

Binding energies of the lithium isoelectronic sequence approaching the critical charge

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The Simon-Zhislin-Hunziker theorem implies that Z_c , the critical charge below which the three electron atom is not bound, is at most 2. The vanishing electron affinity of He implies that Z_c is not less than 2. Hence, $Z_c = 2$. To elucidate the approach to the critical charge, we calculated nonrelativistic binding energies for the third electron in the ground state, $1s^2 2s^2 S$, and in the first and second excited states, $1s^2 2p^2 P$ and $1s^2 3s^2 S$, for nuclear charges approaching Z_c . At this limit the quantum defects for both 2S states are found to approach unity. This implies that the orbital specifying the outer (ns , $n = 2, 3$) electron becomes a very diffuse $(n - 1)s$ -type orbital, except within the relatively tiny space occupied by the inner two-electron shell. For the 2P state the quantum defect approaches zero both as $Z \rightarrow \infty$ and as $Z \rightarrow 2$. An expression for the s - p splitting at $Z \rightarrow 2$ is suggested, that improves upon earlier results based on energies computed (or measured) at integer values of Z . Rigorous large Z asymptotic expressions for the quantum defects in the $1s^2 ns^2 S$ states are presented, exhibiting the expected mild dependence on the principal quantum number.

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I. INTRODUCTION

Insightful clues to the understanding of the relative magnitudes of the energy components that contribute to the s - p splitting in the lithium (and similar) isoelectronic sequences are provided by a consideration of the two limits, as the nuclear charge Z grows to infinity on the one hand and as it approaches the critical charge below which the third electron is not bound, on the other [1]. Whereas the former limit is simply provided by $\frac{1}{2}$ -perturbation theory, the latter requires a more subtle analysis [2]. Current efforts to improve the (already very impressive) accuracy of computed energies and wave functions for light atoms, that are driven by the need to obtain sufficiently precise values for the higher-order QED terms [3,4], provide the computational procedure used in the present paper.

Ionization energies are computed for the three-electron isoelectronic sequences $1s^2 2s^2 S$, $1s^2 3s^2 S$, and $1s^2 2p^2 P$ as well as for the two-electron isoelectronic sequences $1s 2s^{1,3} S$ and $1s 2p^{1,3} P$, emphasizing Z values approaching the critical charge. For the ground 2S state of the three-electron system our energy values are essentially in agreement with Feldmann and King [5] as well as with Guevara and Turbina [6]. Our reservations concerning both Refs. [5] and [6] are specified below.

The computed ionization energies allow the evaluation of the quantum defect for the outermost electron, which, upon approaching the critical charge, turns out to approach unity in the three-electron 2S states, but zero in the 2P state.

Similar behavior is observed for the He isoelectronic sequence: when the nuclear charge approaches its critical value (that for the singly excited states is equal to unity), the quantum defect of the outer electron approaches unity in the $1s ns^{1,3} S$ ($n \geq 2$) states, but it approaches zero in the $1s np^{1,3} P$ states. These results suggest that an essential aspect of the behavior of alkali atoms in that limit is captured by the hard core model studied by Parsons and Weisskopf [7], which completely ignores both correlation and the effect of the outer electron on the core. The threshold behavior of the photodetachment cross sections of negative ions has been interpreted in terms of a similar insight into the form of the outgoing electron (continuum) wave function [8].

The asymptotic forms of the quantum defects suggested by the presently obtained energies yield a physically meaningful expression for the behavior of the $2s$ - $2p$ splitting upon approaching the critical charge.

II. THE CRITICAL CHARGE

If the nuclear charge of an N -electron atom is allowed to decrease continuously, a certain critical charge is encountered below which the N th electron ceases to be bound. The evaluation of this critical charge for the isoelectronic sequences of most members of the periodic table has been studied by several authors, some of whom are referred to below.

Most (neutral) atoms have positive electron affinities, i.e., they form bound singly negative ions. Closed-shell atoms, such as the rare gases (except the element $Z = 118$, closing the $7s^2 7p^6$ shell [9]) and the closed d -shell elements (Zn, Cd, Hg), do not form bound negative ions. It appears that bound doubly negative atomic ions do not exist.

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A theorem due to Simon [10], Zhislin [11], and Hunziker [12] states that N -electron atomic systems have an infinite number of bound states if $Z > N - 1$, and at most a finite number of bound states if $Z \leq N - 1$.

For the ground state of the He isoelectronic sequence the critical charge had been determined fairly accurately. The controversy that still exists involves the fourth digit, beyond $Z_c \approx 0.911$ [6,13]. Indeed, H^- is known to have a (single) bound state [14–16]. Upon approaching the critical charge the ionization energy, whose square root determines the rate of the exponential asymptotic decay, vanishes. Nevertheless, it was shown that at the critical charge the wave function remains bound (square integrable), decaying asymptotically as the exponent of the square root of r [17]. This mode of approach towards the critical charge has been referred to as “absorbing.” A concise review is provided by Hogreve [18].

For the Li isoelectronic sequence the Simon-Zhislin-Hunziker (SZH) theorem cited above implies that the critical charge is at most 2. The fact that He has a vanishing electron affinity implies that the critical charge is not less than 2. This is consistent with an “expanding” mechanism implying that at $Z_c = 2$ the outermost electron becomes infinitely diffuse. This same behavior should be expected to hold for other isoelectronic sequences involving atoms with a single-electron outside a closed shell.

The claim made in Ref. [6] that the critical charge is strictly larger than 2 ($Z_c \approx 2.0090$) is probably a consequence of the fact that these authors’ data analysis involves fitting the total three-electron 2S energy rather than the much smaller ionization energy of the outermost electron, the quantity whose vanishing determines the critical charge. Our nonvanishing binding energy for the $2s$ electron at $Z = 2.001$ (presented in Table IV) and similar results for even lower Z by Feldmann and King [5] (which, as suggested below, are in all likelihood lower than the actual binding energies) are consistent with $Z_c = 2$.

Inspection of ground state atoms may suggest that the absorbing mechanism, which (probably) characterizes the behavior of isoelectronic sequences whose singly negative member is bound, is the more common one. However, apart from a finite number of cases, singly excited states of N -electron atoms cease to be bound when the nuclear charge equals $N - 1$, suggesting that the expanding mechanism (the outermost orbital becoming infinitely diffuse) is the prevailing mode of detachment of the outermost electron upon approaching the critical charge.

As an illustration we consider the $1s2s\ ^{1,3}S$ and the $1s2p\ ^{1,3}P$ states of the helium isoelectronic sequence, whose ground state is absorbing. The pertinent results are presented in Tables I and II, respectively. Upon approaching the critical charge, $Z_c = 1$, the binding energy of the outer electron in both P states approaches the asymptotic form $-\frac{(Z-1)^2}{8}$, characterizing the expected expanding scenario. The binding energy of the outer electron in the two S states approaches $-\frac{(Z-1)^2}{2}$ as Z approaches the critical charge, although the deviation from this asymptotic form takes place much more rapidly upon increase of Z . Hence, the $2s$ electron behaves, close to the critical charge, like a diffuse $1s$ electron, whereas the $2p$ electron, occupying the lowest possible orbital of that

TABLE I. The $2s$ binding energies in the $1s2s\ ^1S$ and $1s2s\ ^3S$ states of the He isoelectronic sequence.

Z	$\epsilon_{2s}(^1S)$	$\frac{\epsilon_{2s}(^1S)}{(Z-1)^2}$	$\epsilon_{2s}(^3S)$	$\frac{\epsilon_{2s}(^3S)}{(Z-1)^2}$	$\frac{E(^1S)-E(^3S)}{(Z-1)^{2.25}}$
2.0	0.1459740	0.14597	0.17522938	0.17523	
1.5	0.04141875	0.16568	0.05263081	0.21052	
1.2	0.00838160	0.20954	0.01107373	0.27684	0.1006
1.1	0.00255789	0.25578	0.003348679	0.33487	0.1406
1.05	0.000773081	0.30923	0.0009732720	0.38931	0.1693
1.02	0.0001517148	0.37929	0.0001743921	0.43598	0.1702
1.01	0.0000422813	0.42281	0.0000468530	0.46853	0.1446

symmetry type, becomes a diffuse hydrogenlike $2p$ orbital at the same limit. The rightmost columns of Tables I and II suggest that close to the critical charge the singlet-triplet splittings satisfy

$$E(^1S) - E(^3S) \approx 0.15(Z-1)^{2.25},$$

$$E(^1P) - E(^3P) \approx 0.25(Z-1)^{4.75}.$$

Attempting to estimate the critical exponent using the “natural” integer Z energies ($Z = 2, 3, \dots$), a considerably lower critical exponent is obtained. Thus, for the $1s2s\ ^{1,3}S$ states such a fit yields $E(^1S) - E(^3S) \approx 0.029(Z-1)^{1.25}$. It is tempting to conjecture that the actual limiting critical exponent for the $^{1,3}P$ splitting is 5, and that for the $^{1,3}S$ splitting is possibly $\frac{5}{2}$.

Atomic doubly excited states present a host of issues that are beyond the scope of the present discussion.

III. THE QUANTUM DEFECT

For the outermost electron in alkali atoms (and corresponding isoelectronic ions) the ionization (binding) energy is expressed, semiempirically, in the form [19]

$$\epsilon_{n,\ell} = -\frac{(Z - N_0)^2}{2(n - \delta_{n\ell})^2}. \quad (1)$$

Here, N_0 is the number of core electrons and $\delta_{n\ell}$ is referred to as the quantum defect. For a given isoelectronic sequence the quantum defect is weakly dependent on the principal quantum number n but strongly dependent on both the nuclear charge Z and the angular momentum quantum number ℓ . The quantum defects presented in Ref. [19] for the $3s$ and $3p$ states of the first four members of the Na isoelectronic

TABLE II. The $2p$ binding energies in the $1s2p\ ^1P$ and $1s2p\ ^3P$ states of the He isoelectronic sequence.

Z	$\epsilon_{2p}(^1P)$	$\frac{8\epsilon_{2p}(^1P)}{(Z-1)^2}$	$\epsilon_{2p}(^3P)$	$\frac{8\epsilon_{2p}(^3P)}{(Z-1)^2}$	$\frac{E(^1P)-E(^3P)}{(Z-1)^{4.75}}$
2.0	0.12384309	0.990745	0.13316419	1.06531	
1.5	0.03122708	0.999267	0.03285671	1.05141	
1.2	0.005021736	1.00435	0.005092757	1.01855	0.1484
1.1	0.001253514	1.00281	0.0012574865	1.00599	0.2234
1.05	0.000312855	1.00114	0.0003130254	1.00168	0.2575
1.02	0.0000500122	1.00024	0.0000500144	1.00029	0.2500
1.01	0.0000125008	1.00006	0.0000125009	1.00007	0.225

sequence sharply decrease upon increasing the nuclear charge, eventually tending to zero. Anticipating our results for the Li isoelectronic sequence, we note that the values of the quantum defects in the Na isoelectronic sequence referred to above are consistent with an extrapolation of the $3s$ quantum defect to 2.0, and the $3p$ quantum defect to 1.0, upon a decrease of Z to 10. This feature suggests that, close to the critical charge, the outermost electron occupies (outside the relatively tiny $1s^2 2s^2 2p^6$ core) a (diffuse) $1s$ -like or a $2p$ -like hydrogenic orbital, respectively.

The binding energies of the outer electron in the singly excited states of the He isoelectronic sequence, reported in Tables I and II, suggest that as Z approaches the critical charge the quantum defects are given by

$$\begin{aligned}\delta(1s2s^3S) &\approx 1 - 8.75(Z - 1), \\ \delta(1s2s^1S) &\approx 1 - 3.30(Z - 1), \\ \delta(1s2p^3P) &\approx 0.6(Z - 1)^2, \\ \delta(1s2p^1P) &\approx 0.7(Z - 1)^2.\end{aligned}$$

The slightly lower quantum defects in the triplet states, compared to the corresponding singlets, are manifestations of Hund's multiplicity rule. The values of the quantum defects suggest that the $2s$ orbital approaches, close to the critical charge, a hydrogenic $1s$ orbital, while the $2p$ orbital approaches a hydrogenic $2p$ orbital in the same limit.

For the large Z members of an isoelectronic sequence the low order $\frac{1}{Z}$ -perturbation theory is adequate. Thus, for the He ground state [13], the Li $1s^2 2s^2 S$ and the Li $1s^2 2p^2 P$ [20] isoelectronic sequences, the following are the leading terms

$$\begin{aligned}E(1s^2 1S) &= -Z^2 + \frac{5}{8}Z + \dots, \\ E(1s^2 2s^2 S) &= -\frac{9}{8}Z^2 + \frac{5965}{5832}Z + \dots, \\ E(1s^2 2p^2 P) &= -\frac{9}{8}Z^2 + \frac{57397}{52488}Z + \dots.\end{aligned}\quad (2)$$

Hence, for the binding energies of the outermost electron in the 2S and 2P isoelectronic sequences we obtain

$$\begin{aligned}\epsilon_{2s} &= -\frac{1}{8}Z^2 + \frac{290}{729}Z + \dots, \\ \epsilon_{2p} &= -\frac{1}{8}Z^2 + \frac{3074}{6561}Z + \dots.\end{aligned}$$

Expanding the expression for the binding energy, Eq. (1), in terms of the quantum defect we obtain

$$\epsilon_{n\ell} = -\frac{(Z-2)^2}{2[n-\delta_{n\ell}(Z)]^2} \approx -\frac{Z^2}{2n^2} + \frac{Z}{2n^2} \left(4 - \frac{2\delta_{n\ell}^{(0)}}{n}\right),$$

where, for large Z , $\delta_{n\ell} \approx \frac{\delta_{n\ell}^{(0)}}{Z} + \dots$. Compared to the binding energies obtained by means of the $\frac{1}{Z}$ -perturbation theory it follows that

$$\begin{aligned}\delta_{2s} &= \frac{596}{729Z} + \dots \approx \frac{0.8176}{Z} + \dots, \\ \delta_{2p} &= \frac{1652}{6561Z} + \dots \approx \frac{0.2518}{Z} + \dots.\end{aligned}$$

For the $1s^2 3s^2 S$ and the $1s^2 4s^2 S$ states, one similarly obtains, using the Slater integrals $F_0(1s, ns)$ and $G_0(1s, ns)$

($n = 3, 4$) evaluated by Butler *et al.* [21] and by Golden [22],

$$\epsilon_{ns} = -\frac{Z^2}{2n^2} + Z[2F_0(1s, ns) - G_0(1s, ns)] + \dots,$$

i.e.,

$$\epsilon_{3s} = -\frac{Z^2}{18} + Z\frac{6331}{32768} + \dots$$

and

$$\epsilon_{4s} = -\frac{Z^2}{32} + Z\frac{1102802}{9765625} + \dots.$$

The corresponding large Z quantum defects are

$$\begin{aligned}\delta_{3s} &= \frac{25671}{32768Z} + \dots \approx \frac{0.7834}{Z}, \\ \delta_{4s} &= \frac{7545672}{9765625Z} + \dots \approx \frac{0.7727}{Z}.\end{aligned}$$

These results, together with δ_{2s} , exhibit the (mild) dependence of the quantum defect on the principal quantum number n (in the large Z limit). Evaluating the Slater integrals $F_0(1s, ns)$ and $G_0(1s, ns)$ for hydrogenic orbitals with higher principal quantum numbers, we obtain the quantum defects $\delta_{ns} \approx \frac{\delta_{ns}^{(0)}}{Z} + \dots$, where

$$\begin{aligned}\delta_{5s}^{(0)} &\approx 0.767889 & \delta_{6s}^{(0)} &\approx 0.765334 \\ \delta_{7s}^{(0)} &\approx 0.763809 & \delta_{8s}^{(0)} &\approx 0.762825 \\ \dots & \delta_{15s}^{(0)} \approx 0.760543 & \dots & \delta_{20s}^{(0)} \approx 0.760149 \\ \dots & \delta_{30s}^{(0)} \approx 0.759868 & \dots & \delta_{40s}^{(0)} \approx 0.759769 \\ \dots & \delta_{50s}^{(0)} \approx 0.759724 & \dots & \delta_{60s}^{(0)} \approx 0.759699 \\ \dots & \delta_{70s}^{(0)} \approx 0.759684 & \dots & \delta_{80s}^{(0)} \approx 0.759675 \quad \dots\end{aligned}$$

In Table III we report our calculated binding energies for the outermost electron in the various three-electron sequences considered, at large Z . The derived values of $Z\delta_{2s}$ appear to depend (for Z not too low) roughly linearly on $\frac{1}{Z}$, yielding

TABLE III. The $2s$, $2p$, and $3s$ binding energies in the Li isoelectronic sequence—high Z behavior.

Z	ϵ_{2s}	$2 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{2s}}}$	$Z\delta_{2s}$
14	19.183252	1.93734	0.8773
13	16.206234	1.93213	0.8823
12	13.479248	1.92598	0.8882
11	11.002307	1.91861	0.8953
Z	ϵ_{2p}	$2 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{2p}}}$	$Z\delta_{2p}$
14	18.317658	1.98258	0.2438
13	15.411699	1.98131	0.2430
12	12.755835	1.97984	0.2419
11	10.350094	1.97813	0.2405
Z	ϵ_{3s}	$3 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{3s}}}$	$Z\delta_{3s}$
14	8.3315346	2.93971	0.8441
13	7.0248252	2.93467	0.8492
12	5.8292425	2.92873	0.8553
11	4.7447916	2.92159	0.8625

$\lim_{Z \rightarrow \infty}(Z\delta_{2s}) \approx 0.81$. Similarly, $\lim_{Z \rightarrow \infty}(Z\delta_{2p}) \approx 0.25$ and $\lim_{Z \rightarrow \infty}(Z\delta_{3s}) \approx 0.78$. These values are in agreement with those provided by first order perturbation theory, presented above.

IV. THE $1s^2 2s^2 S$ ISOELECTRONIC SEQUENCE

The ground state energy of the lithium atom and isoelectronic ions has been one of the early targets of computational quantum chemistry. A review of the early approaches is provided by Ritter *et al.* [23], who obtained ionization energies that agree to about 1% with the experimental results. Current approaches [3–5] yield much higher accuracy.

Our results for the binding energies of the $2s$, $3s$, and $2p$ electron in the low nuclear charge range ($2 < Z \leq 3$) are presented in Tables IV to VI, respectively. These results were obtained using the quadruple precision version of the procedure described in Refs. [3,4]. The higher Z energies presented in Table III were already referred to in the previous section. Some results due to Feldmann and King [5] are appended at the bottom of Table IV. For the $2s$ electron, the quantum defects at low Z are roughly consistent with the asymptotic expression

$$\delta_{2s} \approx 1 - 0.6(Z - 2)^{\frac{2}{3}}; \quad Z \rightarrow 2. \quad (3)$$

Substituting in Eq. (1) and expanding we obtain

$$\epsilon_{2s} \approx -\frac{(Z - 2)^2}{2} + 0.6(Z - 2)^{\frac{8}{3}}. \quad (4)$$

The form of this expression is reminiscent of the Puiseux expansion proposed by Guevara and Turbina [6].

The lowest Z calculation of Feldman and King [5] yields an unreasonable quantum defect. Use of the asymptotic expression for the quantum defect, Eq. (3), suggests that the ionization energy at $Z = 2.000001$ should be about 4.9994×10^{-13} a.u., not 3.75×10^{-13} a.u. Our own results suffer from the same deficiency already at $Z = 2.001$, where the $2s$ binding energy should probably be closer to 49×10^{-8} a.u. than to the reported value, 36.6×10^{-8} a.u., in order to give rise to a reasonable quantum defect. Since these ionization energies are the differences of the three-electron and two-electron ground state energies, the computations reported in Ref. [5] imply an accuracy of some 13 digits. It is remarkable

TABLE IV. The $2s$ binding energies in the Li isoelectronic sequence—low Z behavior. The bottom three lines are from Ref. [5].

Z	ϵ_{2s}	$2 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{2s}}}$	$\frac{1-\delta}{(Z-2)^{\frac{1}{3}}}$
3.0	0.19814691	1.58852	
2.5	0.06053034	1.43704	
2.2	0.01259749	1.26001	0.7603
2.1	0.003708863	1.16109	0.7477
2.05	0.001044725	1.09384	0.6914
2.02	0.000183315	1.04452	0.6042
2.01	0.0000472982	1.02816	0.6067
2.001	0.000000366		
2.0001	4.992988×10^{-9}	1.00070	
2.00001	4.9963×10^{-11}	1.00037	
2.000001	3.75×10^{-13}	1.1547	

TABLE V. The $3s$ binding energies in the Li isoelectronic sequence—low Z behavior.

Z	ϵ_{3s}	$3 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{3s}}}$	$\frac{1-\delta}{(Z-2)^{\frac{1}{2}}}$
3.0	0.0741850	2.59613	0.5961
2.5	0.0209308	2.44378	0.6276
2.2	0.00390067	2.26436	0.5911
2.1	0.00106321	2.16858	0.5331
2.05	0.00028029	2.11179	0.4999

that the asymptotic values of the quantum defect, as used here, provide such a sensitive measure of the ionization energy close to the critical charge.

V. THE $1s^2 2p^2 P$ ISOELECTRONIC SEQUENCE

The ionization energies of the $1s^2 2p^2 P$ state yield quantum defects that are very close to zero near the critical charge. The negative quantum defects (i.e., $2 - \delta > 2$) presented in Table VI for the lowest values of Z suggest that the computation of the corresponding ionization potentials is not sufficiently accurate. The values of the quantum defects obtained imply an error in the third or fourth digit of the ionization energies, i.e., a respective error in the eighth or ninth digit of the total energies. Assuming that the behavior suggested by the quantum defect for somewhat higher nuclear charges is valid we write

$$\delta_{2p} \approx 0.06(Z - 2)^{\frac{3}{2}}.$$

Hence,

$$\epsilon_{2p} \approx -\frac{(Z - 2)^2}{8} + 0.007(Z - 2)^{\frac{7}{2}}.$$

The asymptotic form $\epsilon_{2p} \approx -\frac{(Z-2)^2}{8}$ is adequate.

VI. s - p SPLITTING IN THE LITHIUM ISOELECTRONIC SEQUENCE

Using the asymptotic expressions, close to the critical charge, of the $2s$ and $2p$ ionization energies, the $2s$ - $2p$ splitting, i.e., the difference between the total (or ionization) energies of the $1s^2 2p^2 P$ and the $1s^2 2s^2 S$ states, is given by

$$\Delta\epsilon \approx \frac{3}{8}(Z - 2)^2 - 0.6(Z - 2)^{\frac{8}{3}}.$$

TABLE VI. The $2p$ binding energies in the Li isoelectronic sequence—low Z behavior.

Z	ϵ_{2p}	$2 - \delta = \frac{Z-2}{\sqrt{2\epsilon_{2p}}}$	$\frac{\delta}{(Z-2)^{\frac{3}{2}}}$
3.0	0.130243	1.95933	
2.5	0.0319970	1.97652	0.066
2.2	0.00503257	1.99352	0.072
2.1	0.00125241	1.998074	0.061
2.05	0.000312637	1.999562	0.039
2.02	0.0000499852	2.00030	
2.01	0.0000124814	2.00149	

This expression yields, via the Hellmann-Feynman theorem (differentiation with respect to the nuclear charge), the difference of nuclear attractions

$$\Delta L \approx \frac{3}{4}Z(Z-2) - 1.6Z(Z-2)^{\frac{5}{3}},$$

and, via the virial theorem, the difference of interelectronic repulsions

$$\Delta C \approx -\frac{3}{2}(Z-2) + 0.4(Z+6)(Z-2)^{\frac{5}{3}}.$$

It follows that close to the critical charge, where only the leading term matters,

$$\frac{\Delta C}{\Delta L} \approx -\frac{2}{Z};$$

hence

$$\lim_{Z \rightarrow 2} \frac{\Delta C}{\Delta L} = -1. \quad (5)$$

This result was recently obtained on the basis of a postulated expression of the form $\alpha(Z-2)^\beta$ for the low Z behavior of the s - p splitting, which was crudely fitted to a few integer Z energies, yielding for the critical exponent the value $\beta \approx 1.21$ [1]. It appears that the higher critical exponent, 2, suggested by the present analysis, can only be reliably estimated close enough to the critical charge, as was done in the present paper. The limiting ratio, Eq. (5), does not depend on the value of the critical exponent, provided that it is larger than unity.

VII. CONCLUSIONS

Highly accurate ionization energies were obtained for the $1s2s^{1,3}S$ and the $1s2p^{1,3}P$ states of the He isoelectronic

sequence and for the $1s^22s^2S$, $1s^23s^2S$, and $1s^22p^2P$ states of the lithium isoelectronic sequence, in particular for nuclear charges approaching the critical charges, $Z_c = 1$ and 2, respectively, as closely as the stability of the computational procedure allowed. It was observed that as Z approaches the critical charge the quantum defects corresponding to the computed ionization energies approach unity for the S states and zero for the P states, in both the He and the Li isoelectronic sequences. This behavior can be understood by noting that, close to the critical charge, the outermost electron occupies a diffuse orbital that—most of the time—experiences the two core electrons as a tiny sphere screening the nuclear charge. This behavior, as well as weaker support stemming from the analysis of experimental spectra of heavier alkali metals, suggests the conjecture that $\lim_{Z \rightarrow Z_c} \delta_{n\ell} = N_\ell$, where N_ℓ is the number of ℓ -type shells in the core. Estimates of the asymptotic behavior of the quantum defects near the critical charge yield asymptotic expressions for the ionization energies, and, consequently, the s - p splitting. The high Z limit of the quantum defects was studied as well, providing an asymptotically rigorous assessment of the commonly claimed near independence of the quantum defect on the principal quantum number.

The extraction of asymptotic features out of highly accurate computations near the critical charge appears to suggest insights that would otherwise not be accessible.

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