

Variation of Atomic Wave Functions with Atomic Number

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1. INTRODUCTION

RESULTS of calculations of atomic wave functions and fields, by the method of the self-consistent field with or without exchange, for a number of atoms had already been published before the war. But a systematic survey of these functions and the way in which they vary with atomic number does not seem to have been undertaken till recently, by Löwdin^{1,2} and by the writer,³ and, with reference to atomic fields rather than wave functions, by Mrs. Ridley.⁴

One purpose of such a survey is to provide means for the interpolation of wave functions or fields with respect to atomic number. Whether the results of such an interpolation are going to be used as they stand for the interpolation of other atomic properties, such as x-ray scattering factors, or adopted as initial estimates in a self-consistent field calculation, it is worth taking some trouble to make this interpolation as accurate as possible. This is clear if the interpolated results are going to be used as they stand; and if they are going to be used as initial estimates of a self-consistent field calculation (particularly one with exchange), trouble taken in obtaining these estimates is likely to be repaid many times over in the shortening of the subsequent calculation.

2. SCALING

For a given (nl) wave function, the most obvious variation with increasing atomic number is a decrease in linear dimensions. The linear dimensions of an atomic wave function can be characterized by a dimension R , which will be called the "scale length." This can be chosen in various ways: we may, for example, take R to be r_M , the radius of the main maximum of the radial charge density $P^2(nl; r)$, or to be the mean radius

$$\bar{r} = \int_0^\infty r P^2(nl; r) dr, \quad (1)$$

or the root-mean-square radius,

$$(\bar{r}^2)^{\frac{1}{2}} = \left[\int_0^\infty r^2 P^2(nl; r) dr \right]^{\frac{1}{2}}, \quad (2)$$

or the median radius r_m , that is, the radius such that

the probability of the electron lying within r_m is $\frac{1}{2}$,

$$\int_0^{r_m} P^2(nl; r) dr = \frac{1}{2}. \quad (3)$$

If, for a given (nl), the radial wave functions $P(nl; r)$ for different atoms were replicas of the same function on different linear scales, they would be related by the relation

$$R^{\frac{3}{2}} P(nl; r) \text{ is a function of } r/R \text{ only.} \quad (4)$$

The relation (4) between wave functions of different atoms will be called "pure scaling." It is convenient to write

$$s = r/R, \quad P^*(nl; s) = R^{\frac{3}{2}} P(nl; Rs), \quad (5)$$

and to refer to s as the "reduced radius" and $P^*(nl; s)$ as the "reduced radial wave function." The relations between the inner wave functions of the heavier atoms depart little from the "pure scaling" relation (4), and a relation of this kind has been used by various workers to estimate wave functions or other atomic properties depending on them for one atom from those of an atom of neighboring atomic number.

3. SCREENING PARAMETERS

It is often convenient to express the scale length R for an (nl) wave function in terms of the point charge Z of a Coulomb field for which the (nl) wave function has that value of R . This point charge Z is often called the "effective nuclear charge" for R , and if for an atom of atomic number N this effective nuclear charge is written $N - \sigma$, σ is called the "screening-parameter"* for R . If subscript (H) is used to denote values for hydrogen, σ is given by

$$R = R_{(H)} / (N - \sigma).$$

If for a many-electron atom the (nl) wave function were derivable from that for hydrogen by the pure-scaling relation (4), the screening parameter σ would be independent of the particular dimension R used to define it. However, the outer wave functions of neutral and slightly-ionized atoms, particularly those of negative ions, the ($3d$) wave functions of the atoms of the first long period, and probably the ($4d$) wave functions of the second long period, depart considerably from

¹ P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

² P. O. Löwdin, Phys. Rev. **94**, 1600 (1954).

³ D. R. Hartree, Proc. Cambridge Phil. Soc. **51**, 684 (1955).

⁴ E. C. Ridley, Proc. Cambridge Phil. Soc. **51**, 693 (1955).

* Other terms are "screening constant" and "shielding constant" but these do not seem satisfactory as the quantity σ , so defined, is not a constant for variation of any of the variables of which it might be considered a function.

scaled hydrogen wave functions, and the screening parameter σ may vary quite considerably with the property chosen to define it. For Mn, for example, the values of σ_{3d} defined through the radius r_M of maximum $|P(3d; r)|$ and through \bar{r} differ by as much as 3 units. Thus there is no single "screening parameter" which will represent all the properties of such a function. This is perhaps not always sufficiently realized.

4. CHOICE OF SCALE RADIUS

In the results presented in Sec. 6, the mean radius \bar{r} given by (1) has been adopted as the scale radius R . This choice is perhaps not the best, as it gives rather too much weight to the behavior of the wave function for large r (the root-mean-square radius $(\bar{r}^2)^{1/2}$ gives still more weight to the wave function for large r). A result is that for given atomic number, the values of σ for the outer wave functions, so defined, may show quite a considerable variation with the degree of ionization. The radius r_M of the main maximum of $|P(nl; r)|$ varies less than \bar{r} with the degree of ionization. The main effect of the degree of ionization is on the way the wave function decreases from this maximum as r increases, so that the choice $R=r_M$ would lead to a smaller variation of σ with degree of ionization. On the other hand, three-figure values of the radial wave functions are all that are available in most cases, and in view of the approximations made in deriving the equations from which these wave functions were evaluated, there would be no significance in carrying the solution of these equations to a greater degree of numerical accuracy. But this is not enough to locate the position of the maximum of $|P(nl; r)|$ consistently to the accuracy desirable for the analysis of the variation of the wave functions with atomic number and with the atomic configuration. The values of \bar{r} are easily evaluated to the degree of accuracy justified by that of the values of the radial wave functions themselves, and adoption of this dimension as the scale length, turns out to have some other advantages.

5. BEHAVIOR OF WAVE FUNCTIONS FOR LARGE ATOMIC NUMBER

Although the nonrelativistic Schrödinger equation is not physically significant for large values of the atomic number N , still we can inquire, as a mathematical rather than a physical question, how its solutions behave, as functions of N , as $N \rightarrow \infty$. The results turn out to be useful in the present context: first, because they suggest the most appropriate way of presenting the variation of the screening parameters σ and reduced wave functions $P^*(s)$ with atomic number N , from the point of view of ease of interpolation; and secondly, because by using the asymptotic behavior of σ and $P^*(s)$ with N as $N \rightarrow \infty$, we can make the estimation of wave functions, for atoms of atomic number higher than any for which results are available, an interpolation between available results and the limiting results for $N \rightarrow \infty$, instead of being an extrapolation.

It appears^{5,6} that, for a given configuration, the normalized solutions of Fock's equations (or of the equations of the self-consistent field without exchange) have for large N the asymptotic behavior expressed by

$$P(nl; r) = N^{\frac{1}{2}} [P_{(H)}(nl; Nr) + (1/N)Q(nl; Nr) + (1/N^2)R(nl; Nr) + O(1/N^3)], \quad (6)$$

and consequently that if the screening parameter σ for \bar{r} is defined by

$$\bar{r} = \bar{r}_{(H)} / (N - \sigma). \quad (7)$$

Then

$$\sigma = \sigma_0 + O(1/N), \quad (8)$$

where

$$\sigma_0 = [2/\bar{r}_{(H)}] \int_0^{\infty} P_{(H)}(nl; \rho) Q(nl; \rho) d\rho. \quad (9)$$

Since, from (7), \bar{r} is $O(1/N)$, it follows that (8) can be written

$$\sigma = \sigma_0 + O(\bar{r}), \quad (10)$$

$O(\bar{r}^n)$ denoting a quantity q such that q/\bar{r}^n remains finite as $N \rightarrow \infty$.

It also follows from (6) that, if $s = r/\bar{r}$, the reduced wave function is given by

$$P(nl; s) = P^*_{(H)}(nl; s) + \bar{r} Q^*(nl; s) + O(\bar{r}^2), \quad (11)$$

Q^* being a function which can be expressed in terms of the functions $P_{(H)}$ and Q , which occur in the expression (6). It is clear from formula (11) that, for a given value of s , the Coulomb-field value $P^*_{(H)}(nl; s)$ is the limit of the reduced wave function $P^*(nl; s)$, for large atomic number ($N \rightarrow \infty$, $\bar{r} \rightarrow 0$). For a given (nl) , the limiting value σ_0 of the screening parameter and the function $Q^*(nl; s)$ consist of sums of contributions from the various (nl) groups in the atom.

Equations for the functions Q , R , \dots in (6) can be obtained by inserting this expression into Fock's equations and equating powers of $1/N$. Solutions of these equations (with exchange) for the normal configurations (for large N) of systems of up to 28 electrons have been evaluated by Charlotte Froese, and the values of σ_0 calculated.⁵ Some results from these calculations are included in Figs. 1-3.

Mrs. Ridley⁷ has shown that if the scale length R is taken as the root-mean-square distance of the electron from the nucleus,

$$\left[\int_0^{\infty} r^2 P^2 dr \right]^{\frac{1}{2}},$$

instead of \bar{r} , then the limiting value as $N \rightarrow \infty$ of the corresponding screening parameter σ is

$$\sigma_0 = [1/\bar{r}^2_{(H)}] \int_0^{\infty} \rho^2 P_{(H)}(nl; \rho) Q(nl; \rho) d\rho,$$

⁵ C. Froese, Proc. Roy. Soc. (London), 239, 311 (1957).

⁶ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley and Sons, Inc., New York, 1957), Sec. 7.6.

⁷ E. C. Ridley, Ph.D. thesis, Cambridge (1955).

and if the scale length R is taken as the median radius r_m , such that

$$\int_0^{r_m} P^2 dr = \frac{1}{2},$$

then the limiting value as $N \rightarrow \infty$ of the corresponding screening parameter is

$$\sigma_0 = -2 \int_0^{r_m} P_{(H)}(nl; \rho) Q(nl; \rho) d\rho / r_m [P_{(H)}(nl; r_m)]^2.$$

These values differ from each other and from the value (9) for $R = \bar{r}$; this illustrates the variation of the screening parameter with the property used to define it, and shows that this variation does not vanish in the limit $N \rightarrow \infty$.

Formulas (10) and (11) suggest that a convenient way of presenting the variation of the screening parameters and reduced wave functions $P^*(s)$, with atomic number is to plot σ , and $P^*(s)$ for fixed s , against \bar{r} as abscissa, instead of against the atomic number N . Then the Coulomb-field points σ_0 and $P^*_{(H)}(s)$ can be included on a plot of finite extent, and also the variation of σ and $P^*(nl; s)$ may be approximately linear in \bar{r} , at least for values of N large compared with σ , which would be convenient for interpolation. It is indeed found for a given configuration that these variations are remarkably nearly linear over the whole range from the limit $N \rightarrow \infty$ down to the slightly ionized and neutral atoms.

6. VARIATION OF SCREENING PARAMETERS WITH ATOMIC NUMBER

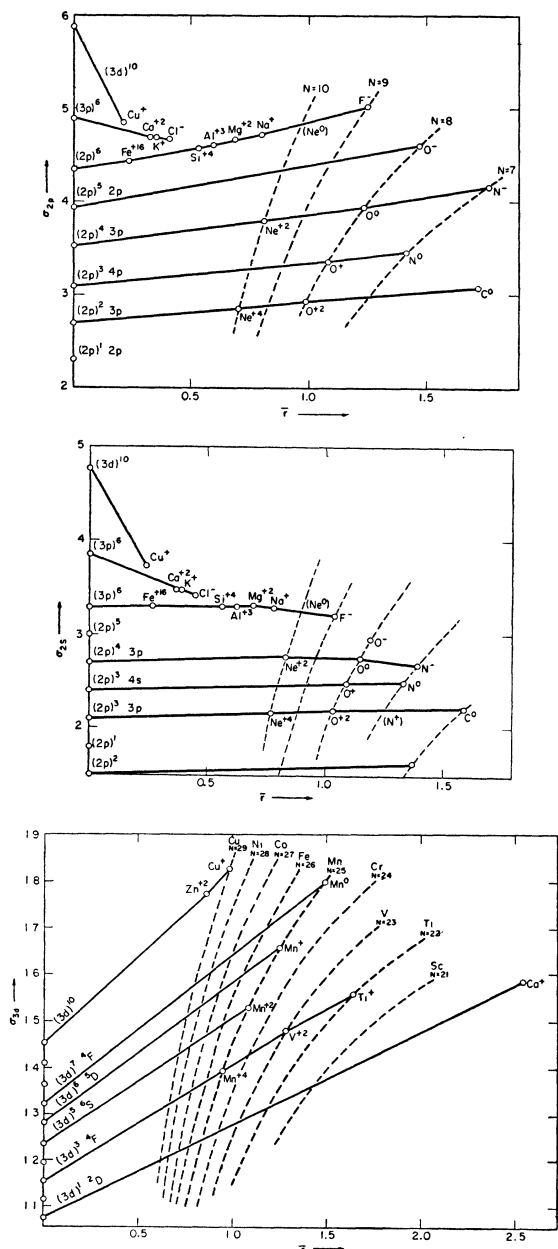
Figures 1-3 show examples of plots of the variation with atomic number of screening parameters for \bar{r} , plotted with the mean radius \bar{r} as abscissa as suggested in the previous section. They refer, respectively, to the $(2p)$, $(2s)$, and $(3d)$ wave functions calculated by the solution of Fock's equations (self-consistent field with exchange). On such a plot of σ against \bar{r} , the points for an atom of atomic number N , in different states of ionization, are the hyperbolas

$$\sigma = N - \bar{r}_{(H)} / \bar{r},$$

spaced at unit intervals from one another, in the direction of the σ axis. These curves are drawn broken in Figs. 1-3. Here $\bar{r}_{(H)}$ has the value⁸

$$\bar{r}_{(H)} = \frac{1}{2} [3n^2 - l(l+1)].$$

For each configuration for which there are enough points to judge, the results for the $(2p)$ wave function (Fig. 1) show remarkably small departures from linear variations with atomic number over the whole range from $\bar{r} = 0$ to the negative ions. In Fig. 2, for the $(2s)$ wave function, the departures from a linear variation of σ with \bar{r} are greater than for $(2p)$; they occur mainly for large \bar{r} , and even then are not large. In Fig. 3, for the $(3d)$ wave function, some of the points are based on results of calculations which are only preliminary, but improvement in the approximation to the solution of Fock's equations is unlikely to make more than minor changes. For the Cu^+ iso-electronic sequence, the considerable variation (nearly 5 units) in σ_{3d} , from 18.3 for Cu^+ to 14.5 in the limit $N \rightarrow \infty$, should be noted; this illustrates how rough an approximation it may be to treat the screening parameter as the sum of contribu-



FIGS. 1-3. Screening parameters σ_{2p} , σ_{2s} , and σ_{3d} , respectively, for the mean radius \bar{r} . From results of self-consistent field calculations with exchange, plotted against \bar{r} .

⁸ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), Table 2^a.

tions from the various (nl) groups, these contributions depending on the configuration only. Moreover, this variation is a decrease with increasing atomic number; this should be compared with the behavior of the screening parameters of Viervoll and Ogrim,⁹ and Qurashi,¹⁰ used in the calculation of atomic scattering factors for x rays; these parameters increase with atomic number, and to a much greater extent. Certainly Viervoll and Ogrim's, and Qurashi's figures refer to neutral or slightly ionized atoms, whereas the uppermost curve in Fig. 3 refers to a constant configuration; no results, calculated with exchange, are currently available for extending Fig. 3 to configurations of more than 28 electrons, but it does not seem likely that the addition of further electron groups, lying mainly outside the ($3d$) group, would increase σ_{3d} by more than a few units. This different behavior of the screening parameters used in calculating atomic scattering factors for x-rays is discussed in the following section.

Figures 1-3 show that when the variation of a screening parameter σ_{nl} with atomic number is expressed by plotting σ against \bar{r} rather than against N , the variation of σ with \bar{r} , for a given configuration, is very nearly linear right from small values of \bar{r} (large values of N), for which the results of Sec. 5 can be expected to apply, to the slightly ionized and neutral atoms, and even in some cases to the negative ions. On account of the small departures from linearity when there are results for more than one state of ionization (in addition to the limit $N \rightarrow \infty$) available, the curves of σ against \bar{r} have been drawn as straight lines unless there is reason to draw them otherwise.

On these figures, the results for constant configuration and those for constant atomic number lie on smooth curves. On the other hand, for atoms in which the (nl) group is incomplete, the values of σ_{nl} for a constant degree of ionization may not lie on a smooth curve, since they refer to terms with different values of (LS), and the coefficients of one or two of the terms in the equation for the corresponding radial wave function have different values for the different terms.

A physical explanation can be given of some of the features shown by Figs. 1-3. Consider, for example, the behavior of σ_{2p} with \bar{r} for the 10-electron iso-electronic sequence. With increasing atomic number, the ($2p$) wave function contracts relative to the ($2s$) function. This is illustrated by the fact that for F^- , Ne^0 , and Na^+ , $\bar{r}_{2p} > \bar{r}_{2s}$, whereas in the Coulomb-field limit, $\bar{r}_{2p} = (5/6)\bar{r}_{2s}$. Consequently for an electron in a ($2p$) wave function, the screening of the nucleus by the electrons in the ($2s$) wave function decreases with increasing atomic number (decreasing \bar{r}), as shown in Fig. 1. A similar explanation applies to the decrease of σ_{3d} with \bar{r} for the ($3d$)¹⁰ configuration.

The screening parameter σ_{3d} for $Ti^+(3d)^3$ is actually

⁹ H. Viervoll and O. Ogrim, *Acta Cryst.* **2**, 277 (1948).

¹⁰ M. M. Qurashi, *Acta Cryst.* **7**, 310 (1954).

smaller than that for $Ca^+(3d)^1$; the reason here is that in Ca^+ the ($3d$) wave function lies largely outside the $(3s)^2(3p)^6$ charge distribution of the argon-like core, whereas in Ti^+ the ($3d$) wave function lies in the same range of radii as the ($3s$), ($3p$) wave functions, and the lessened screening by the $(3s)^2(3p)^6$ groups more than compensates for the screening by the additional electrons in the other two ($3d$) wave functions. A similar explanation can be given of the decrease of σ_{3d} by more than 1 unit between Mn^+ and Mn^{+2} ; on the removal of one ($3d$) electron from Mn^+ , the remaining ($3d$) wave functions contract relative to the $(3s)^2(3p)^6$ groups, and the consequent decrease of the screening of the nucleus by the $(3s)^2(3p)^6$ groups is added to the decrease of screening resulting from the removal of the ($3d$) electron.

Data for plotting σ against \bar{r} for the ($3s$) and ($3p$) wave functions are at present scanty. However, when recently an estimate was required of the difference between the contribution from the argon-like core to the atomic scattering factor for Fe in the configuration $(3d)^6(4s)^2$ and the configuration $(3d)^2(4s)^2(4p)^4$, suggested as an approximation to that in metallic iron, it was found that the available data for the ($3s$) and ($3p$) wave functions, including particularly the limiting values for $N \rightarrow \infty$, were adequate to give the estimates required.

7. SCREENING PARAMETERS FOR CALCULATING ATOMIC SCATTERING FACTORS

Instead of determining screening parameters σ for an (nl) wave function by comparing the value of some dimension R (or some other quantity) with the corresponding value for the (nl) wave function of hydrogen, screening parameters can be specified, without reference to hydrogen wave functions, by assigning arbitrarily a value σ_0 to that wave function of some atom, of atomic number N_0 , and determining the values for other atoms accordingly. To obtain the scaling ratio $R(N)/R(N_0)$ between the values of the scale length R for atomic numbers N and N_0 , the value of σ assigned to atomic number N is given by

$$(N - \sigma)/(N_0 - \sigma_0) = R(N_0)/R(N). \quad (12)$$

This, in effect, is what has been done in the assignment of values of screening parameters[†] for the evaluation of the contributions to the atomic scattering factors from different (nl) groups of electrons in an atom. James and Brindley¹¹ write " s is defined by having values which make the curves of f against $[1/(Z-s)](\sin\theta)/\lambda$ as nearly coincident as possible"; this process is one of pure scaling, using screening parameters (s in James and Brindley's notation) related by formula (12). This formula, however, does not define

[†] The screening parameters σ are written s by James and Brindley¹¹ and p by Viervoll and Ogrim⁹ and Q by Qurashi¹⁰.

¹¹ R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931), p. 89.

a unique set of screening parameters, since if σ_0' , σ' are numbers related by

$$(N - \sigma') / (N_0 - \sigma_0') = (N - \sigma) / (N_0 - \sigma_0); \quad (13)$$

the relation between the wave functions which is expressed by the use of σ_0' and σ' as screening parameters is just the same as that expressed by the use of σ_0 and σ .

The relation between the set of screening parameters σ and the set σ' is

$$\sigma' = N(\sigma_0' - \sigma_0) / (N_0 - \sigma_0) - \sigma(N_0 - \sigma_0') / (N_0 - \sigma_0), \quad (14)$$

and if σ varies only slightly with N , σ' will vary nearly linearly with N . Such a nearly linear variation of screening parameter with atomic number is indeed shown by the values for the (3s), (3p), (3d), and (4s) wave functions given by Viervoll, Ogrim, and Qurashi, shown in Fig. 4. This behavior is strikingly different from that of screening parameters obtained by comparing values of some dimension R with that of the corresponding hydrogen wave function. The most nearly comparable values are

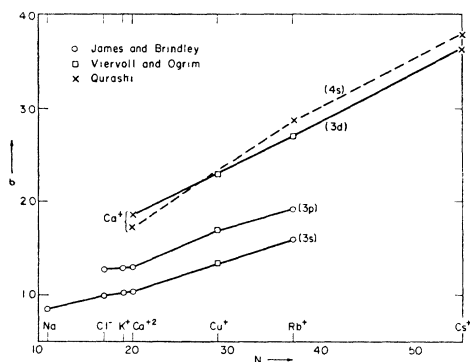


FIG. 4. Screening parameters σ_{3s} , σ_{3p} , σ_{3d} , and σ_{4s} , as used in calculation of x-ray scattering factors, plotted against atomic number N .

those for the screening parameter for the median radius r_m [see Eq. (3)], obtained by Mrs. Ridley⁴ in an analysis of results of calculation of the self-consistent field without exchange, mainly for neutral and slightly ionized atoms of the heavier elements. These values, for the (3s) to (4p) wave functions, are shown in Fig. 5, which is drawn on the same scales as Fig. 4 so as to be easily comparable with it. For $N=29$ to 55 the range of Mrs. Ridley's values of $\sigma(3d)$ is less than 2 units, whereas the values given by Qurashi cover a range of nearly 18 units; that is, the range of σ is not much less than that of $N - \sigma$. A feature of the results shown in Fig. 5 is the initial decrease of $\sigma(3d)$ with increasing atomic number once the (3d)¹⁰ group is complete; the physical reason for this has been considered in Sec. 6. The values of Viervoll, Ogrim, and Qurashi, on the other hand, increase with atomic number over the wide range.

This behavior of the values of the screening parameters used by Viervoll and Ogrim, and Qurashi does not imply that there is anything wrong with these values;

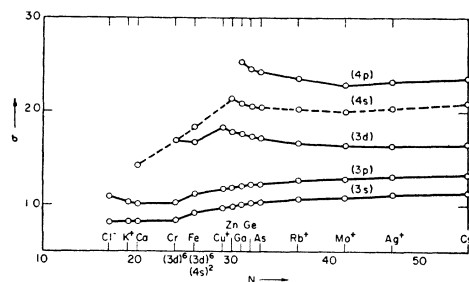


FIG. 5. Screening parameters σ_{3s} , σ_{3p} , σ_{3d} , σ_{4s} , and σ_{4p} for the median radius r_m , from results of self-consistent field calculations without exchange, plotted against N .

any values of σ_0 and σ given by (12) will give the same results when applied to the scaling of wave functions or the evaluation of properties depending on such scaling. However, the smaller the range of a screening parameter the more likely it is that it can be interpolated accurately. A comparison of Figs. 4 and 5 suggests that, for the (3s), (3p), (3d), and (4s) wave functions, a more convenient assignment of screening parameters could be made than that adopted by Viervoll and Ogrim, and Qurashi.

8. VARIATION OF REDUCED WAVE FUNCTIONS WITH ATOMIC NUMBER

Figures 6 and 7 are plots of $P^*(nl; s)$ against \bar{r} for one value of s for each of the (2p) and (2s) wave functions; the values of s for which the figures are drawn have been chosen as being in the neighborhood of the values of s for which the variation of $P^*(s)$ with \bar{r} is greatest for the wave function concerned. In Figs. 6 and 7, points for atoms of the same element in different stages of ionization are joined by broken lines.

The results for the neon-like iso-electronic sequence have been calculated by different workers, Na^+ and Si^{+4} by W. Hartree^{12,13}; Mg^{+2} by Yost¹⁴; F , Al^{+3} , and Fe^{+16} by Charlotte Froese¹⁵; and Al^{+3} also by Kattenbach¹⁶; using

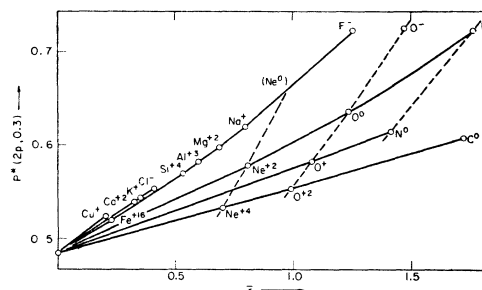


FIG. 6. Reduced wave functions $P^*(2p; s)$ for $s=0.3$, from results of self-consistent field calculations with exchange, plotted against \bar{r} .

¹² D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **193**, 299 (1948).

¹³ Hartree, Hartree, and Manning, Phys. Rev. **60**, 857 (1941).

¹⁴ W. J. Yost, Phys. Rev. **58**, 557 (1940).

¹⁵ C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

¹⁶ K. Kattenbach, Z. Astrophys. **33**, 165 (1953).

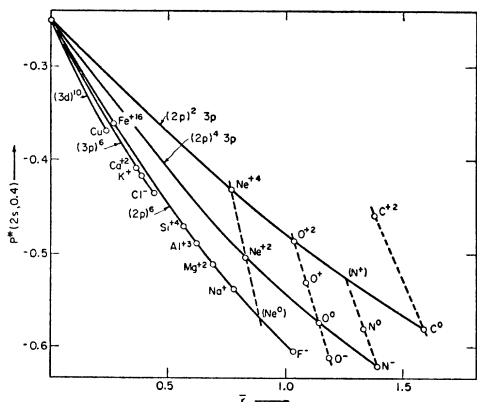


FIG. 7. Reduced wave functions $P^*(2s; s)$ for $s=0.4$, from results of self-consistent field calculation with exchange, plotted against \bar{r} .

different forms of the radial wave equation, different methods for the numerical integration of the equations and for determining the characteristic values of the ϵ parameters in these equations so as to satisfy the two-point boundary conditions and the condition of normalization which the radial wave function must satisfy; and using also different sizes of the interval of integration. The consistency of the reduced $(2p)$ wave functions for the different atoms of the sequence provides a good check on the whole set of calculations. It also indicates that the differences, at fixed s , between the values of the reduced wave function $P^*(nl; s)$ for different configurations in which the $(2p)^6$ group is complete, such as the 10-electron configuration of Ne, the 18-electron configuration of Ar, and the 28-electron configuration of Cu^+ , are significant.

In Fig. 7 for the $(2s)$, the points for Cu^+ , Ca^{+2} , K^+ , Cl^- , Si^{+4} , Mg^{+2} , and Na^+ fall nearly on a straight line, which however does not pass through the Coulomb-field point at $\bar{r}=0$. In the writer's previous paper³ this was commented on as a matter for surprise, if not for suspicion of a mistake. It is clear now that it was a result of trying to pass a single curve through points representing values of the reduced $(2s)$ wave function for different configurations; the subsequently calculated results for Fe^{+16} shows that for atoms in which the $(2p)^6$ group is complete, the variation of the reduced wave function with the configuration, though small, is appreciable. The points for the 10-electron iso-electronic sequence, with the Coulomb-field point at $\bar{r}=0$, fall on a smooth curve which differs little from a straight line.

Figures 6 and 7 show that when, for a given configuration, the variation of a reduced radial wave function with atomic number is expressed by plotting $P^*(s)$, for given s , against \bar{r} , rather than against the atomic number, then the variation of $P^*(s)$, like that of the screening parameter σ , is in many cases nearly linear from $\bar{r}=0$ right to the slightly ionized and neutral atoms. Moreover, the curves of constant atomic number are approximately similar curves with respect to the

Coulomb-field point $\bar{r}=0$. These features of the reduced wave functions can be used to simplify considerably the interpolation of wave functions with respect to atomic number.¹⁷

ADDENDUM

Since this paper was written, solutions of Fock's equations for various 28-electron systems (iso-electronic with Cu^+) have been calculated by Piper.¹⁸ Also Miss Froese¹⁹ has derived the equations for the functions $R(nl; Nr)$ in the expression (6), and has obtained solutions of them for some configurations. These functions give the second-order terms in $1/N$ in the departure of an (nl) wave function from the corresponding hydrogen-like function in the field of a point charge N ; from these results the values of $(d\sigma/d\bar{r})$ at $\bar{r}=0$ for the various configurations and wave functions can be derived.

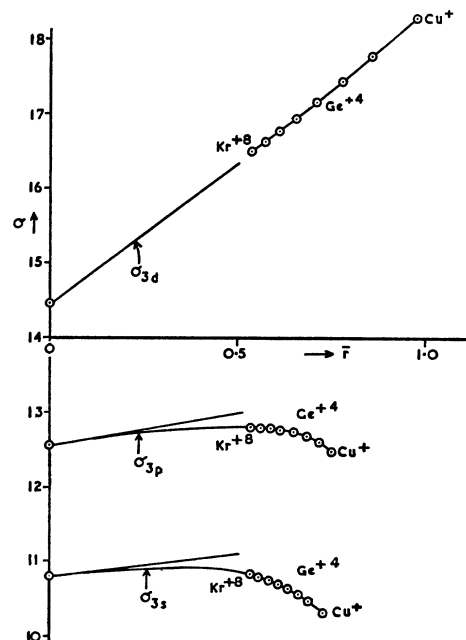


FIG. 8. Screening parameters σ_{3s} , σ_{3p} , and σ_{3d} for 28 electron systems (straight lines drawn from values of σ_0 and $(d\sigma/d\bar{r})_0$ as calculated by C. Froese).

In Fig. 8 the straight lines from $\bar{r}=0$ to 0.5 are drawn from the values of σ_0 and $(d\sigma/d\bar{r})_0$ calculated by Miss Froese for the normal configuration of 28-electron systems. The plotted points give the values of σ derived from the results of Piper's calculations. The departure of σ_{3d} from a linear variation with \bar{r} is remarkably small.

Miss Froese's results for $(d\sigma/d\bar{r})_0$ also confirm the small negative slopes of the curves of σ_{2s} and σ_{2p} against \bar{r} for the 18-electron systems iso-electronic with argon (Figs. 1 and 2) and the much larger negative slopes of the corresponding curves for the 28-electron systems.

¹⁷ C. Froese and D. R. Hartree, Proc. Cambridge Phil. Soc. 53, 663 (1957).

¹⁸ W. W. Piper, Bull. Am. Phys. Soc. Ser. II, 2, 132 (1957).

¹⁹ C. Froese [Proc. Roy. Soc. (London), to be published].