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Letter

Analytical Hartree–Fock wave functions for the atoms Cs to Lr

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Abstract. Analytical approximations to Hartree–Fock wave functions are constructed using Slater-type functions for the ground states of all 49 neutral atoms from Cs ($Z = 55$) to Lr ($Z = 103$). The current compilation is more extensive and more accurate than previous ones. The wave functions are available upon request from the authors or from the Web page http://www.unb.ca/chem/ajit/download.htm on the Internet.

Key words: Hartree–Fock wave functions – Slater–type functions – Atoms Cs to Lr

1 Introduction

Atomic wave functions are used to help solve many problems. The Hartree–Fock (HF) model [1] is a conventional choice for the construction of comprehensive tables of atomic wave functions because HF wave functions are accurate enough for many purposes. Moreover, they serve as a good starting point for the construction of more accurate wave functions. Although atomic HF wave functions can be obtained in numerical form, it is more convenient to tabulate and use wave functions expressed in some analytic form. Procedures for obtaining analytical approximations to HF wave functions in which the radial orbitals are expanded in a set of basis functions, such as Slater-type functions (STFs), are well developed [2–5].

Many compilations of analytical HF (AHF) wave functions built with STFs have been published for the lighter atoms from He ($Z = 2$) to Xe ($Z = 54$) [6–12]; however, there are only two such compilations [13, 14] for the heavier atoms from Cs ($Z = 55$) to U ($Z = 92$) and none at all for the atoms from Np ($Z = 93$) to Lr ($Z = 103$). The purpose of this letter is to report AHF wave functions for the ground states of the 49 atoms from Cs ($Z = 55$) to Lr ($Z = 103$). The current compilation is more extensive and more accurate than the previous ones. Hartree atomic units are used throughout.

2 Computational method

We worked with the experimental ground states [15, 16] in all cases. This means that we consider states different from those used in previous work for the Ce and U atoms. For Ce ($Z = 58$) we consider the $([\mathrm{Xe}]6s^2\ 4f\ 5d)^1\mathrm{G}$ state as opposed to the $([\mathrm{Xe}]6s^2\ 4f\ 5d)^3\mathrm{H}$ state considered earlier. For U ($Z = 92$) we consider the $([\mathrm{Rn}]7s^2\ 5f^3\ 6d)^5\mathrm{L}$ state instead of the $([\mathrm{Rn}]7s^2\ 5f^4)^5\mathrm{I}$ state used earlier.

Our experience with atomic wave functions led us to use $2n_{\mathrm{occ},l} + l + 1$ STFs for each angular momentum quantum number, l, where $n_{\mathrm{occ},l}$ is the number of occupied radial orbitals of that symmetry. A search was made to find an optimal choice of STF quantum numbers that was applicable to as many atoms as possible with the same occupied subshells. At each step in this search, the exponents of the STFs were optimized by minimizing the total energy, E, with the conjugate direction algorithm [17] incorporated in our version [18] of the ATOM program [19]. After wave functions had been obtained for a complete row of the periodic table, we examined the behavior of the exponents and quantum numbers as a function of the atomic number, Z. If we detected nonsmooth behavior or expansion coefficients with an abnormally large magnitude, $|c_i| > 3$, then we perturbed the nonlinear parameters and restarted the optimizations for the offending wave functions. This process was repeated as often as necessary, but smooth behavior could not always be achieved.

Global optimization of large numbers of nonlinear parameters is never complete. At some point, one has to stop and accept the results as they are. We stopped after 6 man-years of effort and uncounted hours of computing time. The next section is devoted to examining the quality of our best ground-state wave functions for the 49 atoms from Cs to Lr.

3 Results and discussion

We need to examine our new wave functions, hereafter referred to as K98, and compare them with the MM81 wave functions of McLean and McLean [13] and both the reoptimized (KT93R) and the improved wave functions (KT93I) of Koga and Thakkar [14]. Note that there are no MM81, KT93R or KT93I wave functions for $Z > 92$. The appropriate reference for AHF wave functions is the numerical HF (NHF) limit; therefore, we

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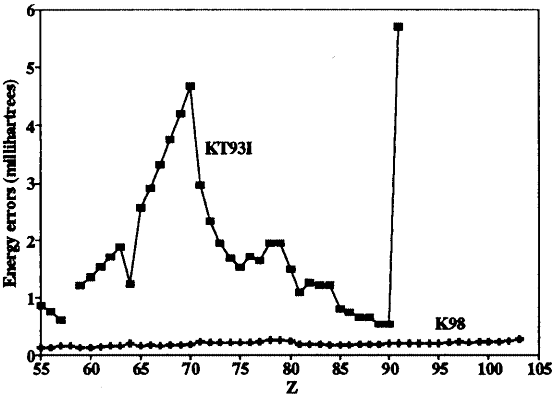

Fig. 1. Energy errors (in millihartrees) relative to numerical Hartree–Fock values

used NHF wave functions and properties for all 49 species computed [20] with our modified and extended version of MCHF72 [21]. All comparisons among the various AHF wave functions are made by examining errors, with respect to the NHF reference, averaged over 36 atoms in the MM81, KT93R and KT93I cases and over 49 atoms in the K98 case.

The energy errors of the current K98 wave functions are compared with the previous best KT93I ones in Fig. 1. In each atom, the lowest energy is predicted by the K98 wave function. Moreover, the errors in the K98 energies vary more smoothly with Z.

Average errors in the total energies and the energies of the outermost orbitals of each symmetry are compared in Table 1. Observe that the total energy errors decrease from 28.5 millihartrees to 0.2 millihartrees in the expected order: MM81, KT93R, KT93I and K98. The errors in the outermost orbitals of each symmetry decrease in a slightly different order: KT93R, MM81, KT93I and K98. Clearly, the improved total energies of the KT93R wave functions were obtained at the expense of the energies of the outermost orbitals.

We investigate the quality of the electron density at the nucleus, $\rho(0)$, the position moments $\langle r^n \rangle, n = -2, -1, \ldots, 4$, the electron momentum density at the momentum-space origin, $\Pi(0)$, and the momentum moments $\langle p^n \rangle, n = -2, -1, \ldots, 4$ in Table 2. The lowest average errors are found for the current K98 wave functions for all properties except $\langle r^{-2} \rangle$, for which KT93I is slightly more accurate. The KT93I wave functions are the second-most accurate for the properties other than $\langle r^3 \rangle$, $\langle r^4 \rangle$, $\Pi(0)$, $\langle p^{-2} \rangle$ and $\langle p^{-1} \rangle$, for which the MM81 wave functions are the second-most accurate. The MM81 wave functions are better than the KT93I ones at describing properties that depend on the outer reaches of the electron density and the related inner region of the electron momentum density.

Table 1. Average energy errors in millihartrees

Energy	MM81	KT93R	KT93I	K98
Total	28.49	26.03	1.84	0.19
Outer *s* orbital	0.25	0.69	0.17	0.03
Outer *p* orbital	3.02	3.69	0.57	0.05
Outer *d* orbital	5.14	5.85	0.79	0.04
Outer *f* orbital	8.26	9.06	0.91	0.05

Table 2. Average percentage errors of various properties

Property	MM81	KT93R	KT93I	K98
$\rho(0)$	0.0360	0.0211	0.0025	0.0010
$\langle r^{-2} \rangle$	0.0084	0.0044	0.0002	0.0004
$\langle r^{-1} \rangle$	0.0012	0.0015	0.0002	0.00004
$\langle r \rangle$	0.0320	0.0603	0.0062	0.0017
$\langle r^2 \rangle$	0.0560	0.2531	0.0557	0.0099
$\langle r^3 \rangle$	0.1724	0.7899	0.2841	0.0332
$\langle r^4 \rangle$	0.3800	1.8365	0.8022	0.0933
$\Pi(0)$	0.9403	2.9132	1.8429	0.3573
$\langle p^{-2} \rangle$	0.3368	1.3696	0.7006	0.1155
$\langle p^{-1} \rangle$	0.0675	0.2731	0.0742	0.0102
$\langle p \rangle$	0.0052	0.0058	0.0015	0.0014
$\langle p^2 \rangle$	0.0004	0.0002	0.00002	0.00001
$\langle p^3 \rangle$	0.0136	0.0071	0.0013	0.0013
$\langle p^4 \rangle$	0.4171	0.3894	0.3569	0.2972

4 Concluding remarks

Analytical approximations to HF wave functions have been constructed for the ground states of all 49 atoms from Cs to Lr. The current compilation is more extensive and more accurate than previous ones. The wave functions are freely available on the Internet at http://www.unb.ca/chem/ajit/download.htm. A limited number of printed tables of the wave functions are available upon request to (T.K. or A.J.T.) for libraries and readers without adequate Internet access. We hope these wave functions will be useful to the wider quantum chemistry community for some time to come.

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