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Theoretical Calculations of the *d*-, *f*-, and *g*-Electron Transition Series*

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Self-consistent-field calculations of the effective quantum numbers for *nd*, *nf*, and *ng* electrons for a large number of atomic configurations from $Z = 2$ to 126 have been made using a Hartree plus statistical-exchange method with first-order correlation and relativistic energy corrections. The computed binding energies agree with experimental values where known (67 configurations), with an average deviation of 1.5%. The sudden decreases with increasing Z in the effective quantum numbers of the *d* and *f* electrons, which precede the onset of the known transition series, are accurately predicted. An interpretation of these changes in effective quantum number is given in terms of the effective potential. The probable existence of a 7*d*, 6*f*, or 5*g* transition series beginning at about $Z = 122$ is examined. The computed abrupt decrease in effective quantum number of the 7*d* and 6*f* electrons at $Z = 120$, and of the 5*g* electron at $Z = 121$, indicates the possible participation of all of these electrons in the ground configuration of such elements. Relativistic corrections strongly affect the calculated relative energies of different possible ground configurations of the elements $Z = 121$ to 126.

I. INTRODUCTION

In an attempt to predict atomic behavior in regions of the periodic system where experimental evidence is incomplete, and to aid in the discovery of atoms not yet observed, it is of interest to do *ab initio* calculations of atomic structure over a wide range of atomic number. Extensive self-consistent-field calculations of atomic structure have been carried out in the past by numerous workers, most notably the numerical Hartree-Fock-Slater (HFS) calculations of Herman and Skillman,[1] the numerical Hartree-Fock (HF) calculations of Froese[2] and Mann,[3] and the analytic HF calculations of Clementi.[4] However to date, these calculations have been largely limited to the ground configurations of atoms and ions. Extensive calculations of excited configurations of atoms have been made only with the rather inaccurate Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) models.[5-7] It is the purpose of this paper to present the results of extensive SCF calculations of excited electronic configurations in order to study systematic changes in one-electron wave functions and binding energies as a function of atomic number.

There is considerable current interest in extending such theoretical calculations to superheavy elements which may be stable enough to be produced and identified chemically.[8] Modern nuclear shell theory suggests two possible regions of relative stability centered around $Z = 114$ and $Z = 126$. The former is perhaps the more likely, but this region of relative stability may extend as high as $Z = 124$. It is thus of interest to try to predict some of the chemical properties of these elements. Larson and Waber[9] have made calculations of the total energies of elements $Z = 122$ to 127 using Hartree wave functions, in order to try to determine the most likely ground configurations of these elements. Liberman, Waber, and Cromer[10] have performed similar calculations for elements $Z = 124$ to 126 by solving the relativistic Dirac equation with Slater's $\rho^{1/3}$ exchange potential.

In this paper we have used a Hartree plus statistical exchange scheme (HX) which is more accurate than either the H or HFS methods, and gives values of one-electron binding energies which agree quite well with HF values,[11] where the latter are available. In addition, the HX method has certain advantages over the HF method which make the former particularly suited for this type of survey problem: The HX method does not require elaborate input values to a computer program; it is less time consuming, and involves essentially no convergence instabilities; unlike the HF method, it gives simple central-field potentials useful for understanding changes in binding energies with atomic number, and in calculating relativistic perturbation corrections.

II. METHOD AND RESULTS

A complete discussion of the HX method is given in Ref. 11. Here we mention only a few clarifying points needed for later discussions.

The radial part of the Schrödinger equation to be solved is

$$\left(-\frac{d^2}{dr^2}+V_{\text{eff}}^{\,i}\right)P_{n_i l_i}(r)=\epsilon^i P_{n_i l_i}(r), \tag{1}$$

where $P(r) \equiv rR(r)$ is r times the radial wave function, and where the effective potential V_{eff} is defined as

$$V_{\text{eff}} = l_i(l_i+1)/r^2 + V^i(r)\ . \tag{2}$$

$V^i(r)$ is the central potential for the HX method, consisting of the familiar Hartree potential term plus a free-electron-type approximation to the non-self-interaction exchange terms.

Once the Schrödinger equation is solved and the radial wave functions obtained, the one-electron energy E^i and the total energy E may be computed from the formulas

$$E^i = (i|-\nabla^2|i) + \left(i\left|-\frac{2Z}{r}\right|i\right) + \sum_{j\neq i} E^{ij} , \tag{3}$$

$$E = \sum_i \left[(i|-\nabla^2|i) + \left(i\left|-\frac{2Z}{r}\right|i\right) + \sum_{j<i} E^{ij} \right], \tag{4}$$

where E^{ij} is the Coulomb interaction energy between electrons i and j (averaged over all magnetic quantum numbers), calculated from the familiar expressions involving Slater integrals.[11]

Theoretical binding energies computed from these expressions (using either HX or HF wave functions) frequently disagree with experiment by 5 – 15% or more, because of neglected correlation and relativistic effects. For heavy elements, it is completely impractical to make high-accuracy calculations of the correlation energy; nor for our purposes is it necessary to make such calculations of relativistic energy. It is, however, possible to significantly improve the theoretical results by means of very simple perturbation calculations. In the case of correlation energy, we use a correction based on the correlation energy of a zero-temperature free-electron gas, modified as described in Ref. 11 to take into account the differences between free and bound electrons (discussed for example, by Slater[12]). For relativistic terms, we use the familiar mass-velocity and Darwin one-electron energies[11] $E_m{}^i$ and $E_D{}^i$. For high-Z elements, this relativistic correction is much too small for the most tightly bound orbitals; however, it is adequate for our purposes of calculating binding energies of the more loosely bound electrons. Thus our final expressions for the one-electron and total binding energies are

$$E_t{}^i = E^i + E_r{}^i + E_c{}^i , \tag{5}$$

$$E_t = E + \sum_i (E_r{}^i + E_c{}^i) , \tag{6}$$

$$\text{where } E_r{}^i = E_m{}^i + E_D{}^i , \tag{7}$$

and $E_c{}^i$ is the one-electron correlation energy.

In the past, the binding energy of an electron i has frequently been measured by the one-electron energy E^i (Eq. 4) [to which corresponds the corrected value $E_t{}^i$, Eq. (5)]; this is valid provided removal of the electron produces little change in the wave functions of the remaining electrons (Koopmans's theorem).[13] However, for many cases these remaining electrons experience significant relaxation effects, and Koopmans's theorem is invalid; for maximum accuracy it is then necessary to compute the binding energy in question by differencing the total energies (6) for the atom and ion in the appropriate configurations.

So far as the correlation energy correction to the binding energy is concerned, the statistical model which we are using is such that ΔE_c is much too large when there are two (and only two) valence electrons i and j; the energies $E_c{}^i$ and $E_c{}^j$ in such cases arise mainly as a result of the mutual presence of these electrons, so that E_c for the atom effectively involves a double counting of a single physical effect (cf. Ref. 11, footnote 38). The error is eliminated by use of $E_c{}^i$ rather than ΔE_c; this procedure is justified because the effect on E_c of wave function relaxation is negligible.

Relaxation effects *are* of great importance in the calculation of relativistic contributions to the binding energies of deeply-buried electrons in heavy atoms. Indeed, they are so important that the perturbation expression (7) appears to be too inaccurate to give reasonable results in some cases whether ΔE_r or $E_r{}^i$ is used. We have thus been forced to omit relativistic contributions completely in computing binding energies of deeply buried d, f, and g electrons for $Z \geqslant 57$; the binding energies given later for these cases can thus be considered as semi-quantitative only.

In summary, we have computed binding energies as

$$E_B{}^i = \Delta E + \Delta E_r + |E_c{}^i| , \tag{8}$$

except with omission of the relativistic term in the cases just mentioned. To avoid excessive significant-figure loss in computing the values of ΔE and ΔE_r, we had to calculate energies to more than eight significant digits; therefore a computer (CDC 6500) with 14 significant figures was employed. Binding energies calculated from Eq. (8) are very sensitive to the self-consistency criteria used for the solution to the Schrödinger equation, and consequently, we used very stringent self-consistency tests.[14]

Typical computed results are shown in Table I. It should be noted that the values of the uncorrected binding energy (ΔE) are usually far too low, and the correlation corrections are definitely needed to obtain good agreement with experiment. The relativistic corrections are relatively small in most cases; however, when the $3d$ and $4d$ electrons undergo large increases in binding energy, these corrections also become significant. Throughout the entire range of 67 configurations for which experimental values were available, we obtained an average deviation of 1.5% (with a maximum deviation of 7%) between theoretical and experimental binding energies. (This is to be compared with corresponding values of 5.8 and 28% when relativistic and correlation corrections were omitted.) It should be noted that most of the larger deviations are at least partially the result of known strong configuration-interaction perturbations, for which we have made no attempt to correct.[15] The above agreement gives some indication of the accuracy which may be expected from this calculational method where experimental data are not available. A more complete comparison of results with experiment is given in Figs. 1 and 2, where both the experimental and theoretical values of the effective quantum numbers of d and f elec-

TABLE I. Theoretical binding energies of d and f electrons with and without relativistic and correlation corrections (Ry). The binding energies are the energies required to remove the d or f electron with no change in the nl values of the remaining electrons. ΔE is the HX binding energy without corrections. The 3rd and 7th columns give the percent deviations of ΔE and ΔE_B from experiment. $E_B = \Delta E + \Delta E_r + |E_c^i|$, where ΔE_r and E_c^i are the relativistic and correlation corrections, respectively.

Atom	ΔE	% deviation	ΔE_r	$-E_c^i$	E_B	% deviation	experiment[a]
Cu $4d$	0.1108	− 1.8	0.0000	0.0033	0.1141	+1.1	0.1128
Ge $4p4d$	0.1181	− 9.4	−0.0006	0.0115	0.1290	−1.1	0.1304
Kr $4p^5 4d$	0.1195	−10.3	−0.0010	0.0125	0.1310	−1.6	0.1332
Rb $4d$	0.1199	− 8.2	−0.0009	0.0115	0.1305	−0.1	0.1306
Sr $5s4d$	0.2063	−16.8	−0.0133	0.0524	0.2454	−1.0	0.2479
Y $5s^2 4d$	0.4243	− 9.5	−0.0303	0.0627	0.4567	−2.6	0.4688
Pd $4d^9 5d$	0.1080	− 3.9	0.0000	0.0043	0.1123	−0.1	0.1124
Xe $5p^5 5d$	0.1294	−14.5	−0.0059	0.0250	0.1485	−1.9	0.1513
Cs $5d$	0.1337	−12.9	−0.0071	0.0261	0.1527	−0.5	0.1535
Ba $6s5d$	0.2684	− 7.9	−0.0310	0.0550	0.2924	+0.4	0.2913
Ba $6s4f$	0.0630	− 6.8	−0.0002	0.0037	0.0665	−1.2	0.0673
Hg $6s5f$	0.0626	− 0.8	−0.0001	0.0008	0.0633	+0.3	0.0631

[a] Difference between the center-of-gravity energy of the levels of the atomic configuration listed and that of the corresponding ion; obtained from C. E. Moore Atomic Energy Levels (U. S. National Bureau of Standards, Circular No. 467, U. S. Government Printing Office, Washington, D. C., 1949–1958), 3 vols.

trons are plotted as a function of Z. In all cases, the configuration of the atom is that configuration containing the electron in question which appears to have the lowest energy. The predicted local irregularities in the curves (due in some cases to irregular changes in the type configuration considered) agree remarkably well with experiment.

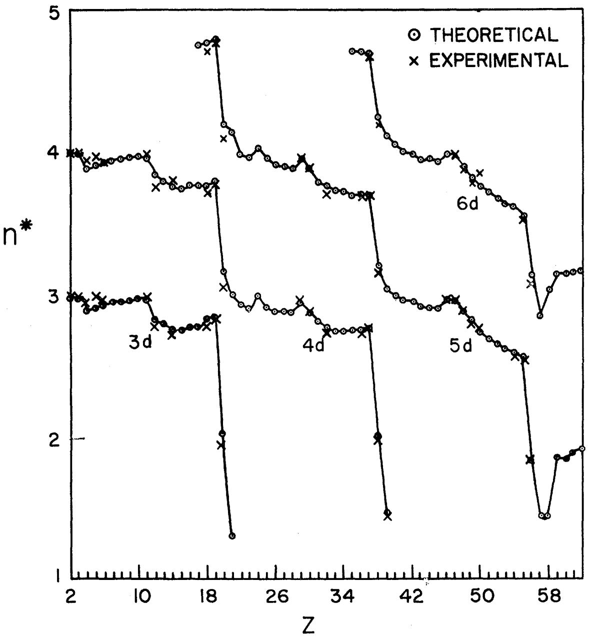

FIG. 1. Effective quantum numbers n^* for d electrons as a function of atomic number; $n^* = E_B^{-1/2}$, where E_B is the energy (in rydbergs) required to remove the d electron from the atom. The theoretical values are calculated from $E_B = \Delta E + \Delta E_r + |E_c^i|$. The experimental values are calculated from the difference between the centers of gravity of the corresponding configurations of the atom and ion.

III. ABRUPT BINDING-ENERGY AND WAVE-FUNCTION CHANGES

Of particular interest in Figs. 1 and 2 are the abrupt changes with Z in the effective quantum number, which precede the beginnings of the various d- and f-electron transition series. In each instance, there occurs a corresponding abrupt change in the nature of the d or f wave function, consisting primarily of an abrupt contraction (or "collapse") to smaller radii; the collapse of the $4f$ and $5f$ wave functions in going from $_{56}$Ba to $_{57}$La is illustrated in Figs. 3 and 4. In the case of f electrons, these apparently discontinuous changes were

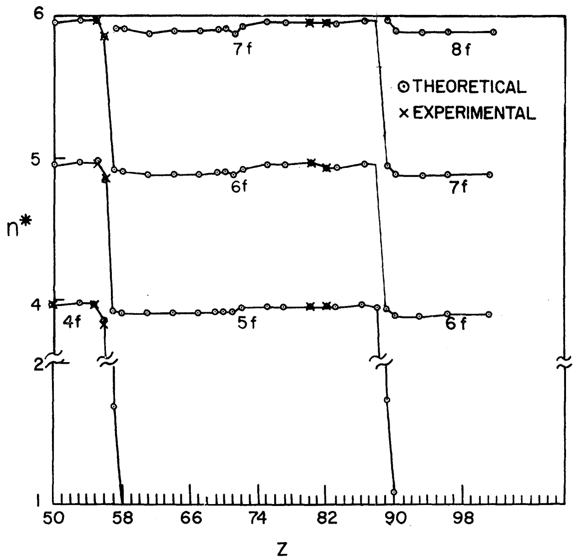

FIG. 2. Effective quantum numbers (n^*) for f electrons as a function of atomic number. A further description is given under Fig. 1.

first predicted by Mayer[5] by means of calculations using Thomas-Fermi potentials. Although the behavior of d electrons is qualitatively similar to that of f electrons, there are important differences; to make these clear, we first repeat Mayer's discussion for f electrons, and also describe certain modifications which arise in SCF calculations.

In hydrogen, the effective potential (2) simplifies to

$$V_{\text{eff}}(r) = l_i(l_i + 1)/r^2 - 2Z/r\,, \qquad (9)$$

with $Z = 1$; for f electrons ($l_i = 3$) this is positive for $r < 6$ Bohr units, and at greater radii there exists a shallow potential well with a minimum at $r = 12$. In multi-electron neutral atoms (of any Z), the core electron-cloud does not extend appreciably beyond $r = 5$ or 6; consequently the effective potential for f electrons for $r > 6$ is very much like that in hydrogen. However, with increasing Z a second (inner) potential well develops at small radii, where the effective nuclear charge is much greater than unity. The two wells are separated by a positive potential barrier, resulting in the existence of two quasi-independent sets of negative-energy levels. Any bound f-electron wave function has appreciable amplitude only within one of the two potential wells – the outer or the inner well, according as the f-electron eigenvalue corresponds to an energy level of the outer or inner well, respectively. For small values of Z the lowest level lies in the outer well, and so the $4f$ electron is concentrated in the outer-well region; for larger Z ($\geqslant 57$) the inner well becomes sufficiently deeper and wider that an inner-well level becomes the lowest one, and the $4f$ electron is concentrated in the inner-well region. These two alternatives are exemplified by Ba and La in Fig. 3.

More generally, if for a given Z the m lowest-lying f levels are in the inner well (the corresponding nf wave functions being those for $n \leqslant m + 3$), then all excited nf wave functions (corresponding to $n > m + 3$) have m nodes within the region of the inner well or the potential barrier, and therefore have $(n - 4) - m$ nodes within the outer well (cf. Fig. 4). Since the excited electron lies almost entirely in the outer-well region and the potential in that region is essentially hydrogenic, the energy must essentially be that of a hydrogenic f electron with $n - 4 - m$ nodes; this implies an effective quantum number $n^* = n - m$, which explains the near-integral quantum defects $(n - n^*)$ of excited f electrons seen in Fig. 2.

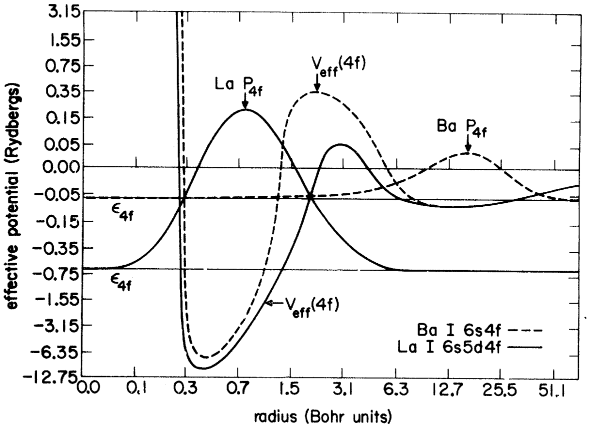

FIG. 3. Plot of the effective potentials $V^i(r) + l_i(l_i + 1)/r^2$ and radial wave functions $P_{n_i l_i}(r)$ of the $4f$ electron of Ba I and La I as a function of r. In order to include all the important features in one plot, nonlinear scales for r and V_{eff} have been used, in which the interval between each point is doubled at each point. Each wave function is plotted on a linear vertical scale, the zero of which lies at the level of the corresponding eigenvalue (ϵ_{nl}).

It is of course conceivable that an inner- and outer-well level might have equal energies. In such a case a resonance would exist and an electron of this energy would, in effect, be divided more or less equally between the two wells; the wave function would have large amplitudes in both wells and an amplitude minimum in the barrier region. For a given (*a priori*) potential, such as a TF or a TFD one, such a situation will certainly exist at some (in general, non-integral) value of Z. For a self-consistent-field calculation, however, such a situation tends to be metastable: If during the iteration process a small portion of the charge of the f electron is (say) transferred from the outer well to the inner well, then other electrons of the atom become more completely shielded from the nucleus and move to regions of larger r; this causes the f electron to be less well shielded and it moves still more toward the inner well – i.e., the inner well becomes deeper and wider, the inner-well level drops, the resonance is destroyed, and the f wave function collapses into the inner well. Conversely, of course, the electron could move completely to the outer well; the correct solution is that which leads to lower total energy of the atom.[16] Relaxation effects of this sort, which are inherent in any SCF method, tend to increase the abruptness (as a function of Z) of the f-wave function collapse and of the binding-energy change.[17]

At $Z = 56$, just before the collapse of the $4f$ wave function occurs, the $4f$ electron is "abnormal" in

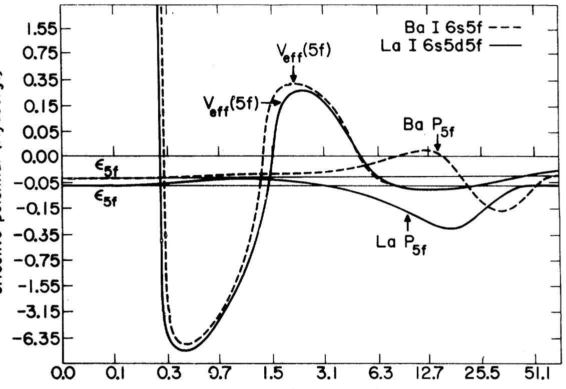

FIG. 4. Plot of the effective potentials and radial wave functions of the $5f$ electron of Ba I and La I. Further description is given under Fig. 3.

the sense that its mean radius $\langle r\rangle_{4f}$ is much greater than the radii for some nine $5s$, $5p$, and $6s$ electrons having $n>4$; similarly the binding energy of the $4f$ electron is much smaller than the energies of these nine electrons. It is important to note that already at $Z=57$ the collapse of the $4f$ wave function from the outer to the inner well results in $\langle r\rangle_{4f}$ becoming less than $\langle r\rangle_{nl}$ for all $n=5, 6, \ldots$ electrons; further contraction of the $4f$ wave function with increasing Z is only slightly more rapid than the contraction of the $4d$ and $5s$ functions, even though electrons are still being added to the $4f$ subshell. The binding energy of the $4f$ electron, on the other hand, remains "abnormal" to quite high Z; although this energy increases by an order of magnitude in going from $Z=56$ to 57, it remains smaller than the $5s$ binding energy until about $Z=77$ – long after the $4f$ subshell has been completed at ${}_{70}$Yb. (The behavior of $5f$ electrons for $Z>88$ is analogous.)

We consider now the situation for d electrons. Mayer[5] noted that double wells with positive energy barriers cannot exist for d electrons in a TF potential, and concluded that abrupt binding-energy and wave function changes were characteristic of f electrons only. Latter's subsequent calculations,[6] however, showed that energy changes similar to those for f electrons *do* occur for d electrons in either a TF or TFD potential,[18] though the changes were computed to occur somewhat gradually – requiring an increase in Z of 2 or 3 units rather than only one. Moreover, Rau and Fano[19] have recently pointed out that positive potential barriers do exist for d electrons when one uses more accurate potentials (in their case, HFS with tail cut-off at $-2/r$).

The existence of potential barriers and abrupt changes in n^* are much more marginal for d than for f electrons. The reason is easily seen from (9). For $l_i=2$, the hydrogenic well begins at $r=3$ and has its minimum at $r=6$. These radii are small enough that the core electrons in multi-electron atoms tend to overlap the inner portion of the hydrogenic well. The overlap will be smallest (and potential barriers most pronounced) when the core is most compact, i.e., for light atoms having a closed-shell core. Thus one of the more pronounced double-well structures occurs for K I $3p^6 3d$ ($\langle r\rangle_{3p}=1.43$), as shown in Fig. 5.[20] Even so, the inner portion of the outer well is appreciably lower than hydrogenic, and n_{3d}^* is somewhat less than 3 (Fig. 1). (More highly excited nd functions have eigenvalues higher than the top of the potential barrier, but the wave functions are still concentrated in the outer well, and show quantum defects $n-n^*$ approximately independent of n.)

In the next element beyond K, the added electron necessarily has a much larger radius than that of $3p$ electrons. Thus in Ca I $3p^6 3d 4s$ the $4s$ wave function ($\langle r\rangle=4.37$) extends far into the outer-well region, and the small potential barrier which exists in K has been wiped out (Fig. 5) simply because the $4s$ electron does not completely shield the barrier region from the added unit of nuclear charge. The corresponding abrupt wave function change in going from K to Ca is shown in Fig. 5; the abrupt binding-energy increases may be seen in Fig. 1. As in the f-electron case, the sharpness of the $3d$ changes is due in part to the outward relaxation of the s electron as the $3d$ electron moves inward from its hydrogenic radius.

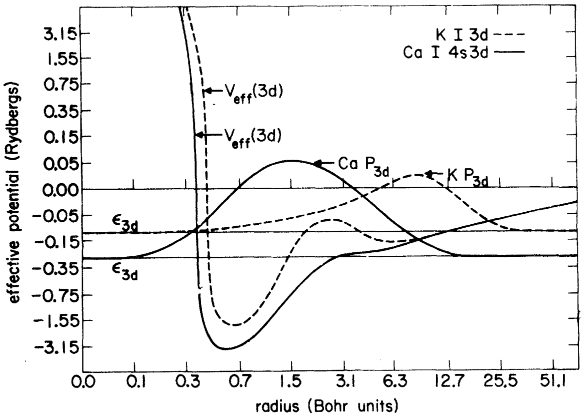

FIG. 5. Plot of the effective potentials and radial wave functions of the *3d* electron of K I and Ca I. A further description is given under Fig. 3.

Although these abrupt changes for d electrons are superficially similar to those for f electrons, there are important differences. In the building up of the periodic system, an nd electron never remains in an outer hydrogenic orbit while electrons with larger n are being added to the atom. Thus an nd electron is never "abnormal" as to radius in the same way as an f electron; the abrupt d-electron change always occurs in the alkaline-earth configuration $np^6 nd(n+1)s$, and the mean radius $\langle r\rangle$ of the nd electron is always smaller than that of the $(n+1)s$ electron. On the other hand, the d electron in the alkaline earth has not yet completely dropped into the inner well (Fig. 5), and the binding energy of the d electron is less than that of the s electron; both radius and energy decrease considerably for another element or two, and the d electron quickly becomes "normal" also as to energy.

The values of Z at which d collapse occurs are clearly much more closely related to the shell structure of the atom than is the case for f electrons. Accurate calculation of the d collapse can therefore be expected only for a self-consistent-field method in which the computed potential takes full account of shell structure. At the same time, the computed width and depth of the inner well must be reasonably accurate. This is illustrated by the results given in Table II, where the observed values of Z at which the binding-energy jump occurs are compared with values computed by four methods in which the effective potential includes: (1) neither exchange nor shell effects (TF), (2) the deeper potential well produced by the effect of exchange (TFD), (3) shell structure only (Hartree), and (4) both exchange and shell effects (HX). The Hartree result for $3d$ shows that the shell structure alone is not the entire story, whereas the TFD results are fairly close to experiment even without the inclusion of shell effects.

TABLE II. Atomic numbers at which *d*, *f*, and *g* electrons penetrate the core: $n^* < 2.5$, 3.5, and 4.5 for *d*, *f*, and *g* electrons, respectively, using eigenvalues as an approximate measure of E_B.

	TF[6]	*TFD*[6]	H[a]	HX[a]	experiment[b]
3*d*	27	22[c]	21	20	20
4*d*	45	37	38	38	38
5*d*	71[c]	59	56	56	56
6*d*	> 92	89	88	88	88 ?
7*d*	• • •	• • •	• • •	120	• • •
4*f*	69	60	58	57	57
5*f*	> 92	89	90	89	89?
6*f*	• • •	• • •	• • •	120	• • •
5*g*	• • •	• • •	• • •	121	• • •

[a] This investigation.

[b] C. E. Moore, Atomic Energy Levels (U. S. National Bureau of Standards, Circular No. 467, U. S. Government Printing Office, Washington, D. C., 1949–1958), 3 vols.

[c] These are borderline cases; the arbitrary criterion on n^* for penetration is very nearly satisifed for $Z = 21$ and 70.

It should be noted that the *d*- (or *f*-) wave function collapse occurs one or two elements in the periodic system prior to the beginning of the corresponding transition series. That is, where the collapse first occurs, the binding energy of the electron (though much greater than hydrogenic) is still small enough that this electron appears only in excited configurations.

Because barriers in *d*-electron potentials are low or absent, and the outer-well region is thus not so close to hydrogenic, the effective quantum numbers n^* for excited electrons are not necessarily close to an integer. The abrupt drops in n^* are therefore not so nearly equal to unity as for *f* electrons, and the n^* curves in Fig. 1 are neither so smooth nor so flat between drops as are the curves of Fig. 2, especially for high *Z* where the core radii are large. An irregularity of particular interest is that which occurs in the 5*d* curve in the region $Z = 56$ to 59, and which is associated with the well-known competition between *d* and *f* electrons in the rare-earth series:[21] the 5*d* electron collapses at $Z = 56$, and becomes part of the ground configuration of $_{57}$La; at La the 4*f* electron also collapses, and both 5*d* and 4*f* occur in the ground configuration of $_{58}$Ce; at $Z = 59$, 4*f* electrons become very tightly bound, but the binding energy of the 5*d* electron decreases substantially and 5*d* no longer appears in the ground configuration.

All of the above discussion pertains only to neutral atoms, and the situation is of course quite different for ions. For singly-ionized atoms the effective potential well for an outer electron is given asymptotically by (9) with $Z = 2$. The radii of the well are then only half as large as in neutral atoms, and core wave functions (which have about the same radii in ions as in neutral atoms) tend to overlap the outer well even of *f* electrons, thus altering the shape of the outer well and producing non-integral values of n^*, much as for *d* electrons in neutral atoms. In Ba II $5p^6nf$, for example, the computed barrier for the *nf* electron is very low, the top lying at an appreciably negative energy. The calculated quantum defect $n - n^*$ is comparatively small for $n = 4$ (where the energy level lies below the top of the barrier), but gradually increases to nearly unity as *n* increases and the barrier becomes gradually of less consequence; i.e., the deep inner well has an increasingly greater effect, comparable for large *n* to that of the inner well of neutral La (namely, unit quantum defect).[22]

A discussion of the effect of ionization for the case of *d* electrons is given in Ref. 23.

IV. THE SUPERHEAVY ELEMENTS

The HX values of the effective quantum numbers of the *d*, *f*, and *g* electrons from $Z = 100$ to 126 are shown in Fig. 6. There are large decreases in the effective quantum numbers of the 6*f* and 7*d* electrons at $Z = 120$, and of the 5*g* electron at $Z = 121$. These are accompanied by corresponding changes of approximately 1.0 in the effective quantum numbers of the 7*f* and 6*g* electrons and a

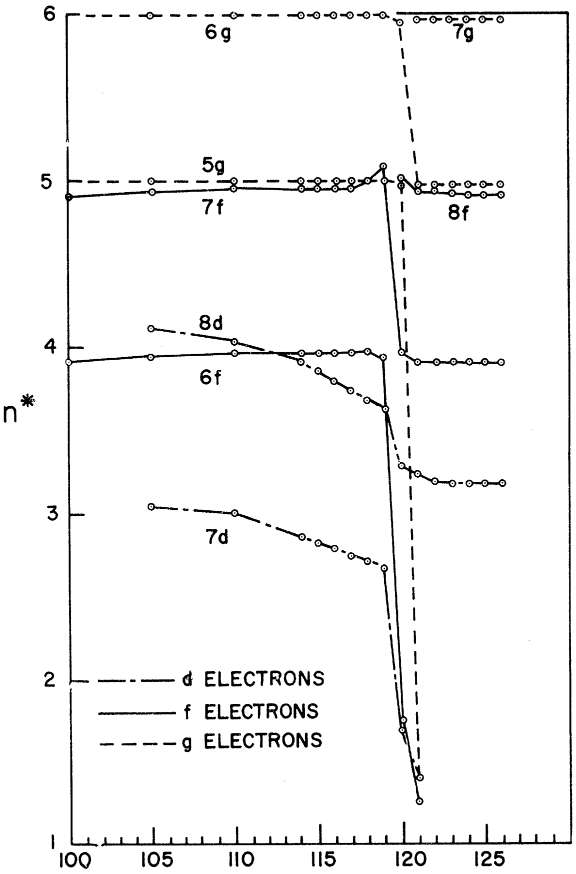

FIG. 6. Effective quantum number n^* as a function of atomic number for *d*, *f*, and *g* electrons in the super heavy elements. A further description is given under Fig. 1.

change of 0.34 in the $8d$ effective quantum number. The explanation of these sudden changes is entirely the same as for the corresponding changes which occur in the d and f electrons of the lighter elements. In Fig. 7 we show the effective potentials and wave functions of the $5g$ electron of $Z = 120$ and 121. As can be seen, a relatively small change in the effective potentials in going from $Z = 120$ to 121 causes an extremely large change in the character of the $5g$ wave function. The depth of the inner well, the height of the barrier, and the outer region being so closely hydrogenic all contribute to the large change in the $5g$ wave function and the corresponding change in the effective quantum number from 4.98 to approximately 1.4.

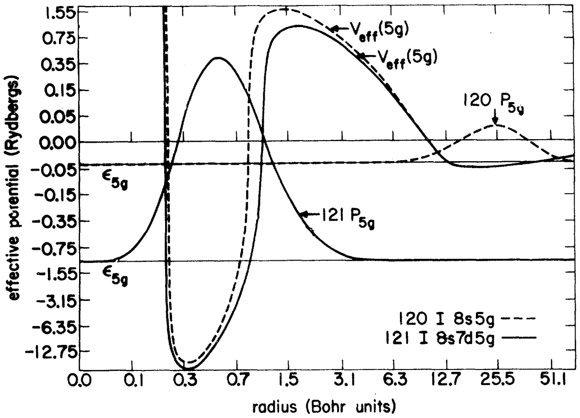

FIG. 7. Plot of the effective potentials and wave functions of the $5g$ electron of $Z = 120$ and 121. A further description is given under Fig. 3.

The curves of Fig. 6 imply the beginning (at $Z = 121$ or 122) of a fifth transition series of elements which Seaborg[8] has called the super actinides. It is likely that in this transition series the $7d$, $6f$, and $5g$ electrons all compete for positions in the ground-state configurations. In order to try to determine the ground configurations of the first few elements of this series, we performed calculations of the total binding energies of the possible ground configurations of elements $Z = 121$ through 126; the results are given in Table III.

It is important to note that the relative stabilities of the possible configurations are quite dependent upon relativistic corrections. The Hartree calculations of Larson and Waber[9] indicate that the most stable configurations of elements 122 through

TABLE III. Theoretical total binding energies $Z = 121$ to 126. (HX without corrections, HX with relativistic corrections, HX with relativistic and correlation corrections, and Dirac-Slater.) All energies are in units of rydbergs.

Configuration[a]	$-E$(HX)	$-(E+E_r)$(HX)	$-(E+E_r+E_c)$(HX)	$-E$(Dirac-Slater)[10]
		$Z = 121$		
$6f$	98 315.907[b]	110 065.865	110 075.467	
$7d$	5.663	66.137	5.735[b]	
		$Z = 122$		
$5g^2$	100 247.726[b]	112 405.051	112 414.739	
$6f5g$	7.779[b]	6.801	6.487	
$7d5g$	7.564	7.088	6.771	
$6f^2$	7.345	8.167	7.853	
$7d6f$	7.014	8.372[b]	8.054[b]	
$7d^2$	6.512	8.452[b]	8.132[b]	
		$Z = 123$		
$5g^3$	102 201.723[b]	114 778.681	114 788.452	
$6f5g^2$	201.759[b]	80.408	90.179	
$7d5g^2$	201.532	80.713	90.480	
$6f^25g$	201.269	81.741	91.511	
$7d6f5g$	200.947	81.964	91.729	
$7d^25g$	200.453	82.061	91.825	
$6f^3$	200.224	82.635	92.404	
$7d^3$	198.434	82.658	92.414	
$7d6f^2$	199.805	82.782[b]	92.547[b]	
$7d^26f$	199.208	82.788[b]	92.551[b]	
		$Z = 124$		
$5g^4$	104 177.878[b]	117 185.244	117 195.099	
$6f5g^3$	7.883[b]	6.953	6.807	
$7d5g^3$	7.667[b]	7.275	7.126	
$6f^25g^2$	7.362	8.274	8.127	
$7d6f5g^2$	7.050	8.515	8.365	
$7d^25g^2$	6.564	8.630	8.478	126 325.434
$7d^4$	1.489	9.011	8.854	5.876

TABLE III. (*continued*)

Configuration[a]	$-E$(HX)	$-(E+E_\gamma)$ (HX)	$-(E+E_\gamma+E_c)$ (HX)	$-E$(Dirac-Slater)[10]
$6f^3 5g$	6.284	9.146	8.999	5.949
$7d^3 5g$	4.520	9.225	9.070	6.009
$7d6f^2 5g$	5.875	9.312	9.161	6.068
$7d^2 6f5g$	5.287	9.337	9.184	6.092
$7d^3 6f$	2.549	9.364	9.208	6.169
$6f^4$	4.624	9.546[b]	9.398[b]	6.344[b]
$7d^2 6f^2$	3.425	9.573[b]	9.420[b]	6.339[b]
$7d6f^3$	4.118	9.633[b]	9.482[b]	6.394[b]
		$Z=125$		
$5g^5$	106 176.286[b]	119 625.021	119 634.951	
$6f5g^4$	76.266[b]	6.719	6.658	
$7d5g^4$	76.061[b]	7.061	6.997	
$7d^5$	65.740	7.765	7.691	
$6f^2 5g^3$	75.717	8.032	7.969	
$7d6f5g^3$	75.417	8.293	8.227	
$7d^4 6f$	67.096	8.353	8.279	129 377.027
$7d^2 5g^3$	74.940	8.428	8.360	6.980
$7d^3 6f^2$	68.266	8.791	8.719	7.395
$7d^4 5g$	69.821	8.831	8.759	7.434
$6f^3 5g^2$	74.611	8.900	8.837	7.451
$7d^3 5g^2$	72.874	9.039	8.968	7.555
$7d^2 6f^3$	69.245	9.073	9.003	7.633
$7d6f^2 5g^2$	74.214	9.087	9.021	7.578
$7d^2 6f5g^2$	73.634	9.132	9.064	7.617
$7d^3 6f 5g$	70.875	9.166	9.095	7.706
$6f^5$	70.626	9.172	9.108	7.747
$7d6f^4$	70.033	9.200	9.133	7.748
$6f^4 5g$	72.922	9.287[b]	9.223[b]	7.825[b]
$7d^2 6f^2 5g$	71.744	9.356[b]	9.287[b]	7.856[b]
$7d6f^3 5g$	72.427	9.395[b]	9.329[b]	7.891[b]
		$Z=126$		
$5g^6$	108 197.042[b]	122 098.296	122 108.320	
$7d^6$	81.243	099.176	09.184	132 499.526
$6f5g^5$	97.001[b]	099.991	10.013	
$7d^5 6f$	82.910	100.009	10.018	500.380
$7d5g^5$	96.808[b]	100.353	10.372	
$7d^4 6f^2$	84.383	100.687	10.697	501.063
$7d^5 5g$	86.415	101.133	11.142	501.384
$7d^3 6f^3$	85.663	101.205	11.217	501.506
$6f^2 5g^4$	96.430	101.301	11.332	
$7d^2 6f^4$	96.746	101.563	11.576	501.808
$7d6f5g^4$	96.141	101.582	11.601	
$7d^4 6f5g$	87.768	101.702	11.712	501.967
$7d^2 5g^4$	95.674	101.738	11.753	501.889
$7d6f^5$	87.629	101.756	11.773	501.982
$6f^6$	88.310	101.785	11.806	502.033
$7d^3 6f^2 5g$	88.930	102.120	12.132	502.311
$6f^3 5g^3$	95.299	102.167	12.189	502.315
$7d^4 5g^2$	90.519	102.186	12.197	502.370
$7d^3 5g^3$	93.592	102.369	12.382	502.472
$7d6f^2 5g^3$	94.914	102.375	12.393	502.456
$7d^2 6f^3 5g$	89.902	102.381	12.396	502.527
$6f^5 5g$	91.261	102.436	12.456	502.600
$7d^2 6f5g^3$	94.344	102.442	12.457	502.516
$7d6f^4 5g$	90.680	102.487	12.504	502.620
$7d^3 6f5g^2$	91.567	102.505	12.513	502.620
$6f^4 5g^2$	93.584	102.558[b]	12.578[b]	502.680[b]
$7d^2 6f^2 5g^2$	92.428	102.670[b]	12.685[b]	502.749[b]
$7d6f^3 5g^2$	93.101	102.688[b]	12.705[b]	502.763[b]

[a] Plus a core of element 120, . . . $7s^2 7p^6 8s^2$.

[b] Most stable forms.

126 are $6f5g^{m-1}$ ($m = 2$, 3, 4, 5, 6 respectively). Without corrections, the HX binding energies give approximately the same results. However, when the relativistic corrections are added to the HX values of $(-E)$, a complete reordering of the stability of configurations takes place. The further addition of correlation corrections does not introduce any additional reordering. The Dirac-Slater binding energies quoted in Table III from Ref. 8 are obtained from the solution of the Dirac equation with Slater's $\rho^{1/3}$ exchange term. It is important to note that the Dirac-Slater values of $(-E)$ and the HX values of $-(E+E_r+E_c)$ predict the same ground configurations of elements 124 through 126. The large differences between the total binding energies determined from HX with corrections and from Dirac-Slater are due to the fact that the first-order relativistic corrections used in the former fail to account for the extremely high-relativistic energies of the inner-core electrons of such heavy elements. However, these large inner-electron relativistic energies change very little from one configuration to the next, and the first-order relativistic corrections appear to be sufficiently accurate to predict the correct ordering of configurations which differ only in the occupation numbers of the outer orbitals. As can be seen, not only are the corrected HX and Dirac-Slater ground configurations the same, but the orderings of the other configurations according to stability are almost identical; the differences which do occur may be due to the inaccuracy of first-order relativistic corrections, but they also may be due to the differences in the HX and Dirac-Slater exchange approximations. The very close agreement of the corrected HX and Dirac-Slater results for the ordering of the configurations from $Z = 124$ to 126 indicates that the corresponding corrected HX results for $Z = 121$ to 123 are probably fairly reliable.

It must be noted that the total binding energies given in Table III are for spherically-averaged atoms, and therefore each value represents the center-of-gravity energy of all levels of the corresponding configurations. It is of course not necessarily true that the lowest energy level of an atom belongs to the configuration with lowest center-of-gravity, because the energy depression from center of gravity to lowest level is not the same for all configurations. More specifically, this depression tends to increase as the number of $7d$ electrons in the configuration is decreased and as the number of $5g$ electrons is increased, because the electrostatic interaction parameters $F^k(nl, nl)$ increase strongly in going from $7d$ to $6f$ to $5g$.[24] To estimate these depressions quantitatively, we have made numerical calculations for a number of the lowest configurations of the elements $Z = 121$ to 125, using methods described elsewhere.[23,25] Differential effects from one configuration to another appear to be small (less than ~ 0.05 Ry), and ground levels appear to belong to the configuration with lowest center of gravity for all cases in Table III except for $Z = 123$, where the lowest level is computed to belong to $7d6f^2$.

There are of course other possible ground configurations than those considered in the table. In Pa I and U I, for example, levels of the configuration $5f^n6d^27s$ lie only about 0.06 Ry above the ground level of $5f^n6d7s^2$.[26] Since calculations of the above type are in agreement with these observations, and predict a similar situation in the super actinides, it seems likely that the ground levels of the latter belong to configurations listed in Table III. However, the basic accuracy of the one-electron model is such that the energy of one center of gravity with respect to another is probably reliable to no better than ± 0.1 Ry for these very heavy elements. It is therefore not possible to conclude much more than that the ground levels of elements 121 to 126 probably belong to one of the configurations marked with a "*b*" in column 4 of Table III.

V. CONCLUSION

The sudden changes with Z in effective quantum number which precede the *d*, *f*, and *g* transition series of elements have been explained in terms of changes in effective potentials. The existence of a double well (i.e. a well-defined potential barrier separating the inner and outer potential regions) is not necessary for such changes to occur, although the magnitude of these changes does depend on the height and definition of the barrier.

The HX results verify the predictions of Seaborg[8] that element 121 is homologous to actinium and lanthanum, and that a super actinide series of elements should exist beginning at $Z = 122$. It appears that both the $6f$ and $5g$ subshells will be filled in a mixed fashion, and there is a strong possibility that many of the ground configurations of the elements of this series will involve one or two $7d$ electrons.

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[14] The self-consistency criteria finally used are as follows: For $Z < 50$ the solution was considered self-consistent when the change in $r_i V_i(r)$ was less than five parts in 10^7 from one primary iteration cycle to the next, and the secondary iteration on the eigenvalues (during each primary cycle) was discontinued when $\Delta\epsilon_i/\epsilon_i$ was less than five parts in 10^{10}. For $Z \geqslant 50$ the change in $r_i V_i(r)$ was made less than one part in 10^8 and the eigenvalue change was required to be less than one part in 10^{11}.

[15] Perturbations of $sd\,^1D$ by $p^2\,^1D$ in Be, Mg, Ca, Sr, and Ba, and of s^2d by $sp^2\,^2D$ in B, are well known, and in most cases are of the proper sign and magnitude to account for much of the apparent error.

[16] These two possible alternatives are the source of considerable convergence difficulties in SCF iterations for certain configurations.

[17] An example can be seen by comparing the potential (Fig. 4) for La I $6s5d5f$ (the f electron *outside* the $6s$ and $5d$ electrons) with that (Fig. 3) for La I $4f6s5d$ (the f electron *inside* the $6s$ and $5d$). Clearly the difference between the $4f$ potentials for Ba and La in Fig. 3 is due primarily to this relaxation effect.

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[21] See, for example, B. Edlén, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1964), Vol. XXVII, pp. 91f; or B. G. Wybourne, Spectroscopic Properties of the Rare Earths (Interscience Publ., New York, 1965), pp. 1–4.

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Measurement of the Total Cross Section for Symmetric Charge Exchange in Helium from 400 - 2000 eV*

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The energy dependence of the total cross section for symmetric charge exchange in helium is measured in the range from 400–2000 eV. Beam-attenuation techniques are used, and all measurements are made on the forward-scattered ions and the high-energy neutrals resulting from the charge exchange. Cross-section values are given at 100–eV intervals, and the results show a cross section decreasing as the energy increases, with a value at 1000 eV of 1.04×10^{-15} cm^2. The absolute cross sections are accurate to ± 12%. Relative cross-section values accurate to ± 6% are reported.

INTRODUCTION

The $\text{He}^+ + \text{He}$ collision has been studied in great detail both experimentally and theoretically in recent years. These studies have led to a better understanding of the collision process and of the molecular states involved. In the energy region from several hundred to several thousand electron volts, the most significant contribution to the total cross section in $\text{He}^+ + \text{He}$ collisions comes from resonant charge exchange. Although there have been many studies of the total cross section for symmetric charge exchange in helium there is still a substantial lack of agreement among the published results.

The typical collision in the $\text{He}^+ + \text{He} \rightarrow \text{He} + \text{He}^+$ process involves very little kinetic-energy transfer between the partners. It is generally a glancing collision resulting in a high-energy neutral atom scattered in the forward direction and a low-energy ion recoiling in a perpendicular direction. The forward-scattered neutral atoms have nearly the same kinetic energy as the incident ions. The