THE INTERPOLATION OF ATOMIC FIELDS

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ABSTRACT. $Z(nl; r)$ is the contribution to $Z(r)$ from an electron in the (nl) wave function. The $Z(nl; r)$ vary systematically with atomic number and, as N becomes large, tend to the corresponding hydrogen-like functions, $Z_H(nl; r)$. A two-parameter method of fitting the $Z(nl; r)$ to the $Z_H(nl; r)$ is described. This involves a 'screening constant' and a 'slope constant', both of which are defined. From published data, the two parameters have been obtained as functions of atomic number. The parameters for an unsolved atom can then be found by interpolation and approximate $Z(nl; r)$ derived by appropriate adjustment of the functions for the nearest atom in the periodic table for which they are known. The method has been tested by interpolating for the $(3d)$ function between Cu^+ and Rb^+ and by preparing estimates of the $Z(nl; r)$ for the unknown structure Mo^+. The results were good for all but $Z(4d; r)$ for Mo^+, where the number of values of the screening and slope constants already known was insufficient for reliable interpolation.

1. *Introduction.* In the preceding paper (3), Hartree has described a method of interpolating atomic wave functions with respect to atomic number. This method is suitable for obtaining a first approximation to a self-consistent field with exchange. For heavy atoms, only calculations without exchange are at present feasible, and for these it is better to make estimates of the contributions to $Z(r)$ from electrons in the various wave functions. In this paper, the problem of interpolating these contributions with respect to atomic number, N, is considered.

2. *The variation of $Z(r)$ contributions with atomic number.* A derivation of the self-consistent field equations, a description of the methods used to solve them, and a survey of most of the calculations so far carried out has been given by Hartree (2). The same notation will be used here.

The contribution to $Z(r)$ from an electron in an (nl) wave function is given by

$$Z(nl; r) = [1 - Z_0(nl, nl; r)]. \tag{1}$$

Then the total $Z(r)$ is $$Z(r) = \Sigma_{n'l'} q(n'l') Z(n'l'; r) + i, \tag{2}$$

where i is the degree of ionization of the atom and $q(n'l')$ is the number of occupied wave functions in the $(n'l')$ group. If the $(n'l')$ group is complete,

$$q(n'l') = 2(2l+1). \tag{3}$$

$Z_0(nl, nl; r)$ is related to the normalized wave function, $P(nl; r)$, by

$$Z_0(nl, nl; r) = \int_0^r P^2(nl; r_1)\, dr_1. \tag{4}$$

Sketches of $P(3s; r)$ and $Z(3s; r)$ are given in Fig. 1. $Z(3s; r)$ decreases from unity at the origin to zero as $r \to \infty$ and has a steeply sloping almost linear region in the neighbourhood of the principal maximum of $P(3s; r)$. This is the region of maximum

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probability for electrons in the $(3s)$ group. The point of inflexion is near to $Z(3s;\, r) = \frac{1}{2}$. The subsidiary maxima of $P(3s;\, r)$ produce in $Z(3s;\, r)$ only small irregularities near the origin. The $Z(nl;\, r)$ curves for other wave functions show similar features.

For a hydrogen-like atom of atomic number N, $Z(nl;\, r)$ is obtained from the corresponding hydrogen function, $Z_{\mathrm{H}}(nl;\, r)$, by a simple scaling process, for

$$Z(nl;\, r) = Z_{\mathrm{H}}(nl;\, Nr). \tag{5}$$

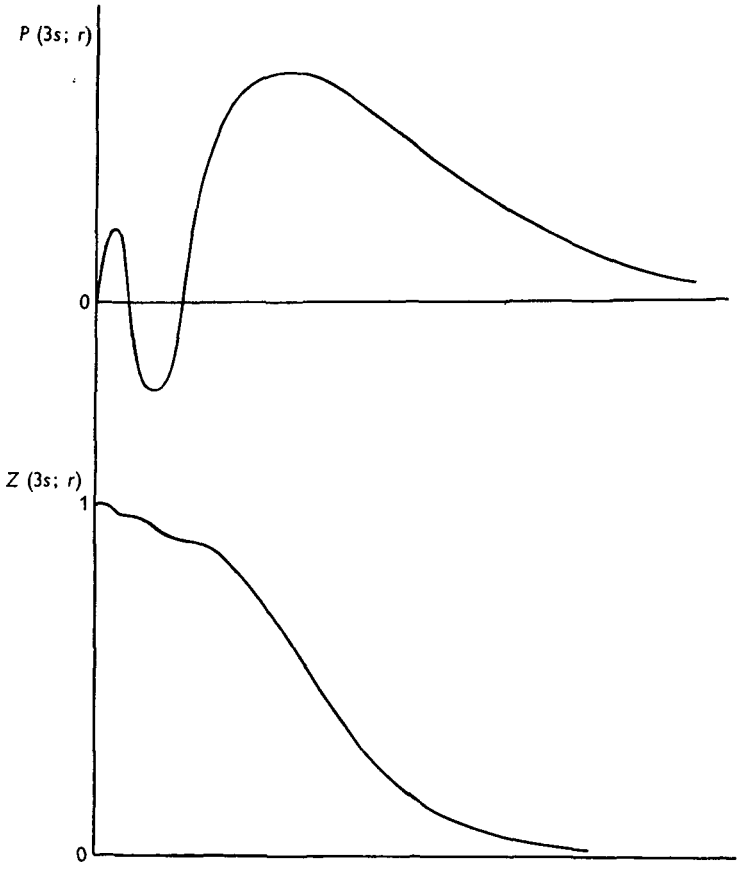


Fig. 1. Sketches of $P(3s;\, r)$ and $Z(3s;\, r)$

Thus, if the $Z(nl;\, r)$ for a series of hydrogen-like atoms are plotted against a logarithmic scale of r, the curves are similar to one another, but displaced relative to $Z_{\mathrm{H}}(nl;\, r)$ by a distance $\log N$ in the direction of decreasing $\log r$.

For a series of nearly neutral atoms, the situation is more complex. The electrons screen the nucleus so that the effective atomic number varies from N, for small r, to i, as $r \to \infty$. Consequently, each $Z(nl;\, r)$ is shifted relative to $Z_{\mathrm{H}}(nl;\, r)$ by an amount less than $\log N$. The curves are no longer similar and the gradient at the point of inflexion varies with atomic number, increasing towards the hydrogen value as N becomes large.

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3. *Screening and slope constants.* It is important that estimates of $Z(nl; r)$ should be accurate in the region where an electron in the (nl) wave function is most likely to be. A satisfactory method of interpolating $Z(nl; r)$ with respect to N will therefore aim at obtaining good results in the region in which $Z(nl; r)$ is varying rapidly.

Fig. 2 shows the form of the graphs of $Z(nl; r)$ against $\log r$ for an atom of atomic number N, and the corresponding function $Z_{\mathrm{H}}(nl; r)$ for hydrogen. The two curves can be brought into coincidence in the most important region by

(a) a shift of the hydrogen curve along the $\log r$ axis to bring the points $Z(nl; r) = \frac{1}{2}$ and $Z_{\mathrm{H}}(nl; r) = \frac{1}{2}$ into coincidence (this is a simple scaling process and cannot superpose the curves over a wide range, as the tangents at their points of inflexion are not parallel); and

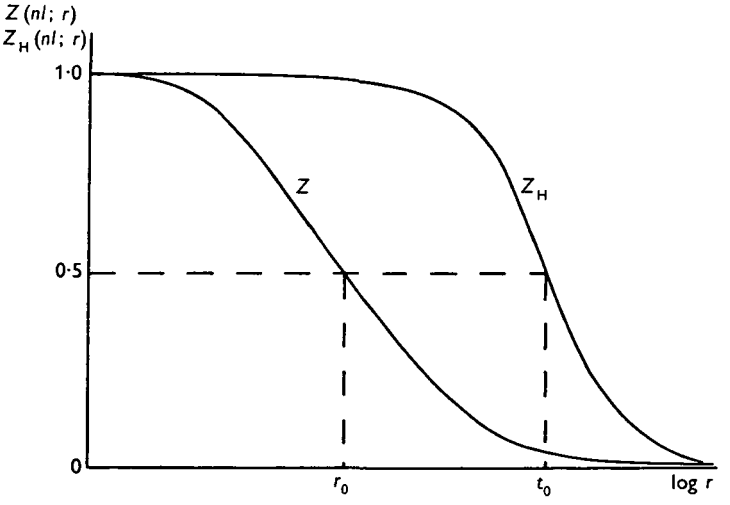


Fig. 2. $Z(nl; r)$ and $Z_{\mathrm{H}}(nl; r)$ plotted against $\log r$

(b) a uniform expansion of the $\log r$ scale for the hydrogen function to make the gradients at the points of inflexion equal, thus compensating for the chief deficiency of simple scaling.

Analytically this can be expressed

$$\log r_0 = \log t_0 - \log [N - \sigma(nl)], \tag{6}$$

$$\log r \doteq \log r_0 + \alpha(nl) \log (t/t_0), \tag{7}$$

where r_0, t_0 and t are defined by

$$Z(nl; r_0) = Z_{\mathrm{H}}(nl; t_0) = \tfrac{1}{2}, \tag{8}$$

$$Z(nl; r) = Z_{\mathrm{H}}(nl; t). \tag{9}$$

Here (6) describes simple scaling corresponding to an effective atomic number $[N - \sigma(nl)]$. Thus, $\sigma(nl)$ is a type of screening constant. $\alpha(nl)$ will be referred to as the 'slope' constant.

Published results of self-consistent field calculations give tables of $q(n'l')\, Z(n'l'; r)$. From these, values of r_0 can be obtained by inverse interpolation. Analytical expressions

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Table 1. *Values of screening constants, σ, and slope constants, α*

Where a group is incomplete, the number of electrons is indicated by a bracketed index above the value of σ.

Atom	Atomic number	Parameters	(1s)	(2s)	(2p)	(3s)	(3p)	(3d)	(4s)	(4p)	(4d)	(4f)	(5s)	(5p)	(5d)
Cl^-	17	σ	0·43	3·54	4·67	8·07	10·89	—	—	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·01	0·025	0·025	0·05	0·05	—	—	—	—	—	—	—	—
		α	1·00	1·10	1·20	1·28	1·57	—	—	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	—	—	—	—	—	—	—	—
K^+	19	σ	0·46	3·60	4·69	8·19	10·26	—	—	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·01	0·015	0·015	0·025	0·025	—	—	—	—	—	—	—	—
		α	1·00	1·09	1·09	1·23	1·30	—	—	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	—	—	—	—	—	—	—	—
Ca	20	σ	0·45	3·61	4·72	8·21	10·14	—	14·27	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·02	0·02	0·01	0·025	0·025	—	0·05	—	—	—	—	—	—
		α	1·00	1·08	1·08	1·21	1·25	—	1·46	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·01	0·005	—	0·01	—	—	—	—	—	—
Cr	24	σ	0·32	3·68	4·74	8·31	10·09	$16·78^{(6)}$	—	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·18	0·10	0·03	0·35	0·10	0·05	—	—	—	—	—	—	—
		α	1·00	1·05	1·07	1·20	1·20	1·89	—	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·04	0·005	0·01	0·05	0·02	0·02	—	—	—	—	—	—	—
Fe	26	σ	0·48	3·66	4·67	9·08	11·01	$16·59^{(6)}$	18·28	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·01	0·03	0·03	0·05	0·05	0·05	0·05	—	—	—	—	—	—
		α	1·00	1·06	1·07	1·20	1·22	1·53	1·57	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	0·005	0·005	—	—	—	—	—	—
Cu^+	29	σ	0·45	3·73	4·77	9·69	11·76	18·25	—	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·02	0·02	0·02	0·05	0·05	0·05	—	—	—	—	—	—	—
		α	1·00	1·06	1·05	1·20	1·23	1·62	—	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·02	0·02	0·01	0·02	0·01	0·01	—	—	—	—	—	—	—
Zn	30	σ	0·35	3·76	4·82	9·87	11·96	17·86	21·35	—	—	—	—	—	—
		$\pm\Delta\sigma$	0·12	0·06	0·03	0·04	0·04	0·04	0·04	—	—	—	—	—	—
		α	1·00	1·05	1·05	1·21	1·22	1·52	1·61	—	—	—	—	—	—
		$\pm\Delta\alpha$	0·02	0·02	0·01	0·02	0·01	0·01	0·03	—	—	—	—	—	—
Ga	31	σ	0·49	3·80	4·86	10·00	12·15	17·55	20·77	$25·26^{(1)}$	—	—	—	—	—
		$\pm\Delta\sigma$	0·11	0·07	0·07	0·04	0·04	0·04	0·06	0·06	—	—	—	—	—
		α	1·00	1·04	1·05	1·20	1·22	1·44	1·53	1·73	—	—	—	—	—
		$\pm\Delta\alpha$	0·02	0·02	0·01	0·02	0·01	0·01	0·03	0·07	—	—	—	—	—
Ge	32	σ	0·51	3·84	4·84	10·22	12·26	17·31	20·50	$24·54^{(2)}$	—	—	—	—	—
		$\pm\Delta\sigma$	0·12	0·07	0·07	0·05	0·05	0·05	0·04	0·04	—	—	—	—	—
		α	0·99	1·06	1·05	1·19	1·21	1·38	1·47	1·68	—	—	—	—	—
		$\pm\Delta\alpha$	0·02	0·02	0·01	0·02	0·01	0·01	0·03	0·03	—	—	—	—	—

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Table 1. (*Cont.*)

Atom	Atomic number	Parameters	(1s)	(2s)	(2p)	(3s)	(3p)	(3d)	(4s)	(4p)	(4d)	(4f)	(5s)	(5p)	(5d)
As	33	σ	0·42	3·78	4·87	10·29	12·33	17·12	20·35	24·29[3]	—	—	—	—	—
		$\pm\Delta\sigma$	0·12	0·07	0·07	0·05	0·05	0·05	0·04	0·04	—	—	—	—	—
		α	1·00	1·04	1·05	1·18	1·21	1·34	1·43	1·66	—	—	—	—	—
		$\pm\Delta\alpha$	0·02	0·02	0·01	0·02	0·01	0·01	0·03	0·02	—	—	—	—	—
Br	35	σ	0·47	3·95	4·84	10·51	12·47	16·49	20·03	24·31[5]	—	—	—	—	—
		$\pm\Delta\sigma$	0·24	0·20	0·20	0·20	0·20	0·20	0·60	0·60	—	—	—	—	—
		α	1·03	1·05	1·05	1·14	1·19	1·23	1·37	1·58	—	—	—	—	—
		$\pm\Delta\alpha$	0·04	0·05	0·01	0·05	0·01	0·01	0·06	0·03	—	—	—	—	—
Rb^+	37	σ	0·48	3·88	4·91	10·63	12·61	16·65	20·22	23·49	—	—	—	—	—
		$\pm\Delta\sigma$	0·02	0·02	0·02	0·01	0·01	0·01	0·05	0·05	—	—	—	—	—
		α	1·00	1·05	1·04	1·16	1·17	1·24	1·34	1·45	—	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	0·005	0·005	0·005	—	—	—	—	—
Mo^+	42	σ	0·48	3·98	5·01	10·90	12·81	16·42	19·97	22·76	31·26[5]	—	—	—	—
		$\pm\Delta\sigma$	0·04	0·03	0·01	0·02	0·01	0·005	0·01	0·005	0·005	—	—	—	—
		α	1·00	1·04	1·04	1·13	1·13	1·18	1·26	1·30	1·67	—	—	—	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	0·005	0·005	0·005	0·005	—	—	—	—
Ag^+	47	σ	0·60	4·03	5·08	11·15	12·98	16·38	20·39	23·16	31·16	—	—	—	—
		$\pm\Delta\sigma$	0·35	0·19	0·07	0·15	0·05	0·04	0·06	0·05	0·02	—	—	—	—
		α	1·00	1·03	1·03	1·11	1·11	1·14	1·23	1·28	1·61	—	—	—	—
		$\pm\Delta\alpha$	0·04	0·04	0·01	0·05	0·02	0·01	0·06	0·02	0·02	—	—	—	—
Cs^+	55	σ	0·46	4·14	5·19	11·33	13·20	16·45	20·88	23·44	29·01	—	33·39	37·22	—
		$\pm\Delta\sigma$	0·04	0·03	0·03	0·02	0·02	0·02	0·02	0·02	0·03	—	0·03	0·03	—
		α	1·00	1·03	1·03	1·09	1·09	1·11	1·19	1·20	1·26	—	1·38	1·50	—
		$\pm\Delta\alpha$	0·005	0·005	0·005	0·005	0·005	0·005	0·005	0·005	0·005	—	0·01	0·005	—
W	74	σ	−0·24	4·16	5·53	11·74	13·52	16·44	23·56	26·26	31·91	41·98	40·06	43·74	56·52[4]
		$\pm\Delta\sigma$	0·70	0·40	0·35	0·25	0·25	0·20	0·20	0·10	0·10	0·10	0·12	0·12	0·12
		α	0·99	1·06	1·02	1·06	1·06	1·07	1·17	1·17	1·21	1·43	1·33	1·38	1·82
		$\pm\Delta\alpha$	0·04	0·04	0·01	0·04	0·01	0·01	0·05	0·03	0·01	0·01	0·05	0·02	0·01
Au^+	79	σ	−0·07	4·31	5·55	11·95	13·66	16·82	23·94	26·66	31·79	40·98	40·44	44·30	55·95
		$\pm\Delta\sigma$	0·60	0·40	0·14	0·27	0·10	0·06	0·20	0·15	0·04	0·03	0·15	0·05	0·03
		α	1·00	1·01	1·02	1·05	1·06	1·07	1·15	1·16	1·17	1·32	1·29	1·34	1·73
		$\pm\Delta\alpha$	0·04	0·04	0·01	0·04	0·01	0·01	0·05	0·03	0·01	0·01	0·05	0·02	0·01
Hg^{++}	80	σ	0·13	4·25	5·39	11·80	13·75	16·67	24·03	26·65	31·90	40·96	40·37	44·23	55·12
		$\pm\Delta\sigma$	0·60	0·40	0·14	0·27	0·10	0·06	0·20	0·15	0·04	0·03	0·15	0·05	0·03
		α	0·98	1·03	1·03	1·07	1·06	1·07	1·16	1·16	1·18	1·32	1·30	1·34	1·65
		$\pm\Delta\alpha$	0·04	0·04	0·01	0·04	0·01	0·01	0·05	0·03	0·01	0·01	0·05	0·02	0·01

for hydrogen wave functions are available (see, for example, Condon and Shortley (1)). From these $Z_H(nl; t)$ can be obtained by numerical quadrature and t_0 by inverse interpolation. $\sigma(nl)$ can then be calculated from (6).

A value for $\alpha(nl)$ was obtained by finding r_a, t_a, r_b and t_b such that

$$Z(nl; r_a) = Z_H(nl; t_a) = 0{\cdot}4 \tag{10}$$

and

$$Z(nl; r_b) = Z_H(nl; t_b) = 0{\cdot}6, \tag{11}$$

and taking

$$\alpha(nl) = [\log(r_a/r_b)]/[\log(t_a/t_b)]. \tag{12}$$

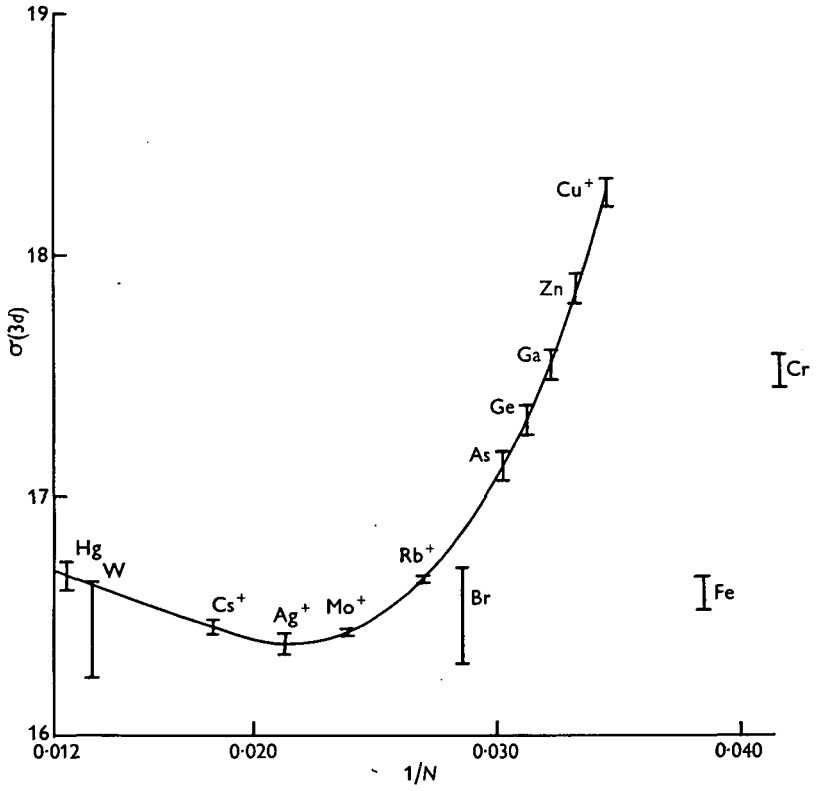


Fig. 3. Plot of $\sigma(3d)$ against $1/N$.

Since the two points used for obtaining the slope constant lie near the point of inflexion, the procedure gives a value of α which brings the important part of the curves into coincidence. r_a, r_b, t_a and t_b may be obtained by inverse interpolation.

Values of the $\sigma(nl)$ and $\alpha(nl)$ have been calculated for those atoms heavier than Ca for which results of self-consistent field calculations without exchange are readily available (Hartree (2), Henry (4), Ridley (5), and a private communication from Hartree, 'Improved self-consistent field for Ag^+'). These are given in Table 1. The ranges of uncertainty, $\Delta\sigma$ in σ and $\Delta\alpha$ in α, have been estimated from the accuracy of the published tables.

$\sigma(nl)$ and $\alpha(nl)$ were plotted against $1/N$. For $(1s)$, $(2s)$, $(2p)$ and $(3s)$, continuous curves could be drawn to lie within the estimated ranges of uncertainty of σ or α. The

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plot obtained for $\sigma(3d)$ is given in Fig. 3 and shows several interesting features. There is a hint of a break in the curve between Br and Rb^+. This would be reasonable, since it is here that the $4p$ group is completed and the new shell begun. However, the accuracy does not enable the nature of the discontinuity to be determined with any confidence, and a continuous curve has been drawn from Cu^+ to Hg^{2+}. The points for Cr and Fe lie well below this curve, as might be expected, since the $(3d)$ group is incomplete and the 'self-screening' of the $(3d)$ electrons is well below its maximum value. The plots for $(3p)$, $(4s)$, $(4p)$ and $(4d)$ show similar physically accountable irregularities. A similarity in the general shape of the curves for $3s$ and $4s$, $3p$ and $4p$,

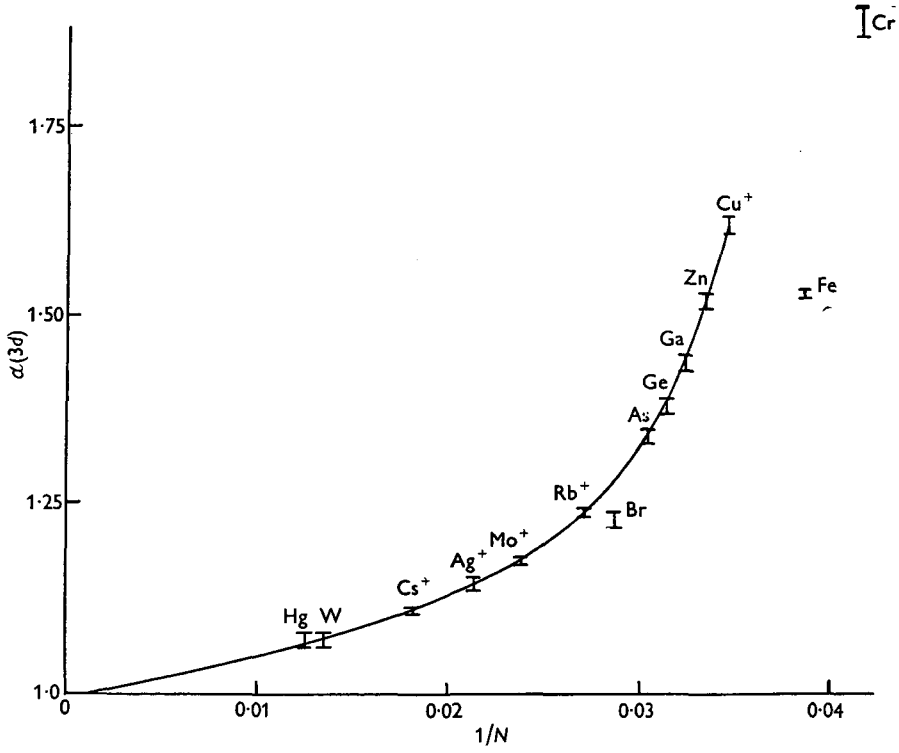


Fig. 4. Plot of $\alpha(3d)$ against $1/N$.

$3d$ and $4d$, enables curves for $4s$, $4p$ and $4d$ to be drawn with greater confidence than is at first sight justified by the sparsity of points. A plot of $\alpha(3d)$ is given in Fig. 4. As $1/N \to 0$, $\alpha \to 1$, since the wave function becomes hydrogen-like. This gives an extra point for the curve.

From the curves $\sigma(nl)$ and $\alpha(nl)$ for any atom between Cu^+ and Hg may be obtained. Graphical interpolation is adequate. For (nl) up to $(3d)$, this gives σ to 0·05 and α to about 0·01. The interpolation is less satisfactory for the outer electrons, since the points available are few at present.

4. *The estimation of* $Z(nl; r)$. Given values of $\sigma(nl)$ and $\alpha(nl)$ for an atom of which the structure is unknown, estimates of the $Z(nl; r)$ may be obtained by adjusting the functions for the nearest atom in the periodic table for which they are known.

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Thus, suppose that $\sigma(nl)_A$ and $\alpha(nl)_A$ for an atom of atomic number N_A have been determined by interpolation and that the functions $Z_B(nl; r)$ for a neighbouring atom of atomic number N_B are known. Then, from (6), (7) and (9),

$$\log r_B \simeq [\alpha(nl)_B/\alpha(nl)_A] \log r_A + \{\log t_0 - \log [N_B - \sigma(nl)_B]\} - [\alpha(nl)_B/\alpha(nl)_A] \{\log t_0 - \log [N_A - \sigma(nl)_A]\} \quad (13)$$

and

$$Z_A(nl; r_A) = Z_B(nl; r_B), \quad (14)$$

Table 2. *Values of* t_0, t_a *and* t_b

nl	$t_a(Z_H = 0{\cdot}4)$	$t_0(Z_H = 0{\cdot}5)$	$t_b(Z_H = 0{\cdot}6)$
1*s*	1·556	1·339	1·143
2*s*	6·372	$5{\cdot}800_5$	5·268
2*p*	$5{\cdot}237_5$	4·673	$4{\cdot}148_5$
3*s*	14·66	$13{\cdot}62_5$	12·63
3*p*	13·60	12·57	11·58
3*d*	$11{\cdot}01_5$	$10{\cdot}00_5$	$9{\cdot}059_5$
4*s*	26·49	24·90	23·33
4*p*	25·46	23·87	22·30
4*d*	23·19	21·60	20·05
4*f*	18·87	17·34	15·89
5*s*	41·93	39·69	37·40
5*p*	$40{\cdot}91_5$	38·67	36·38
5*d*	38·75	$36{\cdot}50_5$	34·23
5*f*	35·07	32·85	30·62
5*g*	28·80	26·68	24·66

Table 3. *Maximum discrepancy between estimated and known values of* $10Z(3d; r)$ *for elements of the second long period*

Atom	Atomic no.	Discrepancy for $10Z(3d; r)$	
		Estimate using σ and α	Estimate using σ only
Zn	30	0·035	0·17
Ga	31	0·08	—
Ge	32	0·095	—
As	33	0·11	0·49

from which $Z_A(nl; r_A)$ can be obtained approximately as a function of r_A by interpolation in the table of $Z_B(nl; r_B)$. Values of t_0 are needed and are given in Table 2, where values of t_a and t_b are also quoted.

This method of obtaining estimates of $Z(nl; r)$ has been tested in two ways:

(*a*) Estimates of $Z(3d; r)$ were derived for Zn, Ga, Ge and As from the function for Cu^+, using the correct values of $\sigma(3d)$ and $\alpha(3d)$. The estimates obtained were compared with the known values of $Z(3d; r)$. In Table 3, the maximum discrepancy between the estimated and known values of $10Z(3d; r)$ is given. The agreement becomes less good as the difference between the atomic numbers increases. For comparison, estimates of $10Z(3d; r)$ for Zn and As were obtained by using only the screening constant, $\sigma(3d)$, and taking $\alpha(3d) = 1$. The maximum discrepancies for these

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are also give in Table 3, and are about $4\frac{1}{2}$ times those obtained when both parameters are used. This shows that the proposed adjustment using both $\sigma(nl)$ and $\alpha(nl)$ is a considerable improvement upon any process of simple scaling.

Table 4. *Discrepancies between estimated and final values of* $Z(nl; r)$ *for* Mo^+. *Estimated and final values of* $\sigma(nl)$ *and* $\alpha(nl)$

nl	Maximum discrepancy per electron	σ (nl)		$\alpha(nl)$	
		Initial	Final	Initial	Final
$1s$	0·001	0·50	0·48	1·00	1·00
$2s$	0·002	3·97	3·98	1·04	1·04
$2p$	0·001	4·99	5·01	$1·03_5$	1·04
$3s$	0·005	10·93	10·90	1·13	1·13
$3p$	0·005	12·82	12·81	$1·13_5$	1·13
$3d$	0·003	16·47	16·42	$1·17_5$	1·18
$4s$	0·017	20·14	19·98	$1·27_5$	1·26
$4p$	0·028	23·25	22·76	$1·32_5$	1·30
$4d$	0·2	29·00	31·26	1·50	1·67

(*b*) Estimates of the $Z(nl; r)$ were made for an unknown structure, Mo^+. Rb^+ and Ag^+ are the nearest known structures. For the inner wave functions up to and including $(4p)$, the estimates were derived from the $Z(nl; r)$ for Rb^+ by the use of formulae (13) and (14), with interpolated values of σ and α for each (nl). The estimate of $Z(4d; r)$ was obtained from the function for Ag^+. The estimates were then used to start a self-consistent field calculation, the results of which are given in a subsequent paper (4). Here, the maximum discrepancies between the estimated and final values of the $Z(nl; r)$ are given in Table 4. The values of $\sigma(nl)$ and $\alpha(nl)$ obtained initially by interpolation are also compared with the final ones. This agreement, obtained for adjustment over five units of atomic number, indicates that the method should prove useful. Now that the structure of Mo^+ has been calculated, interpolation in this region of the periodic table should be straightforward.

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