Bare Coulomb Field and Atomic Reciprocal Form Factor

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ABSTRACT: The reciprocal form factor of N-electron closed shells systems in a bare Coulomb field is shown to be a spherically symmetric, positive, and decreasing function of the radial distance. Nonmonotonicities of the reciprocal form factor appear when studying bare Coulomb field open-shell systems. Analysis of the weight of the interelectronic repulsion term is carried out for some isoelectronic series as well as neutral atoms with $N = 1$–103. © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 106: 485–489, 2006

Key words: bare Coulomb field; reciprocal form factor; momentum density; open- and closed-shell systems; isoelectronic series

1. Introduction

In recent years, several works have been published to clarify monotonicity characteristics of the one-particle density of many-electron systems in position and momentum spaces (see Refs. [1, 2], and references therein). Recently structural properties of the reciprocal form factor, $B(\mathbf{r})$, have been studied [3] for numerous neutral atoms and singly charged ions within a Hartree–Fock framework, whose interest lies in the fact that facilitates the analysis and interpretation of Compton profiles [4]. The reciprocal form factor is defined (see Ref. [5], and references therein) in terms of the one-particle momentum density $\Pi(\mathbf{p})$ as

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

It has been shown [3] that the spherically averaged reciprocal form factor (RFF) $B(r)$ falls throughout the Periodic Table into three different categories attending to the number of its local maxima and minima: (i) (type I) monotonic decrease from the origin, (ii) (type II) maximum at $r = 0$ and a negative minimum $B_{\min}$ at $r_{\min}$, and (iii) (type III) a local maximum at $r = 0$ and a pair minimum–maximum

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(B_{min}, B_{max}), with $B_{max} > 0$, at r_{min} and r_{max}, respectively; attending to the sign of B_{min}, the following subtypes have been distinguished: III-a ($B_{min} < 0$) and III-b ($B_{min} > 0$). In addition, it has been found that the behavior of $B(r)$ is essentially determined by the contribution of the highest occupied subshells.

In the present work, we will analyze the RFF of an electron system moving in a bare Coulomb field (BCF) potential $-Z/r$ (atomic units are used throughout). March [6] showed that the total electron density is a monotonically decreasing function for an arbitrary number of closed shells in the BCF case. In contrast, the same property was also shown for the total momentum density in the closed-shell case [7]. In fact, the one-particle momentum density $\Pi_b(\mathbf{p})$ for $\mathcal{M}$ closed shells is given by (see Ref. [7], and references therein):

$$\Pi_b(\mathbf{p}) = \sum_{j=1}^{\mathcal{M}} \frac{16 p_j^5 j^2}{\pi^2 (p_j^2 + p^2)^4}, \tag{2}$$

with $p_j = Z/j$ [Coulomb potential $V(r) = -Z/r$]. The normalization will be given by

$$\int \Pi(\mathbf{p}) d\mathbf{p} = B(0) = N,$$

where N is the number of electrons in the system.

In this work we will study structural properties of the reciprocal form factor of an electron system moving in a BCF potential and the weight of the interelectronic repulsion term on the structural characteristics of the reciprocal form factor. First, we will consider in Section 2 the analysis of $B(r)$ for an electron system with an arbitrary number of closed shells, and the results of numerical calculations for the isoelectronic series of closed-shell atoms in their ground state are presented. In Section 3 we will analyze $B(r)$ for atomic systems with open shells. In particular, we will study analytically the reciprocal form factor with a BCF potential energy in the general case and its structural changes when adding the interelectronic repulsion term for neutral atoms. In Section 3 we will analyze numerically structural properties of several isoelectronic series for open-shell ground-state atoms.

2. Bare Coulomb Field Reciprocal Form Factor for Closed Shells

For an arbitrary number of closed shells, the BCF reciprocal form factor $B_b(\mathbf{r})$ is obtained analytically from the momentum density $\Pi_b(\mathbf{p}) = \Pi_b(p)$ by means of Eq. (2) and taking into account that the Fourier transform $B(\mathbf{r})$ for a spherically symmetric $\Pi(\mathbf{p})$ reduces to the one-dimensional integral

$$B(\mathbf{r}) = 4\pi \int_0^\infty p^2 \Pi(p) j_0(pr) dp, \tag{3}$$

where $j_0(x)$ is the zeroth spherical Bessel function of the first kind. We have obtained the value

$$B_b(\mathbf{r}) = B_b(r) = \sum_{j=1}^{\mathcal{M}} \frac{2}{3} j^2 e^{-rp_j} (3 + 3p_j r + p_j^2 r^2). \tag{4}$$

Thus, $B_b(\mathbf{r})$ is a positive spherically symmetric function. In addition, its first derivative is given by

$$B_b'(r) = -\sum_{j=1}^{\mathcal{M}} \frac{2}{3} j^2 r p_j^2 e^{-rp_j} (1 + p_j r), \tag{5}$$

which is negative for $r > 0$, so $B_b(r)$ is a monotonically decreasing function for any $\mathcal{M}$. The BCF model for $\mathcal{M}$ closed shells yields the zeroth-order term in the Z^{-1} expansion of $B(r)$:

$$B(r) = B_b(r) + Z^{-1} B_1(r) + Z^{-2} B_2(r) + \ldots, \tag{6}$$

since the Z^{-1} expansion of $\Pi(p)$ is given by [4] $\Pi(p) = \Pi_b(p) + Z^{-1}\Pi_1(p) + Z^{-2}\Pi_2(p) + \cdots$. We have studied the behavior of $B(r)$ in the specific case of the 2- and 10-electron isoelectronic series, which are two sets of atomic systems with closed shells (the neutral and first 20 cationic members of the isoelectronic series of each ground-state atom), in a Roothan–Hartree–Fock framework, using the Koga et al. [8] wave functions. We have observed that $B(r)$ is a non-negative function for the He-isoelectronic series. For the Ne-isoelectronic series, the reciprocal form factor $B(r)$ reaches a minimum B_{min} at r_{min} (type II of the classification pointed out above). Moreover, $B_{min} \to 0$ when Z increases and r_{min} decreases when Z increases, as we would expect from Eq. (6), i.e., $B(r) \sim B_b(r)$ as $Z \to \infty$. To

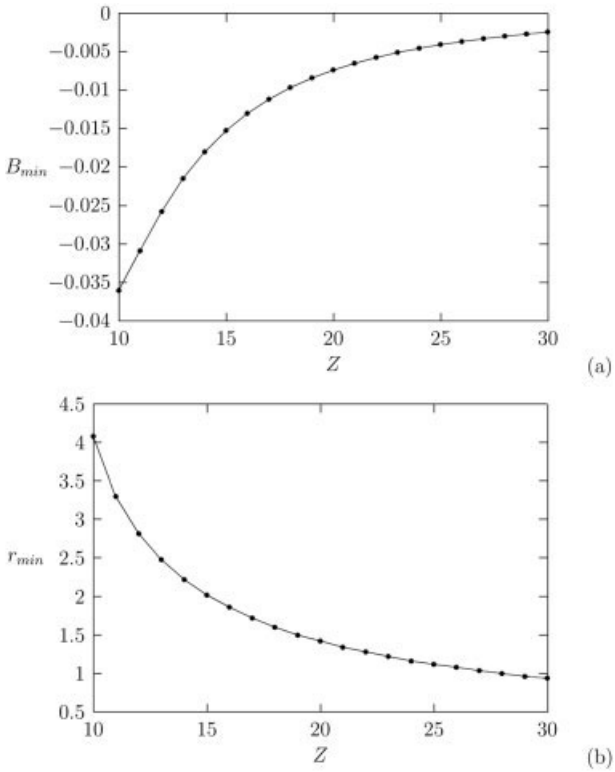

FIGURE 1. Minimum characteristics of $B(r)$ for the Ne isoelectronic serie with nuclear charge $Z = 10$–30. (a) Location of the minimum $r_{\min}$. (b) Value $B_{\min}$ of $B(r)$ at $r_{\min}$. Atomic units are used.

clarify this behavior, Figure 1(a) and 1(b) shows the $B_{\min}$ and $r_{\min}$ values, respectively, when the value of Z increases in the Ne-isoelectronic series.

3. Atomic and Bare Coulomb Field Reciprocal Form Factors

Let us study the effect of the interelectronic repulsion term on the extremum characteristics of the $B(r)$ function for an N-electron atom. In doing so, we first classify, according to the number of local extrema of $B(r)$, the systems with $N = 1$–103 electrons moving in a BCF potential with nuclear charge $Z = N$.

The spherically averaged reciprocal form factor $B_b(r)$ of a BCF atom is given by

$$B_b(r) = \sum_{n,l} N_{nl} B_{nl}(r),$$

where the sum running over all the occupied subshells (n, l), and N_{nl} and $B_{nl}(r)$ are, respectively, the number of electrons and the hydrogenic reciprocal form factor of the subshell (n, l). Normalization of $B_{nl}(r)$ is given by $B_{nl}(0) = 1$. Consequently,

$$B_b(0) = \sum_{n,l} N_{nl} = N.$$

The functions $B_{nl}(r)$ are known [3] to be the product of the exponential $e^{-r/n}$ and a polynomial $P_{2n}(r)$ of degree $2n$ on the radial distance r, whose coefficients are analytically expressed in terms of the quantum numbers (n, l). Hence, all calculations involving $B_b(r)$ in the present work have been analytically carried out.

The number of maxima and minima of $B_b(r)$ (apart from the absolute maximum at $r = 0$), corresponding to systems within the range $N = 1$–103, allows us to classify them into several categories, which are exactly the same that appear when classifying $B(r)$ for neutral atoms [3]. Above we have called these categories types I, II, III-a, and III-b:

Type I: Systems with $N = 1$–16, 19–33, 49–51, and 82 belong to this type.

Type II: This behavior is displayed by systems with $N = 17$–18, 34–36, 52–54, and 83–86.

Type III: This is the case for BCF atoms with $N = 37$–48, 55–81, and 87–103. For $N = 46$ and 77, $B_{\min} < 0$, so that they belong to type III-a, while for $N = 37$–45, 47–48, 55–76, 78–81, and 87–103, $B_{\min} > 0$, so that they are systems of type III-b.

Concerning the present classification, a strong relationship is observed between the category to which a system belongs and shell filling. Such a connection can be described by means of simple rules involving the quantum numbers of the highest occupied subshells. Let us denote by n_s, n_p, and n_d the principal quantum numbers n of the highest occupied subshells with symmetry $l = s, p, d$, respectively, and also ne_s, ne_p, and ne_d the number of electrons in such subshells, respectively. Define the differences $\Delta_{sp} \equiv n_s - n_p$ and $\Delta_{pd} \equiv n_p - n_d$. It is observed that:

1. The $B_b(r)$ function is of type III-a if and only if $\Delta_{sp} = \Delta_{pd} = 0$.
2. When $\Delta_{sp} = 0 < \Delta_{pd}$, the system belongs to type I [if $ne_p(n_p + 1) \leq 18$] or type II (otherwise).
3. For $\Delta_{sp} = 1$, the function is of type I (if $n_p \leq 3$) or type III-b (if and only if $n_p \geq 4$).
4. All systems with $\Delta_{sp} = 2$ belong to type I.

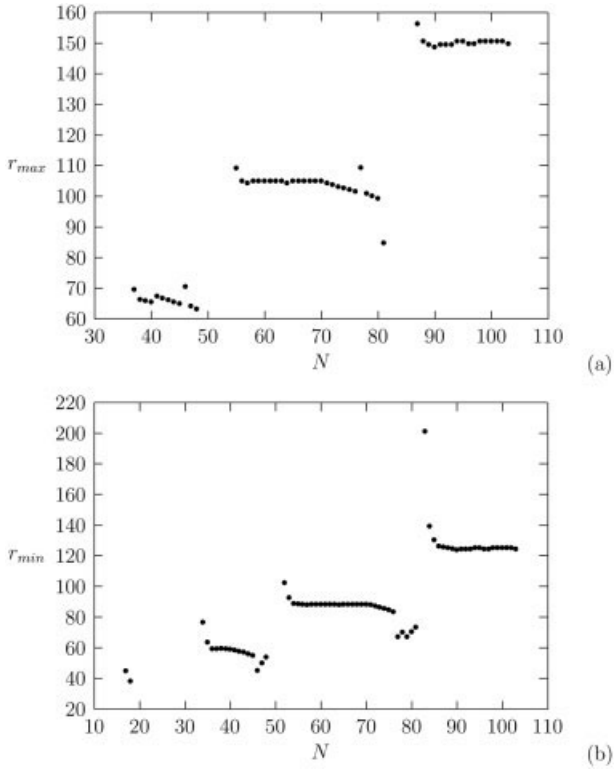

FIGURE 2. Locations of absolute extrema of $B(r)$ for neutral atoms with $N = 1$–103. (a) Maximum r_{max}. (b) Minimum r_{min}. Atomic units are used.

There is only one exception to the above generic rules. According to them, the function $B_b(r)$ for $N = 81$ is expected to be of type I, while it really belongs to type III-b.

Let us study the extremum characteristics of $B_b(r)$ for type II and III categories. It is observed that, within those categories, location of minimum ($r_{\min}$) and maximum ($r_{\max}$) mainly depends on quantum numbers and occupation number of highest subshell. This fact is especially clear in Figure 2. Concerning $r_{\max}$ for type III atoms, its values are grouped into three different ranges [see Fig. 2(a)], each of them associated with one of the values $n_p = 4, 5, 6$ (with $\Delta_{sp} = 1$ in the three cases). Exceptions are $N = 46, 77, 81$ (with $\Delta_{sp} = 0$), which clearly appear away from the corresponding range. Additionally, a small gap is observed for cases in which the highest s-subshell is half-filled ($N = 37, 55, 87$).

Similar comments can be made concerning $r_{\min}$, as displayed in Figure 2(b). Now, a fourth range appears associated with the value $n_p = 3$ ($N = 17, 18$). Additionally, ranges are wider than those of $r_{\max}$ due to the inclusion now of type II systems. Gaps on the left of a range again correspond to an incompletely filled subshell (highest p-subshell, in this case), while those on the right, corresponding to $N = 46$–48 and 77–81, again involve the aforementioned exceptions for $r_{\min}$, $N = 46, 77, 81$. The present analysis of the BCF reciprocal form factor for the systems considered here allows us to state that the values reached by the function $B_b(r)$ at the extrema, i.e., $B_{\min}$ and $B_{\max}$, are also strongly dependent on the quantum numbers n_s, n_p, n_d and the associated occupation numbers. It is also interesting to study the weight of the interelectronic repulsion term on the structural characteristics of the reciprocal form factor.

We have numerically analyzed the structural properties of N-isoelectronic series for $N = 3$–9 (neutral atoms and first 20 cations of each ground state atom) using the analytical Hartree–Fock wave functions [8]. For Li and Be isoelectronic series, the reciprocal form factor is always a decreasing function. For B isoelectronic series, $B(r)$ is of type II, i.e., it reaches a minimum $B_{\min}$ at $r_{\min}$ for $Z = 5$–8 and is of type I, i.e., it is a decreasing function, for $Z = 9$–25. For C isoelectronic series, $B(r)$ is of type II for $Z = 6$–13 and type I for $Z = 7$–26. For N, O, and F isoelectronic series, $B(r)$ is of type II for all cases studied. We would like to remark that $B_{\min} \to 0$ when Z increases in all cases that belong to type II, as we can observe in Figure 3(a). In contrast, $r_{\min}$ decreases when Z increases in almost all type II cases, as shown in Figure 3(b) (there are three exceptions for this behavior: $Z = 8$ in the B-isoelectronic series, $Z = 12$ for the C-isoelectronic series, and $Z = 23$ for the N-isoelectronic series), and $B(r) \sim B_b(r)$ as $Z \to \infty$. This behavior shows that the nonmonotonicities in $B(r)$ are due to terms of higher order than one in the Z^{-1} expansion [Eq. (6)] of $B(r)$.

Now, let us analyze the changes in the BCF classification when adding the interelectronic repulsion term, by comparing it with the known similar one [3] corresponding to ground-state neutral atoms.

There are no modifications for a group of 39 atoms ($N = 1$–4, 11–12, 17–30, 34–36, 42, 44–48, 52–54, 78–80, 83–86); i.e., their $B(r)$ and $B_b(r)$ functions belong to the same type.

A large group of systems (the 46 atoms with $N = 37$–41, 43, 55–77, 87–103) loses the bimodal character (type III) when including the repulsion term, giving rise to a monotonically decreasing (type I) $B(r)$.

For a smaller set of 17 atoms ($N = 5$–10, 13–16, 31–33, 49–51, 82), the type I BCF reciprocal form

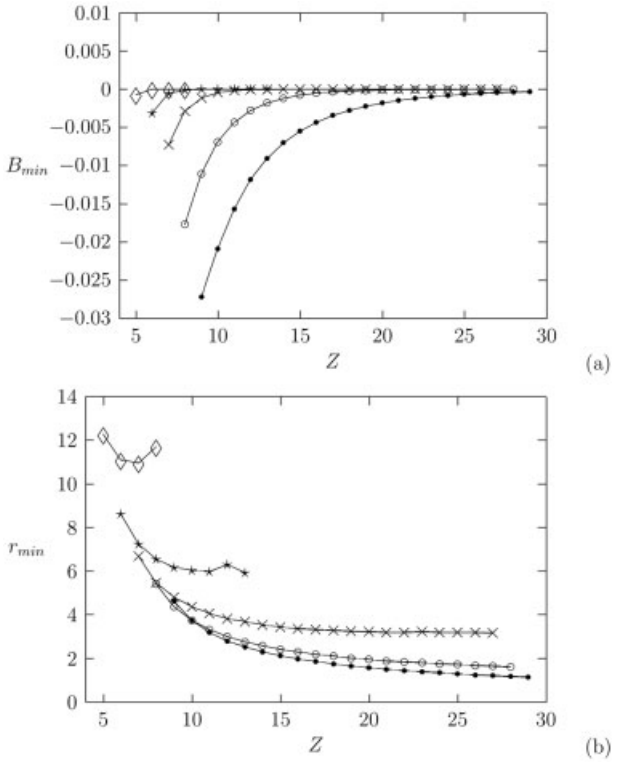

FIGURE 3. Minimum characteristics of type II $B(r)$ for isoelectronic series of B (◇; $Z = 5$–8), C (★; $Z = 6$–13), N (×; $Z = 7$–27), O (○; $Z = 8$–28) and F (●; $Z = 9$–29). Atomic units are used.

factor transforms into a type II one. Again, the system $N = 81$ appears as an special case: the type III-b BCF reciprocal form factor transform into a type II one.

Summarizing, there are two important kinds of modification when adding the interelectronic repulsion term: from type I to type II, and from type III to type I. Let us discuss both cases in terms of shell filling.

Concerning the first one, it is observed that such a change on the structural character of $B(r)$ appears if and only if $\Delta_{pd} > 0 = \Delta_{sp}$ with a low occupation number ne_p of the highest occupied p-subshell. In the present framework, it is empirically induced that "low" means $ne_p(n_p + 1) \leq 18$. The only exception to this rule, as mentioned before, corresponds to $N = 81$, which does not have a type I $B_b(r)$.

In contrast, the change from type III to type I should be discussed by distinguishing the sign of $B_{\min}$ in the type III case. The only system for which the starting function is a type III-a one corresponds to $N = 77$ (with $\Delta_{sp} = \Delta_{pd} = 0$ and $n_p = 5$), characterized by the anomalous shell filling $6s^0 5d^9$. In the remaining cases, $\Delta_{sp} = 1$ for any $n_p \geq 4$ and, additionally, $ne_d \leq 6$ if $n_p = 4$, 5 [except $N = 42$, with $ne_d = 5$ and $n_p = 4$, having a nonvarying $B(r)$].

4. Conclusions

In the present work it has been shown that the reciprocal form factor in a BCF $B_b(\mathbf{r})$ for closed-shell atoms is a spherically symmetric, positive, and decreasing function of r. The study of the reciprocal form factor of 2- and 10-electron atomic isoelectronic series in a Roothan–Hartree–Fock framework reveals that the nonmonotonicities in $B(r)$ arise from those terms of order higher than $B_b(r)$ in the Z^{-1} perturbation expansion of $B(r)$ [see Eq. (6)], so that $B(r)$ tends to $B_b(r)$ when Z increases.

The spherically averaged RFF $B_b(r)$ is classified into three categories for $Z = N = 1$–103. This classification can be described in terms of some rules involving the quantum numbers of highest occupied subshells. Additionally, the study of the reciprocal form factor of several isoelectronic series of open-shell atoms $B(r)$ again shows that $B(r)$ tends to $B_b(r)$ when Z is increasing. Finally, the analysis of the weight of the interelectronic repulsion term on the structural characteristics of $B(r)$ for neutral atoms with $N = 1$–103 shows that three different situations occur: (i) for 39 atoms, $B(r)$ and $B_b(r)$ belong to the same type; (ii) for 46 atoms, $B_b(r)$ loses the bimodal character when the interelectronic term is included, $B(r)$ being a monotonically decreasing function; and (iii) for 17 atoms, $B(r)$ of type II tends to a monotonically decreasing $B_b(r)$ as Z is increasing.

References

1. Angulo, J. C.; Koga, T.; Romera, E.; Dehesa, J. S. J Mol Struct (Theochem) 2000, 501–502, 177.
2. Koga, T.; Matsuyama, H.; Romera, E.; Dehesa, J. S.; Thakkar, A. J. Phys Rev A 1999, 59, 4805.
3. Romera, E.; Angulo, J. C. J Chem Phys 2004, 120, 7369.
4. Weyrich, W.; Pattison, P.; Williams, B. G. Chem Phys 1979, 41, 271.
5. Thakkar, A. J.; Simas, A. M.; Smith, V. H., Jr. Chem Phys 1981, 63, 175.
6. March, N. H. Phys Rev A 1986, 33, 88.
7. Smith, V. H., Jr.; Robertson, D. D.; Tripathi, A. N. Phys Rev A 1990, 42, 61.
8. Koga, T.; Omura, M.; Teruya, H.; Thakkar, A. J. J Phys B 1995, 28, 3113.