Analytical Hartree–Fock Wave Functions Subject to Cusp and Asymptotic Constraints: He to Xe, Li$^+$ to Cs$^+$, H$^-$ to I$^-$

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ABSTRACT: Analytical, variational approximations to Hartree–Fock wave functions are constructed for the ground states of all the neutral atoms from He to Xe, the cations from Li$^+$ to Cs$^+$, and the stable anions from H$^-$ to I$^-$. The wave functions are constrained so that each atomic orbital agrees well with the electron–nuclear cusp condition and has good long-range behavior. Painstaking optimization of the exponents and principal quantum numbers of the Slater-type basis functions allows us to reach this goal while obtaining total energies that, at worst, are a few microHartrees above the numerical Hartree–Fock limit values. The wave functions are freely available by anonymous ftp from okapi.chem.unb.ca or upon request to the authors. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 71: 491–497, 1999

Key words: atoms; Hartree–Fock; Slater-type functions; cusp condition; asymptotic behavior

Introduction

Atomic wave functions are needed often. The Hartree−Fock (HF) model [1] is a customary choice for the construction of comprehensive tables of atomic wave functions because HF wave functions are sufficiently accurate for many purposes. Moreover, even when inadequate, they serve as a 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].

Various compilations of analytical Hartree−Fock (AHF) wave functions have been published. The first comprehensive and widely used collection was that of Clementi [6]. This was later superseded by the compilation of Clementi and Roetti [7]. Improvements to the monumental work of Clementi and Roetti (CR) have appeared recently. Bunge et al. [8] constructed AHF wave functions more accurate than those of CR by using more STFs than CR and by partial optimization of the $\{n\}$ quantum numbers of the STFs. Koga et al. [9, 10] showed that more thorough optimization of the STF exponents in the CR basis sets led to significant improvements in the AHF energies. The most recent advance was made by Koga et al. [11] who obtained the most accurate analytical HF wave functions to date by using more STFs than CR coupled with careful optimization of both the exponents and principal quantum numbers of the STFs.

However, even the most accurate of these AHF wave functions can deviate from the electron−nuclear cusp condition and the asymptotic long-range behavior by uncomfortably large amounts. The goal of this work was to report even more accurate AHF wave functions for the ground states of all the neutral atoms from He to Xe, the cations from Li^+ to Cs^+, and the stable anions from H^- to I^-. These AHF wave functions are built from large STF basis sets and predict energies within a few microHartrees of the numerical HF limit values. Moreover, unlike virtually all others reported in the literature, they are constrained so that each radial orbital $R_{nl}(r)$ with principal quantum number n and angular momentum quantum number l agrees well, but not necessarily perfectly, with the electron−nuclear cusp condition [1, 12, 13]:

$$f'_{nl}(0) = -Zf_{nl}(0)/(l + 1), \qquad (1)$$

in which Z is the nuclear charge and $R_{nl}(r) = r^l f_{nl}(r)$. Moreover, each orbital is constrained to have good long-range behavior [14−17]:

$$R_{nl}(r) \sim \exp\left(-(-2\varepsilon_h)^{1/2}r\right), \qquad (2)$$

in which ε_h is the orbital energy of the highest occupied atomic orbital (AO). More precise matching of the asymptotic behavior, as in the work of Davis et al. [16], was not attempted; the simpler task that we set ourselves proved to be difficult enough. Hartree atomic units are used throughout as in the above equations.

Computational Method

First, we had to choose the number of STFs to use for each species. Our past experience with atomic wave functions [9−11] led us to a prescription for choosing the number of STFs. For each angular momentum quantum number l, we use $2n_{\text{occ}, l} + l + 4$ STFs, where $n_{\text{occ}, l}$ is the number of occupied radial orbitals of that symmetry. One STF of each symmetry was added to the basis sets for the anions to help describe the diffuse orbital occupied by the extra electron and thus obtain anion wave functions of a quality comparable to the cations and neutral atoms. This prescription was found adequate and used in all but a few cases: Five s-STFs were used instead of six in He and its isoelectronic analogs, 10 p-STFs instead of nine were used for Al to Zn and their isoelectronic analogs, and 11 d-STFs instead of 10 were used for Y to Xe and their isoelectronic analogs. Again, the basis sets for the anions isoelectronic to these exceptions had one extra STF of each symmetry.

Since we wanted to impose constraints on the wave function, we chose the $\{n, \zeta\}$ by minimizing, in the jargon of optimization theory, a suitable "objective function" F instead of the energy. We chose the objective function to be

$$F = E + (w_1/n_{\text{occ}}) \sum_{j=1}^{n_{\text{occ}}} |\gamma_j - 1| + w_2|V/T + 2|, \quad (3)$$

in which E, V, and T are the total, potential, and kinetic energies, respectively; w_1 and w_2 are positive weights; $\gamma_j = -(l+1)f_j'(0)/[Zf_j(0)]$ is the cusp ratio for the jth radial orbital; and n_{occ} is the number of occupied radial orbitals. The second and third terms of the objective function F are "penalty" functions that increase F whenever the orbital cusp ratios γ_j deviate from their exact values of unity and whenever the virial ratio, $-V/T$, of the wave function deviates from its exact value of 2. The weights were chosen empirically to achieve cusp ratios of 1 ± 0.001 and a virial ratio of 2 ± 10^{-8}. Their values were $w_1 = 0.1$ and $w_2 = 1000$ for all the second-period atoms and most of the third-period atoms. However, in other cases, our goal for the cusp ratios was not met when these values of w_1 and w_2 were used; we then chose smaller values in the ranges $0.0001 \le w_1 \le 0.1$ and $1 \le w_2 \le 1000$. The constraints on the long-range behavior were handled separately as described below.

Once the size of the basis sets had been fixed, a thorough search was made to determine an optimal choice of $\{n\}$ quantum numbers. At each step in this search, the exponents $\{\zeta\}$ of the STFs were optimized by minimizing F with the conjugate direction algorithm of Powell [18] incorporated in our version [19] of Pitzer's ATOM program [20]. The long-range behavior of the orbitals was constrained in the following manner: After each cycle of the optimization, the smallest STF exponents $\zeta_{\min, l}$ of each symmetry l were set equal to $(-2\varepsilon_h)^{1/2}$. The optimization cycles were repeated until the computed ε_h led to no change in the $\zeta_{\min, l}$; this required very little iteration since all our orbital energies, including ε_h, were always very close to the numerical HF values as discussed in detail in the next section.

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, then we perturbed some of the parameters and restarted the optimization for the offending wave functions. This process was repeated as often as necessary, but smooth behavior could not always be achieved.

It is important to understand that global optimization of large numbers of nonlinear parameters is never complete. At some point, one simply has to stop and accept the results as they are. After six man-years of intense effort and countless hours of CPU time, we stopped the optimizations. The next section is devoted to examining the quality of the resulting 149 wave functions for 53 neutral atoms, 53 cations, and 43 anions.

Results and Discussion

We needed to examine our new wave functions, hereafter referred to as K98 wave functions, and compare them with previous high-quality AHF wave functions: those of Clementi and Roetti [7], Bunge et al. [8], and Koga et al. [11], hereafter referred to as C74, B92, and K95 wave functions, respectively. Since Bunge et al. [8] constructed wave functions only for neutral atoms, there are no B92 wave functions for cations and anions. There is no C74 wave function for Cs^+, and the C74 wave function for Tc^- was omitted because it contains an error [10]. The appropriate reference for AHF wave functions is the numerical (N) HF limit. Therefore, we computed NHF wave functions and properties for all 149 species using our modified and extended version of MCHF72 [21]. All comparisons among the various AHF wave functions were made by examining errors, with respect to the NHF reference, averaged over atoms belonging to the same row of the periodic table. We investigated the quality of the total and orbital energies, the electron density at the nucleus $\rho(0)$, and the moments $\langle r^k \rangle$ ($k = -2, -1, +1, +2$) of the electron density. We inspected the extent to which the wave functions satisfy the virial theorem. We checked how well the orbitals satisfy the cusp condition and how close their long-range behavior is to the correct asymptotic behavior.

Keep in mind that our AHF total energies are variational and lie above the HF limit. This is because the functional F is used only to optimize the nonlinear parameters $\{n, \zeta\}$, that is, to select the basis set; the linear coefficients that are used to expand the atomic orbitals in terms of the STFs are found by solving the restricted HF equations. Some readers may prefer an alternative description: The functional F is used to select the subspace upon which the restricted HF equations are projected and solved.

Table I shows that the average errors in the total energies decrease in the sequence C74, B92, K95, and K98. In fact, the energies improve in this same sequence for all but one of the 149 systems. The sole exception is Y^- where the K95 energy is lower than the K98 energy. The electron configuration of

TABLE I _____

Average errors (in microHartrees) of total energies for K98, K95, B92, and C74 wave functions.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
1	0.000	0.001	0.003	0.0	—	—	—	0.0005	0.0005	—
2	0.005	0.038	0.061	3.8	0.00	0.03	14.	0.005	0.025	78.5
3	0.06	0.20	0.38	5.	0.08	0.25	213.	0.07	0.25	305.
4	1.1	5.0	8.7	60.	0.9	3.5	583.	1.2	3.0	950.
5	4.4	7.9	16.0	5810.	3.8	5.7	11010.	4.5	5.8	16,970.
6	—	—	—	—	5.	9.	—	—	—	—

Y^- is $[Kr]5s^2 4d5p$ and the energy of the very loosely bound $5p$ AO is a mere -0.003 Hartrees. Our basis set does not contain enough p-STF to simultaneously describe the loosely bound $5p$ orbital, get all the p-orbital cusps right, and give the best AHF energy achieved to date. The K98 energies lie only a few microHartrees above the corresponding NHF limit; in the worst case of Y^-, the K98 energy is 9 microHartrees above the NHF limit. The energies are generally most accurate for the cations; this is true for the C74, K95, and K98 wave functions. The anion energy errors for the K95 and K98 wave functions are comparable to those for the neutral species because slightly larger basis sets were deliberately used for the anions to

achieve this result. The energy errors ordinarily increase as one moves to heavier atoms.

Table II shows average errors in the energies of the outermost orbitals of each symmetry. We focused on the outermost orbital energies because they are frequently the least accurate. The errors typically decrease in the order C74, B92, K95, and K98. In three cases, the K95 wave functions have better orbital energies; these are the $5s$ AO of Sb^+ and the $5p$ and $4d$ AOs of Cs^+. The average errors for the K98 wave functions are less than 2.7 microHartrees if we exclude Cs^+.

Table III shows that satisfaction of the virial theorem is achieved to an increasing extent in the sequence C74, B92, K95, and K98. By design, the

TABLE II _____

Average energy errors (in microHartrees) of outermost orbitals of each symmetry.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
Outermost s orbitals										
1	0.0	0.0	1.	10.	—	—	—	0.0	0.0	—
2	0.04	0.05	0.1	13.	0.01	0.00	15.41	0.02	0.07	185.
3	0.16	0.83	0.4	51.	0.12	0.27	115.27	0.07	0.47	457.
4	0.51	1.97	4.1	76.	1.71	2.26	86.36	0.28	1.02	461.
5	0.68	2.61	7.5	660.	2.49	2.17	648.43	0.94	16.87	843.
6	—	—	—	—	4.6	0.6	—	—	—	—
Outermost p orbitals										
2	0.05	0.08	0.0	12.	0.00	0.00	11.42	0.00	0.08	218.
3	0.10	0.55	0.5	61.	0.11	0.21	52.01	0.02	3.47	535.
4	0.54	3.35	6.6	98.	1.78	2.43	72.89	0.16	1.27	819.
5	0.52	3.34	9.9	1026.	2.02	2.17	649.13	0.47	1.31	1668.
6	—	—	—	—	6.1	0.9	—	—	—	—
Outermost d orbitals										
4	0.68	3.41	6.8	83.	2.26	2.91	60.47	0.32	1.68	861.
5	0.80	3.52	11.1	684.	2.67	2.01	730.60	1.97	4.58	1779.
6	—	—	—	—	0.4	0.1	—	—	—	—

TABLE III
Average virial deviations $10^8|V/T + 2|$.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
1	0.0	0.1	56.6	1148.	—	—	—	0.0	0.1	—
2	0.08	0.10	2.51	336.9	0.01	0.18	1227.4	0.00	0.17	1930.0
3	0.00	0.55	0.73	1795.4	0.05	0.90	1026.4	0.00	0.40	1032.2
4	0.01	0.43	1.93	366.7	0.06	0.80	551.0	0.05	0.29	507.8
5	0.08	0.65	0.97	3307.8	0.06	0.34	2776.6	0.21	0.33	4375.1
6	—	—	—	—	0.1	0.3		—	—	—

virial theorem is satisfied to better than 1 part in 10^8 for the K98 wave functions. A simple virial scaling of the wave function [22–24] would achieve exact satisfaction of the virial theorem but the orbitals would then no longer be self-consistent with respect to the HF equations.

It is much easier to obtain a total electron density that satisfies the cusp condition than it is to have the cusp condition satisfied by each orbital. Table IV displays the average errors in the nuclear cusps of all the occupied orbitals of each symmetry. The cusp errors mainly decrease in the order C74, B92, K95, and K98. The exceptions are for the second-period cations where the average error is smaller for the K95 wave functions than for the K98 ones. There are also some cases where the

AOs, usually p-AOs, of the C74 and B92 wave functions have more accurate cusp ratios than those of the K95 wave functions. By design, the K98 orbital cusp ratios do not deviate from unity by more than 0.001.

Table V shows that values of the electron density at the nucleus generally get closer to the numerical HF limit in the sequence C74, B92, K95, and K98. Exceptions are found for third-period cations where the K95 values are better than the K98 ones and for neutral He and third-period atoms where the B92 values are marginally more accurate. The largest errors of the K98 values of $\rho(0)$ are no more than 0.006%. The variational principle tends to produce good values of $\rho(0)$ because it is dominated by the contribution from

TABLE IV
Average cusp errors $10^3|\gamma_J - 1|$ of outermost orbitals of each symmetry.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
Occupied s orbitals										
1	0.05	0.09	0.01	2.04	—	—	—	0.03	0.25	—
2	0.210	0.212	0.408	5.038	0.121	0.092	5.651	0.219	0.255	5.534
3	0.268	0.360	0.515	0.874	0.251	0.287	2.549	0.053	0.223	4.484
4	0.350	0.707	1.256	1.411	0.208	0.454	1.430	0.405	0.515	1.399
5	0.383	0.535	0.564	1.244	0.238	0.454	1.063	0.387	0.579	1.709
6	—	—	—	—	0.236	0.833	—	—	—	—
Occupied p orbitals										
2	0.257	17.055	20.117	13.622	0.339	16.925	8.698	0.090	17.333	14.222
3	0.468	8.343	7.316	7.907	0.316	11.229	12.037	0.437	11.038	11.259
4	0.535	5.113	4.967	10.714	0.477	4.803	10.383	0.637	4.281	12.025
5	0.590	3.612	2.462	16.677	0.457	3.980	16.273	0.599	3.489	16.553
6	—	—	—	—	0.290	3.871	—	—	—	—
Occupied d orbitals										
4	0.346	30.664	30.399	58.290	0.272	30.370	62.013	0.259	31.191	68.603
5	0.459	10.882	11.267	92.251	0.440	9.671	88.677	0.494	12.979	97.026
6	—	—	—	—	0.568	5.892	—	—	—	—

TABLE V
Average $\rho(0)$ errors in 10^{-3} %.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
1	0.64	1.20	0.50	28.45	—	—	—	0.36	3.14	—
2	0.93	1.24	1.99	90.06	0.57	0.93	81.37	0.83	0.92	73.05
3	0.54	0.62	0.53	11.47	0.65	0.48	18.73	0.54	1.13	15.56
4	4.17	11.50	15.60	18.11	1.28	4.40	21.44	4.59	10.74	17.26
5	5.40	8.36	8.74	66.39	3.39	5.20	67.61	3.92	8.58	64.56
6	—	—	—	—	3.74	7.31	—	—	—	—

the 1s electrons which also make the greatest contribution to the total energy.

Table VI shows that the smallest STF exponent $\zeta_{\min, l}$ is close to the asymptotic value $(-2\varepsilon_h)^{1/2}$ only for the K98 wave functions which were constrained in this manner. For the other wave functions, the variational principle does not keep $\zeta_{\min, l}$ close to its asymptotic value because the very long range behavior of the orbitals is irrelevant to the total energy.

Table VII shows that the accuracy of the moments $\langle r^k \rangle$ ($k = -2, -1, +1, +2$) typically increases in the order C74, B92, K95, and K98. Of these four moments, $\langle r^{-1} \rangle$ is most accurately predicted by all the wave functions because it determines the contribution of the electron–nucleus attraction to the total energy. The moments $\langle r^{-2} \rangle$ and $\langle r \rangle$ which sample similar regions of space are the next most accurate, and the $\langle r^2 \rangle$ moments, related to the diamagnetic susceptibility, are the least accurate.

Concluding Remarks

The wave functions presented in this article are the most accurate analytical approximations to true restricted HF wave functions so far obtained for the 53 neutral atoms from He to Xe, the 53 cations from Li^+ to Cs^+, and 43 anions from H^- to I^-. Moreover, unlike most other approximate HF wave functions, the orbitals were constrained to have accurate electron–nuclear cusp ratios and correct long-range behavior.

We will be delighted if this collection of 149 AHF wave functions proves as useful as the venerable collection of Clementi and Roetti has. The wave functions themselves are freely available by anonymous ftp from okapi.chem.unb.ca in the /pub/atoms directory. A limited number of printed tables of the wave functions are available, upon request to one of the authors (T. K. or A. J. T.), for libraries and readers without adequate Internet access.

TABLE VI
Average deviations $10^5|\zeta_{\min, l} - (-2\varepsilon_h)^{1/2}|$ of the smallest STF exponent from the asymptotic value.

Period	Neutrals				Cations			Anions		
	K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
1	0.0	3928.	10,450.	6218.	—	—	—	0.0	4305.	—
2	0.00	10783.	11,514.	8818.	0.03	6630.	15,937.	0.00	11,737.	16,849.
3	0.03	8281.	16,815.	10,410.	0.03	5361.	15,878.	0.00	11,042.	35,220.
4	0.03	6292.	24,312.	16,041.	0.14	11,481.	24,199.	0.03	6283.	33,716.
5	0.08	5034.	33,677.	35,192.	0.15	9511.	50,126.	0.24	5845.	42,382.
6	—	—	—	—	0.44	2025.	—	—	—	—

TABLE VII
Average $\langle r^k \rangle$ relative errors (in 10^{-3} %).

	Period	Neutrals				Cations			Anions		
		K98	K95	B92	C74	K98	K95	C74	K98	K95	C74
$k = -2$	1	0.03	0.07	0.02	2.34	—	—	—	0.00	0.18	—
	2	0.06	0.08	0.18	9.61	0.04	0.05	8.24	0.06	0.06	9.16
	3	0.03	0.05	0.04	4.57	0.05	0.04	1.90	0.03	0.10	2.18
	4	0.31	0.99	1.39	3.14	0.07	0.36	3.41	0.37	0.91	2.11
	5	0.42	0.72	0.74	15.29	0.26	0.43	15.36	0.30	0.75	15.12
	6	—	—	—	—	0.28	0.63	—	—	—	—
$k = -1$	1	0.00	0.00	0.06	0.71	—	—	—	0.00	0.00	—
	2	0.00	0.00	0.01	0.20	0.00	0.00	0.63	0.00	0.00	2.11
	3	0.00	0.01	0.00	0.76	0.00	0.01	0.71	0.00	0.01	1.21
	4	0.01	0.00	0.00	0.22	0.00	0.00	0.38	0.00	0.00	0.55
	5	0.00	0.00	0.00	2.00	0.00	0.00	1.75	0.00	0.00	2.60
	6	—	—	—	—	0.00	0.00	—	—	—	—
$k = +1$	1	0.01	0.01	0.15	3.58	—	—	—	0.00	0.04	—
	2	0.08	0.03	0.12	2.85	0.01	0.03	2.35	0.01	0.06	59.39
	3	0.07	0.19	0.11	8.55	0.06	0.12	12.13	0.05	0.34	284.22
	4	0.42	0.28	0.65	6.83	0.26	0.39	4.47	0.16	0.57	240.44
	5	0.19	0.57	1.12	41.35	0.15	0.24	31.16	1.14	2.84	425.96
	6	—	—	—	—	0.16	0.03	—	—	—	—
$k = +2$	1	0.00	0.00	0.68	15.02	—	—	—	0.04	0.39	—
	2	0.62	0.23	0.54	17.62	0.08	0.14	10.73	0.13	0.84	306.00
	3	0.68	0.93	0.83	43.58	0.49	0.87	58.24	0.99	3.65	1547.15
	4	4.89	2.16	5.55	68.05	1.91	3.78	26.28	2.61	6.88	1820.11
	5	2.58	5.06	10.48	232.91	1.23	2.36	194.41	34.74	35.46	2894.13
	6	—	—	—	—	0.31	0.29	—	—	—	—

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