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Atomic Screening Constants from SCF Functions

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The self-consistent-field function for atoms with 2 to 36 electrons are computed with a minimal basis set of Slater-type orbitals. The orbital exponent of the atomic orbitals are optimized as to ensure the energy minimum. The analysis of the optimized orbital exponents allows us to obtain simple and accurate rules for the 1s, 2s, 3s, 4s, 2p, 3p, 4p, and 3d electronic screening constants. These rules are compared with those proposed by Slater and reveal the need of accounting for the screening due to the outside electrons. The analysis of the screening constants (and orbital exponents) is extended to the excited states of the ground-state configuration and to the positive ions.

I. INTRODUCTION

THE one-electron function of an electron in an atomic system can be obtained numerically with the Hartree-Fock method¹ or analytically with Roothaan's self-consistent-field (SCF) method.² Accurate analytical functions for the first period of the periodic chart of the elements are now available.³ Quite satisfactory functions for the first and second period of neutral atoms and ions were recently published.^{4,5} In addition, the functions for the last six elements of the third period⁶ and those for the complete set of atoms in the third period (including excited states) are computed.⁷ Finally, highly accurate analytical functions for the second and third period are now in the process of being published.⁸ This very large number of accurate data needs to be completed by an equivalent set of data more easily usable for preliminary computations and for those problems where high accuracy is not desired or not feasible with present techniques. The usefulness of functions simpler than the Hartree-Fock functions was recognized long ago. Zener⁹ and Slater¹⁰ made use of a single exponential function to describe an atomic orbital. Physically, the orbital exponent ξ of such functions is $\xi = (Z - \sigma)/n$, where $(Z - \sigma)$ is the effective Z for a given electron (σ is the screening constant) and n is a function of the principal quantum number. In the SCF method the orbital exponent ξ is simply a parameter to be optimized, but when the ξ is obtained for SCF functions, then we can analyze ξ in terms of screening effects.

This paper discusses the screening constant σ . We

give the best value of σ for atoms as obtained by the self-consistent-field method when each individual electron is described by a single exponential function with variable exponents and fixed quantum numbers. This type of self-consistent-field computation is often referred to as a minimal basis set or best atom set.¹¹ Long ago, Roothaan¹² did obtain the best value of σ for the first-row atoms.

II. SCREENING CONSTANT

An electron in an atom is acted upon by the nucleus and all the other electrons. The other electrons reduce the nuclear attraction to some extent. The nuclear charge as seen by a given electron, after the screening of the other electrons, is called the effective Z for that one electron. There have been several rules proposed to compute the Z effective, and we refer to the work of Slater¹⁰ and Pauling and Sherman¹³ for examples of such rules. We are particularly interested in Slater's rules, since they have been widely used in the past as well as today. (For an updated discussion of the Z effective we refer to Slater's new volume on atomic structure.¹⁴)

We have obtained the best orbital exponent ξ in a minimal basis set self-consistent-field calculation for all the atoms and positive ions in the states of the lowest configuration with nuclear charge Z from 2 to 36 and with 2 to 36 electrons.

To do this in a reasonable amount of time, we have prepared a program for the IBM 7090 which generates fully automatically the inputs for all the individual states within the above limits of Z and the number of electrons. This input makes use of the Slater orbital exponents as an initial guess. Then these inputs are processed through the self-consistent-field atomic program, kindly provided to us by Roothaan, to obtain

¹ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

² C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

³ E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.* **127**, 1618 (1962).

⁴ E. Clementi, *J. Chem. Phys.* **38**, 996 (1963).

⁵ E. Clementi, *J. Chem. Phys.* **38**, 1001 (1963).

⁶ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 521 (1961).

⁷ R. E. Watson and A. J. Freeman, *Phys. Rev.* **124**, 1117 (1961); R. E. Watson, *ibid.* **113**, 1934 (1960).

⁸ E. Clementi and C. C. J. Roothaan (to be published).

⁹ C. Zener, *Phys. Rev.* **36**, 51 (1930).

¹⁰ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

¹¹ B. J. Ransil, *Rev. Mod. Phys.* **32**, 245 (1960).

¹² C. C. J. Roothaan, L.M.S.S. Technical Rept., The University of Chicago, 1955.

¹³ L. Pauling and J. Sherman, *Z. Krist.* **81**, 1 (1932).

¹⁴ J. C. Slater, *Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960) Vol. I.

TABLE I. Best values of ξ for the ground state of neutral atoms.^a

<i>Z</i>	1 <i>s</i>	2 <i>s</i>	2 <i>p</i>	3 <i>s</i>	3 <i>p</i>	4 <i>s</i>	3 <i>d</i>	4 <i>p</i>
2.	1.6875							
3.	2.6906	0.6396						
4.	3.6848	0.9560						
5.	4.6795	1.2881	1.2107					
6.	5.6727	1.6083	1.5679					
7.	6.6651	1.9237	1.9170					
8.	7.6579	2.2458	2.2266					
9.	8.6501	2.5638	2.5500					
10.	9.6421	2.8792	2.8792					
11.	10.6259	3.2857	3.4009	0.8358				
12.	11.6089	3.6960	3.9129	1.1025				
13.	12.5910	4.1068	4.4817	1.3724	1.3552			
14.	13.5745	4.5100	4.9725	1.6344	1.4284			
15.	14.5578	4.9125	5.4806	1.8806	1.6288			
16.	15.5409	5.3144	5.9885	2.1223	1.8273			
17.	16.5239	5.7152	6.4966	2.3561	2.0387			
18.	17.5075	6.1152	7.0041	2.5856	2.2547			
19.	18.4895	6.5031	7.5136	2.8933	2.5752	0.8738		
20.	19.4730	6.8882	8.0207	3.2005	2.8861	1.0995		
21.	20.4566	7.2868	8.5273	3.4466	3.1354	1.1581	2.3733	
22.	21.4409	7.6883	9.0324	3.6777	3.3679	1.2042	2.7138	
23.	22.4256	8.0907	9.5364	3.9031	3.5950	1.2453	2.9943	
24.	23.4138	8.4919	10.0376	4.1226	3.8220	1.2833	3.2522	
25.	24.3957	8.8969	10.5420	4.3393	4.0364	1.3208	3.5094	
26.	25.3810	9.2995	11.0444	4.5587	4.2593	1.3585	3.7266	
27.	26.3668	9.7025	11.5462	4.7741	4.4782	1.3941	3.9518	
28.	27.3526	10.1063	12.0476	4.9870	4.6950	1.4277	4.1765	
29.	28.3386	10.5099	12.5485	5.1981	4.9102	1.4606	4.4002	
30.	29.3245	10.9140	13.0490	5.4064	5.1231	1.4913	4.6261	
31.	30.3094	11.2995	13.5454	5.6654	5.4012	1.7667	5.0311	1.5554
32.	31.2937	11.6824	14.0411	5.9299	5.6712	2.0109	5.4171	1.6951
33.	32.2783	12.0635	14.5368	6.1985	5.9499	2.2360	5.7928	1.8623
34.	33.2622	12.4442	15.0326	6.4678	6.2350	2.4394	6.1590	2.0718
35.	34.2471	12.8217	15.5282	6.7395	6.5236	2.6382	6.5197	2.2570
36.	35.2316	13.1990	16.0235	7.0109	6.8114	2.8289	6.8753	2.4423

^a States are the same as given in Table III.

the SCF energy. A control program optimizes Slater's orbital exponent one at a time starting with the innermost electron up to the outermost. This cycle of individual optimizations of the orbital exponents was repeated four times, until the ξ reached the optimal value. The fact that four circles of parameter optimizations,

and not just a single one, were needed is due to the coupling of the orbitals of the same symmetry. It is noted that the coupling is not too strong, since in a minimal basis set SCF computation each Slater function represents to a large extent an individual atomic orbital, and the coupling is mostly due to the orthog-

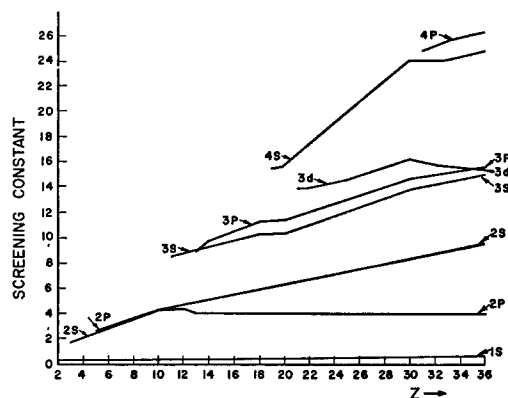


FIG. 1. The screening constants σ are plotted vs the atomic number Z . The values of σ are given in Table I.

onality constraint for the orbitals of the same symmetry. Extension of this work to the fourth and fifth periods of the periodic table will likely require a minimum of five and six optimization cycles, respectively.

In the Slater rules the electrons are divided into groups. Each group is defined as external (or internal) with respect to the others (the nucleus is the origin). In addition, the assumption is made that for a given electron there is no screening due to the electrons of external groups. Finally, it is assumed that the Z effective for a given electron is independent in general (with the exception of the d and f electrons) of the l quantum number. Hence, in general, σ is a function of n and N_i , where n is the principal quantum number and N_i is the total number of electrons minus those belonging to the group outside the one in consideration. These rules hold reasonably well for the first row of the periodic table, less for the second, and not too well above it.

More correctly, the σ constant for a given electron in an atom is a function of the principal quantum number n , of the l quantum number, of N (the total number of electrons), and Z . In addition, for the valency electrons, σ is a function of the total angular momentum of the atom L and the spin multiplicity S . Hence, in contrast with the Slater rules we have $\sigma = \sigma(n, l, N, L, S)$. The latter dependency of σ is confirmed by our work.

The screening constants for the $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, $4p$, and $3d$ electrons as obtained from the final

TABLE III. Total energy for the ground states of neutral atoms (in a.u.).^a

Atom	Best ξ	Slater ξ	Mod. Slater ξ	Hartree-Fock
He	2.8476563	2.8475000	2.8475000	2.8616785
Li	7.4184820	7.4183331	7.4184776	7.432726
Be	14.556740	14.556023	14.556724	14.57302
B	24.498370	24.494952	24.498279	24.52905
C	37.622389	37.618550	37.621822	37.68861
N	54.268899	54.265109	54.267084	54.40091
O	74.540362	74.532946	74.539909	74.80936
F	98.942114	98.931685	98.942037	99.40929
Ne	127.81219	127.79954	127.81218	128.5470
Na	161.12392	161.08810	161.12319	161.85889
Mg	198.85779	198.76642	198.85263	199.61461
Al	241.15376	240.97498	241.14520	241.87665
Si	288.08997	287.82188	288.08546	288.85429
P	339.90989	339.52612	339.90505	340.71871
S	396.62761	396.10959	396.62270	397.50476
Cl	458.52370	457.85088	458.51939	459.48197
Ar	525.76526	524.91686	525.76150	526.81743
K	598.08989	597.04174	598.08710	599.16428
Ca	675.63389	674.31958	675.63237	676.75786
Sc	758.40415	756.70061	758.39861	759.73486
Ti	846.81560	844.47817	846.80664	848.40416
V	940.97195	937.79927	940.95861	942.8803
Cr	1041.0062	1036.8141	1040.9894	1043.3036
Mn	1147.1067	1141.6968	1147.0871	1149.8620
Fe	1259.0855	1252.4142	1259.0691	1262.4423
Co	1377.3744	1369.2604	1377.3604	1381.4123
Ni	1502.0487	1492.3420	1502.0361	1506.8657
Cu	1633.2393	1621.7939	1633.2252	1638.9310
Zn	1771.1509	1757.7974	1771.1310	1777.8451
Ga	1916.5167	1900.9307	1916.5023	1923.2594
Ge	2068.5139	2050.7607	2068.4992	2075.3581
As	2227.1393	2207.2852	2227.1249	2234.239
Se	2392.7274	2370.8130	2392.7175	2399.867
Br	2565.1132	2541.1940	2565.1053	2572.443
Kr	2744.5196	2718.6317	2744.5102	2752.056

^a The computed state is always the ground state of the lowest configuration with the exception of Cr and Cu where the electronic configurations are . . . $3d^4$ and . . . $3d^9$, respectively.

TABLE II. Screening constants for Si atom and Kr²²⁺ ion.

Atomic orbital	Silicon atom			Krypton (22+) ion		
	³ P	¹ D	¹ S	³ P	¹ D	¹ S
1S	0.4255	0.4253	0.4254	0.8064	0.8064	0.8066
2S	4.9800	4.9796	4.9793	10.0782	10.0788	10.0786
3S	9.0969	9.0890	9.0763	11.2749	11.2715	11.2702
2P	4.0549	4.0584	4.0636	3.7604	3.7590	3.7568
3P	9.7148	9.7721	9.8604	11.5196	11.5470	11.5870

SCF computation (after ξ 's optimization) are given in Fig. 1 and in Table I for the neutral atoms of the ground-state configuration. Inspection of Fig. 1 reveals that $\sigma = \sigma(n, l, N_i)$. In Table II, the screening constants for the silicon atom and for the Kr^{22+} ions are compared. Inspection of this table, which is typical of the variation of ξ with different values of L , S , and Z , show that $\sigma = \sigma(n, l, N, L, S, Z)$.

Again by inspection of Fig. 1, some simple rules for the screening constants of the neutral atoms can be derived. Denoting the *number* of electrons of principal quantum n , and angular momentum l , of a given configuration by nl , we propose the following new rules to obtain the screening constant:

$$\begin{aligned}\sigma(1s) &= 0.3(1s-1) + 0.0072(2s+2p) \\ &\quad + 0.0158(3s+3p+4s+3d+4p), \\ \sigma(2s) &= 1.7208 + 0.3601(2s-1+2p) \\ &\quad + 0.2062(3s+3p+4s+3d+4p), \\ \sigma(2p) &= 2.5787 + 0.3326(2p-1) - 0.0773(3s) \\ &\quad - 0.0161(3p+4s) - 0.0048(3d) + 0.0085(4p), \\ \sigma(3s) &= 8.4927 + 0.2501(3s-1+3p) + 0.0778(4s) \\ &\quad + 0.3382(3d) + 0.1978(4p), \\ \sigma(3p) &= 9.3345 + 0.3803(3p-1) + 0.0526(4s) \\ &\quad + 0.3289(3d) + 0.1558(4p), \\ \sigma(4s) &= 15.505 + 0.0971(4s-1) \\ &\quad + 0.8433(3d) + 0.0687(4p), \\ \sigma(3d) &= 13.5894 + 0.2693(3d-1) - 0.1065(4p), \\ \sigma(4p) &= 24.7782 + 0.2905(4p-1).\end{aligned}$$

These rules hold remarkably well as can be noted by the total energies given in Table III. In this table we compare the total SCF energy for the minimum basis set for Slater ξ , best ξ , and those ξ 's obtained with the above rules. The present rules are easily interpreted in terms of Slater's rules. For example, $\sigma(2p)$ has an initial contribution of 2.5787 which can be interpreted as the Slater screening constant for the $1s$ electrons (this is 2×0.85) plus the $2s$ electrons screening (2×0.35); this gives a screening of 2.4 not too different from our value of 2.5787. The $2p$ screening of 0.2216 for the $2p$ should be compared with a screening of 0.35 proposed

by Slater. The additional screening is due to outside electron penetration and is not accounted for by Slater rules.

At this point we should comment on Mulliken's screening constant for the $3s$ and $3p$ orbitals.¹⁵ For the $3s$ screening constant, Mulliken's values are remarkably close to our values; for Na, Mg, Al, Si, P, S, and Cl the screening constants are 0.90, 1.14, 1.37, 1.61, 1.85, 2.08, and 2.32, respectively. For the $3p$ screening constant Mulliken's values are somewhat less accurate than those originally proposed by Slater. Mulliken's values were obtained by interpolation of data from the SCF wavefunctions for Na and Cl atoms. From Fig. 1, one can see that this interpolation holds well for the $3s$ screening constant, but not for the $3p$ screening constants.

The modification of the Slater rules reported above should be somewhat qualified. The interpretation of the ξ parameters is bound to be subjective to some degree. The coupling of the vectors for the basis set of a given symmetry, prevents an objective division of the various contribution to the screening constant. There is not too much physical meaning in the individual terms of a given basis set. Hence, different rules can be obtained from our optimized ξ 's. In this work we have been guided by the principle of formulating rules which are simple to apply and close to those originally given by Slater.

Tables for the screening constants of the excited states for neutral atoms of the ground state electronic configuration and the corresponding states of all the stages of ionization of krypton are deposited with the ADI.¹⁶ In the deposited tables the ξ 's for any positive ion with Z smaller than 36 can be obtained by interpolation of the ξ for the neutral case and the corresponding ξ Kr ion. The accuracy of this interpolation was previously verified.^{3,4}

We are considering extending this work up to the inclusion of the $4f$ electrons. This extension will require some time, however, since, as noted previously, the number of cyclic optimizations of the ξ will increase.

¹⁵ R. S. Mullikan, J. Am. Chem. Soc. **72**, 4495 (1950), Table II, footnote 6.

¹⁶ These tables have been deposited as Document No. 7545 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$27.50 for photoprints or \$7.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.