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Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons

E. CLEMENTI, D. L. RAIMONDI, AND W. P. REINHARDT*

IBM San Jose Research Laboratory, San Jose, California

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Minimal basis-set atomic functions for the ground-state atoms from Rb ($Z=37$) to Rn ($Z=86$) are presented. These functions are analyzed in order to obtain systematic data for the screening constants and atomic radii following the work initiated by Slater.

I. INTRODUCTION

In a previous paper¹ (hereafter referred to as I), self-consistent-field functions were computed with a minimal basis set of Slater-type orbitals for atoms with 2 to 36 electrons. From the analysis of the optimized orbital exponents, atomic screening constants were derived for the $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, and $4p$ electrons. The screening constants were compared with those proposed by Slater in his classical work² and the new "rules" were obtained. The previous work was motivated by the need for simple wavefunctions to complement the large number of highly accurate wavefunctions available for the first-, second-, and third-row atoms. For the atoms of the fourth, fifth, and sixth rows the need for simple wavefunctions is even more apparent, since little data is presently available. They are particularly useful where preliminary computations are desired or where high accuracy is either not feasible with present techniques or not required. In this paper, we give SCF minimal basis-set functions for atoms with 37 to 86 electrons or for the atoms from rubidium to radon in the periodic table. In addition, the previous results are combined with the present data in discussing screening constants and orbital radii. In order to clarify the results to be presented, a short review of the theory follows.

The Slater-type basis set has the form

$$\chi_{n,l,m} = N r^{n-1} \exp(-\zeta_{n,l,m} r) Y_{l,m}(\theta, \varphi), \quad (1)$$

where n , l , and m are the usual quantum numbers, $Y_{l,m}$ is a spherical harmonic, N is a normalization factor, and $\zeta_{n,l,m}$ is the orbital exponent related to the screening constant $\sigma_{n,l,m}$ and to the effective nuclear charge Z_{eff} by the relations

$$\zeta_{n,l,m} = Z_{\text{eff}}/n = (Z - \sigma_{n,l,m})/n. \quad (2)$$

It should be noted that we use integer values for " n " whereas Slater used either integer values (in the first- and second-row elements) and fractional values in the third and higher rows of elements.

* Present address: Harvard University, Chemistry Department, Cambridge, Mass.

¹ E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).

² J. C. Slater, Phys. Rev. **36**, 57 (1930).

II. RESULTS

A. Total Energies and Orbital Exponents

Table I lists atomic number (Z), atomic symbol, outer-shell configuration, electronic state, and the total

TABLE I. Total energy for neutral atoms from Rb through Xe.

Z	Atom	Configuration	State	Energy
37	Rb	$5s(1)$	2S	-2930.6932
38	Sr	$5s(2)$	1S	-3123.7176
39	Y	$4d(1)$	2D	-3324.7806
40	Zr	$4d(2)$	3F	-3531.3152
41	Nb	$4d(3)$	4F	-3745.4783
41	Nb ^a	$5s(1) 4d(4)$	6D	-3745.2448
42	Mo	$4d(4)$	5D	-3967.0362
42	Mo ^a	$5s(1) 4d(5)$	7S	-3966.3422
43	Tc	$4d(5)$	6S	-4196.0510
44	Ru	$4d(6)$	5D	-4432.3593
44	Ru ^a	$5s(1) 4d(7)$	6F	-4432.1106
45	Rh	$4d(7)$	4F	-4676.2624
45	Rh ^a	$5s(1) 4d(8)$	4F	-4676.0290
46	Pd	$4d(8)$	3F	-4927.8059
46	Pd ^a	$5s(0) 4d(10)$	1S	-4927.1726
47	Ag	$4d(9)$	2D	-5187.0706
47	Ag ^a	$5s(1) 4d(10)$	2S	-5186.8939
48	Cd	$4d(10)$	1S	-5454.1909
49	In	$5p(1)$	2P	-5729.0988
50	Sn	$5p(2)$	3P	-6011.6722
51	Sb	$5p(3)$	4S	-6302.0043
52	Te	$5p(4)$	3P	-6600.0386
53	I	$5p(5)$	2P	-6905.9462
54	Xe	$5p(6)$	1S	-7219.7921

^a The filling up of the electronic shells is not exactly consecutive for the ground states of the fourth-row atoms. Therefore, for the fourth-row atoms we have given two states: the lowest one and that which one would obtain if the filling up of the shell would be regular.

energy for atoms from rubidium to xenon. Table II lists the optimized orbital exponents for the same group of atoms. Tables III and IV similarly apply to the atoms from cesium to radon. It is noted that the $4f$ electrons are not well described by a single Slater-type orbital when the number of $4f$ electrons is small. This is attributed to the extreme broadness of the $4f$ orbital. Considerable trouble was involved in obtaining results for

TABLE II. Tabulation of optimized orbital exponents for neutral Rb through neutral Xe in their ground state.

Z	Atom	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p
37	Rb	36.2078	13.5784	16.5194	7.2809	7.1011	3.0970	7.2264	2.7202	0.9969		
38	Sr	37.1911	13.9509	17.0152	7.5546	7.3892	3.3611	7.5754	2.9830	1.2141		
39	Y	38.1756	14.3111	17.5016	7.8505	7.6975	3.5659	8.4657	3.1864	1.2512	3.9896	
40	Zr	39.1590	14.6869	17.9964	8.1205	7.9485	3.7254	8.5223	3.3650	1.2891	3.2679	
41	Nb	40.1423	15.0626	18.4911	8.3905	8.2184	3.9090	8.7847	3.5652	1.3392	3.0796	
41	Nb ^a	40.1423	15.0626	18.4911	8.3905	8.2052	3.8207	8.7490	3.5211	1.1842	2.8094	
42	Mo	41.1256	15.4384	18.9859	8.6605	8.5030	4.1037	9.1097	3.7622	1.3952	3.1110	
42	Mo ^a	41.1256	15.4384	18.9859	8.6605	8.4912	4.0241	9.0761	3.7442	1.2212	2.8481	
43	Tc	42.1090	15.8141	19.4704	8.9304	8.7947	4.2996	9.4510	3.9528	1.4453	3.2205	
44	Ru	43.0923	16.1899	19.9754	9.2004	9.0844	4.4876	9.7981	4.1291	1.4905	3.3470	
44	Ru ^a	43.0923	16.1899	19.9754	9.2004	9.0737	4.4140	9.7863	4.1087	1.2969	3.2032	
45	Rh	44.0756	16.5656	20.4702	9.4704	9.3724	4.6571	10.1478	4.3236	1.5286	3.4937	
45	Rh ^a	44.0756	16.5773	20.4702	9.4795	9.3848	4.6454	10.1350	4.2849	1.3279	3.3606	
46	Pd	45.0589	16.9414	20.9650	9.7404	9.6616	4.8568	10.4989	4.5010	1.5675	3.6476	
46	Pd ^a	45.0589	16.9414	20.9650	9.7404	9.6732	4.7465	10.4837	4.4308	...	3.4044	
47	Ag	46.0423	17.3171	21.4597	10.0104	9.9476	5.0398	10.8503	4.6777	1.6057	3.8064	
47	Ag ^a	46.0423	17.3171	21.4597	10.0104	9.9362	4.9662	10.8466	4.6406	1.3511	3.6907	
48	Cd	47.0256	17.6929	21.9545	10.2804	10.2305	5.2173	11.2023	4.8528	1.6384	3.9692	
49	In	48.0097	18.0618	22.4490	10.5436	10.5069	5.4403	11.5594	5.0922	1.9023	4.2354	1.6940
50	Sn	48.9920	18.4297	22.9427	10.8066	10.7844	5.6645	11.9139	5.3163	2.1257	4.4925	1.8204
51	Sb	49.9744	18.7977	23.4363	11.0697	11.0613	5.8859	12.2666	5.5453	2.3222	4.7436	1.9989
52	Te	50.9568	19.1656	23.9300	11.3327	11.3363	6.1021	12.6131	5.7805	2.5076	4.9900	2.1617
53	I	51.9391	19.5335	24.4237	11.5958	11.6138	6.3243	12.9669	6.0074	2.6807	5.2335	2.3223
54	Xe	52.9215	19.9015	24.9173	11.8588	11.8892	6.5432	13.3156	6.2393	2.8436	5.4733	2.4849

^a These atoms have configurations corresponding to atoms labeled "a" of Table I.

TABLE III. Total energy for neutral atoms from Cs through Rn (in atomic units).

Z	Atom	Configuration	State	Energy
55	Cs	6s(1)	² S	-7 541.3432
56	Ba	6s(2)	¹ S	-7 870.6740
57	La	4f(1)	² F	-8 207.7052
58	Ce	4f(2)	³ I	-8 552.4491
59	Pr	4f(3)	⁴ J	-8 905.3989
60	Nd	4f(4)	⁵ I	-9 267.0675
61	Pm	4f(5)	⁶ H	-9 637.0680
62	Sm	4f(6)	⁷ F	-10 015.325
63	Eu	4f(7)	⁸ S	-10 402.457
64	Gd	4f(8)	⁷ F	-10 797.853
65	Tb	4f(9)	⁶ H	-11 202.707
66	Dy	4f(10)	⁵ I	-11 615.016
67	Ho	4f(11)	⁴ J	-12 038.572
68	Er	4f(12)	³ I	-12 467.338
69	Tm	4f(13)	² F	-12 907.267
70	Yb	4f(14)	¹ S	-13 356.155
71	Lu	5d(1)	² D	-12 816.567
72	Hf	5d(2)	³ F	-14 285.319
73	Ta	5d(3)	⁴ F	-14 763.336
74	W	5d(4)	⁵ D	-15 250.513
75	Re	5d(5)	⁶ S	-15 746.921
76	Os	5d(6)	⁵ D	-16 252.392
77	Ir	5d(7)	⁴ F	-16 767.183
78	Pt	5d(8)	³ F	-17 291.316
79	Au	5d(9)	² D	-17 824.845
80	Hg	5d(10)	¹ S	-18 367.869
81	Tl	6p(1)	² P	-18 920.276
82	Pb	6p(2)	³ P	-19 481.953
83	Bi	6p(3)	⁴ S	-20 052.992
84	Po	6p(4)	³ P	-20 633.317
85	As	6p(5)	² P	-21 223.079
86	Rn	6p(6)	¹ S	-21 822.323

the atoms from lanthanum ($Z=57$) to promethium ($Z=60$). In fact, for La, Pr, Nd, and Pm 2 STO's were required to get convergency. In Table IV these cases are apparent by the use of a second 4f STO (labeled 4f'). In each case the first 4f STO given is the dominant one. In the case of La and Ce the extremely small orbital exponent indicates the diffusiveness of the 4f electron, since the orbital exponent is inversely proportional to the radius of maximum charge density.

B. Screening Constants and Orbital Radii

The screening constants reported in I were presented with the following qualifications. If one wishes to identify the σ 's with the ζ 's via Eq. (2), then one should restrict himself only to those orbitals which have no other orbital of the same symmetry in the atom. For example, if one considers the neon atom, the correspondence between ζ and σ is unambiguous for the 2p but not for the 1s and 2s orbitals. The reason is simply that the complete basis set of a given symmetry is used in building the orbitals of that symmetry.

In other words, as noted in I, the coupling of the vectors for the basis set of a given symmetry prevents an objective division of various contributions to the screening constants. The problem becomes clearly more acute the larger the basis set of a given symmetry. In Fig. 1, the screening constants calculated from Eq. (2) are plotted versus atomic number for the atoms from helium to radon. Certainly, discontinuities should exist where new orbitals begin to fill, and these are evident. But a detailed discussion of these results is clouded by the ambiguities discussed above. There is a simple way by which these ambiguities may be in part removed. Let us consider again the neon atom. In the minimal basis

TABLE IV. Tabulation of optimized orbital exponents for neutral Cs through neutral Rn in their ground state.

Z	Atom	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f	4f'	5d	6p
55	Cs	53.9043	20.2558	25.4098	12.1258	12.1926	6.7606	13.6602	6.4644	3.0889	5.7096	2.7302	1.0605				
56	Ba	54.8861	20.6234	25.9048	12.3852	12.4388	6.9800	14.0081	6.7008	3.3239	5.9460	2.9601	1.2625				
57	La	55.8683	20.9767	26.3978	12.6477	12.7132	7.1991	14.3534	6.9266	3.5622	6.1813	3.1792	1.5520	0.3400	3.5230		
58	Ce	56.8481	21.3700	26.8912	12.8864	12.9865	7.4200	14.6951	7.1516	3.7827	6.4152	3.3931	1.7994	0.4190			
59	Pr	57.8306	21.7310	27.3847	13.1670	13.2748	7.5833	15.0508	7.2642	3.5226	6.5743	3.0567	1.2911	5.2752	0.5000		
60	Nd	58.8132	22.1081	27.8783	13.4476	13.5630	7.7466	15.3856	7.5035	3.7485	6.7023	3.3922	1.5511	5.5665	0.5800		
61	Pm	59.7958	22.4852	28.3719	13.7282	13.8513	7.9099	15.6994	7.6558	3.7671	6.9350	3.2828	1.5659	5.7835	0.6500		
62	Sm	60.7783	22.8674	28.8655	14.0088	14.1395	8.0731	16.0763	7.7720	3.6498	7.0599	3.2562	1.3353	5.8829			
63	Eu	61.7609	23.2354	29.3590	14.2894	14.4280	8.2170	16.4176	7.9687	3.7180	7.2352	3.3110	1.3536	6.0800			
64	Gd	62.7435	23.6085	29.8527	14.5699	14.7164	8.3610	16.7590	8.1617	3.7764	7.4084	3.3528	1.3691	6.2534			
65	Tb	63.7261	23.9861	30.3462	14.8505	15.0049	8.5050	17.0995	8.3497	3.8341	7.5775	3.3922	1.3834	6.4662			
66	Dy	64.7086	24.3547	30.8398	15.1311	15.2935	8.6480	17.4433	8.4565	3.8608	7.7545	3.4254	1.3906	6.6340			
67	Ho	65.6912	24.7278	31.3334	15.4117	15.5818	8.8280	17.7823	8.6407	3.9152	7.9179	3.4678	1.4065	6.8674			
68	Er	66.6737	25.1008	31.8270	15.6923	15.8703	9.0580	18.1201	8.7773	3.9436	8.0678	3.4944	1.4127	6.9946			
69	Tm	67.6563	25.4739	32.3206	15.9728	16.1587	9.2844	18.4581	8.9970	4.0074	8.2360	3.5456	1.4307	7.1585			
70	Yb	68.6389	25.8470	32.8142	16.2534	16.4455	9.3794	18.7989	9.1005	4.0300	8.3974	3.5663	1.4322	7.3580			
71	Lu	69.6195	26.2249	33.3055	16.5115	16.7221	9.5673	19.1396	9.2976	4.1910	8.8223	3.7360	1.4674	7.7328		4.0226	
72	Hf	70.6016	26.5949	33.7994	16.7705	16.9944	9.7443	19.4766	9.4824	4.3666	8.8810	3.9170	1.5274	8.0524		3.3239	
73	Ta	71.5837	26.9649	34.2932	17.0305	17.2668	9.9397	19.8137	9.6837	4.5387	9.0810	4.0947	1.5875	8.3676		3.2736	
74	W	72.5657	27.3349	34.7871	17.2900	17.5392	10.1397	20.1508	9.8871	4.7083	9.2933	4.2651	1.6424	8.6777		3.3484	
75	Re	73.5478	27.7049	35.2810	17.5495	17.8115	10.3391	20.4849	10.0933	4.8714	9.5136	4.4288	1.6860	8.9812		3.4766	
76	Os	74.5299	28.0749	35.7749	17.8091	18.0839	10.5238	20.8249	10.2860	5.0190	9.7145	4.5820	1.7205	9.2882		3.5994	
77	Ir	75.5119	28.4449	36.2688	18.0686	18.3563	10.7120	21.1620	10.4785	5.1691	9.9343	4.7322	1.7611	9.5862		3.7392	
78	Pt	76.4940	28.8149	36.7627	18.3281	18.6287	10.9097	21.4991	10.6826	5.3176	10.1575	4.8839	1.7919	9.8765		3.8815	
79	Au	77.4761	29.1849	37.2566	18.5876	18.9010	11.1033	21.8361	10.8867	5.4655	10.3820	5.0340	1.8230	10.1624		4.0253	
80	Hg	78.4581	29.5547	37.7505	18.8471	19.1734	11.3112	22.1732	11.1015	5.6222	10.6170	5.1934	1.8589	10.4402		4.1712	
81	Tl	79.4409	29.9421	38.2431	19.1397	19.4555	11.5197	22.5114	11.3042	5.8244	10.8472	5.4177	2.1366	10.7169		4.4050	2.0423
82	Pb	80.4195	30.2150	38.7383	19.3841	19.7165	11.7232	22.8489	11.5084	6.0263	11.0799	5.6060	2.3500	10.9922		4.6304	2.0655
83	Bi	81.3982	30.5880	39.2335	19.6285	19.9774	11.9268	23.1805	11.7126	6.2058	11.3098	5.8042	2.5400	11.2673		4.8488	2.2233
84	Po	82.3768	30.9609	39.7286	19.8729	20.2383	12.1304	23.5240	11.9168	6.4046	11.5168	6.0049	2.7218	11.5396		5.0608	2.3701
85	As	83.3554	31.3338	40.2238	20.1173	20.4992	12.3339	23.8615	12.1210	6.5867	11.7624	6.2080	2.8833	11.8101		5.2678	2.5272
86	Rn	84.3341	31.7068	40.7190	20.3617	20.7602	12.5375	24.1991	12.3253	6.7786	11.9857	6.3942	3.0540	12.0828		5.4706	2.6793

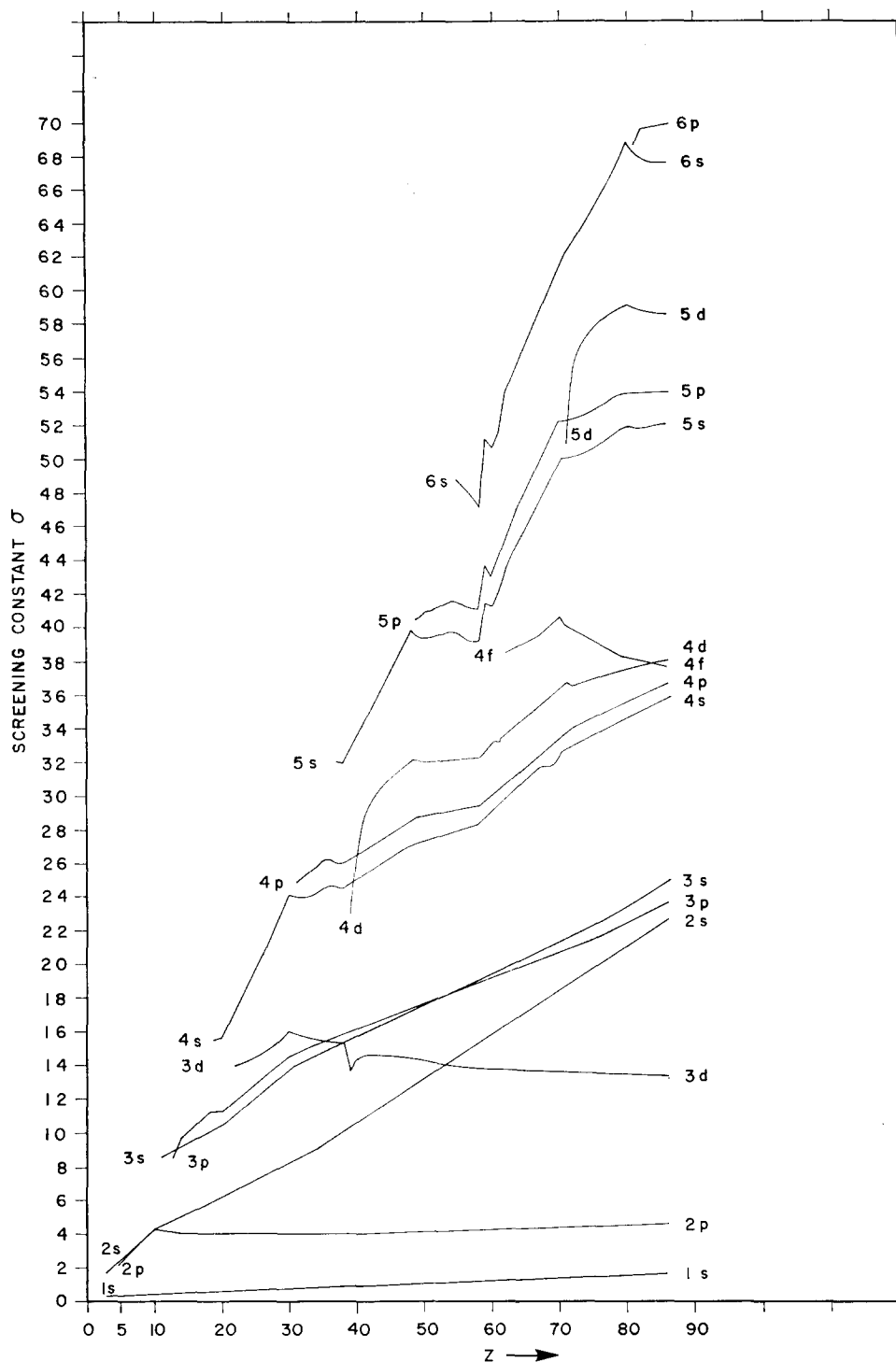


FIG. 1. The screening constants σ calculated from Eq. (2) are plotted vs atomic number Z .

set—SCF formalism, we use one $1s$ STO, one $2s$ STO, and one $2p$ STO. The radial part of the SCF orbital, $f(r)$, is characterized by the value of r for which $rf(r)$ has an extrema or a node. If the minimal basis set is well optimized the extrema and nodes are unambiguously determined by plotting the radial functions.

Therefore, one can obtain two sets of ζ 's. The first set contains the ζ 's which correspond to the optimized minimal basis set. The second set contains the ζ 's which correspond to STO's, not used in the computation, but which have the same r_{\max} as given by the first set. Since the minimal basis set of STO's gives an orthogonal set

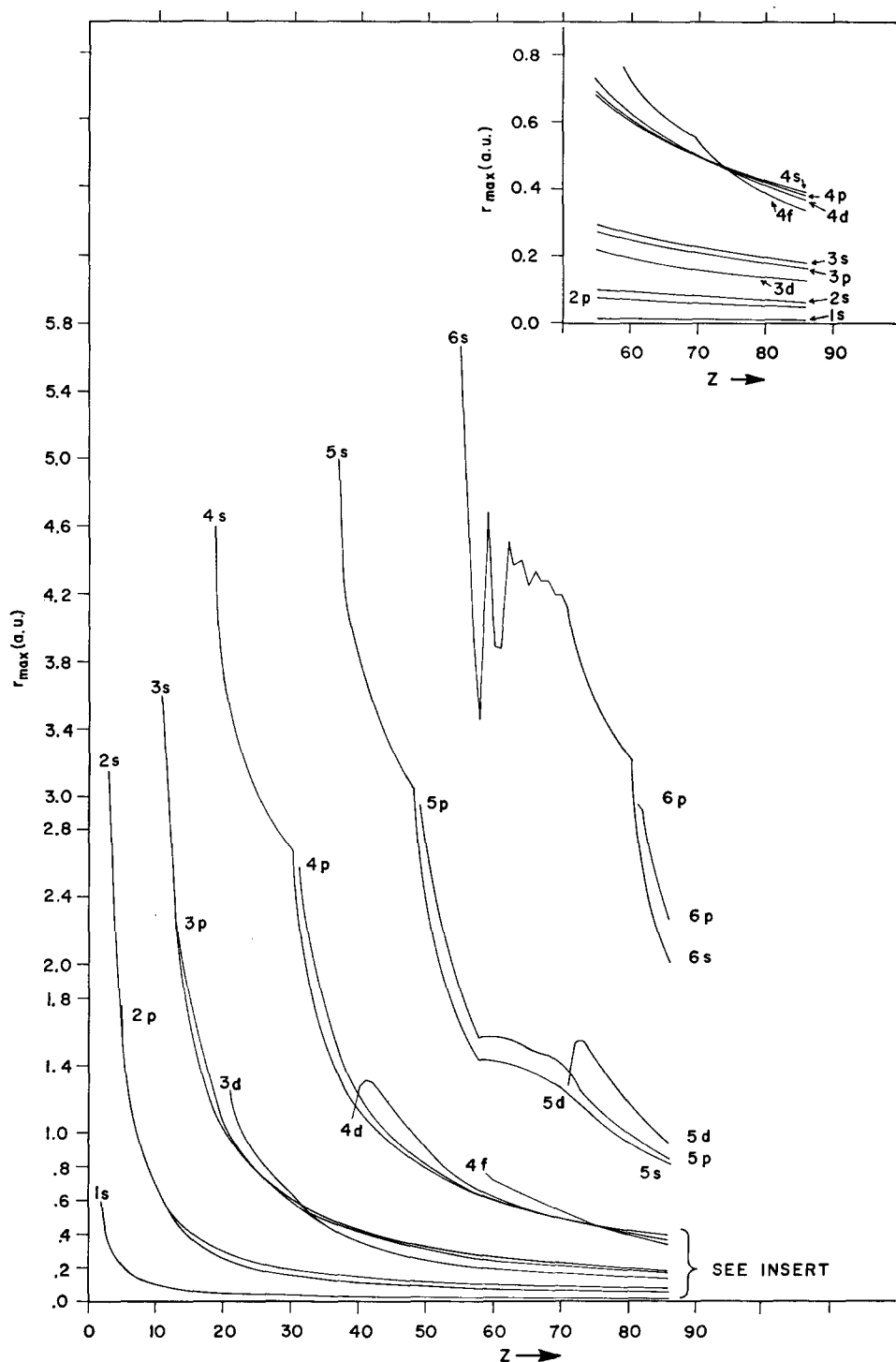


FIG. 2. Radii of maximum charge density r_{\max} are plotted vs atomic number Z .

of SCF orbitals and since the STO's are nodeless functions, the only r_{\max} of $r f(r)$ which should be considered is that corresponding to the main and outermost lobe from the nucleus. This presents no ambiguity since the main lobe is distinct from the orthogonality lobes of the SCF orbitals. For example, using again the case of the

neon atom, the minimal basis set is

$$\begin{aligned}
 1s(\text{SCF}) &= f(r_{1s}) Y_{00} = 0.99735\chi(1s) + 0.01092\chi(2s), \\
 2s(\text{SCF}) &= f(r_{2s}) Y_{00} = -0.25499\chi(1s) + 1.02937\chi(2s), \\
 2p(\text{SCF}) &= f(2p) Y_{1m} = \chi_{2p},
 \end{aligned} \tag{3}$$

																	He 0.31
Li 1.67	Be 1.12											B 0.87	C 0.67	N 0.56	O 0.48	F 0.42	Ne 0.38
Na 1.90	Mg 1.45											Al 1.18	Si 1.11	P 0.98	S 0.88	Cl 0.79	Ar 0.71
K 2.43	Ca 1.94	Sc 1.84	Ti 1.76	V 1.71	Cr 1.66	Mn 1.61	Fe 1.56	Co 1.52	Ni 1.49	Cu 1.45	Zn 1.42	Ga 1.36	Ge 1.25	As 1.14	Se 1.03	Br 0.94	Kr 0.88
Rb 2.65	Sr 2.19	Y 2.12	Zr 2.06	Nb 1.98	Mo 1.90	Tc 1.83	Ru 1.78	Rh 1.73	Pd 1.69	Ag 1.65	Cd 1.61	In 1.56	Sn 1.45	Sb 1.33	Te 1.23	I 1.15	Xe 1.08
Cs 2.98	Ba 2.53	La (6.22)	Hf 2.08	Ta 2.00	W 1.93	Re 1.88	Os 1.85	Ir 1.80	Pt 1.77	Au 1.74	Hg 1.71	Tl 1.56	Pb 1.54	Bi 1.43	Po 1.35	At 1.27	Rn 1.20
		Ce (5.05)	Pr 2.47	Nd 2.06	Pm 2.05	Sm 2.38	Eu 2.31	Gd 2.33	Tb 2.25	Dy 2.28	Ho 2.26	Er 2.26	Tm 2.22	Yb 2.22	Lu 2.17		

FIG. 3. Atomic radii (Ångstroms), determined from minimal-basis-set SCF functions.

where $\chi(1s)$, $\chi(2s)$, and $\chi(2p)$ are normalized STO's with orbital's exponents equal to 9.6421, 2.8793, and 2.8792, respectively. From $rf(r)_{\max}$ one would obtain the following set of ξ 's:

$$\begin{aligned}\xi'(1s) &= 9.6339, \\ \xi'(2s) &= 2.7933, \\ \xi'(2p) &= 2.8792,\end{aligned}\quad (4)$$

which is different than the set used in the computation of the SCF function. Since we are using minimal basis sets, the difference will not be too large for those cases

where the number of STO's of the same symmetry is small. However, the differences will be considerably greater for atoms with large numbers of electrons.

In addition to the usefulness of the orbital radii maxima for the screening constant analysis, these data are interesting in themselves for consideration of atomic radii. Certainly, there is a correlation between atomic radii and the radius of maximum charge density in the outermost shell of the atom. In a recent paper, Slater³ has found a good correlation between his empirically determined radii and radii calculated from the wavefunctions of Liberman, Waber, and Cromer.^{4,5} Thus, in Fig. 2 we give radii of maximum charge density for each

TABLE V. Comparison of R_{\max} for rare-gas atoms determined by using SCF functions of varying basis-set dimension (in atomic units).

Atom	Basis set	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p
He	A ¹	0.593										
He	B ^a	0.568										
He	C ^a	0.569										
Ne	A ¹	0.104	0.716	0.695								
Ne	B ^a	0.103	0.687	0.623								
Ne	C ^a	0.103	0.683	0.635								
Ar	A ¹	0.057	0.346	0.286	1.23	1.35						
Ar	B ^a	0.057	0.338	0.280	1.18	1.30						
Ar	C ^a	0.057	0.339	0.280	1.18	1.30						
Kr	A ¹	0.028	0.162	0.126	0.489	0.471	1.46	0.436	1.66			
Kr	B ^a	0.028	0.158	0.126	0.476	0.469	1.37	0.408	1.56			
Kr	C ^a	0.028	0.158	0.125	0.475	0.467	1.38	0.412	1.57			
Xe	A	0.019	0.106	0.081	0.301	0.279	0.700	0.227	0.710	1.81	0.760	2.04
Xe	B ^a	0.018	0.102	0.080	0.291	0.279	0.687	0.225	0.705	1.74	0.752	1.96

A, Single zeta.

B, Double zeta.

C, Hartree-Fock.

^a Preliminary results of Clementi.

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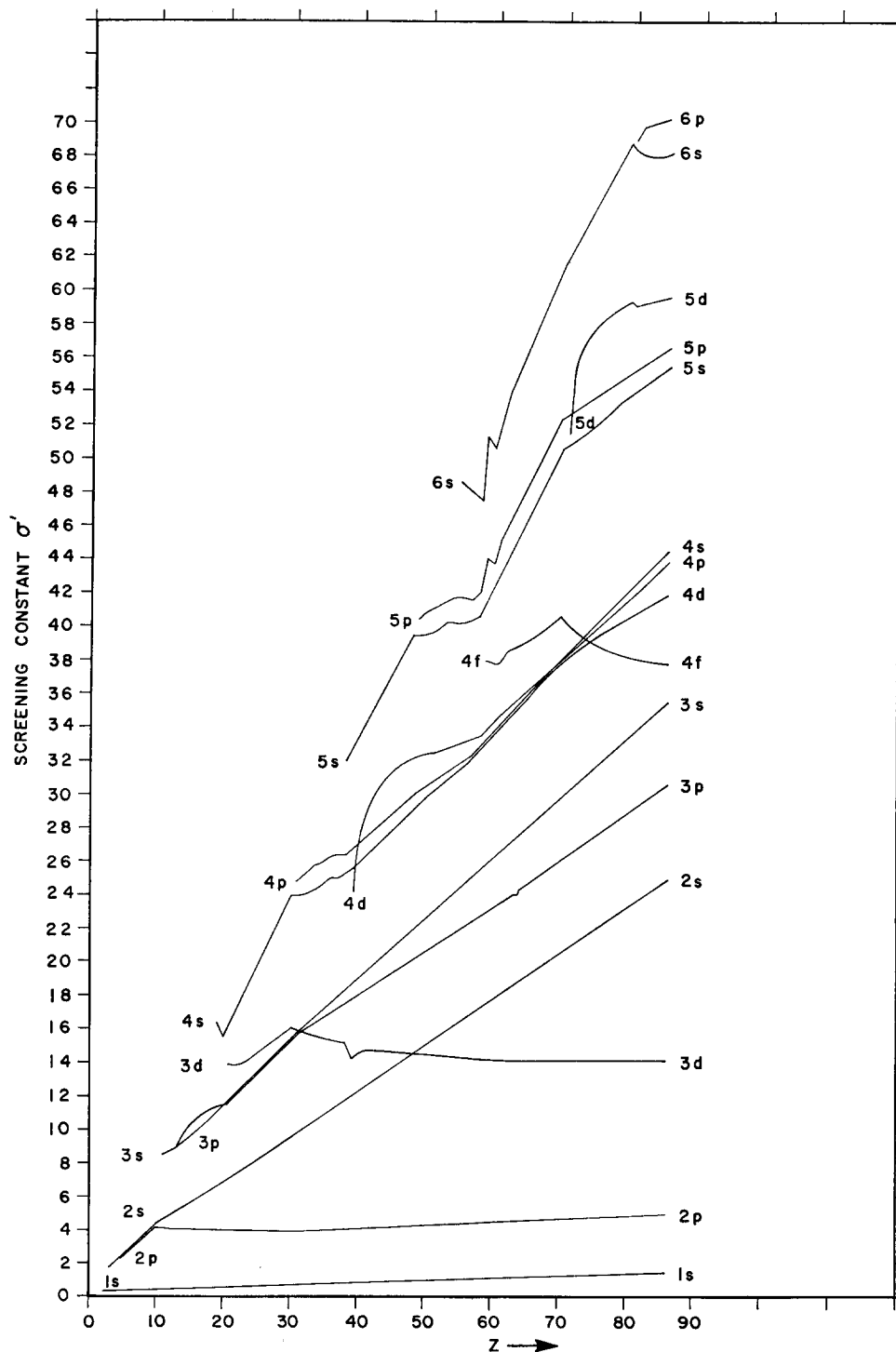


FIG. 4. The screening constants σ' calculated from r_{\max} are plotted vs atomic number Z .

of the orbitals for atoms from helium to radon, and in Fig. 3 the atomic radii in angstroms are given for helium to radon as calculated from the minimal-basis-set wavefunctions described above. Apart from some peculiarities, notably the behavior of the $6s$ orbital as the $4f$ shell is being filled, the variations with increasing

atomic number are relatively smooth. The contraction of the d and f orbitals is certainly evident in the Fig. 2 insert. Due to the qualitative nature of these simple wavefunctions, a detailed discussion of these results is postponed until a similar analysis is made on the more accurate wavefunctions which are available for atoms

from helium to xenon. This is exemplified in Table V where we have compared orbital radii for the rare gas atoms (helium, neon, argon, krypton, and xenon) as determined from wavefunctions of varying basis set dimensions.⁶ In the outer shells, large deviations are evident.

In Fig. 4 we have plotted the screening constants determined from the orbital radii by the technique described above. Although the trends are similar, these data are not clouded by the coupling of the vectors of orbitals of the same symmetry. One difference which stands out is the screening of the $4s$, $4p$, $4d$, and $4f$

electrons. Because of the contraction of the $4f$, $4d$, and $4p$ orbitals the screening constants for these orbitals should in the limit of high Z be less than the screening constant for the $4s$ orbital. Considering radon, in Fig. 1 the order of increasing values of the screening constants are $4s$, $4p$, $4f$, and $4d$. But in Fig. 4, we have similarly $4f$, $4d$, $4p$, and $4s$ which is the correct description. Again a more detailed analysis is postponed until this analysis can be applied to more accurate wavefunctions.

So that all the data is available to the reader, tables of orbital radii for the atoms from helium through radon are available upon request to the authors.⁷

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Temperature Dependence, Orientation Correlation, and Molecular Fields in Second-Harmonic Light Scattering from Liquids and Gases

D. L. WEINBERG*

Lincoln Laboratory,† Massachusetts Institute of Technology, Lexington, Massachusetts

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The properties of second-harmonic light scattering in fluids are derived in terms of the molecular polarizabilities, orientation correlation among molecules, and the molecular field F_α . Measurements of scattering intensity in CCl_4 and water, from about 10° to 60°C , are reported. The variations with temperature, and therefore apparently the effects of changes of orientation correlation, are slight. The influence of preferred orientation in CCl_4 , of the type deduced from x-ray diffraction, is calculated. The third-rank molecular polarizability tensor consists of a fourth-rank tensor contracted with F_α , in addition to the term previously known, which is independent of F_α . With F_α arising from molecular multipole moments, the new term explains some measured depolarizations in liquids, and accounts for the spectral line, but not the background, observed in methane gas. In the case of molecular dipole moments, the new term can cause spectral narrowing.

I. INTRODUCTION

Second-harmonic light scattering has been observed in liquids and fused quartz¹ and methane gas.² When an optical electric field of angular frequency ω is incident on matter, Rayleigh scattering arises from local, e.g., molecular, induced electric dipoles, (neglecting higher-order induced moments) radiating independently of each other at the fundamental frequency ω . Second-harmonic scattering is related, but the nonlinear response at 2ω is pertinent. Raman scattering differs from both, in that the scattered light differs from a harmonic of ω by a natural frequency of the medium. Finally there are effects in which the local dipoles oscillate coherently, i.e., in definite phase relations with

each other, such as harmonic generation and stimulated emission.

The formulation which Buckingham and Stephen³ (BS) applied to Rayleigh scattering is used. Let the dipole moment of an isolated molecule in an electric field G_α be

$$p_\alpha = \mu_\alpha + \alpha_{\alpha\beta} G_\beta + \frac{1}{2} \beta_{\alpha\beta\gamma} G_\beta G_\gamma + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta} G_\beta G_\gamma G_\delta + \dots \quad (1)$$

This can be applied to a molecule in a fluid, where $G_\alpha = E_\alpha + I_\alpha + F_\alpha$, if the fields are sufficiently homogeneous. E_α is the optical field in the medium, $E_\alpha + I_\alpha$ is the local optical field, and F_α is the field with no incident light beam. (The present $I_\alpha + F_\alpha$ is the F_α of BS.) Since 2ω is well below the frequencies of the strong absorption bands in the cases to be considered, the polarizability tensors are approximately symmetrical in all pairs of indices. They will be assumed to be exactly so. Table I relates the elements of $\beta_{\alpha\beta\gamma}$ and of $\gamma_{\alpha\beta\gamma\delta}$ for some molecules of interest here.

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* Present address: NASA Electronics Research Center, Cambridge, Mass.

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