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Quantum defects and atomic core radii

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The dynamical origin of the quantum defect Δ of the valence electron of alkali-metal atoms is attributed solely to an unspecified potential of the inner core, and it is demanded that Δ is stationary with respect to variation in the values of atomic core radius r^*. It is seen that this conjecture, when supplemented by a reasonable description of the core interaction, simultaneously produces numbers for r^* and Δ that help visualize the conceptual aspects of the problem. Corrections to the quantum-defect data due to core polarization are considered from a slightly different point of view. Problems in extending the present model for multivalent atoms are discussed.

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The many-body problem in physics is, in general, not exactly soluble and one such typical example is furnished by the atomic structure calculation. Thus, over the years, the N-electron problem has been discussed and treated within the framework of various approximation schemes [1]. While the general many-electron problem is still largely unsolved, the structure and spectra of alkali-metal atoms can be understood relatively simply because they are made of closed shells with one valence electron. The situation is similar to the hydrogen atom except that the potential on the valence electron is not purely Coulombic but is shielded by the core electrons resulting in the removal of l degeneracy. The effect of the inner screening is well taken care of by the so-called quantum-defect theory (QDT) [2]. Here the energy eigenspectrum is still described by a hydrogenic formula with the principal quantum number n being replaced by an effective quantum number n^* and the quantum defect Δ is written as

$$\Delta = n - n^* . \tag{1}$$

The quantity Δ is almost constant in a particular series (constant l and varying n) of terms and is obtained traditionally by fitting the experimental binding energy. However, application of the QDT to atoms and/or computation of the values for Δ without resorting to use of the experimental data is an interesting problem [3] to deal with. The present report is an effort in this direction.

The quantum defect for alkali-metal atoms can be explained by the use of the WKB approximation method [4] and for the ground state of a Z-electron atom, Δ is given by [5]

$$\Delta = \frac{1.33}{\pi} Z^{1/3} \int_0^{x^*} \left[\left[\frac{\chi(x)}{x} \right]^{1/2} - \left[\frac{1}{Zx} \right]^{1/2} \right] dx . \tag{2}$$

The upper limit x^* of the integral in (2) is related to the radius r^* of the core of closed shells by

$$x^* = \frac{r^*}{a}, \quad \text{with } a = 0.885\,34 Z^{-1/3} . \tag{3}$$

In writing (2) we have assumed that the potential field of the valence electron is proportional to r^{-1} only for $r > r^*$ and the unspecified potential inside the core is given by the Thomas-Fermi model of the atom. The Thomas-Fermi function $\chi(x)$, which satisfies the universal differential equation

$$\frac{d^2\chi(x)}{dx^2} = \frac{[\chi(x)]^{3/2}}{x^{1/2}} , \tag{4}$$

is subject to the boundary condition $\chi(0)=1$, together with a suitably chosen initial tangent inclination.

For a given value of the atomic core radius, the quantum defect Δ can be obtained from (2) by means of a single quadrature. Different rather arbitrary methods are adopted to fix the value of r^* from the experimentally measured internuclear distance between two ions in an ionic crystal. The most widely accepted method is due to Pauling [6]. However, we feel that, as with quantum defect, a purely theoretical approach in respect of this is also an equally involved problem with a host of connections in several areas of physics [7] and [8]. We, therefore, ask the following: Can one compute values for both r^* and Δ by some judicious exploitation of (2)? An answer to this question appears to call for a relatively closer look into the dynamics of the alkali-metal atom.

The valence electrons of alkali-metal atoms are s electrons and have a high probability to lie in the immediate vicinity of the nucleus. In the graphic language of Bohr, orbits of these electrons constitute the so-called penetrating orbits such that their wave functions and energy eigenvalues are significantly affected due to interactions with the core. One way of realizing this is to demand that Δ is a maximum with respect to variation in the core radius. We thus have

$$\frac{d\Delta}{dx^*} = 0 . \tag{5}$$

Equations (2) and (5) can be combined to write

$$\chi(x^*) = \frac{1}{Z} , \tag{6}$$

which tells us that computation of the numerical result for x^* involves only numerical solutions of the Thomas-

TABLE I. Core radii and quantum defects for alkali-metal atoms from ^{3}Li to ^{55}Cs. The numbers in parentheses are from Kostelecky and Nieto [10], Friedrich [2], and Ham [11].

Element	Core radius (a.u.) $\tilde{r}^*$	r^*	Quantum defect $\tilde{\Delta}$	Δ	$\delta\Delta$
Li	0.838	0.859	0.3564	0.3477 (0.4000)	0.0155
Na	1.719	1.831	1.3644	1.3816 (1.3500)	0.0138
K	2.078	2.147	2.0080	2.0228 (2.2296)	0.0466
Rb	2.518	2.524	3.0154	3.0346 (3.1952)	0.0551
Cs	2.785	2.794	3.7527	3.7888 (4.1307)	0.0700

Fermi equation with a sufficiently closed mesh. Appropriate numerical results for r^* and Δ calculated on the basis of (2) and (6) will be presented in due course. Meanwhile, we like to deal with a function

$$\tilde{\chi}(x)=\frac{1}{(1+\alpha x)^2}, \quad \alpha=0.53625 \tag{7}$$

and thereby construct closed-form analytical expressions for x^* and Δ. The function $\tilde{\chi}(x)$ was introduced by Tietz [9] as a fair approximation to the universal Thomas-Fermi function $\chi(x)$ for a neutral atom. From (2), (6), and (7) we get

$$\tilde{x}^*=\frac{1}{\alpha}[Z^{1/2}-1] \tag{8a}$$

and

$$\tilde{\Delta}=\frac{2.66}{\pi\alpha^{1/2}}Z^{1/3}\left[\tan^{-1}(\alpha\tilde{x}^*)^{1/2}-\left[\frac{\alpha\tilde{x}^*}{Z}\right]^{1/2}\right]. \tag{8b}$$

Results in (8a) and (8b) represent our desired analytical expressions. We have used a tilde over x^* and Δ only to indicate that these quantities refer to the approximate Thomas-Fermi function introduced in (7). Obviously, the exact values of core radii and quantum defects will be determined from (2) and (6) in conjunction with a delicate numerical solution of (4).

In Table I, we present our results for quantum defects of the alkali-metal series for both r^* and $\tilde{r}^*$. Appropriate results quoted by earlier workers [2], [10], and [11] are given in braces. The two sets of data, namely those taken from the standard literature and new ones, are expected to provide a useful check on the ansatz of our theoretical model for the quantum-defect method. Looking closely into our numbers we see that $r^*>\tilde{r}^*$ for all Z and except for ^{3}Li, an increase in the value of core radius tends to produce a larger quantum defect. Further, the value of Δ for ^{3}Li is in variance with that of Kostelecky and Nieto [10] by 13%. The reason for this may be attributed to the inadequacy of the Thomas-Fermi model for a small atom like lithium.

Interestingly, our result for ^{11}Na does not differ appreciably from that in Ref. [10]. But as we go to higher atoms, our Δ values again start deviating from the corresponding quantum defects obtained from experimental term energies. However, the deviation in question always remains less than 9%. Note that the reference value for ^{19}K is taken from a relatively recent literature [2] while the source for the corresponding results of ^{37}Rb and ^{55}Cs is the classic work of Ham [11] albeit quite antique. We feel that relativistic effects may be responsible for the discrepancy observed in high Z atoms.

From the discussion presented above, it is clear that despite inadequate treatment of the interaction in the core region, the present model yields results for Δ that are not off the mark with regard to numerical accuracy. An added realism to our theory is that it simultaneously gives an estimate for the ionic core radii. Significantly, these results were obtained by a purely theoretical approach in that we did not require the use of experimental information to compute our results.

One of the tasks in developing a theory for the quantum-defect method consists in confronting its consequences with experimental data. This will involve consideration of polarization effects in the atomic potential $V(r)$. In the presence of the polarization potential $V_p(r)$, the atomic potential is not purely Coulombic in some region beyond the ionic core. Thus, it is rather tricky to deal with the effects of $V_p(r)$ within the framework of QDT. On the other hand, such effects may be quite significant. For example, the correct description of the core polarization by the field of valence electron of alkalis bears considerably on the photospectroscopy of these atoms [12].

We note that there exists a direct procedure [11] to approximate the change in quantum defect induced by $V_p(r)$. This change is given by

$$\pi\delta\Delta=\int_{r_1}^{r_2}\left[-\frac{1}{n^2}-V(r)-\frac{(l+1/2)^2}{r^2}\right]^{1/2}dr-\int_{r_1}^{r_2'}\left[-\frac{1}{n^2}+\frac{2}{r}-\frac{(l+1/2)^2}{r^2}\right]^{1/2}dr\ . \tag{9}$$

The expression in (9) is based on the WKB method with Langer modification. Here l stands for the orbital angular momentum and

$$V(r)=-\frac{2}{r}+V_p(r)\ . \tag{10}$$

While the lower limit r_i of the integral in (9) may conveniently be taken near the core radius, the quantities r_2 and r_2' refer to appropriate outer turning points.

To describe the motion of the valence electron in the alkali-metal atoms, Marinescu, Sadeghpour, and Dalgarno [13] have recently derived a parametric model potential of the form

$$V_l(r)=-\frac{Z_l(r)}{r}+V_p(r) \tag{11}$$

with

$$Z_l(r)=1+(Z-1)e^{-a_1 r}-r(a_3+a_4 r)e^{-a_2 r}\ , \tag{12}$$

$$V_p(r)=-\frac{\alpha_c}{2r^4}(1-e^{(r/r_c)^6})\ . \tag{13}$$

Here r_c and α_c stand for the cutoff radius and the core polarizability, respectively.

For a fixed value of α_c, the parameters in (11) were determined from a nonlinear fit to alkali-metal atom Rydberg energies. The potential in (11) exhibits appreciable angular momentum dependence for $l \leq 3$. This may lead to new significance for the dependence of Δ on l. However, we note that one of the features of the result in (11) is that it exactly reproduces the experimental polarizabilities for each of the atoms in the alkali series. In view of this we have used the expression for $V_p(r)$ by Marinescu, Sadeghpour, and Dalgarno [13] to compute the change in quantum defect ($\delta\Delta$) due to core polarization. The value of r_i in (9) was fixed exactly at the core radius of the atom under consideration. The upper limits were however, determined by the prescription given above.

Values of $\delta\Delta$ for the valence electron in the s state are given in column six of Table I. These results should be subtracted from the corresponding data obtained by the omission of long-range polarization. Our results for $\delta\Delta$ are highly augmented compared to those given in Ham [11]. The difference between our numbers and those of Ham are presumably due to different handling of the polarization effect. Interestingly, the present choice for $V_p(r)$ could also produce the results of Ref. [11] provided we had agreed to work with values for r_i quoted there.

In this work we presented a recipe to compute values for ionic core radii and quantum defects for monovalent atoms without making use of experimental results. An extension of the idea developed to deal with multivalent atoms would be quite interesting. But we feel that this is a more involved problem. Even for the traditional quantum-defect method, the task is not as simple as with monovalent atoms. In the presence of more than one valence electron, the term values of the neutral atom do not follow the Ritz law with the accuracy found in the alkali-metal atoms. In the case of alkali-metal atoms, the slow variation of quantum defects as a function of energy can be understood in a relatively simple manner by postulating the existence of an inert core. But rapid variations occur in systems like the alkaline earth metals and other atomic systems in which the core can be excited rather easily. In such cases one is required to perform close-coupling calculations [14].

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