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Asymptotic description of the Rydberg states with L > 0 in a two-electron atom

I.A. Ivanov[a]

Institute of Spectroscopy, Academy of Sciences of Russia, Troitsk 142092, Russia

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Abstract. The energies of the levels belonging to a Rydberg series $1snp$ ^{1,3}P in a two electron atom have been determined by means of the quantum defect theory for a two-electron atom with nuclear charge Z considered as a parameter. Comparison with configuration interaction calculations suggests that the analytic quantum defect expression for the energy levels may be in fact asymptotically exact as $Z \to 1$, providing an analytic description of the disappearance of the Rydberg states with $L > 0$ when Z approaches the value of 1.

PACS. 31.10.+z Theory of electronic structure, electronic transitions, and chemical binding – 31.15.-p Calculations and mathematical techniques in atomic and molecular physics (excluding electron correlation calculations)

1 Introduction

Properties of the eigenvalues $E_n(Z)$ of a two-electron atomic system, *i.e.*, quantum mechanical system described by the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \qquad (1)$$

as functions of the nuclear charge Z is a subject which received considerable attention. The reason behind is clear, the system is simple enough for $E_n(Z)$'s to be accurately computed numerically. Studying $E_n(Z)$'s one may hope to gain some understanding of exact solutions of a very complicated quantum mechanical problem.

The ground state eigenvalue, $E_0(Z)$, of this Hamiltonian and its properties as a function of the parameter Z is the best studied one. It was rigorously proved by Kato [1] that $E_0(Z)$ is an analytic function of Z.

It is clear that for sufficiently small positive Z-values system described by (1) does not have bound states. All bound states must disappear when moving from large to small Z-values. It could be expected that this disappearance is reflected in some properties of $E_0(Z)$, *e.g.*, $E_0(Z)$ could have a singularity at the point $Z = Z_{\rm crit}$ where bound state disappears. The position of this singularity can in principle be located by studying numerically coefficients of the perturbation series in powers of $1/Z$. These coefficients up to the terms of large order have been computed in a number of works [2–4]. They have been analyzed using different techniques [5–8] such as the ratio test or Pade analysis.

In the paper of Baker *et al.* [9], the authors performed high-precision calculations of the first 400 coefficients of the perturbation series for the ground state of the He-like ions. Upon analysis of the asymptotic behavior of these coefficients, they obtained the value $Z_{\rm crit} \approx 0.911029$ as the position of the singular point of $E_0(Z)$ for the ground state. These authors also resolved a long-standing controversy by proving that it is exactly at the singular point $Z = Z_{\rm crit}$ that the ground state ceases to be a bound state. Their value of the critical point has been subsequently refined [10–12].

Other properties of $E(Z)$ for the ground state of a two-electron system have been studied, such as possible existence of other singular points in the complex Z-plane [5,13]. In [14,15] a dispersion relation for $E(Z)$ has been proposed and verified by means of a complex rotation calculation.

As far as excited states and properties of their energies as functions of Z are concerned, much less is known. It was conjectured that all the states belonging to a given Rydberg series cease to be bound states for $Z = 1$ [9]. In the paper [16] we proposed a simple model based on the quantum defect theory (QDT), which seems to provide accurate description of the energies of the Rydberg series $1sns$ ^{3}S for Z-values in the neighborhood of 1. The overall agreement between values obtained in framework of QDT and computed ones, allowed to conjecture that QDT might provide in fact leading term of some still unknown asymptotic expansion, that $E_n(Z)$'s for this series possess.

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[a] e-mail: `iivanov@pub.iams.sinica.edu.tw`

In the present paper we generalize the treatment given in [16] for the case of the states with $L > 0$ (L-total angular momentum). Taking as an example $1snp\ ^{1,3}\mathrm{P}$ Rydberg series, we show that QDT using only two parameters provides quite accurate description of Z-behavior of the low-lying members of Rydberg series.

The case of the states with $L > 0$ is perhaps more interesting then that of S-states since it gives more clear evidence that the QDT description of the system (1) is adequate when Z assumes values in the neighborhood of 1. For $L > 0$-states QDT, as we shall see, predicts variation of quantum defects along the series for a given Z in complete agreement with the results of the numerical calculation.

2 Theory

As in [16] we consider a very simple model of a Rydberg state of a two-electron system with nuclear charge Z, *viz.*, we consider a particle moving in a combination of Coulomb and short-range fields. The corresponding model Hamiltonian reads

$$\hat{H}_{\mathrm{mod}} = -\frac{1}{2}\nabla^2_{\boldsymbol{R}} - \frac{z}{R} + V_{\mathrm{sr}}(R), \qquad (2)$$

where $z = Z - 1$ and $V_{\mathrm{sr}}(R)$ is a short-range potential vanishing outside some sphere.

For simplicity we consider below only P-states of a two-electron system, modification of the derivation given below for higher partial waves being straightforward.

Essential steps of the derivation below are the same as for S-states considered in [16]. We reproduce them in details for the sake of completeness.

In framework of the QDT formalism the equation which defines positions of the poles of T-matrix for this model system reads for p-wave [17]

$$M\left(k^2, z\right) = -\frac{2}{9} z\tau(k)\left(k^2 + z^2\right), \qquad (3)$$

where $M(k^2, z)$ can be found if solution of the Schrödinger equation in the inner region where short-range interaction is present is known, the function $\tau(k)$ can be expressed as

$$\tau(k) = \ln(k) + \frac{1}{2}\left[\Psi(\mathrm{i}\eta) + \Psi(-\mathrm{i}\eta)\right] + \frac{\mathrm{i}\pi}{\mathrm{e}^{2\pi\eta} - 1}, \qquad (4)$$

where $\Psi(x)$ is the digamma function [18] and $\eta = -z/k$.

QDT approach to the description of the Rydberg states relies on the fact that the function $M(k^2)$ is an analytic function of k^2 [17].

This is a consequence of a general statement about the analicity of solutions of a differential equation as functions of a given parameter. From the same general statement it follows that the function $M(k^2, z)$ is also an analytic function of z.

Introducing variables $k = i\kappa$ and $u = z/\kappa$ and using known properties of the digamma function [18], equation (3) can be rewritten as

$$\frac{M(k^2, z)}{z(k^2 + z^2)} = -\frac{2}{9}\left(\ln z - \ln u + \pi\cot\pi u + \frac{1}{2u} + \Psi(u)\right), \qquad (5)$$

where $M(k^2, z)$ is an analytic function of both arguments. Introducing new function $\beta(k^2, z) = -9M(k^2, z)/2$ (analytic in both arguments), equation (5) can be rewritten as

$$\frac{\beta(k^2, z)}{z^3\left(1 - \frac{1}{u^2}\right)} - \ln z = -\ln u + \pi\cot\pi u + \frac{1}{2u} + \Psi(u). \qquad (6)$$

We are interested in the solutions of this equation for which $u \to C$, where C-positive constant, when $z \to 0$. It is easy to see that equation (6) has such solutions of the form $u = n + \delta(z)$, and hence $\kappa = z/(n + \delta)$, where $\delta \to 0$ when $z \to 0$. That gives for the energy the well-known Rydberg formula, δ being the quantum defect. Retaining only the two leading terms in z it is easy to show that $\delta(z)$ is given by the following expression

$$\delta = \frac{z^3\left(1 - \frac{1}{n^2}\right)}{\beta(z)}, \qquad (7)$$

where it is understood that it is legitimate to retain only two leading terms of the z expansion of the function $\beta(z)$

$$\beta(z) \approx \beta_0 + \beta_1 z, \qquad (8)$$

where β_0, β_1 are some numbers independent of energy (account of their energy dependence would introduce terms of higher orders in z).

Recalling that parameter z in our model is $z = Z - 1$, where Z is the charge of the nucleus, we arrive at the following tentative expression for the energy levels of the Rydberg series $1snp$ for $Z \to 1$

$$E(Z) = -\frac{Z^2}{2} - \frac{(Z - 1)^2}{2(n + \delta)^2}, \qquad (9)$$

with $n = 2, 3...$ and

$$\delta = \frac{(Z - 1)^3\left(1 - \frac{1}{n^2}\right)}{\beta(Z)}, \qquad (10)$$

where function $\beta(Z)$ is analytic in the neighborhood of $Z = 1$ and has an expansion

$$\beta(Z) = \beta_0 + \beta_1(Z - 1) + ..., \qquad (11)$$

where both β_0 and β_1 do not depend on n.

As we shall see equations (9, 10) do seem to describe behavior of level energies of $1snp$ series of a two electron system for the charge of the nucleus Z close enough to 1. A feature of the equation (10) not present in the case of S-states is dependence of the quantum defect on the quantum number n through the factor $1 - 1/n^2$. If shown to be correct, this dependence is a good demonstration of the overall validity of the approach. Indeed, this factor has a pure Coulomb origin (it is in fact related to the normalization of the Coulomb radial wave functions).

The numerical results presented in the next section seem to confirm this n dependence of the quantum defect for the $1snp$ series.

3 Numerical results

Numerical calculation of the energies of $1snp$ series does not pose any serious problems. As in the case of the of $1sns$ ^{3}S series considered in [16] the numerical evidence suggests that for Z close to 1, these states exhibit simple hydrogenlike properties (the circumstance which actually makes the present approach possible). Therefore straightforward calculation using simple Slater type basis which is sufficiently large, gives energies accurate enough to verify formulas (9, 10). More specifically, we used the split-exponential basis set constructed of the orbitals

$$\phi_{ilm}(\boldsymbol{r}) = r^i \left(a\mathrm{e}^{-Zr} + \delta_1^l b\mathrm{e}^{-(Z-1)r} \right) Y_{lm}(\hat{\boldsymbol{r}}). \tag{12}$$

The radial parts were chosen in this particular form so as to describe adequately the series $1snp$ (hence the second term $\delta_1^l b\mathrm{e}^{-(Z-1)r}$ in the radial function, which is present only for $l = 1$).

Proper combinations of the products of $\phi_{ilm}(\boldsymbol{r})$ coupled and symmetrized to correspond to a given symmetry of the state (either ^{1}P$^\mathrm{o}$ or ^{3}P$^\mathrm{o}$) have been formed. Finding the eigenvalues amounted to the solution of the generalized eigenvalue problem

$$\det\left(H_{ij} - ER_{ij}\right) = 0, \tag{13}$$

where H_{ij} and R_{ij} are Hamiltonian and overlap matrices respectively.

Both for singlet and triplet P-states the parameters i and l of the orbitals (12) were chosen as follows: all orbitals with $l < 9$ which by symmetry considerations could be coupled to produce P-states were used. For each l the parameter i in equation (12) assumed values $i = l + 1, ..., l + 10$. This resulted in overall dimension $N = 850$ of the eigenvalue problem (13). The energy levels for the first few members of Rydberg series for singlet and triplet P-states are shown in Tables 1–2 (second column). A few words should be said about possible accuracy of these values (the issue which is very important in the present problem where we are interested in numerically small effects). We performed a few separate diagonalizations for larger basis set ($N = 1100$ both for singlet and triplet P-states). The results for the low-lying members of the Rydberg series were stable within first eight digits. Thus the accuracy of the results reported in Tables 1–2 must be on the order of 10^{-8} a.u. This, as we shall see, will be sufficient to detect effects which are predicted by the formulas (9, 10).

Table 1. Level energies, quantum defects, and $\beta(Z)$-values for $1snp$ ^{1}P states.

Z	E (a.u.)	δ	$\beta(Z)$	δ (Eq. (10))
1.04	–0.54099998	0.00009101	0.52743653	0.00009108
	–0.54088888	0.00010782	0.52763661	0.00010795
	–0.54085000	0.00011200	0.53569178	0.00011385
	–0.54083200	0.00011719	0.52426955	0.00011658
	–0.54082222	0.00012450	0.49976131	0.00011807
1.05	–0.55156245	0.00016162	0.58006582	0.00016164
	–0.55138887	0.00019322	0.57505371	0.00019157
	–0.55132812	0.00019969	0.58683255	0.00020205
	–0.55130000	0.00020501	0.58532985	0.00020690
	–0.55128472	0.00020929	0.58066426	0.00020953
	–0.55127551	0.00020637	0.59334930	0.00021112
	–0.55126953	0.00021505	0.57218149	0.00021215
1.06	–0.56224989	0.00025227	0.64216925	0.00025592
	–0.56199996	0.00030005	0.63990400	0.00030332
	–0.56191248	0.00031648	0.63984681	0.00031991
	–0.56187199	0.00032295	0.64208488	0.00032758
	–0.56184999	0.00033003	0.63631113	0.00033175
	–0.56183673	0.00033291	0.63557766	0.00033427
	–0.56182812	0.00032713	0.64996861	0.00033590
1.08	–0.58399962	0.00047604	0.80664658	0.00051962
	–0.58355542	0.00056951	0.79913330	0.00061585
	–0.58339994	0.00060214	0.79716219	0.00064953
	–0.58332797	0.00061730	0.79623937	0.00066512
	–0.58328887	0.00062072	0.80193441	0.00067358
	–0.58326529	0.00064442	0.77830184	0.00067869
	–0.58324999	0.00064008	0.78740549	0.00068200
1.09	–0.59506190	0.00059730	0.91536225	0.00069034
	–0.59449978	0.00071893	0.90134575	0.00081818
	–0.59430303	0.00076111	0.89795303	0.00086293
	–0.59421195	0.00078105	0.89602783	0.00088364
	–0.59416247	0.00079216	0.89470917	0.00089489
	–0.59413263	0.00079883	0.89396262	0.00090167
	–0.59411327	0.00079972	0.89732035	0.00090607
1.10	–0.60624910	0.00071638	1.04692350	0.00088757
	–0.60555523	0.00086777	1.02434126	0.00105194
	–0.60531236	0.00092064	1.01831584	0.00110947
	–0.60519992	0.00094527	1.01558501	0.00113609
	–0.60513884	0.00095687	1.01604543	0.00115056
	–0.60510201	0.00096459	1.01555324	0.00115928
	–0.60507811	0.00096786	1.01706802	0.00116494
1.11	–0.61756125	0.00082749	1.20636121	0.00111164
	–0.61672177	0.00101094	1.17030734	0.00131750
	–0.61642792	0.00107468	1.16110049	0.00138955
	–0.61629189	0.00110367	1.15773621	0.00142290
	–0.61621799	0.00111879	1.15662926	0.00144101
	–0.61617343	0.00113098	1.15284156	0.00145193
	–0.61614450	0.00113214	1.15727899	0.00145902
1.13	–0.64056037	0.00100791	1.63481967	0.00164119
	–0.63938810	0.00126019	1.54967808	0.00194511
	–0.63897777	0.00134771	1.52828642	0.00205148
	–0.63878781	0.00138815	1.51937269	0.00210072
	–0.63868461	0.00140925	1.51567611	0.00212746
	–0.63862238	0.00142276	1.51266879	0.00214359
	–0.63858198	0.00142883	1.51359381	0.00215406

4 Discussion

The third column of Tables 1–2 contains results for the quantum defects. The quantum defects were computed using formula (9) as a definition. The overall n-dependence of the quantum defects along the Rydberg series for a fixed Z is obvious. The extent to which this n-dependence is reproduced by the factor $1 - 1/n^2$ following from the QDT analysis can be judged using the data from the

Table 2. Level energies, quantum defects, and $\beta(Z)$-values for $1snp$ ^{3}P states.

Z	E (a.u.)	δ	$\beta(Z)$	δ (Eq. (10))
1.04	–0.54100003	–0.00013349	–0.35958656	–0.00013289
	–0.54088890	–0.00015374	–0.37003748	–0.00015750
	–0.54085000	–0.00017599	–0.34093159	–0.00016611
	–0.54083200	–0.00017187	–0.35748753	–0.00017010
	–0.54082222	–0.00017249	–0.36072410	–0.00017227
	–0.54081633	–0.00016493	–0.38012033	–0.00017357
1.05	–0.55156258	–0.00024859	–0.37712147	–0.00025134
	–0.55138892	–0.00029384	–0.37813882	–0.00029789
	–0.55132814	–0.00030972	–0.37836103	–0.00031418
	–0.55130001	–0.00031497	–0.38098838	–0.00032172
	–0.55128473	–0.00032637	–0.37235814	–0.00032581
	–0.55127551	–0.00032870	–0.37252862	–0.00032828
1.06	–0.56225019	–0.00041254	–0.39269016	–0.00042100
	–0.56200006	–0.00048738	–0.39394215	–0.00049896
	–0.56191253	–0.00051368	–0.39421521	–0.00052625
	–0.56187202	–0.00052422	–0.39555678	–0.00053888
	–0.56185001	–0.00053393	–0.39331093	–0.00054574
	–0.56183674	–0.00053408	–0.39618171	–0.00054987
	–0.56182813	–0.00054039	–0.39346607	–0.00055256
1.08	–0.58400074	–0.00092036	–0.41722609	–0.00094025
	–0.58355581	–0.00108255	–0.42040485	–0.00111438
	–0.58340011	–0.00113951	–0.42123262	–0.00117532
	–0.58332806	–0.00116561	–0.42168554	–0.00120353
	–0.58328892	–0.00118128	–0.42138988	–0.00121885
	–0.58326533	–0.00118828	–0.42208312	–0.00122809
	–0.58325001	–0.00119173	–0.42291329	–0.00123408
1.09	–0.59506380	–0.00128065	–0.42693315	–0.00130117
	–0.59450045	–0.00150320	–0.43107957	–0.00154212
	–0.59430333	–0.00158089	–0.43231201	–0.00162646
	–0.59421210	–0.00161804	–0.43252292	–0.00166549
	–0.59416256	–0.00163666	–0.43304567	–0.00168670
	–0.59413269	–0.00164831	–0.43324615	–0.00169948
	–0.59411331	–0.00165874	–0.43262234	–0.00170778
1.10	–0.60625216	–0.00172177	–0.43559722	–0.00173611
	–0.60555630	–0.00201580	–0.44096163	–0.00205761
	–0.60531283	–0.00211927	–0.44236835	–0.00217014
	–0.60520017	–0.00216734	–0.44293928	–0.00222222
	–0.60513899	–0.00219360	–0.44320924	–0.00225051
	–0.60510211	–0.00220732	–0.44379330	–0.00226757
	–0.60507817	–0.00222115	–0.44318166	–0.00227865
1.11	–0.61756591	–0.00224942	–0.44378057	–0.00224932
	–0.61672340	–0.00262688	–0.45038707	–0.00266587
	–0.61642865	–0.00275919	–0.45223837	–0.00281166
	–0.61629227	–0.00282096	–0.45295251	–0.00287913
	–0.61621822	–0.00285495	–0.45325716	–0.00291579
	–0.61617357	–0.00287581	–0.45338143	–0.00293789
	–0.61614460	–0.00289060	–0.45326371	–0.00295224
1.13	–0.64057008	–0.00357877	–0.46042308	–0.00352535
	–0.63939150	–0.00415767	–0.46970794	–0.00417820
	–0.63897928	–0.00436039	–0.47236353	–0.00440669
	–0.63878860	–0.00445484	–0.47344482	–0.00451245
	–0.63868508	–0.00450763	–0.47385754	–0.00456990
	–0.63862267	–0.00454024	–0.47402016	–0.00460454
	–0.63858218	–0.00456017	–0.47425258	–0.00462703

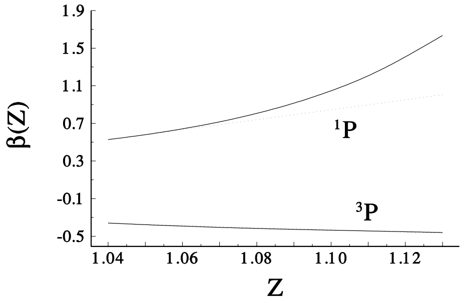

Fig. 1. Function $\beta(Z)$ for ^{1}P^o and ^{3}P^o states, computed according to equation (7) (solid lines), and linear approximations (14) (dashed lines).

fourth column of Tables 1–2. This column contains numerical values of $\beta(Z)$ computed using equation (7) as a definition. As one can see, for a given Z sufficiently close to 1, $\beta(Z)$ remains pretty much constant for the low-lying members of the singlet and triplet $1snp$ Rydberg series. This is in complete agreement with the n-dependence for the quantum defects predicted by the formula (7). One could repeat the observation we made above that this agreement is a direct evidence of Coulombic nature of these levels, since the factor $1 - 1/n^2$ which seems to provide quite adequate description of quantum defects behavior with n, is of purely Coulombic origin.

The second aspect of the problem is the behavior of the quantum defects with Z. Figure 1 plots the function $\beta(Z)$ defined by equation (7) for singlet and triplet states. When computing the values of the function $\beta(Z)$ we used corresponding energies for the lowest member of the series $1s2p$ ^{1,3}P. For larger Z-values, the β-values for different n are different, but, anyway, our approach is expected to be valid for Z sufficiently close to 1. Figure 1 shows that for triplets $\beta(Z)$ is pretty much a linear function of Z for Z as large as $Z \approx 1.15$. For singlets the domain where $\beta(Z)$ could be approximated by a linear function is more narrow ($Z < 1.08$). The dashed straight lines on the figures represent linear approximations to $\beta(Z)$ both for singlet and triplet states. The coefficients of these approximations were determined by means of the numerical analysis of the data in the fourth column of Tables 1–2 and were found to be

$$\begin{aligned} \beta(Z) &\approx 0.315 + 5.3(Z-1) && \text{singlet states} \\ \beta(Z) &\approx -0.314 - 1.18(Z-1) && \text{triplet states.} \end{aligned} \qquad (14)$$

The functions $\beta(Z)$ for the triplet and singlet states behave quite differently. The reason of this difference cannot, of course, be accounted for by means of the present not truly *ab initio* approach.

With these linear approximations for $\beta(Z)$ the quantum defects were computed by means of the equation (7). The results are presented in Tables 1–2 (fifth column). The values predicted by the formula (7) and the "true", numerically calculated quantum defect values, presented in the third column of Tables 1–2 agree quite well, showing strong indication that present approach captures at least leading Z and n behavior of the quantum defects. Indeed,

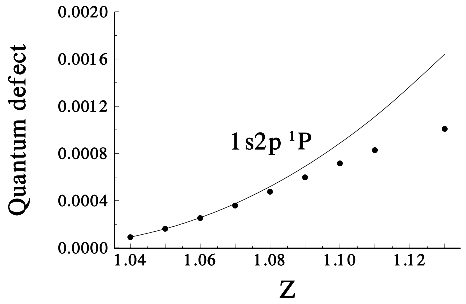

Fig. 2. Quantum defects: given by equations (10, 14) (solid line) and numerically computed (solid circles) for $1s2p\ ^1\mathrm{P}$ state.

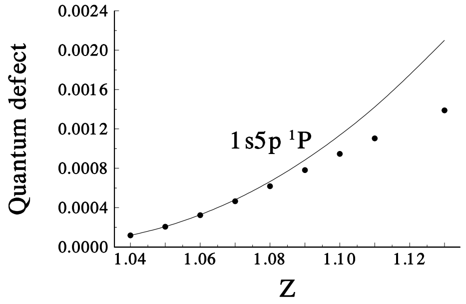

Fig. 3. Quantum defects: given by equations (10, 14) (solid line) and numerically computed (solid circles) for $1s5p\ ^1\mathrm{P}$ state.

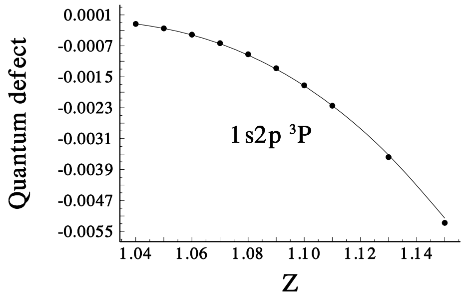

Fig. 4. Quantum defects: given by equations (10, 14) (solid line) and numerically computed (solid circles) for $1s2p\ ^3\mathrm{P}$ state.

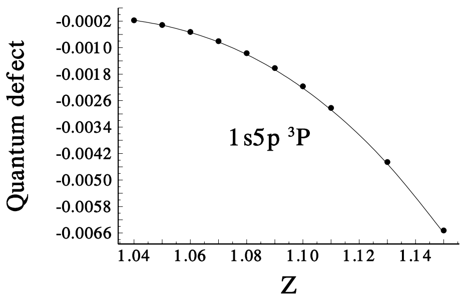

Fig. 5. Quantum defects: given by equations (10, 14) (solid line) and numerically computed (solid circles) for $1s5p\ ^3\mathrm{P}$ state.

the predicted results for the quantum defects presented for all Z and n were obtained using only two parameters. To illustrate the point more clearly we present in Figures 2–5 numerically computed and predicted (using the formulas (7, 14)) quantum defects for levels $1s2p\ ^1\mathrm{P}$ (Fig. 2), $1s5p\ ^1\mathrm{P}$ (Fig. 3), $1s2p\ ^3\mathrm{P}$ (Fig. 4) and $1s5p\ ^3\mathrm{P}$ (Fig. 5).

To our opinion, the observed agreement of predicted values and the "true" ones for a given value of Z and for different n along the Rydberg series gives enough evidence that the present QDT approach is valid. As we discussed above, the origin of the factor $1 - 1/n^2$ is purely Coulombic. This factor in the formula (7) seems to reproduce reasonably well n-dependence of the quantum defects. This favorably distinguishes $L > 0$-states from the S-states, where arguments similar to those leading to the formulas (9, 10) produce quantum defect independent of n [16] for different members of the Rydberg series. In this respect the case of P-states is perhaps more interesting as it demonstrates more clearly that the present approach does work.

From the other hand the agreement of the Z dependencies demonstrated in Tables 1–2 may not be so conclusive since virtually any function in a narrow domain can be represented as a linear function. It might be desirable to obtain numerical values for the quantum defects for Z even closer to 1 (*e.g.* $Z \approx 1.01$) to verify formulas (14). We did not succeed in performing reliable calculation for such Z due to the problems of numerical character, the levels becoming more and more densely spaced when Z approaches 1.

5 Conclusion

Similar procedure, with only minor modifications, could be applied as well for the states with larger momenta, though numerical verification of the formulas analogous to (9, 10) would be much more difficult task (it is easy to see that in the leading order the present approach produces $(Z-1)^{2l+1}$ dependence for the quantum defects).

We believe, however, that triplet S-states considered in [16] and P-states presented in this paper give enough evidence that the present approach captures essential features of energy levels behavior near $Z = 1$. This circumstance, we believe, is interesting by itself, since there are no many examples of analytic results for a two-electron system, especially in the region of $Z \approx 1$, where role of correlations, for example for the bound $^1\mathrm{S}^\mathrm{e}$ state is predominant. A natural question is why is it possible to get such a simple analytic description in a seemingly untractable problem. Numerical calculation shows that the Rydberg states considered in the present paper are becoming progressively more and more "hydrogenlike" when $Z \to 1$. This provides ground for the possibility of the description of these states by means of QDT.

An interesting question is the mathematical status of the formulas (9, 10). Basing on the numerical evidence, one might argue that this formulas provide asymptotic description of level energies behavior when $Z \to 1$. QDT approach presented in the paper is a single channel one, all other closed channels being neglected. The apparent success of the single channel approach could be explained if the contribution due to these neglected channels becomes numerically small when $Z \to 1$ comparing to the contribution given by equations (9, 10). Of course, it by no means signifies that the formulas (9, 10) can provide an insight into analytic character of a possible singularity of $E_n(Z)$'s at $Z = 1$. Contributions of the neglected channels, though numerically small, might well introduce additional terms singular when $Z \to 1$.

Another question is for what value of Z the levels belonging to a Rydberg series disappear. It seems probable (though has not been proved rigorously) [9] that all these levels cease to be bound states at $Z = 1$ precisely. Our formulas (9, 10) and their agreement with the results of numerical calculation support this view, though, of course, one cannot exclude the possibility that at Z much closer to 1 something dramatic may happen.

Mathematically rigorous description of the behavior of the energies in vicinity of $Z = 1$ is an extremely difficult task and the present elementary approach can by no means pretend to give such a complete and rigorous description. However, agreement of the numerical data and expressions offered by QDT approach suggests that QDT captures some essential features of the phenomena, possibly giving leading terms of some asymptotic expansions.

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