THE INTERPOLATION OF ATOMIC WAVE FUNCTIONS

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ABSTRACT. If $\bar{r}_{nl}$ is the mean radius for the radial wave function of a complete (nl) group in an atom of atomic number N, the variation of $1/\bar{r}_{nl}$ with N is nearly linear. Further the variation of a given (nl) radial wave function with N is such that for a given value of $(r/\bar{r}_{nl})$, the variation of the quantity $(\bar{r}_{nl})^{\frac{1}{2}} P(nl; r)$ with $\bar{r}_{nl}$ is nearly linear. These relations between the radial wave functions for different atoms are examined from the point of view of using them as a means of interpolating, with respect to atomic number, between results for atoms for which solutions of Fock's equations have been carried out.

1. *Introduction.* Wave functions for a number of atoms and ions have been calculated by the method of the self-consistent field, with exchange for the lighter atoms (up to Cu), and without exchange for the heavier atoms (for a survey, see (5)). But from time to time wave functions, fields or charge distributions are wanted for other atoms or ions, either for direct use for calculating atomic properties such as X-ray scattering factors, or to provide the first estimates to use in further self-consistent field calculations. For either purpose, the required wave functions or fields can be obtained by interpolation, with respect to atomic number N, between the results for atoms for which calculations have already been carried out; and in this interpolation, it is worth while going to some trouble to obtain good approximations to the unknown wave functions or fields. If the interpolated results are to be used directly, this is self-evident. It still applies if they are to be used as initial estimates in a self-consistent field calculation (and particularly in one with exchange), since the amount of work involved in such a calculation depends very much on how good or bad the initial estimates are; if the calculation is done by hand (as contrasted with the use of a high-speed automatic digital machine), two man-days spent in obtaining good initial estimates may well save several man-weeks of work in the subsequent calculation.

Experience with self-consistent field calculations has led to the conclusion that in calculations with exchange it is best to start from estimates of the wave functions themselves, whereas in calculations without exchange it is best to start from estimates of contributions to $Z(r)$ ($= r^2 \times$ (field at radius r)). Also calculations without exchange are a good deal shorter and less involved than those with exchange, so that if results without exchange (which are the only ones which it is at present practicable to obtain for heavy atoms) are wanted, it may often be worth while to estimate the contributions to $Z(r)$ by interpolation and to obtain the wave functions by integrating the radial wave equation, rather than to interpolate the wave functions themselves. Thus the problem of interpolation with respect to the atomic number N has two aspects, one concerned with the interpolation of wave functions, with emphasis on those for light atoms calculated with exchange, and the other on the interpolation of the contributions to Z, with emphasis on the results without exchange for the heavier atoms. Only the first of these aspects is considered in the present paper; the second is the subject of the

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following paper (8) by Mrs E. C. Ridley, whose work has suggested several of the ideas of the present paper.

2. *Scaling and departures from pure scaling.* Consider the normalized radial wave function $P(nl;\, r)$ for given quantum numbers (nl) and the different values of the atomic number N. Let R be a typical length specifying the linear scale of the wave function; a convenient quantity to take is the mean radius $\bar{r} = \int_0^\infty rP^2 dr$, but there are several possible alternatives, for example, the root-mean-square radius $\left[\int_0^\infty r^2P^2dr\right]^{\frac{1}{2}}$, the radius r_M of the main maximum of $P(r)$, or the median radius r_m, that is, the radius such that the probability of the electron lying within a sphere of radius r_m is $\frac{1}{2}$. The choice of the scale radius R is discussed in § 3. For any particular choice, let

$$s = r/R. \tag{1}$$

If the wave functions for different atoms could be derived from one another simply by changes of scale of r, the function

$$P^*(nl;\, s) = R^{\frac{1}{2}}P(nl;\, Rs), \tag{2}$$

which will be called a 'reduced wave function', would be the same function of s for all N. The process of deriving an approximate wave function for atomic number N by taking $P^*(nl;\, s)$ to be the same function of s as it is for atomic number N_0, for which it is supposed known, will be called 'pure scaling' from N_0 to N. One process for interpolating wave functions with respect to N is to obtain a set of functions—let them be written $P_0(nl;\, r)$—for atomic number N by pure scaling from known results for different atomic numbers N_0, and then interpolate with respect to N_0 between the functions $P_0(nl;\, r)$ so obtained. This process, using $R = r_M$, was used to interpolate wave functions for S^+ to serve as a starting point for a self-consistent field calculation by A. S. Douglas of which the results were used by Garstang (3) in the course of an investigation of departures from (LS)-coupling in the lighter elements. The procedure explained below appears, however, to be a considerable improvement.

Although for large N the equations of the non-relativistic self-consistent field become physically inapplicable, we may still inquire what is the form of the solution of these equations for large N. If suffix (H) is used to indicate values for the hydrogen atom, we have

$$R = R_{(\mathrm{H})}/N + O(1/N^2) \tag{3}$$

and (see (4), formula (5))

$$P^*(nl;\, s) = P_{(\mathrm{H})}(nl;\, s) + (1/N)P_{(1)}(nl;\, s) + O(1/N^2). \tag{4}$$

Substitution of $(1/N)$ in (4) from (3) gives

$$P^*(nl;\, s) = P_{(\mathrm{H})}(nl;\, s) + (R/R_{(\mathrm{H})})\, P_{(1)}(nl;\, s) + O(R^2). \tag{5}$$

It seemed that (5) would be a more useful formula than (4) to use for expressing the departures from pure scaling, for the following reason. The partial screening of the nucleus by the other electrons can be taken into account by writing (3) as

$$R = R_{(\mathrm{H})}/(N - \sigma), \tag{6}$$

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where σ is a screening number, in the sense that if $(N-\sigma)$ is substituted for N in the relation $NR = R_{(H)}$ for hydrogen-like wave functions, the correct value of R is obtained. And part of the term of order $1/N^2$ in (4) could be included in the second term in this formula by replacing this term by

$$[1/(N-\sigma^*)]\,P_{(1)}(nl;\, s). \tag{7}$$

Now although there is no reason to expect the 'best' value of σ^*, in the sense of the value which minimizes the mean-square residual, to be exactly the same as σ, it seemed likely that the result of taking $\sigma^* = \sigma$ would include in the term of order $1/R$ in (5) a substantial part of the term of order $1/N^2$ in (4).

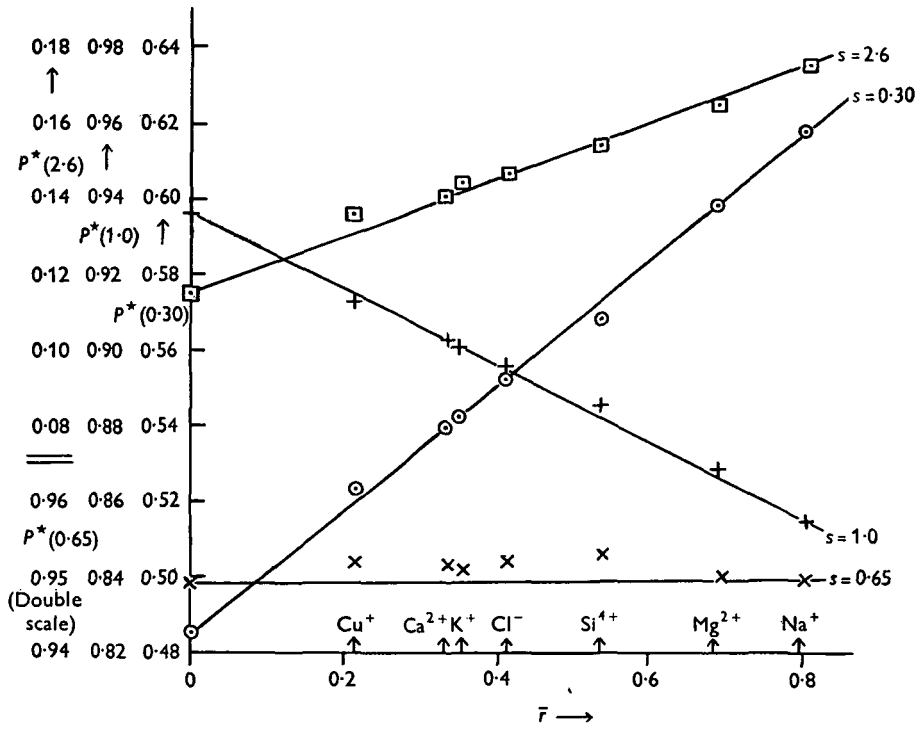

Fig. 1. Reduced wave function $P^*(2p;\, s)$, calculated with exchange, as a function of $\bar{r}$ for $s = 0{\cdot}30,\ 0{\cdot}65,\ 1{\cdot}0,\ 2{\cdot}6$. The values for $s = 0{\cdot}65$ are plotted on double the vertical scale of the others.

If wave functions were derived from one another by pure scaling, the variation of $P^*(nl;\, s)$ with N would be zero, and this is known to be not a bad approximation over small ranges of N. The argument of the previous paragraph suggests that such variation of $P^*(nl;\, s)$ with N, for given s, as does occur will be nearly linear in R, so that a set of plots of $P^*(nl;\, s)$ against R, for various values of s, should be a convenient means of interpolating wave functions with respect to N. Since this variation is likely to be small compared with the maximum of $|P^*(nl;\, s)|$, it can be plotted on a relatively open scale, so that graphical interpolation can be made to adequate accuracy. The

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close approach to such a linear variation of $P^*(nl;\, s)$ with R is illustrated by the results shown in Fig. 1, which are discussed in §4.

3. *The choice of the scale radius R.* In some preliminary work, the typical length R, giving the scale of the wave functions, was taken as the radius of the main maximum of $|P(nl:\, r)|$. However, the calculated wave functions $P(nl;\, r)$ are only tabulated to three or four figures (and the approximation of the self-consistent field method is such that the last figure is hardly likely to be physically significant, so that there is no point in carrying out the numerical work to such an accuracy as to give more figures); the abscissa of the maximum of a function so tabulated cannot be determined very closely, and, moreover, is sensitive to the rounding errors in the tabular values in the immediate neighbourhood of the maximum, and not at all to others.

A better choice for R seems to be the mean radius $\bar{r}$ or the median r_m of the radial probability distribution. The determination of $\bar{r}$ involves a further integration, but the better-determined character of the result seems to justify the extra calculation. The root-mean-square radius could be used, but is too dependent on the exponential 'tail' of the wave function for large r to be convenient. The mean radius $\bar{r}$ seems the most convenient when the purpose is to interpolate wave functions, for use either as they stand or as initial estimates for a calculation of the self-consistent field with exchange; r_m is the more convenient when the purpose is to interpolate contributions to Z as initial estimates for a self-consistent field calculation without exchange, since the determination of r_m only involves an interpolation in a table of the contribution to Z.

For hydrogen, the value of $\bar{r}$ is a simple function of the quantum numbers (nl), namely (see Condon and Shortley (2) chap. 5, Table 2[5])

$$\bar{r}_{(\mathrm{H})} = \tfrac{1}{2}[3n^2 - l(l+1)], \tag{8}$$

which gives

(nl)	$(1s)$	$(2s)$	$(2p)$	$(3s)$	$(3p)$	$(3d)$	$(4s)$	$(4p)$	$(4d)$	$(4f)$
$\bar{r}_{(\mathrm{H})}$	1·5	6	5	13·5	12·5	10·5	24	23	21	18

4. *Variation of reduced wave function with atomic number, for fixed s.* The data available for examining the variation of wave functions, calculated with exchange, with atomic number are slight except for $(nl) = (1s)$, $(2s)$ and $(2p)$; and the departure of the $(1s)$ wave function from a scaled hydrogen wave function is so small except for the lightest atoms that it is not of great interest. For $(nl) = (2s)$ and $(2p)$, the variation is considerable, and the data cover a considerable range of atomic number (carbon, $N = 6$, to copper, $N = 29$; for detailed references see Table 1 of (5)).

A diagram showing the variation of the reduced wave function $\bar{r}^{\frac{1}{2}}P(nl;\, \bar{r}s)$ as a function of N or of $\bar{r}$, for a number of different values of $s = r/\bar{r}$, is either large (to avoid crossing of the curves for different values of s) or complicated (because of the crossing of these curves), so only results for a few values of s are shown as examples in Fig. 1, which refers to the $(2p)$ wave function in atoms for which the $(2p)^6$ group is complete. For a given atom, the difference $|P^*(2p;\, s) - P^*_{(\mathrm{H})}(2p;\, s)|$ has maxima at about $s = 0{\cdot}3$, $1{\cdot}0$ and $2{\cdot}6$, and zeros at about $s = 0{\cdot}65$ and $1{\cdot}4$; in Fig. 1, $P^*(2p;\, s)$ is plotted against $\bar{r}$ for the values $s = 0{\cdot}3$, $1{\cdot}0$ and $2{\cdot}6$ which give about the greatest

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positive and the greatest negative variation, and also for $s = 0{\cdot}65$, for which $P^*(p;\, s)$ is almost independent of $\bar{r}$.

The full lines in Fig. 1 are straight lines drawn through the points for $\bar{r} = 0$ and $\bar{r} = 0{\cdot}796\,(Na^+)$. They are not intended to imply that a linear variation is to be expected over this range; they are inserted simply as a means of exhibiting the extent of the departures from linearity in $\bar{r}$. These departures are small, at most 5 parts in 1000 of the maximum of $|P|$, and they may in part arise from computational causes. For example, the process of successive approximation to the self-consistent field may

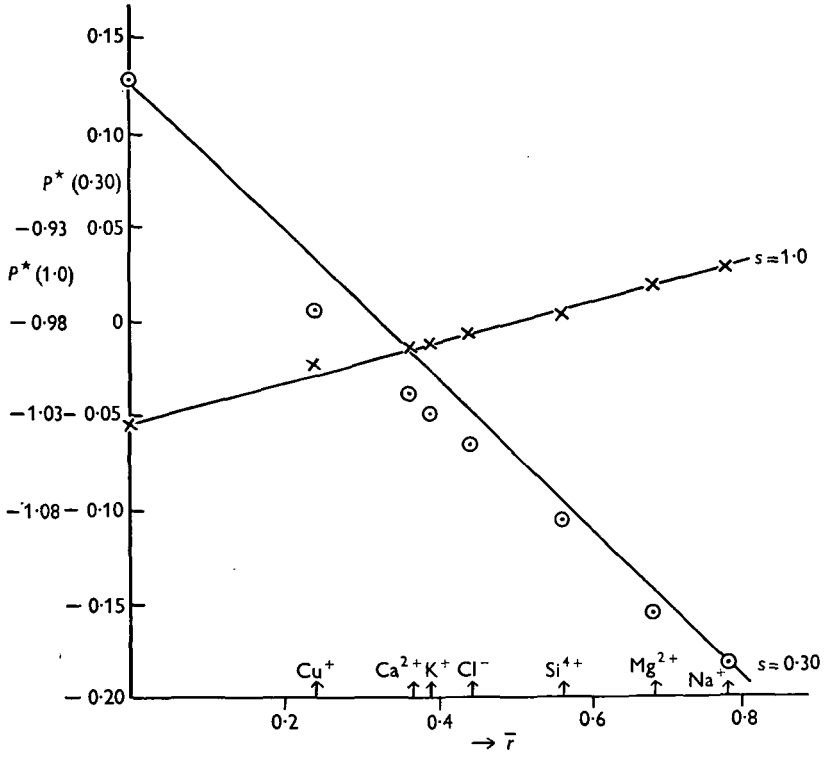

Fig. 2. Reduced wave function $P^*(2s;\, s)$, calculated with exchange, as a function of $\bar{r}$ for $s = 0{\cdot}30,\ 1{\cdot}0$.

not have been carried far enough to establish the last figure in the tabulated values of $P(nl;\, r)$ to a few units; and there will be rounding errors in the values of $\bar{r}$ and in the interpolation for exact values of $s = r/\bar{r}$. However, it is believed that the departures are real, in the sense that they represent—though of course not accurately—features of the behaviour of the solutions of Fock's equations; whether there is anything corresponding to them in the exact solution of Schrödinger's equation for a many-electron system is another matter.

These departures appear at first sight to be somewhat irregular; the irregularities may also be partly computational, but it seems probable that in part they are consequences of the irregular set of configurations for which calculations have been made,

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neither for a single iso-electric sequence nor for atoms all ionized to the same degree. The wave functions for inner complete groups are only slightly affected by the occupation of wave functions of outer groups, and such effect as there is, is mostly expressed by a change of scale (see § 5), so that the effect on the reduced wave function is small; but the irregularities we are considering are small, and they may well be real, in the sense of the previous paragraph.

Fig. 2 shows corresponding results for the (2*s*) function, for the radii ($s = 0{\cdot}3$ and $1{\cdot}0$) in the neighbourhood of which the greatest positive and greatest negative variations

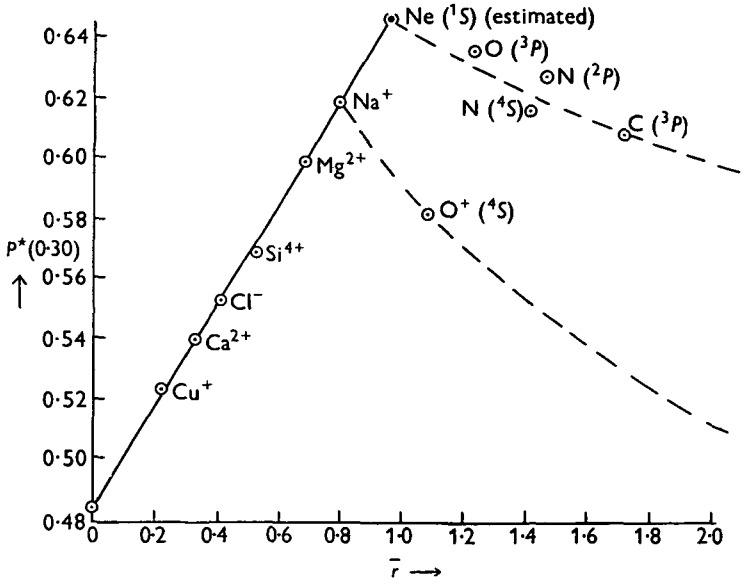

Fig. 3. Reduced wave function $P^*(2p;\, s)$, calculated with exchange, as a function of $\bar{r}$ for $s = 0{\cdot}3$, including values for some configurations with incomplete (2*p*) groups.

of $P^*(2s;\, s)$ with N occur. For $s = 0{\cdot}3$, the hydrogen-like value ($\bar{r} = 0$) lies some way from the best straight line through the points for Na^+ to Cu^+; this is surprising, in view of the close fit of these points to a straight line.

Fig. 3 shows results for the (2*p*) function including some for light atoms in which the (2*p*) group is incomplete. For these, a single configuration gives several states with different values of L and S, and the radial wave functions for these states are appreciably different; thus both the value of $\bar{r}$ and the reduced wave function $P^*(nl;\, s)$, for given s, are different for the different states. This is illustrated in the figure. It has the consequence that points for the normal states of different atoms cannot be expected to lie on a smooth curve.

5. *Variation of mean radius $\bar{r}$ with atomic number.* For the (2*p*) wave function

$$\bar{r} = 5/(N - \sigma)$$

(see formulae (6) and (8)). The values of σ calculated from this formula are shown, plotted against $\bar{r}$, in Fig. 4. In this diagram, $\bar{r}$ rather than the atomic number N is used

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as abscissa, since σ cannot vary linearly with N over a large range of N, whereas for a set of isoelectronic structures it may vary approximately linearly with $\bar{r}$. The second decimal in σ is uncertain to a few units for atoms heavier than Na, but the trend of the variations in σ is probably real (in the sense that it represents a property of the solution of Fock's equations). The variation from Cl^- to Ca^{2+} is in the sense to be expected, since with increasing N the $(3s)$ and $(3p)$ wave functions contract relatively more than the $(2s)$ and $(2p)$ functions, and also the subsidiary maxima of $|P|$ for the $(3s)$ and $(3p)$ functions become more prominent, so that although these ions form an iso-electronic sequence, the screening of the $(2s)$ and $(2p)$ wave functions by the charge distribution of the electrons in the $(3s)$ and $(3p)$ wave functions increases with N.

When the L-shell is still incomplete, σ for the $(2p)$ wave function (and similarly for the $(2s)$ function) varies considerably with N, as would be expected, and also with the degree of ionization; and it is also appreciably different for the different states arising from a configuration of incomplete groups. But once the L-shell is complete, only minor variations of σ with increasing N occur. These variations show breaks between the different iso-electronic sequences of which those atoms for which calculations have been carried out are members; the breaks correspond to the building up of the various outer groups. Values of $1/\bar{r}$ correspondingly show a variation with N which is on the whole linear, with slight irregularities related to the building up of outer groups, in much the same way as do the values of $(\nu/R)^{\frac{1}{2}}$ for energy levels of the X-ray spectra, as discussed long ago by Bohr and Coster (1) (see also (9), figs. 16·12, 16·15, 16·16.).

It would be interesting to have some results for a few highly-ionized atoms such as Fe^{16+} (iso-electronic with neon) to show the variations of σ, and of the reduced wave functions P^*, for an iso-electronic sequence over a wide range. But I know of no results calculated with exchange for such states of high ionization.

6. *Interpolation of wave functions.* Use of results of the kind illustrated in Figs. 1–4 involves four steps for each (nl); (a) an interpolation of σ, which determines $\bar{r}$, (b) the interpolation of $P^*(nl;\, s)$ with respect to $\bar{r}$ for a set of values of s, (c) the interpolation of $P^*(nl;\, s)$ with respect to s, so as to obtain values of $\bar{r}^{\frac{1}{2}}P(nl;\, r)$ at specified values of r, and finally (d) multiplication of these values by $1/\bar{r}^{\frac{1}{2}}$ to give values of $P(nl;\, r)$. It is as well to verify by a quadrature that the results are normalized, and that those for each value of l and different values of n are orthogonal; if the results are going to be used as a starting point for a solution of Fock's equations, these checks can be made as by-products of the evaluation of functions like $Z_0(nl, nl;\, r)$ which have to be calculated in any case.

If the values of σ are plotted against $\bar{r}$ as in Fig. 4, the first step, (a) of the previous paragraph, formally requires the solution of an implicit equation

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

in which the variation of σ with $\bar{r}$ is given. But for a complete (nl) group this gives no difficulty, as σ varies only slightly with $\bar{r}$, and an iterative process converges rapidly.

The second step, (b), requires the use of a set of plots of $P^*(s)$ against $\bar{r}$ for various values of s, of which those in Fig. 1 are representative. It seems advisable to take the

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intervals in s such that Bessel's or Everett's formula to second differences is adequate for the interpolation with respect to s required for step (c). For ($2s$) and ($2p$) the following intervals seem to be suitable:

$$s = 0\,(0{\cdot}02)\,0{\cdot}30\,(0{\cdot}05)\,0{\cdot}80\,(0{\cdot}1)\,1{\cdot}6\,(0{\cdot}2)\,4{\cdot}0\,(0{\cdot}5);$$

for larger values of $(n-l)$ (which determines the number of nodes) smaller intervals might be required for small r. Alternatively, it would be possible to divide $P(r)$ by a polynomial having nodes at the zeros of $P(r)$, which are well determined by the numerical data, and carry out an interpolation process on the quotient, as suggested

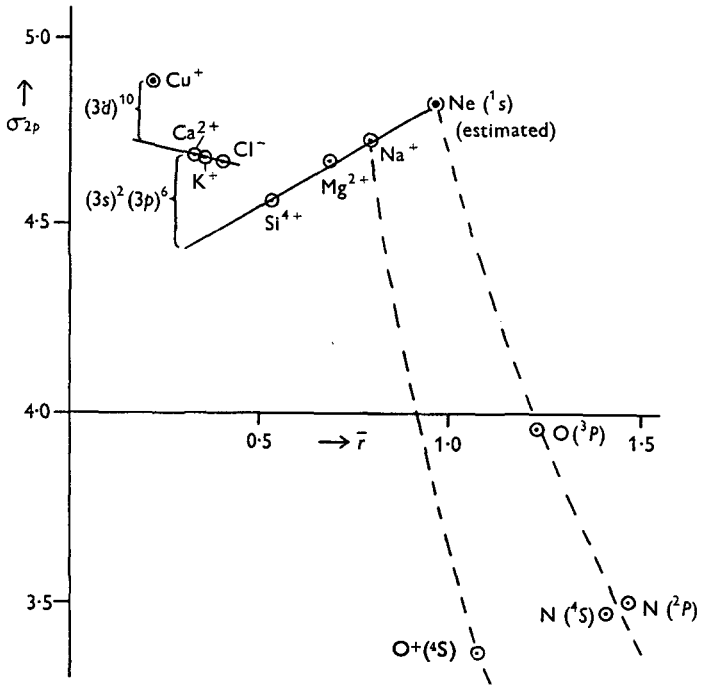

Fig. 4. Screening number for $\bar{r}_{2p}$, $\sigma_{2p} = N - 5/\bar{r}_{2p}$, as a function of $\bar{r}$, for wave functions calculated with exchange.

by Löwdin (7) (who, however, suggests carrying out the interpolation by fitting an analytical formula to the quotient). However, the method here suggested seems adequate for wave functions with values of n up to 3, and no calculations with exchange have yet been done for configurations involving higher values of n.

This method was used to estimate wave functions for Mn^{2+}, and preliminary results (6) show that the interpolation was very satisfactory; for ($3p$) the greatest error in the interpolated wave function $P(3p)$ was 1·2 % of the maximum of $|P|$, and even for $P(3d)$, interpolated between results for Ca^+ and Cu^+, the method produced a useful first estimate, despite the very different circumstances of the ($3d$) wave function in the three ions.

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