Monotonicity of the electron momentum density for atomic closed shells in a bare Coulomb field

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For the bare Coulomb potential energy $-Ze^2/r$, it is shown that the total electron momentum density $\overline{\Pi}_0(p)$ for an arbitrary number of closed shells is a monotonically decreasing function of p. Since it is known that $\Pi(p)$ is nonmonotonic for all atomic ground states with completely closed shells except helium, the implication of this result is that the observed nonmonotonicity is due to terms of higher order than $\Pi_0(p)$ in Z^{-1} perturbation theory. Numerical calculations are presented and analyzed for the ten-electron isoelectronic series.

I. INTRODUCTION

Although not yet formally proven,[1,2] there is numerical evidence[3-5] that the spherically averaged charge density $\overline{\rho}(r)$ is a monotonically decreasing function of r for atomic ground states. The corresponding quantity in momentum space, the spherically averaged momentum density $\overline{\Pi}(p)$, is known[6-11] to be a monotonic function of p for some atomic systems and nonmonotonic for others. In particular, for all of the noble gases except helium, $\overline{\Pi}(p)$ exhibits nonmonotomic behavior. As shown by Westgate, Simas, and Smith[11] in their thorough study of the behavior of $\overline{\Pi}(p)$ for the atoms from hydrogen to uranium, it is the orbitals of the two outermost shells which are responsible for the appearance of nonmonotonic behavior. There are two distinct types of maxima by which the nonmonotonic behavior may be characterized. The first type occurs for values of p in the slower momentum region $(0.0,0.6)\hbar a_0^{-1}$ and a second type which occurs in the faster momentum region $(0.7,1.6)\hbar a_0^{-1}$ and for which $\Pi(p_{\max})$ may be very small or large as compared to the momentum density at the origin.

March[1] has recently established that in the case of the bare Coulomb potential energy $(v=-Ze^2/r)$ $\overline{\rho}(r)$ is a monotonically decreasing function of r for any arbitrary number N of closed shells, i.e., $d\overline{\rho}/dr<0$. This result for the bare Coulomb model, which is the zeroth-order contribution[1,12,13] in a Z^{-1} expansion,[14-16] is in agreement with the numerical evidence, mentioned above, for the atomic ground states.

It is the purpose of the present paper to consider the behavior of the momentum density $\overline{\Pi}(p)$ for the bare Coulomb model. We shall do that in Sec. II. In Sec. III, we present the results of numerical calculations for the ten-electron isoelectronic series and discuss them in the light of our result for the bare Coulomb model.

II. BARE COULOMB FIELD

For N closed shells, the spherically averaged momentum density, $\overline{\Pi}_0(p)$, may be written[12,17] as a sum[18] over the contribution from each of the N closed shells, i.e.,

$$\overline{\Pi}_0(p)=\sum_{j=1}^{N}\frac{16p_j^5j^2}{\pi^2(p_j^2+p^2)^4}=\sum_{j=1}^{N}j^2\overline{\Pi}(p_j,p)\ , \tag{1}$$

where

$$\overline{\Pi}(p_j,p)=16p_j^5/\pi^2(p_j^2+p^2)^4\ , \tag{2}$$

$p_j=Z/j$ and the number of electrons N_e,

$$N_e=\sum_{j=1}^{N}2j^2=\frac{N(N+1)(2N+1)}{3}\ . \tag{3}$$

Differentiation yields

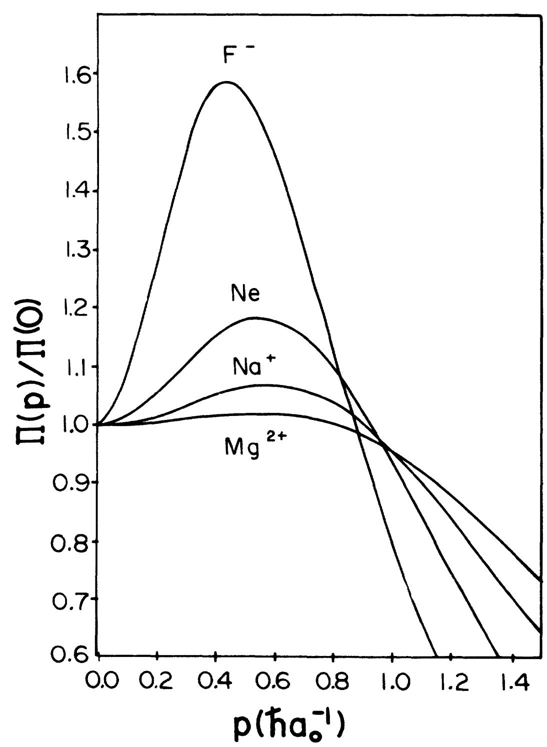

FIG. 1. The spherically averaged momentum density $\overline{\Pi}(p)$ for the ten-electron atomic ions.

$$[\overline{\Pi}_0(p)]' = -p\left[\sum_{j=1}^{N} \frac{128 p_j^5 j^2}{\pi^2(p_j^2+p^2)^5}\right], \tag{4}$$

which vanishes at the origin and which is less than zero for all positive p. Hence $\overline{\Pi}_0(p)$ is a monotonically decreasing function of p.

III. THE TEN-ELECTRON ISOELECTRONIC SERIES

Since the bare Coulomb field model for N closed shells yields the zeroth-order term in the Z^{-1} expansion[16] of $\overline{\Pi}(p)$,

$$\overline{\Pi}(p) = \overline{\Pi}_0(p) + Z^{-1}\overline{\Pi}_1(p) + Z^{-2}\overline{\Pi}_2(p) + \cdots \tag{5}$$

for a 2-,10-,28-, . . . , electron system; the result obtained in Sec. II,

$$[\overline{\Pi}_0(p)]' < 0, p > 0 \tag{6}$$

means that in the particular case of the ten-electron isoelectronic series the observed nonmonotonicity[8–11] for neon is due to one or more of the correction terms to $\overline{\Pi}_0(p)$ in Eq. (5) and that the nonmonotonicity would disappear as $Z \to \infty$. Whether one is discussing the exact or Hartree-Fock (HF) $\overline{\Pi}(p)$, an expansion of the form (5) is applicable.

We examine this by considering the results of our calculations of $\overline{\Pi}(p)$ using the self-consistent-field (SCF) wave functions of Clementi and Roetti[19] for various members of the ten-electron series (e.g., F^-, Ne, Na^+, Mg^{2+}, Al^{3+}, etc.). In Fig. 1, $\overline{\Pi}(p)/\overline{\Pi}(0)$ is plotted for several members of the sequence. Examination of this figure shows that the degree of nonmonotonicity, as measured by $\overline{\Pi}(p_{\max})/\overline{\Pi}(0)$, decreases towards 1 (the value for a monotonic function) as Z increases. The value of the location of the maximum, $p_{\max}$, becomes successively smaller as Z increases for $Z \geq 11$ while $p_{\max}/Z$ decreases towards zero (the location of the maximum for a monotonic function) as Z increases for $Z \geq 10$. Hence the nonmonotonicity disappears as $Z \to \infty$.[20]

IV. SUMMARY

We have shown that the momentum density of the bare Coulomb model for the ground states of fully closed-shell atomic systems is monotonically decreasing. In the specific case of the ground states of the ten-electron atomic systems the HF results indicate that the degree of nonmonotonicity decreases as Z increases. Since the monotonic $\overline{\Pi}_0(p)$ of the bare Coulomb model is the asymptotic limit for this series, the observed deviations from nonmonotonicity are due to $\overline{\Pi}_{HF}(p) - \overline{\Pi}_0(p)$.

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[1]N. H. March, Phys. Rev. A **33**, 88 (1986).

[2]M. Hoffman-Ostenhoff and T. Hoffman-Ostenhoff, Phys. Rev. A **16**, 1782 (1977), have shown that within the infinite nuclear mass approximation, the atomic $\overline{\rho}(r)$ is a convex monotonically decreasing function outside a sphere whose radius depends on the ionization energy and the electron-nucleus attraction. See also M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[3]G. Sperber, Int. J. Quantum Chem. **5**, 189 (1971).

[4]H. Weinstein, P. Politzer, and S. Srebrenik, Theor. Chim. Acta **38**, 159 (1975).

[5]A. M. Simas, R. P. Sagar, A. C. T. Ku, and V. H. Smith, Jr., Can. J. Chem. **66**, 1923 (1988).

[6]W. Weyrich, P. Pattison, and B. G. Williams, Chem. Phys. **41**, 271 (1979).

[7]A. J. Thakkar, A. M. Simas, and V. H. Smith, Jr., Chem. Phys. **63**, 175 (1981).

[8]A. J. Thakkar, J. Chem. Phys. **76**, 747 (1982).

[9]A. Harmalkar, A. M. Simas, V. H. Smith, Jr., and W. M. Westgate, Int. J. Quantum Chem. **23**, 811 (1983).

[10]S. R. Gadre, S. J. Chakravorty, and R. K. Pathak, J. Chem. Phys. **78**, 4581 (1983).

[11]W. M. Westgate, A. M. Simas, and V. H. Smith, Jr., J. Chem. Phys. **8**, 4054 (1985).

[12]M. S. Yusaf, G. P. Lawes, and N. H. March, Int. J. Quantum Chem. **17**, 833 (1980).

[13]N. H. March, Phys. Lett. **111A**, 47 (1985).

[14]D. Layzer, Ann. Phys. (NY) **8**, 271 (1959).

[15]J. Linderberg, Phys. Rev. **121**, 816 (1961).

[16]S. R. Singh and V. H. Smith, Jr., Z. Phys. **255**, 83 (1972).

[17]V. Fock, Z. Phys. **98**, 145 (1936).

[18]It is interesting that the contribution from shell j is of the form of a 1s contribution [P. Kaijser and V. H. Smith, Jr., Adv. Quantum Chem. **10**, 37 (1977)] with the appropriate p_j and weighted by j^2.

[19]E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[20]It should be noted that the present results are for N_e fixed and Z variable. If $N_e = Z$, the Thomas-Fermi (TF) theory, which is asymptotically exact [E. H. Lieb and B. Simon, Adv. Math. **23**, 22 (1977)] as $Z \to \infty$, has $\overline{\Pi}(p) = (Z^2/3\pi^2)(\frac{1}{2}p^2 + |E_F|)^{-3}$, where $E_F = -Z^{4/3}/18^{1/3}$. This expression is nonmonotonic as well. If one considers the plots of $Z^{2/3}\overline{\Pi}_0(p)$ vs $pZ^{-2/3}$, one notes that Eq. (1) becomes indistinguishable from the TF expression above as N_e increases.