Numerology, hydrogenic levels, and the ordering of excited states in one-electron atoms

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We show that the observed ordering of Rydberg states of one-electron atoms can be understood by assuming that these states are basically hydrogenic in nature. Much of the confusion concerning this point is shown to arise from the failure to differentiate between hydrogenic ordering as the nuclear charge approaches infinity, and hydrogenic ordering for an effective charge of one. The origin of k ordering of Rydberg levels suggested by Sternheimer is considered within this picture, and the predictions of k ordering are compared with those obtained by assuming hydrogenic ordering.

A number of recent papers have pointed out quite unexpected systematic structure in the energy levels of some "simple" atomic systems: one-electron[1] and He-like[2-6] atoms and ions. The presence of unexplained structure in such presumably well understood systems has naturally elicited a great deal of interest, and several authors have attempted to explain the observations.[1-6] The purpose of this Communication is to offer an explanation of the results in one-electron atoms and ions.

Sternheimer, in a series of papers,[1] suggested that $k = n + l$ is approximately a good quantum number ("k ordering") for one-electron atoms for values of $l < l_1$. For $l > l_1$, the ordering of states becomes hydrogenic, that is, states having the same n are almost degenerate ("n ordering"). The value of l_1 varies from atom to atom, but is constant for all Rydberg states of a particular atom. Thus, for example, in Na, $l_1 = 2$, and the states $7s$, $6p$, $5d$, $5f$, and $5g$ are approximately degenerate. We shall refer to this type of combined k and n ordering as modified k ordering. Sternheimer[1] suggests that the existence of modified k ordering is indicative that the field felt by the Rydberg electron is quite nonhydrogenic for $l < l_1$. As we shall see, this conclusion is not supported by the present analysis.

Typically, when one speaks of hydrogenic ordering of states in a many-electron atom, the implication is that states having the same principal quantum number are approximately degenerate. This is the situation in very highly ionized atoms, where the electron-nucleus interaction swamps the electron-electron interaction. There, the electronic states correspond roughly to hydrogenic states for Z equal to the bare nuclear charge. These states become exactly hydrogenic as the nuclear charge goes to infinity. This is clearly not the case in neutral or few times ionized atoms. Another definition of hydrogenic states can be used in this case, however, which we shall show explains quite well the observed ordering of states of one-electron atoms.

Let us begin by considering the $1s^2 2s^2 2p^6 nl$ states of Na. We first make the extreme assumption that the field produced by the core is of the form $-1/r$. The resulting allowed energies of the nl electron are obviously hydrogenic. To describe our results we will use the $(j_1 j_2)$ representations of SO(4):

$$\vec{j}_1 = (\vec{L} + \vec{M})/2, \quad \vec{j}_2 = (\vec{L} - \vec{M})/2 ,$$

where $\vec{M}$ is the Lenz vector and $\vec{L}$ is the orbital angular momentum. Since our potential is hydrogenic, we must have $j_1 = j_2$. The lowest energy state is a (00), the first excited state a $(\frac{1}{2}\frac{1}{2})$, etc. The (00), which under the reduction SO(4) $\supset$ SO(3) contains only an s state, has energy -1 Ry; the $(\frac{1}{2}\frac{1}{2})$, which contains both s and p states, has energy $-\frac{1}{4}$ Ry, etc.

At this point, we must recall that in a many-electron atom, the principal quantum number of an electron n is not directly related to its energy, but rather to how many orbitals of the same l exist with lower energy. Thus, in Na, we would label the $(00)s$ Rydberg electron as the $3s$, since there are $1s$ and $2s$ electrons present in the core. Likewise the $(\frac{1}{2}\frac{1}{2})s$ would be labeled the $4s$, with the $(\frac{1}{2}\frac{1}{2})p$ being called the $3p$, since the $2p$ is present in the core. That is, due to the way principal quantum numbers are defined in the many-electron atom, the "$4s$" and "$3p$" will be degenerate in energy, both having the energy of a $2s$ or $2p$ hydrogenic electron. Because of the nomenclature, we would be forced to say that the $4s$ has a quantum defect of 2, the $3p$ a quantum defect of 1. Nevertheless, both are completely hydrogenic in this model, and the "quantum defect" is really a "nomenclature defect." Table I shows how principal quantum numbers would be assigned in this picture to higher states. Note that, in this case, $k = n + 1$ is a good quantum number for $l < 2$, and that above that value, n becomes a good quantum number, i.e., $l_1 = 2$.

Of course, it is clear that the potential felt by the nl

TABLE I. Hydrogenic energy levels in Na.

		SO(4) representation				
	Core	(00)	$(\frac{1}{2}\frac{1}{2})$	(11)	$(\frac{3}{2}\frac{3}{2})$	(22)
Na	$1s^2 2s^2 2p^6$	$3s$	$4s$ $3p$	$5s$ $4p$ $3d$	$6s$ $5p$ $4d$ $4f$	$7s$ $6p$ $5d$ $5f$ $5g$

TABLE II. Normal ordering.

		2	3	4	5
Core	n_H SO(4)	$(\frac{1}{2}\frac{1}{2})$	(11)	$(\frac{3}{2}\frac{3}{2})$	(22)
K I	$1s^2 2s^2 2p^6 3s^2 3p^6$	$4s$ $4p$	$5s$ $5p$ $3d$	$6s$ $6p$ $4d$ $4f$	$7s$ $7p$ $5d$ $5f$ $5g$
Tl I	$...6s^2$	$7s$ $6p$	$8s$ $7p$ $6d$	$9s$ $8p$ $7d$ $5f$	$10s$ $9p$ $8d$ $6f$ $5g$
Ba II	$...5p^6$		$6s$ $6p$ $5d$	$7s$ $7p$ $6d$ $4f$	$8s$ $8p$ $7d$ $5f$ $5g$

Rydberg electron in a one-electron atom is not hydrogenic all the way to the origin. Thus, the above argument requires some modifications when applied to a real atom. The first is that the wave function is changed somewhat from its hydrogenic form. One of the most obvious changes is to give the wave function extra nodes such that it is orthogonal to all of the core wave functions of the same symmetry. These nodes generally occur at relatively small r, however, and do not greatly alter the large r shape of the wave functions.

The second required modification results from the fact that at intermediate r, the effective potential seen by the nl electron is "shallower" than the Coulombic potential; this is reflected in the fact that in all the one-electron atoms, the ionization energy of the ground state is considerably less than 1 Ry, being typically of the order of $\frac{1}{3}$ Ry for the neutral one-electron atoms. As a consequence, the lowest hydrogenlike state which can appear in this potential is not the (00), which would have an energy of -1 Ry, but rather the $(\frac{1}{2}\frac{1}{2})$, which has an energy of $-\frac{1}{4}$ Ry. This implies, for example, that the lowest lying s and p states in one-electron atoms might be considered to belong to the $(\frac{1}{2}\frac{1}{2})$. This, in turn, implies that the next three excited states should be those of the (11), i.e., s, p, and d. Assigning principal quantum numbers as above to these states, one obtains results such as shown in Table II. For many of the one-electron ions, the potential is too shallow to support even the $(\frac{1}{2}\frac{1}{2})$ state. That is, the ionization energy is less that $Z^2/4$ Ry, where Z is the asymptotic charge of the core plus nucleus. As a result, the lowest state which appears is a (11). The resulting ordering is also shown for a typical case in Table II.

We have also shown in Table II the hydrogenic principal quantum number, n_H for each state. Each of these states will have a "hydrogenic quantum defect," $\delta_H = n - n_H$, which is produced simply because the n labeling in a many-electron atom is different from that in hydrogen. The total quantum defect can then be written as $\delta = \delta_H + \delta_p$, where δ_p is the part of

the quantum defect produced by the deviation of the potential from hydrogenic. A nonzero δ_p indicates the breaking of the exact energy degeneracy of the hydrogenic states. As we shall show below, δ_p is relatively small for most of the one-electron atoms and ions.

A third modification of the hydrogenic picture relates to the fact that electrons of different l penetrate into the core differently. This modification introduces a certain ambiguity into our classification, as we shall see presently.

We shall refer to orderings based on this hydrogenic picture as "normal." Since, as shown in Table II, the designation of the lowest SO(4) state suffices to define the representations of all of the higher states in this scheme, we can indicate the kind of ordering being considered by the SO(4) label of the lowest set of atomic states.

We have used the schemes given above to study the orderings of the levels given by Sternheimer in his papers[1]: The alkali metals, neutral and singly ionized alkaline earths, Ga I, Ga II, In I and II, Sn II, Tl I, Pb II, Zn I, and Al III. Of course, as noted above, there is a breaking of the normal symmetry due to the nonhydrogenic parts of the potential. One therefore hopes to see, not exact degeneracies, but rather nonoverlapping groupings of levels which can be identified with particular "normal" SO(4) representations.

We began by assigning the lowest-lying states to the SO(4) representations suggested by consideration of the lowest ionization limit, as described above (e.g., Table II). This procedure worked perfectly for all of the alkalis and for all of the singly ionized alka-

line earths and for Al III. That is to say, *all* of the levels given by Sternheimer[1] for *each* of these elements naturally fell into SO(4) representations such that all of the states belonging to a representation (aa) are lower in energy than any state belonging to $(a + \frac{1}{2}a + \frac{1}{2})$, and higher in energy than any state belonging to $(a - \frac{1}{2}a - \frac{1}{2})$.

The situation is slightly more complicated for the "pseudo-one-electron atoms" of the alkaline earths, neutrals of group III, and first ions of group IV. For the neutrals of group III, we find that the correct ordering is of the type $(\frac{1}{2}\frac{1}{2})$, with the states of $(\frac{1}{2}\frac{1}{2})$ being given by the ns^2np and $ns^2(n+1)s$. For the first ions of group IV, again the correct ordering is of the type $(\frac{1}{2}\frac{1}{2})$, but now the np has been pulled down in energy sufficiently that it must be considered approximately degenerate with the ns. That is, the ns and np form the $(\frac{1}{2}\frac{1}{2})$; the (11) is then formed by the $ns^2(n+1)s$, $ns^2(n+1)p$, and ns^2nd, etc. Again, *all* of the levels given by Sternheimer[1] are ordered correctly by these assignments.

The neutrals of the alkaline earths provide the greatest difficulty for this scheme for two reasons: the instability of low-lying d orbitals, and perturbations caused by excitations which are not of the "one-electron" type. Low-lying d orbitals are known to be very unstable, since very small changes in potential can cause them to localize either inside or outside the core. This is reflected quite clearly in the spectrum of Ca I: the $3d$ does not fit at all in a hydrogenic ordering scheme. However, if the $3d$ is simply ignored as being defined by the nonhydrogenic portion of the potential, all remaining levels are successfully ordered by a $(\frac{1}{2}\frac{1}{2})$ scheme, where the $(\frac{1}{2}\frac{1}{2})$ is composed of the $4s$ and $4p$. Similar, but less striking behavior is found in Sr I. Here, one can almost order all the levels, including the $4d$, as a $(\frac{1}{2}\frac{1}{2})$; the difficulty in this spectrum is caused by a perturbation to the np states which occurs between $n = 7$ and $n = 8$, and persists for the higher np states. If one does as in Ca I and discards the $4d$ as being "nonhydrogenic," the resulting $(\frac{1}{2}\frac{1}{2})$ classification successfully orders all levels. There is no such difficulty in Zn I and In II, where the $3d$ and $4d$, respectively, are well within the core. In Zn I, the $4p$ and $5s$ form a $(\frac{1}{2}\frac{1}{2})$; in In II, it is the $5s$ and $5p$ which form a $(\frac{1}{2}\frac{1}{2})$. In both cases, the resulting ordering is perfect.

One finds, in general, that several ordering schemes reproduce quite well the observed ordering of the one-electron states. Thus, for example, although modified k ordering seldom coincides with normal ordering, Sternheimer found relatively few cases in which the excited states did not follow modified k ordering.[1] This ambiguity is due to the fact that all ordering schemes are broken, so that there is

some uncertainty as to which group a particular level belongs. This is particularly true of the np states in one-electron atoms and ions, for which, in general, $n_{np}^* \cong \frac{1}{2}(n_{ns}^* + n_{n+1,s}^*)$. As a result, the np can be considered to belong to the same representation as the ns, which is generally what was done above, or the same representation as the $(n+1)s$. The latter assignment follows naturally in the hydrogenic picture if we assume that the lowest ns state in one-electron atoms and ions is produced in a very nonhydrogenic part of the potential, with the next highest state being the hydrogenic (11), etc. Table III shows some typical assignments obtained with this scheme. Such a procedure leads, in general, to a modified k ordering which differs from that of Sternheimer only in the value found for l_1. This difference seems not to be significant, however, since the data do not give this value unambiguously. We note that modified k ordering is not followed completely in this scheme by Cs (Table III) where the f states are out of order. Cs was one of the cases found by Sternheimer to violate k ordering: The ordering shown in Table III agrees with that which is observed.

A fairly stringent test of the approximate ordering schemes involves the width of the grouping produced by the symmetry breaking, which should be as small as possible, and the separation of the groupings, which should be as large as possible. We have found three cases where the straightforward application of normal ordering as discussed above does not lead to the best groupings within these criteria. In Ca II, if one again ignores the $3d$ as being nonhydrogenic, and orders the remaining states according to a $(\frac{1}{2}\frac{1}{2})$, very good grouping of levels occurs. In Al III, the groupings are much better if a $(\frac{1}{2}\frac{1}{2})$ ordering is used, rather than a (11), and in Cs I, the best groupings are found if one assumes that the $6p$, $5d$, and $7s$ form a (11), as shown in Table III. The normal or-

TABLE III. Normal ordering with nonhydrogenic lowest ns state.

			SO(4) representation		
	Core		(11)	$(\frac{3}{2}\frac{3}{2})$	(22)
K I	...$3p^6$	$4s$	$5s$	$6s$	$7s$
			$4p$	$5p$	$6p$
			$3d$	$4d$	$5d$
				$4f$	$5f$
					$5g$
Cs I	...$5p^6$	$6s$	$7s$	$8s$	$9s$
			$6p$	$7p$	$8p$
			$5d$	$6d$	$7d$
				$4f$	$5f$

dering which produces the best grouping is shown for each element considered in Table IV.

The quality of the groupings shown in Table IV can be compared roughly with those obtained from modified k ordering by considering the difference between the effective quantum numbers of the highest and lowest members of a group Δ_w and the difference between the effective quantum numbers of the lowest member of one group and the highest member of the group immediately below that group Δ_s. These numbers will be constant, with their sum equal to one, over the whole spectrum to the extent that the quantum defects are independent of n. Table IV also shows the ratio Δ_s/Δ_w, for the elements studied in both normal and modified k ordering. It is seen that, in general, this ratio is much larger for normal ordering that for modified k ordering, thus indicating that the groupings are more narrow and the separation between groupings wider in the former than in the latter.

As noted above, if the states are really relatively hydrogenic, one would expect that δ_p would be small, and that δ_H would give a good indication of the value of δ. This is generally found to be the case. For example, referring to Table II, we see that δ_H for Ti I is 5, 4, 3, and 1 for the $9s$, $8p$, $7d$, and $5d$ states, respectively. The measured quantum defects for these states are 4.76, 4.21, 3.1, and 1.03, respectively. For Ba II, δ_H is 3, 3, 2, and 0 for the $7s$, $7p$, $6d$, and $4f$, respectively. The corresponding values of δ are 3.62, 3.23, 2.44, and 0.31. Finally, for K, $\delta_H = 2$, 2, 0, 0, and $\delta = 2.19$, 1.73, 0.23, 0.0 for the $6s$, $6p$, $4d$, and $4f$, respectively.

In the discussion above, we have shown that the assumption that Rydberg states of one-electron atoms are approximately hydrogenic, combined with rules concerning how to assign principal quantum numbers in many-electron atoms, leads to a "normal" ordering scheme for Rydberg states. The resulting predictions of ordering were found to be in perfect agreement with observations. In addition, this approach leads to a simple explanation of certain observed variations in principal quantum number as a function of angular momentum. A slight modification of the argument was shown to lead to modified k ordering,[1] which predicts only slightly less well the observed orderings. Specific comparisons to decide which ordering is "best," however, are relatively useless, and fall further into the realm of numerology, since both schemes are quite approximate. The important point is that both of these schemes result from a very hy-

TABLE IV. Orderings of one-electron atoms (see text for discussion).

Element	SO(4)	Δ_s/Δ_w Present work	Sternheimer (Ref. 1)
Na I	$(\frac{1}{2}\frac{1}{2})$	1.0	0.5
K I	$(\frac{1}{2}\frac{1}{2})$	0.9	0.2
Rb I	$(\frac{1}{2}\frac{1}{2})$	0.5	0.5
Cs I	(11)	0.9	a
Mg II	$(\frac{1}{2}\frac{1}{2})$	1.7	0.1
Ca II	$(\frac{1}{2}\frac{1}{2})$	1.8	0.2
Sr II	(11)	0.4	0.3
Ba II	(11)	0.3	0.2
Ra II	(11)	1.2	a
Al III	$(\frac{1}{2}\frac{1}{2})$	1.1	0.1[b]
Ga I	$(\frac{1}{2}\frac{1}{2})$	1.0[c]	1.0[c]
In I	$(\frac{1}{2}\frac{1}{2})$	0.9	(a)
Tl I	$(\frac{1}{2}\frac{1}{2})$	1.2	(a)
Ge II	$(\frac{1}{2}\frac{1}{2})$	1.3	0.4
Sn II	$(\frac{1}{2}\frac{1}{2})$	1.5	0.1
Pb II	$(\frac{1}{2}\frac{1}{2})$	1.3	0.1
Ca I	$(\frac{1}{2}\frac{1}{2})$	0.9	0.5
Sr I	$(\frac{1}{2}\frac{1}{2})$	0.9	0.3
Zn I	$(\frac{1}{2}\frac{1}{2})$	1.1[c]	1.1[c]
In II	$(\frac{1}{2}\frac{1}{2})$	1.5	0.1

[a]Modified k ordering not followed.
[b]n ordered by Sternheimer (Ref. 1).
[c]Modified k ordering and normal ordering coincide.

drogenic picture of the Rydberg states. Effects such as core polarization, or other many-body effects are not needed to explain the observed orderings. These effects are present, as indicated by nonzero values of δ_p and by such effects as inverted fine structure in certain levels, but they are not needed to explain the gross structure of the observed orderings.

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