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Roothaan-Hartree-Fock wave functions for atoms with $Z \leq 54$

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The widely used Roothaan-Hartree-Fock wave functions of Clementi and Roetti [At. Data Nucl. Data Tables **14**, 177 (1974)] for the atoms from He through Xe are improved by reoptimization of the exponents of the Slater-type basis functions. The largest improvement in the energy is 0.053 hartree for Cd.

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Hartree-Fock (HF) wave functions for atoms may be computed numerically by standard methods [1]. Algebraic approximations to HF wave functions in which the radial orbitals are expanded in a set of basis functions, such as Slater-type functions (STF), by the Roothaan procedure [2] are known as Roothaan-Hartree-Fock (RHF) wave functions. RHF wave functions are more convenient for some purposes, and are in great demand as indicated by the large number of citations [3] to the tabulation of Clementi and Roetti [4].

The work of Clementi and Roetti (CR) [4] was a *tour de force* when it appeared in 1974. However, Fig. 1 shows that the differences between their energies and numerical HF values [1,5,6] behave erratically as a function of atomic number. Moreover, some of their wave functions predict virial ratios significantly different from the exact value of -2; the most egregious case is Cd where the CR virial ratio differs from exactness by one part in 10^4.

Unaware of the related work undertaken by Bunge, Barrientos, Bunge, and Cogordan (BBBC) [7], we carried out a variational reoptimization of the exponents of the STF in the CR wave functions using the conjugate direction algorithm of Powell [8]. All RHF calculations were carried out with a modified and corrected [9] version of Pitzer's program [10]. We used exactly the same number and type of STF's as CR did except that in some atoms, we had to modify the n quantum number of one STF to avoid problems with computational linear dependence. In all cases, our optimized wave functions predict virial ratios within 1.0×10^{-7} of the exact value.

Table I shows that our reoptimized RHF wave functions predict energies with errors, relative to the numerical HF limits [1,5,6], significantly smaller than those of CR; the largest improvement is seen for Cd where our reoptimization reduces the error by 0.053 hartree. Moreover, Fig. 1 shows that our errors vary relatively smoothly with atomic number.

For the atoms from He to Kr, the residual errors in our energies are no more than 0.1 mhartree, and our valence orbital energies are closer to the numerical HF values than the CR values. For Rb through Xe our total energies are lower than those of Clementi and Roetti [4],

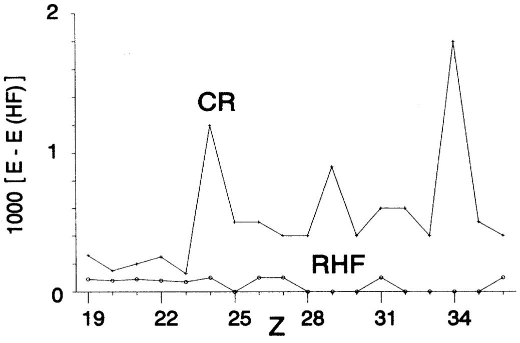

FIG. 1. Energy errors (in mhartree) of the Clementi-Roetti (CR) and present RHF wave functions with respect to the numerical Hartree-Fock (HF) limit.

TABLE I. Clementi-Roetti (E_{CR}), reoptimized (E_{RHF}), and numerical Hartree-Fock (E_{HF}) energies in hartrees.

Z	Atom		STF's	$-E_{\mathrm{CR}}$[a]	$-E_{\mathrm{RHF}}$	$-E_{\mathrm{HF}}$[b]
2	He	(^1S)	5s	2.861 679 9	2.861 680 0	2.861 680 0
3	Li	(^2S)	6s	7.432 725 7	7.432 725 8	7.432 726 9
4	Be	(^1S)	6s	14.573 021	14.573 021	14.573 023
5	B	(^2P)	6s4p	24.529 057	24.529 058	24.529 061
6	C	(^3P)	6s4p	37.688 612	37.688 616	37.688 619
7	N	(^4S)	6s4p	54.400 924	54.400 931	54.400 934
8	O	(^3P)	6s4p	74.809 370	74.809 395	74.809 398
9	F	(^2P)	6s4p	99.409 300	99.409 344	99.409 349
10	Ne	(^1S)	6s4p	128.547 05	128.547 09	128.547 10
11	Na	(^2S)	8s5p	161.858 90	161.858 91	161.858 91
12	Mg	(^1S)	8s5p	199.614 61	199.614 63	199.614 63
13	Al	(^2P)	8s8p	241.876 68	241.876 70	241.876 71
14	Si	(^3P)	8s8p	288.854 31	288.854 36	288.854 36
15	P	(^4S)	8s8p	340.718 69	340.718 77	340.718 78
16	S	(^3P)	8s8p	397.504 85	397.504 89	397.504 90
17	Cl	(^2P)	8s8p	459.481 87	459.482 07	459.482 07
18	Ar	(^1S)	8s8p	526.817 39	526.817 51	526.817 51
19	K	(^2S)	11s6p	599.164 53	599.164 70	599.164 79
20	Ca	(^1S)	11s6p	676.758 03	676.758 10	676.758 18
21	Sc	(^2D)	11s6p5d	759.735 52	759.735 63	759.735 72
22	Ti	(^3F)	11s6p5d	848.405 75	848.405 92	848.406 00
23	V	(^4F)	11s6p5d	942.884 20	942.884 26	942.884 33
24	Cr	(^7S)	11s6p5d	1043.355 2	1043.356 3	1043.356 4
25	Mn	(^6S)	11s6p5d	1149.865 7	1149.866 2	1149.866 2
26	Fe	(^5D)	11s6p5d	1262.443 2	1262.443 6	1262.443 7
27	Co	(^4F)	11s6p5d	1381.414 2	1381.414 5	1381.414 6
28	Ni	(^3F)	11s6p5d	1506.870 5	1506.870 9	1506.870 9
29	Cu	(^2S)	11s6p5d	1638.962 8	1638.963 7	1638.963 7
30	Zn	(^1S)	11s6p5d	1777.847 7	1777.848 1	1777.848 1
31	Ga	(^2P)	10s9p5d	1923.260 4	1923.260 9	1923.261 0
32	Ge	(^3P)	10s9p5d	2075.359 1	2075.359 7	2075.359 7
33	As	(^4S)	10s9p5d	2234.238 2	2234.238 6	2234.238 6
34	Se	(^3P)	10s9p5d	2399.865 8	2399.867 6	2399.867 6
35	Br	(^2P)	10s9p5d	2572.440 8	2572.441 3	2572.441 3
36	Kr	(^1S)	10s9p5d	2752.054 6	2752.054 9	2752.055 0
37	Rb	(^2S)	11s7p3d	2938.347 0	2938.353 1	2938.357 4
38	Sr	(^1S)	11s7p3d	3131.537 9	3131.541 7	3131.545 7
39	Y	(^2D)	11s7p5d	3331.671 2	3331.680 7	3331.684 2
40	Zr	(^3F)	11s7p5d	3538.982 1	3538.991 4	3583.995 1
41	Nb	(^6D)	11s7p5d	3753.584 5	3753.591 7	3753.597 7
42	Mo	(^7S)	11s7p5d	3975.533 8	3975.543 0	3975.549 5
43	Tc	(^6S)	11s7p5d	4204.775 3	4204.783 9	4204.788 7
44	Ru	(^5F)	11s7p5d	4441.526 4	4441.531 0	4441.539 5
45	Rh	(^4F)	11s7p5d	(4685.883 3)	4685.872 6	4685.881 7
46	Pd	(^1S)	9s7p5d	4937.907 1	4937.909 1	4937.921 0
47	Ag	(^2S)	11s7p5d	5197.685 2	5197.689 0	5197.698 5
48	Cd	(^1S)	11s7p5d	5465.072 2	5465.125 3	5465.133 1
49	In	(^2P)	11s9p5d	5740.157 0	5740.163 8	5740.169 1
50	Sn	(^3P)	11s9p5d	6022.922 0	6022.927 1	6022.931 7
51	Sb	(^4S)	11s9p5d	6313.475 5	6313.481 3	6313.485 3
52	Te	(^3P)	11s9p5d	6611.774 8	6611.780 3	6611.784 0
53	I	(^2P)	11s9p5d	6917.972 7	6917.977 3	6917.980 9
54	Xe	(^1S)	11s9p5d	7232.130 2	7232.135 0	7232.138 4

[a] From Ref. [4]. The result for Rh (^4F) is in error; it can be reproduced by assigning the incorrect sign to a vector coupling coefficient.

[b] From Refs. [1,5,6].

but this improvement has taken place at the expense of worsened valence orbital energies. Clearly, greater numbers of STF are needed to obtain "near" HF accuracy for these fourth-row atoms.

The very recent RHF wave functions of BBBC [7] are more accurate than ours. Nevertheless, our results have value because our basis sets are similar than theirs. Our wave functions are available upon request from the third author and will be presented separately in the near future.

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