PHYSICAL REVIEW A **74**, 012714 (2006)

Stepwise rise of quantum defects along the periodic table

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(Received 7 November 2005; published 19 July 2006)

The stepwise behavior of quantum defects along the periodic table of the elements is related to the $(n+\ell,n)$ building-up rule in the table.

DOI: 10.1103/PhysRevA.74.012714 PACS number(s): 03.65.Nk, 32.30.−r, 03.65.−w, 31.15.−p

The stepwise behavior of quantum defects along the periodic table of the elements—i.e., with variation of atomic number Z—has been known for a long time [1,2]. Originally it was found in theoretical analysis and immediately received an appropriate physical explanation, as discussed in more detail below. The special regularities in the position of the steps on the Z scale are less known. The objective of the present paper is to reassess the latter issue by updating, putting together its different aspects, and exposing it in a broad theoretical context. The systematical improvement of theoretical results and experimental data on the individual quantum defects for special values of Z and the Rydberg electron orbital momentum ℓ does not preclude interest in the general overall trends.

The stepwise behavior is well seen in the results of early calculations [1,2] of quantum defects $\mu_\ell(Z)$ across the periodic table. The "empirical" position of the steps $Z^{(d)}_{\mathrm{emp}}$ for d waves (i.e., for the orbital quantum number of an active electron $\ell=2$) and $Z^{(f)}_{\mathrm{emp}}$ for f waves ($\ell=3$) extracted from the plots provided by Manson [1] are listed in Table I further explained below. The plots actually depict the phase shift $\delta_\ell(Z,\epsilon=0)$ for zero energy ϵ, but since Seaton's paper [3] the relation to quantum defects is universally known:

$$\pi\mu_\ell(Z)=\delta_\ell(Z,\epsilon=0). \tag{1}$$

The increment of μ_ℓ at each step is roughly equal to 1.

The stepwise structure had received a fully adequate explanation right at the moment of its recovery. The effective potential seen by the active electron

$$U_{\mathrm{eff}}(r)=U(r)+\frac{\ell(\ell+1)}{2r^2} \tag{2}$$

(atomic units are used throughout the paper) exhibits two wells separated by a potential barrier, as first noticed by Goeppert Mayer [4] (see also discussion by Manson and Cooper [5]). The short-range potential $U_{\mathrm{s}}(r)$ is operative mostly in the inner well, while in the outer well $U(r)$ reduces to pure Coulomb attraction $-Z_0/r$. Here Z_0 is the charge of a residual core seen by the outer (active) electron ($Z_0=1$ if the spectrum of a neutral atom is considered). Now we resort to citations from Manson [1]: "Increasing Z, the inner well gets deep enough to support a bound d state so that the first loop of the continuum wave function is in the inner region even at $\epsilon=0$. The same thing happens for f waves: here, however, the barrier is wider and higher, so that it is more effective in keeping $\epsilon=0$ waves essentially nonpenetrating up to the values of Z around where the first f state becomes bound in the inner well…. For f waves it is seen that at $\epsilon=0$ the curve $[\delta_\ell(Z,\epsilon=0)]$ is a step function since it depends essentially only on the outer region of the potential and on the number of bound states the inner well can support…. The s and p waves, being very penetrating, are determined by the potential over entire range of r…." A similar discussion was given by Fano *et al.* [2].

The separation of inner and outer wells can be further analyzed by using the well-known Thomas-Fermi potential for $U_{\mathrm{s}}(r)$ [6]:

$$U_{\mathrm{s}}(r)=-\frac{Z}{r}\varphi(x),\quad x=rZ^{1/3}/b, \tag{3}$$

where $b=\frac{1}{2}(3\pi/4)^{2/3}\approx 0.885$. The Thomas-Fermi function $\varphi(x)$ does not have a closed-form expression but could be well approximated by the simple analytical formula

$$\varphi_{\mathrm{T}}(x)=\frac{1}{(1+\alpha x)^2} \tag{4}$$

suggested by Tietz [7,8]. He used two different methods to choose the parameter α: the normalization condition in momentum space [7] gave $\alpha_{\mathrm{n}}=(\pi/8)^{2/3}\approx 0.569$ while the variational principle [8] led to $\alpha_{\mathrm{v}}=2^{-4}(35\pi/4)^{2/3}\approx 0.538$. Both these values ensure a good approximation in the intermediate range of x (or r) most important for considering an atomic ground-state or zero-energy scattering shift. For large r the behavior of $\varphi(x)$ and $\varphi_{\mathrm{T}}(x)$ differ, but in this domain the asymptote of $\varphi(x)$ is known to be of little physical sense. The quality of the approximation (4) is quite robust against variation of α; Ref. [9] suggested to use

TABLE I. Position of steps in dependence of quantum defects $\mu_\ell(Z)$ on atomic quantum number Z and assignment of quantum numbers $N=n+\ell$ (see text for details).

N	5	6	7	8
$(n\ell)_N$ for $\ell\geq 2$	$3d$	$4d$	$4f,5d$	$5f,6d$
Z^{rule}_N	21	39	57	89
$Z^{(d)}_{\mathrm{emp}}$	19	37	55	87
$Z^{(f)}_{\mathrm{emp}}$			55	87

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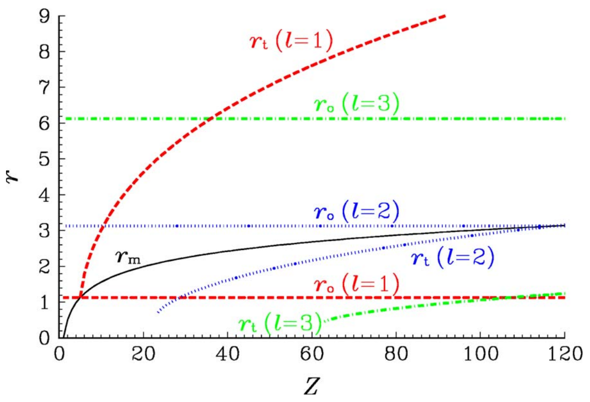

FIG. 1. (Color online) Dependence on atomic number Z of the turning points r_{t} and r_{o} in the effective atomic potential for various values of orbital momentum ℓ. The matching distance r_{m} is also shown; see text for details.

numerologically attractive value $\alpha_{\mathrm{DO}}=\frac{1}{2}$ which also gave good result.

Combining formulas (3) and (4) we obtain the analytical approximate one-electron potential in an atom:

$$U_{\mathrm{s}}^{(\mathrm{an})}(r) = -\frac{Z}{r(1+r/R)^2}, \quad R = \alpha^{-1}Z^{-1/3}b. \tag{5}$$

The Tietz approximation is often omitted when simple atomic models [10] or the Thomas-Fermi approximation [11] are discussed. Schwinger and Englert [12–14] undertook an extensive study of the Thomas-Fermi approximation, but were not aware of the Tietz approximation until 1985 when it was successfully used [15,16]. On the other hand, the approximation has been actively employed in the well-known collection of problems in quantum mechanics [17] and used in various applications until now [18,19]. The beautiful analytical properties of the approximate potential revealed by Demkov and Ostrovsky [9] add to its value; see the brief discussion below.

Following Latter [20] (see also Ref. [21]) we match the potential $U_{\mathrm{s}}^{(\mathrm{an})}(r)$, Eq. (5), with the Coulomb tail; the matching point r_{m} is defined from $U_{\mathrm{s}}^{(\mathrm{an})}(r_{\mathrm{m}})=-1/r_{\mathrm{m}}$. The dependence $r_{\mathrm{m}}(Z)$ is shown by the solid curve in Fig. 1 (parameter value α_{n} was employed). The outer turning point r_{o} for $\epsilon=0$ lies in the domain where only the attractive Coulomb potential $-1/r$ and repulsive centrifugal potential $(\ell+\frac{1}{2})^2/(2r^2)$ are operative (the well-known Langer correction is applied). The position of r_{o} does not depend on Z, being given by the horizontal lines for $\ell=1,2,3$ in Fig. 1. For the motion in the inner potential well the turning points are defined from the condition $U_{\mathrm{s}}^{(\mathrm{an})}(r)+(\ell+\frac{1}{2})^2/(2r^2)=0$. The inner right turning point $r_{\mathrm{t}}(Z)$ is also shown in Fig. 1 for $\ell=1,2,3$. Inspecting the figure one sees that for d and f waves the ordering of radial points of interest is

$$r_{\mathrm{t}}(Z) < r_{\mathrm{m}}(Z) < r_{\mathrm{o}} \tag{6}$$

(the analytical expressions for all these magnitudes are straightforward; they are not cited here for brevity). This means that the inner and outer domains of classically allowed electron motion are separated by a potential barrier, which supports the early reasoning cited above and thus explains the stepwise behavior of $\mu_\ell(Z)$. The matching of potentials occurs inside the barrier and does not influence simple semiclassical formulas. On the contrary, for p waves (moreover for s waves not shown in Fig. 1) the ordering (6) is violated, which means that the outer and inner wells are not separated by a barrier but merge.

The application of Thomas-Fermi theory to various problems in atomic physics has a long and fruitful history [24]. The literature is very extensive; here we refer to the comprehensive review by Spruch [11], the series of papers by Schwinger [12] and Englert and Schwinger [13–15], and book by the latter author [16]. The semiclassical (Thomas-Fermi) method is indispensable when the trends along the periodic table are explored. "The HF method is designed for the investigation of individual atoms with given nuclear charge and number of electrons. In contrast, the semiclassical approach is meant to deal as a whole with the periodic table" [14].

In their recent paper, Kolomeisky and Timmins (KT) [22] look for manifestation of the *Zel'dovich effect* in the evolution of atomic Rydberg spectra along the periodic table of the elements. The effect appears in the energy spectrum of a potential $U(r)$ with a Coulomb tail and some short-range behavior $U_{\mathrm{s}}(r)$ for small separations r from the force center. Since the terminology seems to be introduced for the first time, the authors choose to summarize Zel'dovich's [23] findings in the following terms:"… he stated that as the dimensionless coupling constant w [potential parameter] increases, the spectrum of the problem $E_n(w)$ evolves in a fashion resembling decreasing staircase. The steps are located at critical values of w at which bound states occur in $U_{\mathrm{s}}(r)$ only."

Following Zel'dovich, KT limit consideration to s states and come to the conclusion that such a "peculiar reconstruction" of the bound-state spectrum is absent for atoms. Instead, they show that "along the periodic table of elements, the Zel'dovich effect manifests itself as a systematic periodic variation of the Rydberg spectra proportional to the cubic root of the atomic number" or atomic nucleus charge Z. Thus, in this alternative definition of the effect, the staircase behavior originally put forward by Zel'dovich is substituted by an actual smooth modulation. The terminological dilemma might be formulated as follows: should the name *Zel'dovich effect* be reserved to the stepwise behavior of quantum defects for any potential with a Coulomb tail (including those with centrifugal repulsion), or it should be applied to an arbitrary (including smooth) behavior of quantum defects as the short-range s-wave potential $U_s(r)$ deepens and new bound states appear. A possible resolution is provided by KT who talk about *Zel'dovich modulations* with $Z^{1/3}$ scale when a smooth behavior is discussed.

It is well established that $Z^{1/3}$ is a natural characteristic parameter within the Thomas-Fermi scheme (see bibliography above and also Ref. [25]). In view of this, the attempted separation of Zel'dovich modulations from the similar but more pronounced $Z^{1/3}$ modulations induced by atomic shell structure [11–16] is not easy, as justly indicated by KT, and not without some artificial flavor.

As exposed above, the stepwise behavior is found in the periodic table as long as one lifts restriction to consider only *s* states. The physical background is quite obvious: Zel'dovich [23] stressed that the stepwise behavior appears under condition of resonance scattering of low-energy particles by potential $U_s(r)$. Such a shape resonance emerges for potentials with a barrier, but a barrier is absent in one-electron potential for atomic *s* states. On the contrary, for high enough electron orbital momentum ℓ the barrier is clearly manifested in the effective potential (2).

The arguments cited above of early papers [1] on the stepwise behavior were based on considering wave function and oscillatory behavior (loops) inside the potential well. The similar arguments were applied also by Zel'dovich [23] along with a more quantitative construction. The paper by Zel'dovich [23] was not referred to in the original interpretation of the stepwise behavior of quantum defects [1,2,5]. This circumstance finds its historical explanation in the fact that different, but in many aspects parallel, theoretical schools and traditions existed; in particular, Zel'dovich's paper was addressed primarily to the solid-state community.

The early reasoning [1,2,5] complemented by the later studies [18,26–28] and by the simple arguments put forward above could successfully conclude the quest for search and explanations of the stepwise effect in atomic spectra. However, under a deeper scrutiny, the peculiar features are revealed that add a quite special flavor to the effect. As the first "phenomenological" observation one might notice that the *locations of the steps* $Z_{\text{emp}}^{(f)}$ *for f waves coincides with these of the steps* $Z_{\text{emp}}^{(d)}$ *for d waves*; see Table I. This is not a mere coincidence, but a reflection of the general structure of the periodic table of the elements well described by $(n+\ell,n)$ Aufbau (or building-up) rule. I remind the reader that according to this rule (i) the one-electron orbitals $(n\ell)$ in the ground-state neutral atoms are filled in the order of increasing sum $N\equiv n+\ell$ and (ii) for a fixed N in the order of increasing n. Sometimes this rule is referred to as the Madelung [29] (1936) rule although it was Karapetoff [30] (1930) who published it first. The rule was rediscovered several times as traced in detail in Ref. [31] where a vast bibliography related to the rule is analyzed. The works by Klechkovskii [32,33] summarized in his book [34] should be particularly praised since this author studied systematically different aspects of the $(n+\ell,n)$ rule in much detail. Although the rule allows a number of exceptions, it describes adequately the general Aufbau pattern, while the alternative (n,ℓ) rule breaks down completely for higher Z, as illustrated graphically by Demkov and Ostrovsky [9].

The really quantum-theoretical interpretation of this rule requires an operator with eigenvalues depending on $n+\ell$. This particular linear combination of quantum numbers had never appeared as a result of solution of any Schrödinger equation [this situation can be compared with that for a pure Coulomb field where in the course of a detailed mathematical solution the combination $n_r+\ell+1$ (where n_r is the radial quantum number) naturally emerges in the expression for the bound-state energy, subsequently being designated as the principal quantum number n]. The puzzle was resolved by Demkov and Ostrovsky [9] when it was noticed that the Schrödinger equation for the potential (5) allows an exact analytical solution, but only for the energy $\epsilon=0$. This means that setting $\epsilon=0$ one can quantize the potential strength or, equivalently, the potential parameter Z, with the result

$$Z_N=\left[\frac{\alpha}{2b}N(N+1)\right]^{3/2}. \tag{7}$$

In the literature such a statement of the quantization problem is known as Sturmian. The specific quantum number N appears naturally in this treatment, as testified by analytical expression (7). For $Z=Z_N$ the zero-energy bound states exist on the border between the scattering continuum, $\epsilon>0$, and the bound states domain, $\epsilon<0$. Most remarkably, the bound states with the same sum $N\equiv n+\ell$ are *degenerate*. In other words, as Z increases, the energy levels with the same $n+\ell$ but different ℓ (and n) appear (at $\epsilon=0$) *simultaneously* at $Z=Z_N$; the ordering of appearance is described by the first part of the $(n+\ell,n)$ rule. This degeneracy explains aforementioned observation that $Z_{\text{emp}}^{(f)}\in Z_{\text{emp}}^{(d)}$. For $Z>Z_N$ the bound-state energies become negative and the *degeneracy is lifted*. The ordering of the levels within the given N group was established by perturbative analysis [9]. In this way the second part of the $(n+\ell,n)$ was reproduced. This completes the quantum *ab initio* (i.e., without using empirical information or fitting) derivation of the $(n+\ell,n)$ building-up rule [9]. The specific linear $(n+\ell)$ degeneracy intrinsic for the potential (5) was rediscovered 13 years later by Englert and Schwinger [15], albeit only in the semiclassical approximation.

Denote as Z_N^{rule} the lowest value of the ordering number Z at which the states with given N appear according to the $(n+\ell,n)$ rule. As seen from the Table I, these values are very close to the values $Z_{\text{emp}}^{(d)}$, $Z_{\text{emp}}^{(d)}$. This allows us to assign the labels N to the "empirical" values $Z_{\text{emp}}^{(\ell)}$, as shown in the table. Actually the values of Z_N^{rule} are by two units larger than $Z_{\text{emp}}^{(\ell)}$. This has clear interpretation since (i) the $(n+\ell,n)$ rule refers to filling orbitals in the ground state atoms and (ii) the orbitals are filled for larger Z than the appearance values $Z_{\text{emp}}^{(\ell)}$.

In order to test performance of formula (7), the ratio

$$K_N=\frac{Z_{\text{emp}}^{(\ell)}}{[N(N+1)]^{3/2}} \tag{8}$$

is depicted in Fig. 2 for different N. It is seen that K_N only weakly depends on N in agreement with Eq. (7), albeit the numerical value of the ratio proves to be somewhat different from this that follows from Eq. (7).

Another closely related issue is the $(n+\ell)$ grouping in atomic spectra. Klechkovskii [33] and Sternheimer [35] empirically noticed that the excited energy levels in the one-electron spectra of some atoms and singly charged positive ions form groups with the same value of the sum $n+\ell$. It is operative in some interval of orbital momenta, $0\leq\ell\leq\ell_0$, where the limiting value ℓ_0 depends on Z. The quantum defects are small for $\ell>\ell_0$: $\mu_\ell\ll 1$. Such a grouping is distinct from that of the slightly distorted Coulomb

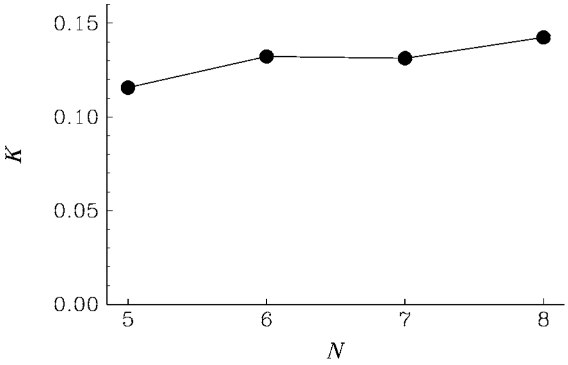

FIG. 2. The ratio K_N, Eq. (8), as a function of quantum number $N=n+\ell$ only weakly depends on N in agreement with formula (7); see text for details.

potential where levels with the same n and different ℓ form clusters. The $n+\ell$ groups do not overlap if the following condition is satisfied:

$$\max_{\ell}[\mu_{\ell-1}(Z)+\ell]-\min_{\ell}[\mu_{\ell}(Z)+\ell]<1. \qquad (9)$$

The grouping was discussed in Refs. [27,36]. It was related to the $(n+\ell,n)$ rule in Refs. [26,28], although probably a more detailed study is needed here.

This brief paper is limited to outlining specifics of the stepwise behavior of quantum defects. I omit many physically important and interesting issues, such as the shape of classical electron trajectories in the potential (5) with unusual focussing properties [9], its generalizations [37], peculiar behavior of s states [28], clustering of resonances in different partial waves [38], or symmetrical (group-theoretical) aspects of the problem [28,39]. I note only that the dynamical group of the atomic potential was constructed in Ref. [28]. An alternative construction was suggested by Kitagawara and Barut [40]. Although it contains some interesting observations, the ultimate goal was not achieved, as argued in Ref. [39].

In conclusion some general remarks are in order. The steplike behavior of $\mu_\ell(Z)$ found in Refs. [1,2] by numerical integration might be reproduced also by using a well-developed arsenal of the semiclassical approximation, such as comparison (or etalon) equation and uniform approximations intended to describe the situation with closely lying turning (or other singular) points [see, for instance, the book by Child [41]; for the potential (5) some correction terms in quantization condition were discussed also in Ref. [42]]. The development of this kind needs some calculations, not difficult in principle, but probably a bit cumbersome. It seems that such an exercise hardly would substantially improve our *qualitative* understanding of $\mu_\ell(Z)$ features (i.e., the stepwise Zel'dovich effect), as described above. If the most *quantitatively* accurate results are required, then the numerical integration is unavoidable, but the efforts are to be directed towards improving the interaction potential, for instance, by taking into account the core polarization at large r and going beyond the Thomas-Fermi approximation in the inner region of $U(r)$, for example, by effectively accounting for electron-electron correlations (for more discussion see Ref. [2]). In any case, when the "old" problems are reexamined one has to take a full account of earlier achievements.

As a summary, in the present study the stepwise behavior of quantum defects along the periodic table of the elements is analyzed and its specific feature is emphasized: the degeneracy of the step positions with respect to the electron orbital momentum ℓ, for d and f Rydberg series. The degeneracy is related to the $(n+\ell,n)$ rule of filling one-electron states in the periodic table.

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