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Scaling in the S and P States of the Helium Isoelectronic Sequence

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Mean values of r_1^n and r_{12}^n for the ground and several excited states of the helium isoelectronic sequence are used to demonstrate that a simple scaling which superimposes the distribution function $f(r_{12})$ as a function of the atomic number leads to a similar result for the electron density distribution $D(r_1)$. On the basis of a screening interpretation of the scaling parameter δ, it is concluded that screening is greater in the singlet than the triplet state of a particular configuration, that screening is greater in the P states than the corresponding S states, and that the screening approaches the limiting value of 1 for the highly excited states. The perturbation expansions of Scherr and Knight are used to determine the limiting value of δ when $Z \to \infty$ and the relationship between the scaling parameter and the scale factor, chosen so that a trial wave function satisfies the virial theorem, is discussed. A brief discussion of the scaling of the Coulomb hole is presented.

Key words: Atomic screening constants – Mean values of r_1^n and r_{12}^n in two-electron atoms – Scaling – Helium isoelectronic sequence, screening in the ~

1. Introduction

The introduction of the distribution function of the interelectronic distance $f(r_{12})$ and the definition of the Coulomb hole as the difference between the exact $f(r_{12})$ and the Hartree-Fock $f(r_{12})$ by Coulson and Neilson [1] has stimulated many recent investigations of electron correlation in atoms. Detailed discussions have been presented of the Coulomb hole in the ground states of helium [1–4], beryllium [5] and neon [6] and some of the excited states of helium [7]. Closely related studies include an analysis of correlation effects in terms of the expectation values of the electron-nuclear attraction and the interelectronic repulsion in the ground states of several atoms [8] and a discussion on the effect of the Pauli principle in atoms in terms of the difference between the $1s2p$ singlet and triplet state $f(r_{12})$ distributions in the He isoelectronic sequence [9]. Several authors have calculated mean values of $1/r_{12}$ which is related, of course, to $f(r_{12})$ by Eq. (1)

$$\langle r_{12}^n \rangle = \int_0^\infty r_{12}^n f(r_{12})\, dr_{12} \tag{1}$$

and compared the results for states of different multiplicity arising from the same configuration [7, 10–12]. Also we should note that a distribution function for the interelectronic angle in atomic systems has been proposed by Banyard and Ellis [13] and used to study angular correlation in two- and four-electron atoms.

In a recent paper [7] on the Coulomb hole in some excited states of helium, it was observed that the distribution function $f(r_{12})$ for a particular state can be approximately represented by a single curve for all atomic numbers Z. Thus, by plotting $f(r_{12})/(Z-\delta)$ versus $(Z-\delta)\,r_{12}$, the distribution functions can be nearly superimposed with an appropriate choice of the scaling parameter δ. The scaling parameter is significantly larger for the 2^1S state than for the 2^3S state of the He isoelectronic sequence [7] and as a consequence it has been suggested that δ be interpreted physically as a screening constant, although it should be stressed that atomic screening constants refer to the radial distance r_1 and not to r_{12} and, therefore, δ should not be confused with the conventional concept of atomic screening constants. The purpose of this paper is to determine whether or not the electron density distribution function $D(r_1)$ can also be scaled by the same procedure and to determine whether or not there is a simple relationship between the δ which scales $D(r_1)$ for a particular state and the δ which scales $f(r_{12})$.

2. Scaling Procedure

There are at least two procedures by which we may study the scaling of the distribution functions of an operator such as r_1 or r_{12}. We could compute the distribution functions $f(r_{12})$ and $D(r_1)$ for a particular state for several values of the atomic number and then determine the value of δ which maximizes the overlap of the scaled curves. If the overlap between the distribution functions for any two values of Z is large for a particular choice of δ, we may conclude that the distribution functions are well represented by a single curve. Or equivalently separate values of δ could be chosen to maximize the overlap of the distribution functions associated with any two values of Z. If the δ's obtained in this manner are nearly independent of Z, we arrive at the same conclusion.

Both variations of the above procedure are quite tedious. An alternative procedure which eliminates the necessity of working directly with the cumbersome distribution functions is based on the expectation values associated with the distribution functions. Another advantage of the second procedure is that Pekeris *et al.* [12] have reported accurate expectation values of r_1^n and r_{12}^n, $n=1,2$, for many excited states of the He isoelectronic sequence. Thus a convenient set of data is available for investigating the scaling of $D(r_1)$ and $f(r_{12})$ in many states of two-electron atoms.

If a distribution function, such as $f(r_{12})$, for a particular state and isoelectronic sequence is scaled as a function of the atomic number by plotting $f(r_{12})/(Z-\delta)$ versus $(Z-\delta)\,r_{12}$, the scaled mean values $\langle r_{12}'^n\rangle$ are related to the unscaled mean values $\langle r_{12}^n\rangle$ by

$$\langle r_{12}'^n\rangle = (Z-\delta)^n \langle r_{12}^n\rangle\,. \tag{2}$$

Furthermore, if the distribution functions for several values of the atomic number can be well approximated by a single curve, then the δ which makes Eq. (2) very nearly constant should be nearly independent of n. This statement is subject to the condition that, for a particular n, δ is relatively insensitive to a change in the atomic number. Similarly we note that if the distribution functions are not well represented by a single curve, the scaling does not effectively superimpose the distribution functions and the values of δ which make Eq. (2) nearly constant are very different for different n.

In the subsequent sections of this paper, δ will be chosen to minimize the sum S_δ defined in Eq. (3).

$$S_\delta^2 = \sum_{i=1}^{N} \left[\langle r_{12}'^{n} \rangle_i - \langle r_{12}'^{n} \rangle_{av} \right]^2 . \tag{3}$$

In this expression, the summation extends over N members of the isoelectronic sequence and $\langle r_{12}'^{n} \rangle_{av}$ is the average of the N scaled mean values defined by Eq. (2). Of course, Eq. (1), (2), and (3) can be rewritten in terms of r_1 and $D(r_1)$. And finally to conclude this section we note that, because Pekeris *et al.* [12] have reported accurate expectation values of r_1^n and r_{12}^n for the He isoelectronic sequence, up to $Z = 10$, the summation in Eq. (3) will be taken only over the 9 two-electron atoms from He up to and including Ne^{+8}. The inclusion of more highly charged ions will have only a relatively small effect on the calculated values of δ and will not alter the principal observations of this paper.

3. Scaling in the Ground State of the He Isoelectronic Sequence

The most accurate expectation values available for the ground state of two-electron atoms are those reported by Pekeris [14–16] for H^-, He and Li^+. Expectation values of comparable accuracy have not been reported for the more highly charged positive ions. However, Scherr and Knight have reported an approximate sixth-order perturbation wave function for the ground state of two electrons about a nucleus of charge Z and used their wave function to compute perturbation expectation expansion coefficients for many operators through to sixth order [17]. Expectation values computed from the expansion coefficients of Scherr and Knight are compared with the accurate variational results of Pekeris in Table 1. It is clear that the sixth-order expectation values become

Table 1. Expectation values for ground state of He isoelectronic sequence[a]

Operator	H^-		He		Li^+	
	Pekeris[b]	Scherr and Knight[c]	Pekeris[d]	Scherr and Knight	Pekeris[e]	Scherr and Knight
r_1	2.170178	2.543604	0.929472	0.929290	0.572774	0.572768
r_1^2	11.913692	9.506842	1.193483	1.192343	0.446279	0.446255
r_{12}	4.412694	4.097613	1.422070	1.421730	0.862315	0.862305
r_{12}^2	25.202010	20.434759	2.516439	2.514189	0.927065	0.927018

[a] In atomic units.

[b] Ref. [14].

[c] Calculated from the data given in Ref. [17].

[d] Ref. [15].

[e] Ref. [16].

much better as the atomic number increases. As Chong and Weinhold [18] have noted the discrepancy for Li^+ is about 1 part in 10^5 for $\langle r_1 \rangle$, and $\langle r_{12} \rangle$ and about 5 parts in 10^5 for $\langle r_1^2 \rangle$ and $\langle r_{12}^2 \rangle$. The perturbation values should be more accurate for the more highly charged ions and, therefore, for the purpose of determining the values of δ which are appropriate for the ground state we shall use the Pekeris expectation values for He and Li^+ and the Scherr and Knight values for Be^{+2} through to Ne^{+8}.

The results of the scaling of the ground state expectation values by the procedure described in the preceding section are shown in Table 2 for r_1, r_1^2, r_{12} and r_{12}^2. The near constancy of the scaled expectation values for each operator is indicated in the accuracy column which is calculated by expressing S_δ as a percentage of the average of the scaled expectation values. Thus it can be seen that for each operator there exists a δ which makes Eq. (2) or an equivalent expression nearly constant. It will be convenient to defer a discussion of the significance of the δ values for the ground state to a later section so that the ground and excited states may be discussed collectively.

The Scherr and Knight sixth-order perturbation expansions can be applied to ions whose atomic number is greater than 10. In fact, the limiting value of δ for high Z can be evaluated directly from the expansion coefficients. If an operator q is expressed as a perturbation expansion in $1/Z$ to sixth order, then it follows from Eq. (2) that the scaled expectation values of q^n are given by

$$\langle q'^n \rangle = (Z-\delta)^n \left[\frac{c_0}{Z^n} + \frac{c_1}{Z^{n+1}} + \cdots + \frac{c_6}{Z^{n+6}} \right]. \tag{4}$$

As discussed above, the scaled expectation values $\langle q'^n \rangle$ should be nearly constant for all Z if the distribution functions can be nearly superimposed and, therefore, we set the partial derivative of the right hand side of Eq. (4) with respect to Z equal to zero. From the resulting expression, it follows that as $Z \to \infty$

$$\delta \sim \frac{c_1}{n c_0}. \tag{5}$$

Substitution of the Scherr and Knight perturbation expansion coefficients into Eq. (7) yields the limiting values of δ listed in Table 2. This approach can be

Table 2. Scaling parameters for ground state of He isoelectronic sequence

Operator	δ^a	Accuracy[b]	Limiting value[c]
r_1	0.39	0.2	0.375
r_1^2	0.42	0.4	0.398
r_{12}	0.46	0.1	0.471
r_{12}^2	0.46	0.3	0.462

[a] Evaluated from expectation values of Pekeris (He and Li^+) and Scherr and Knight (Be^{+2} through to Ne^{+8}).

[b] Calculated by expressing S_δ as a percentage of the average of the scaled expectation values.

[c] Limiting value of δ at high Z as calculated from the Scherr and Knight expansion coefficients.

used to demonstrate that the value of δ varies only slowly as the power n increases (δ equals 0.418, 0.434 and 0.448 for r_1^3, r_1^4, and r_1^5 respectively).

4. Scaling in Some Excited States of the He Isoelectronic Sequence

Scaling parameters based on the data of Pekeris *et al.* [12] and optimized by the criterion defined in Eq. (3) are listed in Table 3 for sixteen excited states. The accuracy of the scaling (see Table 2) is again of the order of one per cent or less.

Table 3. Scaling parameters for excited states of He isoelectronic sequence[a]

State	Operator			
	r_1	r_{12}	r_1^2	r_{12}^2
2^3S	0.54	0.60	0.61	0.61
3^3S	0.73	0.77	0.77	0.77
4^3S	0.81	0.84	0.84	0.84
5^3S	0.86	0.87	0.88	0.88
2^1S	0.74	0.83	0.82	0.82
3^1S	0.85	0.90	0.89	0.90
4^1S	0.90	0.93	0.93	0.93
5^1S	0.93	0.94	0.94	0.94
2^3P	0.80	0.88	0.90	0.89
3^3P	0.90	0.95	0.95	0.95
4^3P	0.94	0.97	0.97	0.97
5^3P	0.96	0.98	0.97	0.98
2^1P	0.89	0.99	0.97	0.99
3^1P	0.95	1.00	1.00	1.00
4^1P	0.98	1.00	1.00	1.00
5^1P	0.99	1.00	1.00	1.00

[a] Evaluated from the expectation values of Ref. [12].

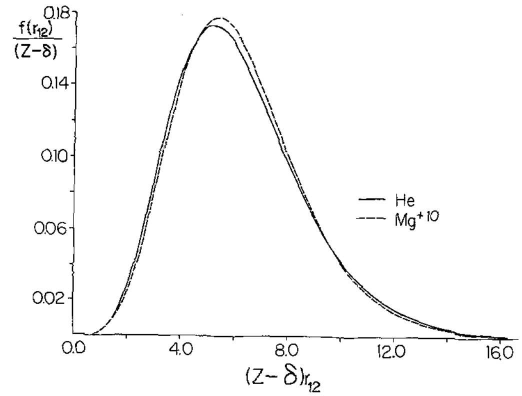

Fig. 1. The $f(r_{12})$ distribution function for the 2^3S state of He and Mg^{+10}. $\delta = 0.6$ and r_{12} in atomic units

For all the cases considered in this paper, it should be stressed that the scaling is not exact in the sense that Eq. (2) and similar equations for the other operators are not identically equal to a constant. If the scaling were exact, S_δ would be equal to zero. Although the ratio of S_δ to the average of the scaled mean values provides a quantitative measure of the accuracy of the scaling, it is interesting to consider the graphical representation in Fig. 1 of the superimposition of $f(r_{12})$ in the 2^3S state of He and Mg^{+10}. The correlated wave functions of Hart and Herzberg [19] used for this plot provide a good approximation to the exact distributions: 0.66060 and 0.50154 a.u. for $\langle r_{12}\rangle$ and $\langle r_{12}^2\rangle$ respectively for Ne^{+8} compared with the exact [12] values of 0.66061 and 0.50155 a.u. respectively. The scaled curves for Li^+, Be^{+2}, B^{+3}, O^{+6} and Ne^{+8} lie between the He and Mg^{+10} curves shown in Fig. 1 and, therefore, we conclude that the scaling leads to a good superimposition of $f(r_{12})$.

5. Discussion

From the data listed in Tables 2 and 3, it can be seen that there is an excellent agreement between the δ's derived from r_{12} mean values and those derived from r_{12}^2 mean values. This indicates that the $f(r_{12})$ curves for all the states studied in this paper can be superimposed quite well by the scaling procedure discussed above. Also we note that there is a fairly good correlation between the δ's based on r_1^n mean values and those based on r_{12}^n mean values and that the correlation improves as we proceed to more highly excited states. This implies that the $D(r_1)$ distributions can be effectively superimposed by the same procedure as the $f(r_{12})$ distributions and, therefore, we might expect that an interpretation attached to δ in the case of $D(r_1)$ should also hold for $f(r_{12})$.

In view of the above observations, it would appear to be reasonable to interpret δ as a screening constant, or at least as a measure of the screening, associated with the screening by one electron of the nuclear charge experienced by the second electron. With this interpretation, we may note that on the basis of the results presented in Table 3:

a) screening is greater in the singlet state than the triplet state of a particular configuration of two-electron atoms,

b) screening is greater in the P states than the corresponding S states of two-electron atoms, and

c) the screening approaches the limiting value of 1 (for two-electron atoms) for highly excited states.

The first observation is consistent with the relative magnitudes of the electron-electron repulsion terms and the electron-nuclear attraction terms in the 2^1S and 2^3S states and the 2^1P and 2^3P states of He. Thus contrary to the common interpretation of Hund's rule, electron repulsion is greater in the triplet state than the singlet state of the $1s2s$ [7] and $1s2p$ [9] configurations of He. But because the triplet state is lower in energy, the virial theorem requires the electron-nuclear attraction to be larger for the triplet than for the singlet state. This is consistent with the observation that the screening is greater in the singlet than the triplet state of a particular configuration.

At this point, it is convenient to discuss the scaling parameters determined from the distribution functions $f(r_{12})$ and $D(r_1)$ in connection with the scale factors associated with what Löwdin [20] has called the scaling problem in quantum mechanics. The scale factor is defined by subjecting a trial wave function to a scale transformation, in which all the coordinate vectors of the trial function from a given origin are uniformly stretched by a certain scale factor η in order to get a better fit of the trial function to the domain of space occupied by the system under consideration [20]. From this statement it is difficult to determine whether or not the scaling parameter δ and the scale factor η are related. However, by consideration of some results obtained by the application of perturbation theory to the ground state of two-electron atoms, it can be shown that η and δ are related in a certain sense.

The scale factor can be written as

$$\eta = Z + \frac{a_1}{2a_0} \tag{6}$$

where a_0 and a_1 are coefficients in the expansion for the energy [20]

$$E = a_0 Z^2 + a_1 Z + a_2 + a_3/Z + \cdots . \tag{7}$$

In the limit when $Z \to \infty$, the "effective nuclear charge" equals the scale factor and $(-a_1/2a_0)$ is interpreted as the charge by which each electron is screened by the other electron [20]. For the ground state of the He isoelectronic sequence, $a_0 = -1$, $a_1 = \frac{5}{8}$ and, therefore, the screening is 0.3125. The second term of Eq. (6) is quite similar to the limiting value of δ defined in Eq. (5) and, in fact, the limiting value of δ obtained from the Scherr and Knight [17] expansion coefficients for $\langle r_1^{-1} \rangle$ is also 0.3125. Thus we see that there is a link between the screening derived from the scale factor and the screening interpretation attached to the scaling parameter.

The value of δ which corresponds to the screening derived from the scale factor is somewhat smaller than the results listed in Table 2. This difference can be attributed to the superimposing of different regions of the distribution functions. Thus the scaling of the mean values of the inverse powers of the operators r_1 and r_{12} is strongly affected by the corresponding distribution functions at small distances. This applies in the case of r_1^{-1}, whereas for positive powers, the scaling is governed to a greater extent by the distribution functions at larger distances. Of course, the scaling parameter would be independent of the power of the operator if the scaling were exact. Also it should be noted that the superimposition illustrated in Fig. 1 is not destroyed by small variations in δ and that the observations listed above would not be altered significantly if negative powers of r_1 and r_{12} were used. It is important, however, to use similar sets of data to compare the scaling of different states.

To conclude this paper, let us briefly consider the scaling of the Coulomb hole. The scaling procedure described in the second section of this paper preserves the normalization of a distribution function such as $f(r_{12})$. In contrast, the charge moved by the Coulomb hole is not necessarily constant for a particular state of an isoelectronic sequence and, therefore, a different scaling procedure is required for the Coulomb hole. Thus, Curl and Coulson [3] have observed that the Coulomb hole in the ground state of the helium isoelectronic sequence, with the exception of H^-, can be represented by a single curve by plotting $\Delta(r_{12})$, the function which describes the Coulomb hole [1], in terms of $(Z-0.38)\,r_{12}$. In this case the abscissa is scaled but the ordinate is not. A recent study [21] of the Coulomb hole in the $2\,^3S$ state as a function of the nuclear charge indicates that the scaling observed by Curl and Coulson is not general for two-electron atoms. With the exception of He, the product of the atomic number and the radius [1] of the Coulomb hole in the $2\,^3S$ state appears to be nearly constant. Also the minimum value of $\Delta(r_{12})$, or depth of the Coulomb hole, is not independent of Z and therefore, it is clear that the procedure which superimposes the Coulomb holes in the $1\,^1S$ state does not lead to a similar result for the $2\,^3S$ state. There is, however, one remarkable similarity between the Coulomb holes of the ground and first excited states of the helium isoelectronic sequence. Thus, the Coulomb hole of the lowest member of the helium isoelectronic sequence for both the ground state [3] and the first excited state [21] appears to differ significantly from the Coulomb holes of the other members of the isoelectronic sequence.

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