

The Quantisation of the Screening Constant

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Abstract

Relationships are given in which the 'screening defect' is expressed in terms of the quantum numbers n and l for both the ground and excited states of neutral atoms for which the electron configuration can be considered as one electron and a core of completed shells. It is further shown that the same functions determine the ground-state energies for any series of neutral atoms with the same outer shell configuration. An explanation is offered in terms of wavefunctions with fewer nodes than the corresponding hydrogen wavefunctions.

1. Introduction

An energy level E of the single electron in a hydrogen-like atom is given by

$$E = Z^2 E_0 / n^2, \quad (1)$$

where E_0 is the energy for the ground state of hydrogen and Z is the nuclear charge. The valence electrons of atoms heavier than helium are generally assumed to occupy orbitals corresponding to the excited states of hydrogen. For the valence electron of such a neutral atom, if the remaining electrons exactly screen their equivalent nuclear charge, then the energy levels would be given by (1), with $Z = 1$. Instead, the electrons in the ground states and lower excited states (with 'lower' defined as having fewer nodes added to the wavefunction through excitation rather than the actual energy level itself) are generally, *but not always*, significantly more tightly bound than would be predicted by (1). These levels can be expressed in one of two forms (Edlen 1964)

$$E = Z^{*2} E_0 / n^2 \quad \text{or} \quad E = E_0 / n^{*2}. \quad (2, 3)$$

Thus we have $n^* \equiv n/Z^*$ where n^* (termed a defective quantum number) or Z^* (termed a screening constant) is used to reflect the higher potential required to obtain the required binding energy. There are assumed to be various contributing terms to n^* or Z^* ; for the present their sum will be termed screening defects. Screening defects are generally considered to arise through polarisation or penetration of the inner core by the valence electron. Waller (1926) derived a term which gave good estimates for the absolute values of such polarisation for nearly hydrogen-like states. Calculations gave energies in good agreement with experiment when n and l were large, either

through semiclassical calculations (Jaffe and Rheinhardt 1977), or wave mechanical calculations (Freeman and Kleppner 1976). The semi-empirical estimation of an effective field has allowed calculations of the screening terms in good accord with experiment for a number of atoms (Jastrow 1948), and generally it is understood that the theory that the inner electrons imperfectly screen the nuclear charge, through the polarisation or penetration of the core by the outer electron, is basically correct, even if accurate calculations are somewhat intractable for n and l small. This theory has been reviewed recently (Metcalf 1980).

The only alternative to this hypothesis is that the deviations from hydrogen-like behaviour arise through a quantum effect. In this context Sternheimer (1979) noted that energies of excited states appear to be grouped according to a quantum number k , where

$$k = n + l. \quad (4)$$

The position for ground states is similar. Expressions have been found for the screening in isoelectronic series (Layzer 1959), and the required orbital exponents have been expressed in terms of quantum numbers (Clementi and Raimondi 1963) for series of atoms. It is not simple, however, to relate one series to another.

While the calculations of the energies of the electrons has proved extremely difficult, attention has been paid to their relative energies to obtain the order of the filling of electron shells. In a simple Coulomb field we have $E = f(n)$; in practice we have $E = f(n, l)$. This is conventionally described as arising from differential screening, but as early as 1926, Madelung noted that the levels were grouped according to $n + l$, i.e. Sternheimer's ordering. Further, Neubert (1970) has offered an explanation in terms of a new (but otherwise unexplained) quantum number $c = \pm \frac{1}{2}$, and a constant χ defined by

$$\lambda = 2\chi(n' + l + 1), \quad (5)$$

where n' is the radial quantum number, l the angular quantum number, and when $\chi = \frac{1}{2}$, $\lambda = n$ is the principal quantum number. Neubert noted that when $\chi = 1$ (which required n' even) and by using c , the order of filling the levels could be obtained, since with n' even the equivalence between radial and angular motion required by the Coulomb field was broken. The quantum defect was represented in terms of a wave number k_{n^*} by

$$k_{n^*} = \chi k_0 / \lambda = k / n^*. \quad (6)$$

An alternative method of ordering energy levels was then devised (Novaro and Berrondo 1972; Berrondo and Novaro 1973). From considerations of group theory, it was argued that $E = f(l)$ arises through the direct product of two hydrogen-like levels; this product generated non-hydrogen-like terms and allowed the ordering of the filling of the periodic table to be obtained. While two empirical constants were required, it was claimed that the 'aufbau' principle could be obtained 'from geometric considerations alone'.

Armstrong (1982) has provided an alternative qualitative explanation for ordering which commences by invoking wavefunctions with fewer nodes. The observed order of the energy levels in spectra could be explained if the lowest state is $(0, 0)$, which has zero nodes, while the next level $(\frac{1}{2}, \frac{1}{2})$, and at one-quarter the energy of the

(0, 0) state, has one node. A problem with the explanation given is that the apparent ground state, from energy considerations, appears arbitrary: for example, RbI ($\frac{1}{2}, \frac{1}{2}$); CsI (1, 1); CaII ($\frac{1}{2}, \frac{1}{2}$); SrII (1, 1); PbII ($\frac{1}{2}, \frac{1}{2}$); SrI ($\frac{1}{2}, \frac{1}{2}$). A second problem lies in demonstrating that the underlying wavefunctions are orthogonal to the outer shells.

All such hypotheses have to address one further problem, namely that the spectral levels are ordered oppositely from the energies of the ground-state shells, even though the order of filling is the spectral order. For example, the observed spectral order for Rb is $5s < 5p < 5d$, and the first ground-state electron occurs in that order. The ground-state energies, as obtained from ionisation potentials [which required Koopmans' (1933) theorem to apply], are -4.2 , -5.8 and -7 eV respectively for Rb, In and Hf (Weast 1977-8). It seems unlikely that deviations from Koopmans' theorem could account for such a significant difference. Such an order can be explained in terms of screening defects; the difficulty with this explanation is that it cannot give quantitative estimates, and even at the qualitative level, there is no uniform approach.

There are two basic classes of approach in the above work. The standard approach assumes that the screening constant could only be calculated from a full quantum mechanical solution, although to make progress approximations are generally made. The second and distinctly minority approach proposes that the screening constant is largely determined through the properties of a wave associated with the motion being different to that assumed in the first approach.

This second approach requires certain assumptions to hold. The motion of a single electron is described in terms of a single valued wavefunction. There are a number of characteristics of this wavefunction; it has a number of zeros (i.e. nodes) and maxima; it is describable in terms of an analytical function (at least in principle); and from the wavefunction the expectation values of certain mechanical properties can be derived. These characteristics are termed here the wave structure. From these wavefunctions, orbitals can be obtained which describe the spatial distribution of electron charge. This description does not imply that the electrons actually reside in such orbitals, but merely that such orbital descriptions contain certain information of value. Thus, when an electron is removed from the atom, certain energy and angular momentum are also removed. The wavefunction itself is designed to be consistent with this information. Such an orbital description has been of considerable value, particularly for chemical calculations where it has been particularly profitable to consider each valence electron in isolation.

For the reason that such orbital descriptions are of considerable interest for chemical calculations, this study investigates the possibility that a fresh set of one electron wavefunctions may describe the energy levels of free atoms better than the one electron wavefunctions currently used.

2. General Approach

The first step is to find a convenient model in which to represent the mechanical properties in terms of the wave structure, and in terms of a reference wave structure. The corresponding states of the hydrogen spectrum (i.e. states with the same values of n and l) will be taken as reference states; the associated mechanical variables will be termed hydrogen-like and denoted by the subscript zero. Wavefunctions with a different wave structure and their associated variables will be termed non-hydrogen-

like. Examination of (1) shows that changes in Z can be expressed in terms of momentum p , defined as $p = (2mE)^{1/2}$, with m the electron mass; as such, these changes in momentum which arise from non-hydrogen-like effects will be expressed through a term defined by

$$\mathcal{M} = p/p_0, \quad (7)$$

i.e. the term expresses the momentum which would arise from the use of non-hydrogen-like orbitals in units of the momentum of the corresponding hydrogen-like state.

Either hydrogen-like or non-hydrogen-like orbitals may be subject to screening defects through the well-known correlation effects. In particular, if there are n_i electrons with the same value of n and l , then defective screening from this cause is expected when $n_i > 1$. Defective screening alters the field as seen by the electron, and introduces an additional term. This term will clearly be dependent on the electron configuration of the atom, and empirically this group term C_N (an approximate expression for which is given below in terms of electron configuration) is considered as additive to \mathcal{M} , i.e. it is expressed also in units of p_0 . Thus, we have

$$Z^* = \mathcal{M} + C_N + \delta, \quad (8)$$

where δ measures the deviation between the observed value of Z^* and the sum of \mathcal{M} and C_N , and ideally is equal to zero. If δ has a significant magnitude or trend, then this indicates incompleteness of the model.

The model to be used incorporates action as an important function. The mechanical variables can be related to action through a diagrammatic method first outlined by Planck (1915, 1916). Here the motion is represented as cells in phase space; boundaries to the cells are the expectation values of the momentum p and a distance r which defines the expectation value of the potential energy in the Coulomb field. The area of these cells defines the action S ; the requirement that the corresponding wavefunction be single-valued (Keller 1958) is

$$S = pr = nh. \quad (9)$$

While Planck's original work considered electron trajectories, such trajectories are not part of quantum mechanical considerations nor of this treatment. Nevertheless, the phase-space representation has attractive features for a model, particularly when the concept of trajectories is dispensed with and the cell shape is used merely as a relative accounting tool. In this case, the cell shape is determined from the expectation values of p and r . Of particular interest to the argument is the fact that the phase-space cell is divisible into two sheets; the sheets do not have to be equivalent, nor do they have to pass continuously from one to the other (Percival 1977). Thus, the possibility exists that a proposed effect could take place on one or both sheets. The value of this will be seen below. There is clear evidence (e.g. spectral analysis) that if there are non-hydrogen-like orbitals, the total action, and its distribution between angular and radial motion, is given by the appropriate quantum numbers of the hydrogen-like orbitals. This is also required for the periodic table. The quantum numbers are used here, and they are considered to define the quanta of action associated with the orbital, but they do not characterise the nodal structure of the wavefunction.

As a working hypothesis, it is assumed here that the wave structures differ from the hydrogen-like ones, and the screening constant is the observable parameter associated with this effect. The tenability of the hypothesis is tested by whether relationships for the screening constant can be obtained from the hypothesis.

The postulate is, therefore, that some special effects may increase the magnitude of p , with a corresponding decrease in r , while holding S constant. This postulate is not compatible with motion in a Coulomb field, as in such a field $S \propto r^{1/2}$. Thus, an additional variable is required if the proposition is to be consistent with other general physics. The obvious additional variable is the field; the potential field is assumed to adopt a value at the inner spatial regions of the wave which permits a contraction of the overall value of r . The model therefore postulates that:

The values for the screening constant $Z^ > 1$ permitted for orbitals of heavy atoms arise from the properties of the wavefunction of the electron being screened, and are not a primary property of the orbitals of the remaining electrons.*

Thus it is proposed that the defective screening constant is a property of the electron being screened. The orbital being screened may in fact have a number of potential solutions, and the inner core will determine which one is adopted because the possible magnitude of the defective screening constant will be limited by the structure of the inner core.

Before developing this model further, however, it will be useful to consider how this model applies to the one-electron wavefunctions of the hydrogen atom.

3. Hydrogen-like Wave Properties

The motion in a central field can be separated for the purposes of calculation into radial and angular components, i.e. in terms of the action

$$S = S_r + S_\theta, \quad (10)$$

and following Schiller (1962) (keeping radial and angular terms separately bracketed)

$$n = (n_r + \frac{1}{2}) + (l + \frac{1}{2}), \quad (11)$$

where n_r and l count the number of radial and angular nodes respectively. Each component is required, by the uncertainty principle, to have $\hbar/2$ of action. Thus, when $l = 0$, there is $\hbar/2$ of angular momentum; this has been confirmed experimentally for s orbitals (Kuhn 1962).

Comparison of equations (1), (2) and (11) leads to the requirement

$$n^* = n/Z^* = (n_r + \frac{1}{2}) + (l + \frac{1}{2}). \quad (12)$$

Clearly, a reduced number of nodes in the wavefunction is possible if

$$Z^* = n/x, \quad (13)$$

where x is an integer and $0 < x < n$, but such a wavefunction would be indistinguishable

from an underlying wavefunction because

$$n_r + l < n - 1. \quad (14)$$

Since n_r and l must be integers, if there were fewer nodes present for any value of n than for the hydrogen-like case, the inequality (14) requires that at least one pair of waves would be identical apart from differences in arbitrary labelling. This would violate the Pauli principle. This issue was not discussed by Armstrong (1982) when he proposed wavefunctions with fewer nodes. One conclusion from this is that, if the above analysis is correct, the hydrogen-like wavefunctions are the only ones based on one fundamental vibration and which are consistent with the Pauli principle.

4. Non-hydrogen-like Wave Properties

The use of two sheets as proposed above allows for a model to be constructed that contains more than one fundamental vibration. For the model to be useful, however, a separation into component vibrations must be made in a non-arbitrary fashion, and once the separation is carried out, a method must be found by which proposed non-hydrogen-like effects can lead to a lowering of the overall energy, and the effect(s) can be made to quantitatively account for \mathcal{M} .

The wavefunction can only be altered by reducing the number of nodes on one or both sheets; if the total action remains constant then the action per phase-space cell is proportionately increased. Since S is constant, and since p is required to increase (to account for observation) and r to correspondingly decrease to account for these changes, it is proposed that:

Proposition 1. The values of \mathcal{M} which arise through the nodal structure of a wave being altered to permit defective screening is proportional to the total action available to the component divided by the number of phase-space cells into which the action is distributed.

Proposition 1 gives the fundamental route by which non-hydrogen-like effects are postulated to arise.

The reduction in the total number of nodes clearly affects the action enclosed by the nodal surfaces, but examination of (12) shows that for each of the two degrees of freedom, $\hbar/2$ of action is independent of these nodal surfaces.

Thus, when $l = 0$, $\hbar/2$ of action is associated with the uncertainty of orientation of any radial axis with respect to an external frame of reference, and since these requirements arise from the uncertainty principle, and not from the nodal structure, these requirements should remain unaltered through variations in the nodal structure. As each sheet contributes half of each effect, we expect that:

Proposition 2. For each non-hydrogen-like sheet, at least $\hbar/2$ of the action is unavailable to affect \mathcal{M} as outlined in Proposition 1.

A primary non-hydrogen-like effect is thus argued to arise from the reduction in the number of nodes on one or both sheets; whichever eventuates will depend on the ability of the atom to provide the necessary screening defect. The reduction in the number of nodes should not be arbitrary, and it is proposed that for a ground state, each sheet should be either hydrogen-like or have zero nodes; excited states should have an appropriate increase in the number of nodes on both ground-state sheets.

Furthermore, if the ground state has one non-hydrogen-like sheet, the effect on \mathcal{M} , apart from the question of available action, should be half that of when both sheets are involved. Furthermore, should all the action be available, and with no reduction in the number of nodes on either sheet, the formula should give the hydrogen-like formula of $\mathcal{M} = 1$. Consideration of these observations leads to:

Proposition 3. The value of \mathcal{M} for the primary non-hydrogen-like effect is given by one of two equations: (a) if both sheets are non-hydrogen-like then

$$\mathcal{M}_1 = \frac{S_{av}}{1 + \text{number nodes}}; \quad (15)$$

(b) if one sheet only is non-hydrogen-like then

$$\mathcal{M}_1 = \frac{S_{av} + 1}{2 + \text{number nodes}}, \quad (16)$$

where S_{av} is the available action, and the number of nodes refers to the number of nodes on the non-hydrogen-like sheet(s).

In the arguments above, there has been no explicit dependence of any variable on l , but it is known that $E = f(n, l)$. Hence, with $l \neq 0$, a second term \mathcal{M}_2 is required to account for this dependence on l .

The non-equivalence of excited states can be seen immediately from (15) and (16). If, for example, an s level is to be converted to a p (or d) level, an angular node(s) must be added to each sheet; for the hydrogen-like sheet, a corresponding reduction can occur in the number of radial nodes, and energy equivalence is maintained. For the proposed non-hydrogen-like sheet, however, there are no radial nodes to remove, and hence l half-nodes must be imposed on each non-hydrogen-like sheet, which will raise the energy. Thus, the transition Na 3s \rightarrow 3p involves raising the energy of the electron, and 3p is an excited state of sodium.

For ground states, however, the position is reversed. For energy equivalence, on the non-hydrogen-like sheet all nodes should be removed. However, for the hydrogen-like sheet, assuming only one sheet is non-hydrogen-like, all nodes, including the angular nodes, are present and these impose angular distributions on the electron charge in real space. However, the charge associated with the $(n' + \frac{1}{2})\hbar$ associated with radial motion should have the same angular distribution on each sheet, and hence the angular distribution of the hydrogen-like sheet is effectively imposed on the non-hydrogen-like sheet. The reduction of the spatial range of the $(n' + \frac{1}{2})\hbar/2$ associated with radial motion is reduced to that imposed by the l half-nodes; a reduction in positional uncertainty leads to a corresponding increase in momentum through the uncertainty principle. The spatial conditions leading to such a reduction in positional uncertainty are termed a constraint.

The reduction in positional uncertainty arising from such a constraint, however, can be partly offset by the degeneracy of the orbitals. For example, if to the spherical distribution of the primary non-hydrogen-like effect is added the formal constraint of l nodes, the electron has $2l + 1$ constrained orbitals to choose from, or interchange between. As it is not known which orbital the electron is in, positional uncertainty is increased, partly offsetting the magnitude of the effect of the imposition of the l

nodes. Thus it is proposed that:

Proposition 4. Further terms in \mathcal{M} arise for each independent constraint to a non-hydrogen-like orbital; the value of \mathcal{M} for each term is proportional to the number of nodes required to impose the constraint, the action per phase-space cell affected by the constraint, and is inversely proportional to the degeneracy resulting from the constraint.

These propositions allow the calculation of ground and excited state values of \mathcal{M} , and hence energy levels. By Propositions 2 and 3 we have

$$S_{av} = (l + n' + h_s)\hbar/2, \quad (17)$$

where h_s is the number of hydrogen-like sheets. For the case of one hydrogen-like sheet, if $l \neq 0$, the secondary term from Proposition 4 is

$$\mathcal{M}_2 = (n' + \frac{1}{2})l/2(2l+1). \quad (18)$$

By inserting (17) into (16), adding (18), and rearranging we get

$$\mathcal{M} = \frac{1}{2}\{1 + l + (n' + \frac{1}{2})(1 + l)/(2l+1)\}, \quad (19)$$

which in the special case of $l = 0$ reduces to

$$\mathcal{M} = \frac{1}{2}n + \frac{1}{4}. \quad (20)$$

If both sheets are non-hydrogen-like, and when $l = 0$, we have

$$\mathcal{M} = n - 1. \quad (21)$$

When $n_i = 0$, the model is formally free of experimental constants. When $n_i \neq 0$, the term defined here as C_N has been observed to be linear with n_i , and a theoretical explanation (Condon and Odabasi 1980, pp. 526–7) has been offered for $l = 0$ and 1. Rather than use these expressions, the following equation is proposed on purely empirical grounds, largely because it covers l where $0 \leq l \leq 3$:

$$C_N \approx (C_N)_0 + (n_i - 1)/(2 + l^4), \quad (22)$$

and $(C_N)_0$ is ideally equal to zero. Equations (19), (21) and (22) are proposed as sufficient to account for ground-state energies.

Ionisation Energies of Ground States

A comparison with experimental observations is given in Table 1 for elements where $n_i = 1$, and hence $C_N = 0$. As can be seen there is excellent agreement, apart from boron, and there is a clear implication that $Z^* = f(n, l)$ as given by equation (19). The remaining main-group elements are given in Table 2, where an empirical value of C_N is used. That C_N is constant seems adequate apart from groups VI–VIII, where agreement is improved by the addition of a further group constant when $n \geq 4$. The comparison is shown in Table 2.

Table 1. Calculated values of Z^* for group I and III elements

Element	\mathcal{M}^A	δ^B	Element	\mathcal{M}^A	δ^B
Li	1.25	+0.009	B	1.333	+0.229
Na	1.75	+0.096	Al	2.000	-0.009
K	2.25	+0.010	Ga	2.667	-0.010
Rb	2.75	+0.022	In	3.333	-0.067
Cs	3.25	-0.039	Tl	4.000	-0.019

^A Defined by equation (19).

^B This term must be added to \mathcal{M} to give Z^* as derived from experimental values of the ionisation potential (Weast 1977-8) through equation (2).

Table 2. Calculated values of Z^* for main-group elements with more than one electron in the highest occupied level

Element	$(\mathcal{M} + C_N)^A$	δ^B	Element	$(\mathcal{M} + C_N)^A$	δ^B
Be	1.735	-0.079	C	1.735	+0.084
Mg	2.235	+0.014	Si	2.402	-0.080
Ca	2.735	-0.054	Ge	3.068	+0.023
Sr	3.235	0	Sn	3.735	-0.061
Ba	3.735	-0.021	Pb	4.402	+0.028
Ra	4.235	+0.127			
	$C_N = 0.485$			$C_N = 0.401$	
N	2.025	+0.043	O	1.976	+0.025
P	2.692	-0.058	S	2.642	-0.025
As	3.358	+0.039	Se*	3.394	-0.007
Sb	4.025	-0.040	Te*	4.061	+0.008
Bi	4.692	-0.300	Po*	4.727	-0.002
	$C_N = 0.691$			$C_N = 0.642$	(+0.085)
F	2.266	-0.004	Ne	2.542	-0.023
Cl	2.932	+0.003	A	3.209	+0.022
Br*	3.748	-0.012	Kr*	3.058	+0.001
I*	4.415	+0.011	Xe*	4.724	-0.002
	$C_N = 0.934$	(+0.149)		$C_N = 1.208$	(+0.183)

^A Here \mathcal{M} is given by equation (19) and C_N is given below the group. For the elements with asterisks the extra term in parentheses must be added to C_N .

^B This term must be added to $\mathcal{M} + C_N$ to give Z^* as derived from experimental values of ionisation potentials (Weast 1977-8).

There are no marked trends in δ apart from the sign of the difference from the median value; this sign is negative when $n-l$ is even and positive when it is odd. Since there is no obvious dependence of δ on n , this indicates that Z^* is a function of n as required by equation (19).

The significance of δ is not immediately obvious. It has been recognised that the ionisation potentials in a group of elements fall onto one of two curves, depending on whether $n+l$ is odd or even. It has been stated (Condon and Odabasi 1980, pp. 522-5) that, from a dynamical group theory treatment, this can arise as follows: 'Because two representations of $SO(3, 2)$ occur in the particular representation $SO(4, 2)$, whose multiplicity pattern coincides with the structure of the periodic table, the neutral elements are sorted into two groups according to whether $n+l$ is even or odd.'

In Table 3 the values of C_N as found from Table 2 are listed, using values of C_N when $n \geq 4$ and assuming a new series commences with spin pairing (Condon and

Table 3. Comparison between the empirical C_N and that calculated from (22) for main-group elements

n_i	C_N (empirical)	C_N (from equation 22)	
		$(C_N)_0$ assumed	C_N calculated
s electrons			
1	0.02	0	0
2	0.49	0	0.5
p electrons			
1	0.02 ^B	0	0
2	0.40	0	0.33
3	0.69	0	0.66
p electrons ($n > 4$)			
4 ^A	0.73	0.73	0.73
5	1.08	0.73	1.06
6	1.39	0.73	1.39

^A This group is used to determine $(C_N)_0$ for $n_i > 4$ and $n > 4$.

^B Boron omitted.

Odabasi 1980). The agreement is sufficient to suggest that if the discontinuity in C_N for groups V–VIII is real (and not that an incorrect function is masked by δ), then the light elements are anomalous.

5. Elements where $l = 2$ and 3

In the transition elements, the series proceeds by the addition of d electrons, but the first ionised state seldom has the configuration of the ground state less one d electron (Moore 1971). Nevertheless, if the ionisation potentials are used to derive values of Z^* , these values can be plotted against the number of d electrons, as shown in Fig. 1 for the early d electrons. The dependency on n , as required by equation (19), is shown by the vertical bars, while the slopes of the lines show the dependency on the number of electrons required by equation (21). Fig. 2 shows a similar plot for elements where $l = 3$. As can be seen, the agreement is quite good for the early members of each series.

Towards the end of the transition metal series, the ionisation invariably involves s electrons, but Z^* does not parallel its behaviour for the Ia or IIa elements. In Table 4, however, a correlation is given with Z^* from equation (21) which is fairly good. When $n = 4$, Z^* is consistently too low, but it should be noted that if the sign of δ follows the rule outlined above, δ will be positive for $n = 3$ and 5, and negative for $n = 4$. Thus, 2δ should be subtracted from the mean values for $n = 3$ and 5 to predict the value for $n = 4$.

Therefore, it appears that the s electrons, in the presence of adjacent d electrons, adopt a different wavefunction from that of s electrons in the absence of filled d orbitals. Once an arbitrary screening defect explanation is abandoned, of course, this is required to explain why the chemistry of the s electrons of copper, silver and gold is so different from potassium, rubidium and caesium. That these elements can use d electrons is beside the point; the s electrons themselves behave so differently. As an example, the reactivity increases as n increases from K to Cs, but the reverse occurs

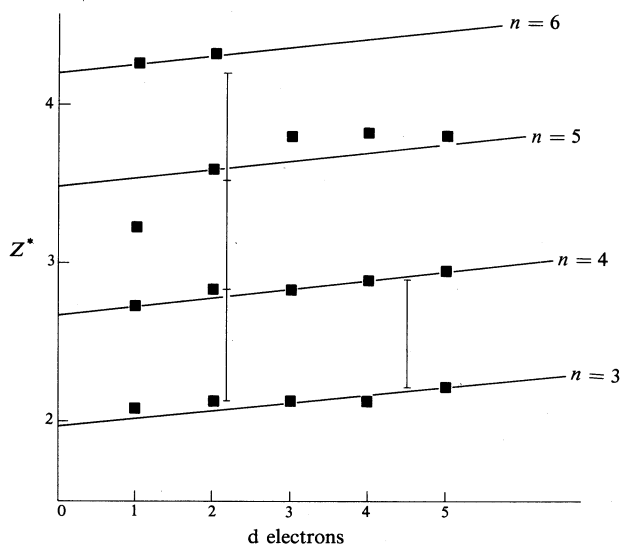


Fig. 1. Values of Z^* derived from ionisation potentials against the number of d electrons for the early transition metals. The gradient of lines is defined by equation (22), with the vertical bar lengths as required by (19), both assuming $l = 2$.

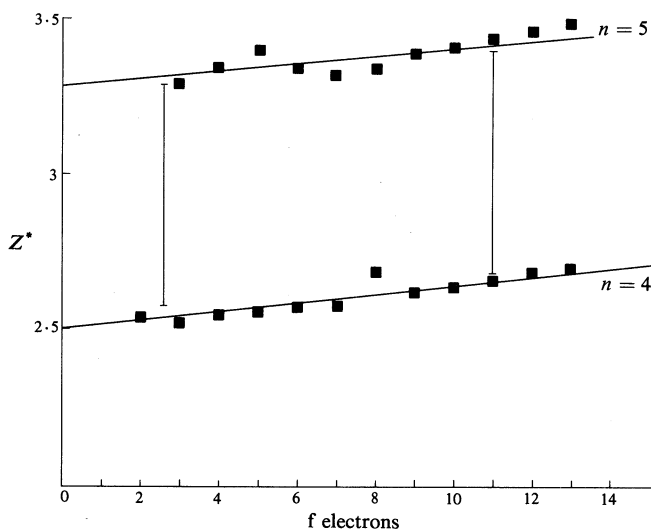


Fig. 2. Values of Z^* derived from ionisation potentials against the number of f electrons for the rare earths. The gradient of lines is defined by equation (22), with the vertical bar lengths as required by (19), both assuming $l = 3$. Ionisation potentials are taken from Weast (1977-8) and Martin *et al.* (1974).

from Cu to Au. For the main-group elements, covalent bonds are generally stronger the higher the ionisation potential of the atom, yet the transition metals with high ionisation potentials, such as Au and Hg, form weak bonds. A fundamental change in the nature of the wavefunction seems to accommodate these observations.

Table 4. Comparison between values of Z^* as required by (2) and those calculated from (21)

Element	\mathcal{M}^A	Z^{*B}	Element	\mathcal{M}^A	Z^{*B}
Co ^C	3	3.12	Ni ^D	3	2.99
Rh ^C	4	3.83	Pd ^D	4	3.72
Ir ^C	5	4.88	Pt ^D	5	4.88
	$ \delta _{av}^E = 0.085$			$ \delta _{av}^E = 0.133$	
Cu	3	3.01	Zn	3	3.32
Ag	4	3.73	Cd	4	4.07
Au	5	4.94	Hg	5	5.25
	$ \delta _{av}^E = 0.13$			$ \delta _{av}^E = 0.11$	

^A \mathcal{M} calculated from equation (21). ^B Ionisation potentials from Weast (1977-8) or Martin *et al.* (1974). ^C $d^7s^2 \rightarrow d^7s$, and energy levels from Martin *et al.* (1974). ^D $d^9s \rightarrow d^9$, and energy levels from Martin *et al.* (1974). ^E Mean magnitude of the deviation δ , assuming the same sign convention for δ as observed for the main-group elements.

6. Excited States

If the proposed model is correct, an immediate prediction follows. The action associated with radial motion is $(n-l-\frac{1}{2})\hbar$. If this is to be distributed such that there is more than one quantum of action per phase-space cell, the required condition for a non-hydrogen-like orbital in the absence of radial nodes is

$$n-l-\frac{1}{2} > 1. \quad (23)$$

Thus, inequality (23) requires that if the lowest orbital in a series is 2p, 3d and 4f, the orbitals are hydrogen-like (provided they arise through excitation and are not ground states), i.e. $\mathcal{M} = 1$, while the 3p, 4d and 5f orbitals are not if the 2p, 3d and 4f levels are not available.

In Table 5 empirical values of Z^* , as required by equation (2), are listed for the excited states of elements where the excitation can be considered to involve one electron and leave an inert core. The selection chosen consists of the excited states of the alkali metals, those of the group III elements which can be assigned the s^2 closed subshell, and the excited states of the Cu subgroup of elements which can be assigned as having the d^{10} closed subshell. Energy levels and their assignments for excited states have been taken from an NSRDS compilation (Moore 1971).

For the alkali metals, when $l = 1$, the Li 2p level has $Z^* = 1.02$, while the Na 3p level has $Z^* = 1.417$. When $l = 2$, the Na 3d level and the K 3d level have $Z^* = 1.003$ and 1.051 respectively, while the Rb 4d level has $Z^* = 1.446$. All of the alkali metals have 4f levels available, but no non-hydrogen-like effect is predicted for $l = 3$. The observed values for K, Rb and Cs are 1.002, 1.003 and 1.005 respectively. Thus, for a first order analysis, this is excellent agreement.

For group 3 elements, no analysis is possible for $l = 1$ (ground states have an additional term), while for $l = 2$ again $Z^* = 1.4$ when $n = 4$, although $Z^* = 1.14$ when $n = 3$. This would seem to be rather poor agreement, but it should be noted that the addition of a radial node actually increases the value of Z^* . This is atypical and is suggestive of a large additional effect. When $l = 3$, $Z^* = 1.015$ when $n = 4$, but 1.26 when $n = 5$. Thus, with the possible exception of the Al 3d state, the commencement of this non-hydrogen-like effect occurs exactly where it is required by inequality (23).

Table 5. Values of Z^* derived from experimental energy levels by (2)

NA indicates the level is not available and an asterisk that one radial node is present through excitation

Element	n	$l = 0$	$l = 1$	$l = 2$	$l = 3$
Li	2	1.259	1.02		
Na	3	1.843	1.417	1.003	
K	3	NA	NA	1.051	
	4	2.259	1.792	1.052*	1.002
Rb	4	NA	NA	1.446	1.003
	5	2.77	2.19	1.349*	
Cs	4	NA	NA	NA	1.005
	5	NA	NA	1.96	
	6	3.21	2.58	1.701*	
B	3	1.485*		0.998	
Al	3	NA	NA	1.14	
	4	1.828*	1.495*	1.167*	
Ga	4	NA	NA	1.408	
	5	2.318*	1.869*	1.314*	
In	4	NA	NA	NA	1.015
	5	NA	NA	1.772	
	6	2.705*	2.207*	1.581*	
Tl	5	NA	NA	NA	1.258
	6	NA	NA	2.076	1.207*
	7	3.190*	2.597*	1.796*	
Cu	4	NA	2.156	1.344	
	5	2.090*	1.717*	1.257*	
Ag	4	NA	NA	NA	1.003
	5	NA	2.681	1.676	
	6	2.467*	2.050*	1.504*	
Au	5	NA	NA	NA	1.256
	6	NA	3.486	2.022	
	7	2.983*	2.533*	1.761*	

The Cu elements have their 3d levels filled, but for $l = 3$, the Ag 4f level has $Z^* = 1.003$, while the Au 5f level has $Z^* = 1.256$. Thus it seems that the observed deviations from hydrogen-like behaviour occur exactly where required by (23).

Discontinuities in a series of screening constants have been recognised and have been explained in terms of core penetration (Foley 1979). The argument is that there is a steep potential well within the core, the depth of which increases rapidly with nuclear charge. As the nuclear charge increases an antinode develops in the inner region giving a sudden phase increase of π . The development of this antinode is assisted by increasing nuclear charge, but this is offset by the centrifugal forces present with large l . It is required that this antinode develops quite suddenly at a certain nuclear charge, particularly when $l = 2$ or 3.

The values of Z^* , as empirically determined from equation (2), for the 5s and 5p levels of Ga (2.32 and 1.87) are similar to those for the 4s and 4p levels of K (2.26 and 1.79). Now, if this reflects that the depths of potential wells are roughly the same, then one might expect the Ga 4d (or 5d) levels to correspond to the K 3d (or 4d) levels. As can be seen from Table 5, they do not, exactly as required by (23). While this argument is stronger when the magnitudes of Z^* are calculated, the probability that some unrelated factor could follow (23) by accident is exceedingly small.

Calculation of Excited State Energies

This model requires that the value of \mathcal{M} for excited states be obtained from (15) and (16). The two equations can be generalised by defining a term x , equal to 2 if one sheet is non-hydrogen-like and 1 if both sheets are non-hydrogen-like, the number n_e of additional quanta of action generated through excitation (this can be negative e.g. $6s \rightarrow 5f$), and n_s which is $n_g - \frac{1}{2}$ if $x = 2$ and $n_g - 2$ if $x = 1$, with n_g being the principal quantum number for the ground state:

$$\mathcal{M} = (n_s + n_e + 1)/(x + n_r + \Delta l'). \tag{24}$$

It should be noted that (24) is written such that $\Delta l'$ is the total change in the number of angular nodes. If angular nodes are removed through excitation, e.g. $3p \rightarrow 4s$, then $\Delta l'$ is negative. The excited state energy levels follow the form of (24) reasonably well, but a considerable improvement is made if minor modifications are made to its parameters.

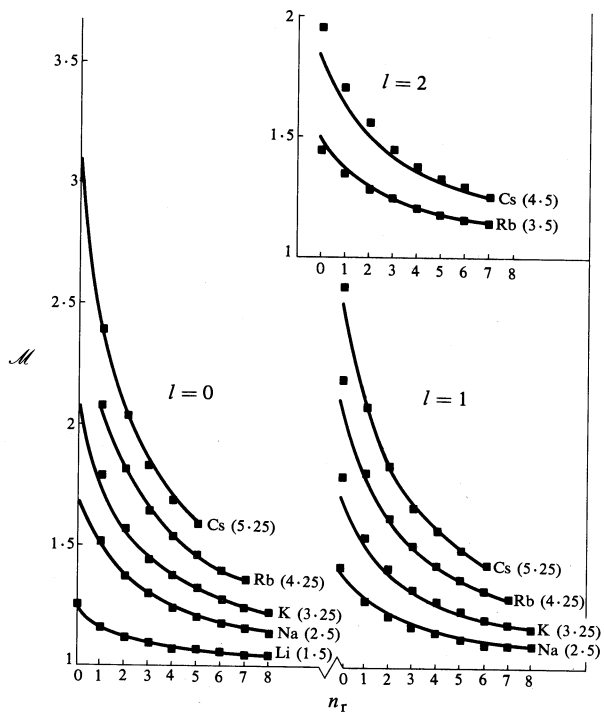


Fig. 3. Comparison between Z^* from observation (squares) and the value of \mathcal{M} required by equation (26) (curves) for non-hydrogen-like excited state levels for the alkali metals.

If $x = 2$ (i.e. one non-hydrogen-like sheet) and for the ground state $l = 0$ (i.e. s state), the best agreement is found when

$$\Delta l' = \Delta l/2. \tag{25}$$

The reason for this is not clear but is presumably a consequence of the requirement

to generate half a node from the non-hydrogen-like sheet. The $l/2$ term could arise if there was a 50% probability that this could come from the hydrogen-like sheet.

The second cause for modification is if minor changes can be made to the value of n_s ; i.e. increased amounts of action may be unavailable. In the following, it has been assumed that such shifts can take place in minimum amounts of $\hbar/4$ (Keller 1958). Specific elements are now considered.

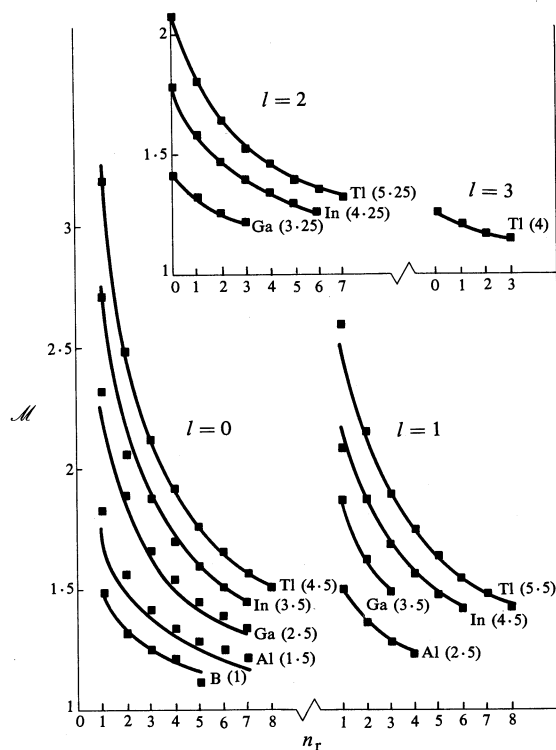


Fig. 4. Comparison between Z^* from observation (squares) and the value of M required by equation (27) (curves) for non-hydrogen-like excited state levels with s^2 subshells for the group III elements.

7. Alkali Metals

A comparison between Z^* as derived from equation (2) and calculated as detailed below is given in Fig. 3. As might be expected, the alkali metals follow the proposed theory most closely, fitting the equation

$$M = (n_s + n_e + 1)/(2 + n_r + \frac{1}{2}l), \quad (26)$$

with $n_s = n_g - \frac{1}{2}$, sufficiently well that the energies of the excited states for Li and Na can be calculated to within about 4% (after applying inequality 22), and frequently the results are better. For K, Rb and Cs the agreement is poorer, and systematic trends are observable. The systematic errors occur in the s and p series, but not in the d series and this may indicate an interaction with the vacant d orbitals. Much better

agreement is found for these three elements when $n_r \neq 0$ by putting $n_s = n_g - \frac{3}{4}$, and the curves in Fig. 3 are calculated on this basis for the s and p series.

Thus, while (26) can give quite an accurate account of the energy levels of the alkali metals, it should be noted that the errors are also of roughly the same magnitude as the deviations for $\mathcal{M} = 1$ for the 2p levels of Li and the 3d levels of K for which (23) requires $\mathcal{M} = 1$. These deviations may well accurately represent the polarisation of the underlying inert gas electron core.

8. Group III Metals

This discussion is limited to those lines which are considered to arise from the excitation of the ground-state p electron, leaving an inner s^2 shell which is assumed to be inert. Comparative data are found in Fig. 4. The group III elements follow an equation of the form

$$\mathcal{M} = (n_s + n_e + 1)/(1 + n_i + l). \quad (27)$$

The term n_s , however, is not constant, being $n_g - \frac{1}{2}$ for the p series, $n_g - \frac{3}{4}$ for the d series and $n_g - 1$ for the f series. (For the f series of Tl n_g is also reduced from 6 to 5.) For the s series, however, n_s is reduced to $n_g - \frac{3}{2}$ for the heavier elements, while for B, best results are obtained when $n_s = n_g - 1$.

The significance of this result is not clear. That boron does not fit well is not unexpected, as it gave a poor fit when considering ionisation potentials. The remaining elements appear to fit their series quite well, which is strong support for this proposed model, but it is clear that there is a minor systematic effect which has not been considered. Ga and Al have systematic deviations of similar magnitude to these deviations from $Z = 1$ for the Al 3d level, where it is required that $\mathcal{M} = 1$ by (23). The deviations may arise through the neglect of polarisation.

For the group III elements we have $x = 2$, but the value of l in the ground state has been subtracted out in (27) for convenience.

9. Group Ib Metals

Our discussion is limited to those lines which are considered to arise from the excitation of a ground-state s electron, leaving an inner d^{10} shell which is assumed to be inert. Detailed data are shown in Fig. 5. The elements follow equation (27). For the p, d and f series we have $n_s = n_g - 1$, while for the s series a tolerable fit is found with $n_s = n_g - 2$, and an improved fit with $n_s = n_g - \frac{7}{4}$. In general, the agreement between calculated and derived values of Z^* is good, although some levels agree only poorly, such as the lowest p level for Au, which has an observed value of $Z = 3.486$ and a calculated value of $\mathcal{M} = 3.000$. Since n_s is constant for the p and d series, the same value is used to calculate the 5f level for Au and, after making the correction for the reduction of n from 6 to 5, the calculated value of \mathcal{M} is 1.250, in excellent agreement with the observed value of $Z = 1.256$.

10. Conclusions

The equations proposed here give a good, but not exact, means of calculating the energies for ground states and for any series of the excited states of these atoms where an inert core can be assumed. Clear relationships between the calculated and derived values of Z^* are too extensive to be a series of accidental coincidences, and the

equations proposed here do not appear to be able to be derived from an alternative theory. This is considered as strong evidence supporting the proposition that the orbitals concerned are fundamentally different from the corresponding excited states of hydrogen.

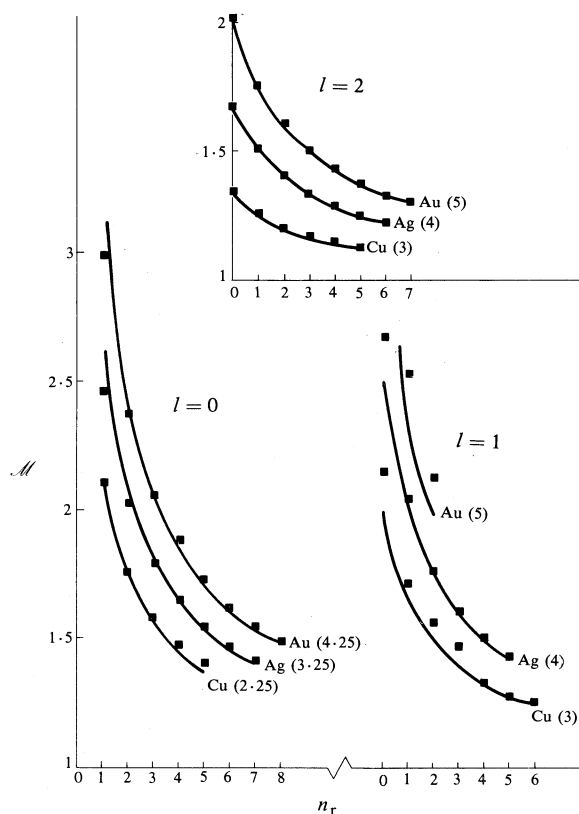


Fig. 5. Comparison between Z^* from observation (squares) and the value of M required by equation (27) (curves) for non-hydrogen-like excited state levels with d^{10} shells for the group Ib elements.

The purpose of this paper has been to explore the consequences of assuming that the nodal properties of atomic orbitals differ from those of the excited states of hydrogen. The postulated requirements for such an hypothesis leads to two qualitative achievements: it has shown that the orbitals may be hydrogen-like or non-hydrogen-like, and it accurately predicts where the transition occurs, and secondly it quite accurately predicts both the form of a given spectral series and the relationships between series and elements. Minor alterations to the value of some terms are required for quantitative agreement, but agreement is quite extensive following these corrections. These calculations have been carried out on the lower levels, and good agreement has been obtained for these levels, where conventional theory has not been particularly successful. Good agreement has been obtained for numerous levels in many series which hitherto have not been numerically related.

For the ground states, good agreement is found for group I and group III elements, i.e. those for which an inert core can be expected. While an empirical correction is

required to make calculations on the remaining elements, the relationships between elements *in the same group* are the same as for the group I and III elements. Of particular significance for the ground-state elements is the term in l ; the dependence on l is accurately given *and it is of the opposite sign* to all other theoretical predictions known to this author. Of further significance is the explanation for the different behaviour of the s electrons for transition metal elements, i.e. that they have a different wavefunction from the alkali metal case. Apart from being numerically accurate, a simple explanation is given of the fundamentally different chemistry between, say, Cs and Au, which is not readily given by the orthodox screening explanation.

The agreements for the excited states are also very good once certain corrections are made. It could be argued that these corrections seem somewhat arbitrary; they are, however, consistent through series of elements. A limited number of elements give poor agreement; it is suggested that these differences are consequences of the fact that the treatment is only first order, and that significant factors, such as polarisation and magnetic interactions, have been omitted. The relationships between series, however, is encouraging, since when there are significant corrections to be made, these apply consistently to a large number of levels.

The concept that the screening defect should depend on the orbital structure, and that orbitals with fewer nodes than those of the corresponding hydrogen orbitals could exist, should have further chemical ramifications.

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