Nonmonotonicity of the atomic electron momentum density

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The observed nonmonotonic behavior of the atomic electron momentum density of neon and some members of its isoelectronic sequence at the Hartree-Fock level is investigated. Further evidence is provided by showing that the nonmonotonicity observed for the neon series at the Hartree-Fock level is still present when a cusp condition and the correct asymptotic behavior are imposed onto the Hartree-Fock wave function. This result is also observed for the results obtained from highly correlated configuration-interaction wave functions. Furthermore, we substantiate the argument that the observed nonmonotonicities are most probably due to higher-order terms in the Z^{-1} perturbation theory.

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I. INTRODUCTION

Momentum-space properties, and in particular momentum-space densities, $\Pi(\mathbf{p})$, are gaining increasing interest since the advent of techniques such as Compton scattering [1] and $(e,2e)$ or electron momentum spectroscopy (EMS) [2] which allow the experimental determination of this property. Hence, besides the theoretical interest, there is a need for a complete characterization of these densities in order to substantiate experimental results.

One interesting aspect of the atomic ground-states' spherically averaged momentum densities is the nonmonotonic behavior for some elements of the periodic table. This is quite unlike the more familiar position space-charge density where, although not formally proven, except for some regions of space [3,4], there is numerical evidence at the Hartree-Fock level for ground states to suggest monotonicity [5–7].

There have been several investigations [8–11] into the nature of the nonmonotonicities in the spherically averaged momentum density, $\Pi(p)$, which has led to the analysis of related quantities such as the radial momentum distribution function, $I(p)=4\pi p^2\Pi(p)$ [8,12], and the Laplacian $\nabla^2\Pi(p)$ [13], in the context of shell structure analysis.

Analysis into the nature of the nonmonotonicity at the Hartree-Fock (HF) level [9] revealed that it is the orbitals of the two outermost shells which are responsible for the nonmonotonicities. Furthermore, the maxima may be classified into two distinct types; i.e., those that occur in the *slow* region (0.0, 0.6) $\hbar a_0^{-1}$ and those in the *fast* region (0.7, 1.6) $\hbar a_0^{-1}$ [9]. Also, the appearance of nonmonotonicities in $\Pi(p)$ of atoms seems to be dependent on the basis set used [8] with nonmonotonicities appearing in better-quality wave functions at the HF level while the lesser-quality wave functions produce monotonic momentum densities. Indeed, these results raise interesting questions about the physical validity of these nonmonotonicities and the possibility that this effect is an artifact of the basis set or of a wave function that does not obey known constraints such as the cusp condition [14] and asymptotic behavior [3,4]. We hope to address these conjectures in this paper.

Smith, Robertson, and Tripathi [15] have shown that for the bare Coulomb potential model [16], $-Ze^2/r$, the total electronic momentum density for an arbitrary number of closed shells, $\Pi_0(p)$, is a monotonically decreasing function of p. Since all closed-shell systems (with the exception of helium) display nonmonotonicities at the HF level, it was suggested that the observed nonmonotonicities were due to higher-order terms occurring in the Z^{-1} perturbation expansion [15,17], i.e.,

$$\Pi(p)=\Pi_0(p)+Z^{-1}\Pi_1(p)+Z^{-2}\Pi_2(p)+\cdots \tag{1.1}$$

for 2,10,18,... electron systems, where the bare Coulomb model for N closed shells corresponds to the zeroth-order term, $\Pi_0(p)$. Therefore as $Z\rightarrow\infty$, the contribution from $\Pi_0(p)$ should dominate, and the nonmonotonicity disappears. This claim was substantiated by calculations at the HF level for the neon isoelectronic sequence, by noting that the degree of nonmonotonicity as characterized by $\Pi(p_{\max})/\Pi(0)$ decreased towards one as Z increases. Likewise, $p_{\max}$ becomes smaller as Z is increased for $Z\geq 11$, and $p_{\max}/Z$ decreases to zero as Z increases for $Z\geq 10$ [15].

The purpose of this paper is to investigate numerically the nonmonotonicities in the momentum density of the neon isoelectronic sequence with the aid of highly accurate configuration-interaction (CI) wave functions that have recently become available [18]. These functions represent the final stage of a convergent sequence in the *position-space* charge density. This type of procedure, recently used in the construction of beryllium and lithium isoelectronic sequences, has been shown to yield highly accurate one-electron momentum-space quantities [19,20]. In this manner, we hope to ascertain the effects of electron correlation, beyond the HF framework, on the nonmonotonic behavior. We will also examine the claim (with the CI functions) that the nonmonotonicities arise from higher-order terms in the Z^{-1} perturbation expansion.

II. RESULTS

We have computed the positions of the maximum in $\Pi(p)$, $p_{\max}$, along with the quantity, $\Pi(p_{\max})/\Pi(0)$ from

TABLE I. Values of p_{max} and $II(p_{max})/II(0)$ computed from HF and CI wave functions for the neon isoelectronic sequence.

	Hartree-Fock		Configuration interaction	
Atom	p_{max}	$II(p_{max})/II(0)$	p_{max}	$II(p_{max})/II(0)$
F^-	0.441 76	1.587 5	0.435 31	1.662 71
Ne	0.546 26	1.173 4	0.542 34	1.184 54
Ne[a]	0.553 60	1.168 1		
Ne[b]	0.542 85	1.158 1		
Na^+	0.588 62	1.068 0	0.590 44	1.073 2
Mg^{2+}	0.552 68	1.021 5	0.552 10	1.022 1
Al^{3+}	0.423 07	1.003 6	0.422 12	1.003 6

[a]Values obtained from a wave function constructed [22] with the addition of diffuse p orbitals to the Clementi and Roetti basis set [21].

[b]Values obtained from a wave function constructed [22] with the cusp condition and asymptotic behavior imposed as constraints.

the self-consistent-field (SCF) functions of Clementi and Roetti [21] for members of the neon isoelectronic sequence. In addition, with the ATOMSCF computer program in the MOTECC package [22], we have constrained a neon HF wave function to satisfy the cusp [14] and asymptotic behavior [3] conditions. We have also obtained an extended neon HF wave function by adding to the basis set [21] two diffuse p-type orbitals. The p_{max} and $II(p_{max})/II(0)$ values were also obtained from these functions. These values were also calculated from highly correlated CI wave functions. The CI wave function for neon has been previously documented [23]. For the other members of the sequence, the wave functions were built in $\{7s,7p,4d,4f,2g\}$ basis sets which produce CI expansions of 723 terms (with single and double excitations) accounting for over 92% of the correlation energy [18].

The results are presented in Table I. Note that for the higher-Z members of the sequence (Si^{4+},P^{5+},S^{6+},Cl^{7+}), nonmonotonicities in either the HF or CI wave functions were not found.

First of all, the nonmonotonicity present at the HF level in neon is still present when the cusp and asymptotically constrained HF wave function is used. This is also observed with the extended HF wave function that includes diffuse p orbitals. The values of p_{max} and $II(p_{max})/II(0)$ do not change significantly among the three wave functions. These results thus support the argument that the nonmonotonicity is neither a problem of the basis set nor of wave-function quality at the near-HF level. Additionally, in consideration of all members, one can see that the nonmonotonicities present at the near HF level are always present at the CI level. Also, the positions of the maxima and $II(p_{max})/II(0)$ show small changes on comparison of HF and CI values, indicating a small dependence on electron correlation for these values. The $II(p_{max})/II(0)$ value is slightly larger for the CI than in the HF case. These results serve to substantiate our argument that these nonmonotonicities are not just a consequence of the HF framework, but rather are also present when dynamic electron correlation is taken into account.

The degree of nonmonotonicity as characterized by $II(p_{max})/II(0)$ is seen to decrease (a value of one means a monotonic momentum density) as Z increases. This behavior, present at the HF level, is also present at the CI level and lends weight to the argument [15] that the nonmonotonicity is a result of higher-order terms in Z^{-1} perturbation theory. The p_{max} and p_{max}/Z values at the CI level are also observed to display similar trends to the HF case when going across the isoelectronic sequence.

III. SUMMARY

We have attempted to establish that the nonmonotonicities in $II(p)$ of the neon atom, present at the HF level, are not a consequence of the basis set or wave-function quality. We have shown this by comparison of results obtained from a cusp and asymptotically constrained wave function and one where diffuse orbitals have been included in the basis set. We have gone beyond the HF level and shown that the nonmonotonicities are also present with CI quality wave functions, thus establishing that this behavior is not an artifact of the HF model. Lastly, our results support the argument that the nonmonotonicities arise from the higher-order terms in the Z^{-1} perturbation expansion of $II(p)$.

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