543(-4)	8.86	-2.097(-4)
52	9.38	-1.103(-3)	7.99	-9.459(-4)	7.57	-4.778(-4)
53	8.28	-1.396(-3)	7.21	-1.322(-3)	6.76	-9.076(-4)
54			6.58	-1.692(-3)	6.17	-1.336(-3)
55					5.70	-1.768(-3)
81			1.36(1)	-8.182(-5)		
82			1.10(1)	-2.053(-4)		
83			9.35	-3.656(-4)		
84			8.36	-6.327(-4)		
85			7.60	-8.926(-4)		
86			6.98	-1.156(-3)		

linear dependence on $1/Z$ within each subshell, with a correlation coefficient always greater than 0.975. The same is true for atoms with a type-III reciprocal form factor. Figure 2 shows the inverse of the location r_{\min} for type-II and type-III atoms, and the above linear behavior corresponding to atoms with the same principal quantum number n and symmetry l of the outermost subshell.

When an isoelectronic serie has a type-II or a type-III $B(r)$ we always observe inequality $r_{\min}^+ < r_{\min}^0 < r_{\min}^-$. This behavior conforms with the behavior observed in r_{\min} for the neon isoelectronic series in Ref. 10. There is no regular behavior for B_{\min} in singly charged ions and neutral atoms with type-II or type-III reciprocal form factors or for B_{\max} in singly charged ions and neutral atoms with type III.

The total $B(r)$ is the sum of subshell contributions, i.e., $B(r) = \sum_{nl} B_{nl}(r)$; so, the different types of $B(r)$ may be understood in doing an analysis of the different behaviors of the contributions $B_{nl}(r)$. This analysis allows us to say that the behavior of $B(r)$ is essentially determined by the contributions of the highest occupied subshells. Let n_l be the principal quantum number of such subshells with symmetry l ($=s, p$ or d); next rules are verified:

1. Type-I modality appears when $n_s > n_p, n_d$.

TABLE II. Extremum characteristics of type-III reciprocal form factors for atoms. $A(\pm n)$ means $A \times 10^{\pm n}$.

Z	Atom	r_{\min}	B_{\min}	r_{\max}	B_{\max}
Neutral atoms					
42	Mo	4.15	1.036(-2)	4.48	1.038(-2)
44	Ru	3.48	1.021(-2)	4.44	1.063(-2)
45	Rh	3.25	1.006(-2)	4.36	1.082(-2)
46	Pd	3.12	-5.163(-3)	9.17	4.227(-5)
47	Ag	2.88	9.669(-3)	4.18	1.118(-2)
48	Cd	2.82	2.307(-2)	3.25	2.321(-2)
78	Pt	3.18	4.857(-3)	4.64	5.938(-3)
79	Au	3.01	4.677(-3)	4.56	6.115(-3)
80	Hg	2.91	1.244(-2)	3.69	1.287(-2)
Anions					
45	Rh ⁻	3.41	3.090(-2)	3.95	3.101(-2)
46	Pd ⁻	3.16	3.024(-2)	3.93	3.058(-2)
47	Ag ⁻	2.96	2.959(-2)	3.89	3.026(-2)
Cations					
23	V ⁺	3.28	-5.784(-3)	8.45	5.791(-5)
24	Cr ⁺	3.06	-6.049(-3)	7.83	6.285(-5)
27	Co ⁺	2.64	-6.246(-3)	7.05	6.721(-5)
28	Ni ⁺	2.53	-6.280(-3)	6.81	6.747(-5)
29	Cu ⁺	2.41	-6.325(-3)	6.55	6.731(-5)
30	Zn ⁺	2.41	1.712(-2)	2.81	1.727(-2)
41	Nb ⁺	3.72	-4.850(-3)	9.10	5.752(-5)
42	Mo ⁺	3.46	-5.339(-3)	8.39	6.593(-5)
43	Tc ⁺	3.39	8.201(-3)	4.34	8.781(-3)
44	Ru ⁺	3.12	-5.965(-3)	7.66	7.513(-5)
45	Rh ⁺	2.96	-6.259(-3)	7.30	7.971(-5)
46	Pd ⁺	2.83	-6.530(-3)	6.98	8.411(-5)
47	Ag ⁺	2.69	-6.802(-3)	6.67	8.815(-5)
48	Cd ⁺	2.59	6.957(-3)	3.81	9.094(-3)
49	In ⁺	2.57	1.947(-2)	3.05	1.973(-2)

2. Type-II modality appears when $n_s = n_p > n_d$ (always due to outermost p subshell).

3. Type-III modality appears when $n_s = n_p + 1 = n_d + 1$ and there is a sufficient d contribution.

4. The negativity of the minimum in the type-III cases is always associated to the anomalous shell filling $(n + 1)s^0 nd^m$, so $n_s = n_p = n_d$.

In addition, numerical examination shows that the contributions from the outermost s subshell has a maximum at $r=0$ (type-I contribution), the outermost p subshell has a type-II contribution to the total $B(r)$ and d and f outermost subshells have a type-III contribution.

Finally, taking into account that $B(r)$ and the spherically averaged electron momentum density $\Pi(p)$ are related by a Fourier transform, we can consider how the $B(r)$ classification matches up with the $\Pi(p)$ one.¹¹⁻¹⁴ T. Koga and co-workers have studied that according to $\Pi(p)$ modalities the atoms that have been studied in this work can be separated into three distinct categories:^{13,14}

- Type A. Atoms with a unimodal $\Pi(p)$ with its maximum located at the origin ($p_{\max}=0$); i.e., a monotonically decreasing momentum density.
- Type B. Atoms with a unimodal $\Pi(p)$ with its maximum located away from the origin $p_{\max}>0$; i.e., the momentum density has a minimum at the origin.
- Type C. Atoms with a bimodal $\Pi(p)$ with one maximum at the origin and the other maximum out of the origin,

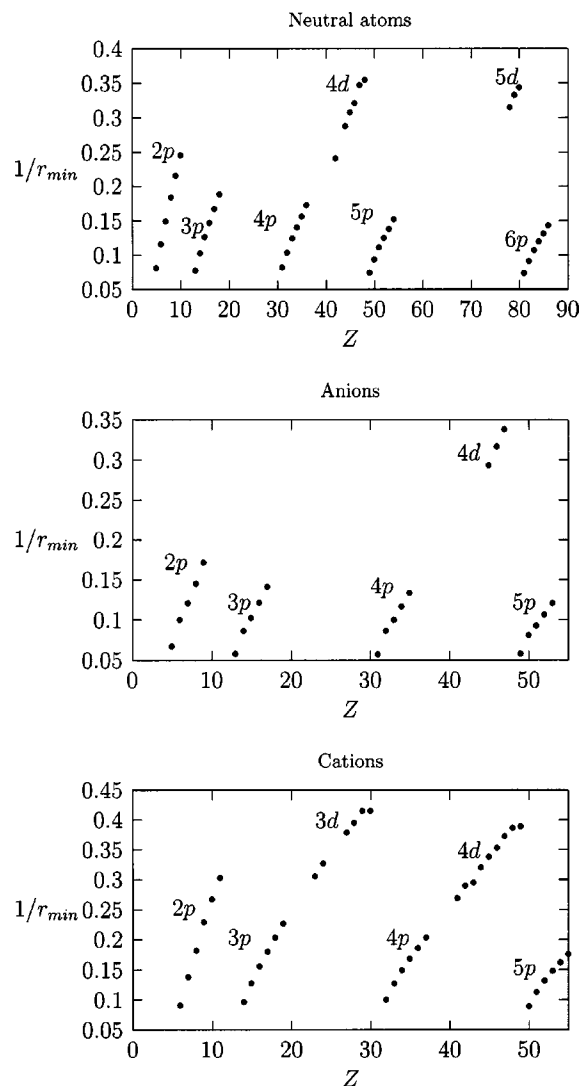


FIG. 2. Inverse of the location r_{\min} of the minimum of $B(r)$ with the principal quantum number and symmetry (nl) of the outermost subshell for each atom. Atomic units are used.

at $p_{\max} > 0$, and a local minimum at p_{\min} with $0 < p_{\min} < p_{\max}$.

Thakkar *et al.*¹⁵ found that a negative second derivative of $\Pi(p)$ at the origin, $\Pi''(0) < 0$, is an indicator of a momentum density of type A or C, while $\Pi''(0) > 0$ corresponds to a type-B one.

The analysis of the relation between both classifications can be summarized as follows:

- For atoms having a $\Pi(p)$ of type C the function $B(r)$ is always positive, so they have a type-I or a type-III-b $B(r)$.
- If the atoms have a $\Pi(p)$ of type B, then the corresponding $B(r)$ is negative in some interval. In fact, these atoms have a type-II or -III-a $B(r)$, with the only exception of Y^- ($Z = 39$) that has a type-I $B(r)$.
- All atoms with a $B(r)$ of type I match up to atoms with a $\Pi(p)$ with second derivative at the origin negative [$\Pi''(0) < 0$]. The Y^- anion constitutes an exception of this property and has $\Pi''(0) > 0$.
- All atoms with $B(r)$ of type II correspond with a $\Pi(p)$

unimodal (type A and B). For anions we observe that a type-II $B(r)$ always matches up to a type-B $\Pi(p)$.

- Atoms with $B(r)$ of type III-a have a $\Pi(p)$ of type B and atoms with $B(r)$ of type III-b have a negative $\Pi''(0)$.
- For anions, a $B(r)$ of type III corresponds with a $\Pi(p)$ of type C.

III. HYDROGENIC ATOMS

In this section, some of the aforementioned structural properties of the spherical function $B(r)$, numerically obtained for atomic systems (both neutral atoms and ions), as well as additional ones, are analytically studied for one-electron atoms in terms of the quantum numbers (n, l) of the subshell to which the electron belongs.

In what follows, and for the sake of simplicity, we will only consider the case of nuclear charge $Z = 1$, having in mind that all monotonicity properties concerning the corresponding functions for arbitrary Z , namely $\Pi_Z(p)$ and $B_Z(r)$, are Z independent due to the scaling

$$\Pi_Z(p) = \frac{1}{Z^3} \Pi(p/Z),$$

$$B_Z(r) = B(Zr).$$

In Ref. 16, it is proved that the (n, l) reciprocal form factor is

$$B_{nl}(r) = e^{-r/n} P_{2n}(r) = e^{-r/n} \sum_{j=0}^{2n} a_j r^j \quad (6)$$

with $a_0(n, l) = 1$ and

$$a_j(n, l) = \frac{(-1)^{j+1}}{(j+1)! n^{j-1}} \times \sum_{k=k_{jl}}^{n-1} \frac{2^{2k+1} (n+k)! k!^2}{(n-1-k)! (k+l+1)! (k-l)! (2k+1)!} \times P_{2k+2-j}^{(j-1, 2)}(0)$$

for $j \neq 0$, with $k_{jl} \equiv \max\{l, [(j-1)/2]\}$ and $P_m^{(\alpha, \beta)}(x)$ being a Jacobi polynomial. Some comments are in order:

(i) The comparison between the McLaurin expansions of $e^{-r/n} B_{nl}(r)$ and $B_{nl}(r)$, which coefficients are proportional, respectively, to a_j and $B^{(j)}(0)$, provides an expression of a_j for low j in terms of the radial expectation values $\langle p^m \rangle$ of $\Pi_{nl}(p)$. So, the first few coefficients for arbitrary (n, l) are given by

$$a_0 = 1, \quad a_1 = \frac{1}{n}, \quad a_2 = \frac{1}{3n^2}, \quad a_3 = 0,$$

$$a_4 = \frac{n-2l-1}{15n^4(2l+1)}.$$

(ii) The leading coefficients a_{2n-2} , a_{2n-1} , and a_{2n} are obtained as particular cases of the general expression of a_j :

TABLE III. Coefficients a_l of the reciprocal form factor $B_{nl}(r)$ of hydrogen atom ($Z=1$) at (n, l) state for $n=1, 2, 3$. Atomic units are used.

nl	a_1^{-1}	a_2^{-1}	a_4^{-1}	a_5^{-1}	a_6^{-1}
1s	1	3			
2s	2	12	240		
2p	2	12	-720		
3s	3	27	1215/2	-10 935/2	229 635/2
3p	3	27	∞	10 935	-229 635
3d	3	27	-6075/2	-54 675	1 148 175

$$a_{2n-2} = (-1)^l \frac{4^{n-1} n! (n-2)!}{(n+l)! (n-l-1)! (2n-1)! n^{2n-2}} \times \left[n^3 - \frac{11}{2} n^2 + 10n - \frac{11}{2} l(l+1) \right], \quad (7)$$

$$a_{2n-1} = (-1)^{l+1} \frac{4^{n-1} (n-2)(n-1)!^2}{(n+l)! (n-l-1)! (2n-1)! n^{2n-1}}, \quad (8)$$

$$a_{2n} = (-1)^l \frac{2^{2n-1} (n-1)!^2}{(n+l)! (n-l-1)! (2n+1)! n^{2n-1}}. \quad (9)$$

(iii) The sign of $B_{nl}(r)$ at large distances is determined by the angular momentum quantum number l as $(-1)^l$.

(iv) The quotient a_{2n-1}/a_{2n} is $n(2-n)(2n+1)$. Consequently, $a_{2n-1}=0$ if and only if $n=2$. Taking into account that the mean location of the zeros of $P_{2n}(r)$ is given by $-a_{2n-1}/(2na_{2n})$, such a location is $(n-2)(n+1/2)$, i.e., it only depends on the principal quantum number n .

Having in mind the third comment, the $B_{nl}(r)$ function corresponding to odd values of the quantum number l (e.g., p and f subshells) necessarily reaches negative values from some large enough r_0 on (i.e., it would not belong to type-I functions). In principle, negativity could also occur for additional finite regions within the interval $(0, r_0)$ (e.g., $4f$), as well as for even l (e.g., $3d$).

It is interesting to study the particular cases corresponding to some different (n, l) values. The explicit expressions of $P_{2n}(r)$ for values of the principal quantum number $n=1, 2, 3$ are given by Table III with $a_0=1$ and $a_3=0$ for arbitrary (n, l) .

Concerning the classification of $B_{nl}(r)$ according to the number of its local extrema (similarly to the one given for neutral atoms), the most remarkable point is the appearance of additional *types* when considering higher values of the principal quantum number n . In fact, such a situation should be expected because of the factorization of $B_{nl}(r)$ as an exponential and a polynomial of degree $2n$. However, we have not yet been able to determine, in general, if the $2n$ zeros of the derivative are simple or not and how many of them belong to the real positive axis.

IV. SUMMARY

Different structural properties of the spherically averaged reciprocal form factor $B(r)$ have been studied for ground-state neutral atoms and single ions. All those systems are classified into three different groups, attending to the number of local extrema of $B(r)$. A detached study of this function for each subshell of the system makes clear that the valence electrons appear to be the main responsables for such a structure.

An analytical study has been carried out for excited states of hydrogenic ions. Observed are (i) the appearance of additional groups in the aforementioned classification when increasing the degree of excitation (i.e., the value of the principal quantum number n), and (ii) the analogy between both classifications attending to the value of the angular momentum quantum number l of the more external electron.

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