

**Highly excited Rydberg states of a rubidium atom: Theory versus experiments**M. Pawlak,<sup>1,2,\*</sup> N. Moiseyev,<sup>1,3</sup> and H. R. Sadeghpour<sup>4</sup><sup>1</sup>*Schulich Faculty of Chemistry, Technion–Israel Institute of Technology, Haifa 32000, Israel*<sup>2</sup>*Faculty of Chemistry, Nicolaus Copernicus University, Gagarina 7, 87-100 Torun, Poland*<sup>3</sup>*Faculty of Physics, Technion–Israel Institute of Technology, Haifa 32000, Israel*<sup>4</sup>*ITAMP, Harvard-Smithsonian Center For Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138, USA*

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There has been increasing interest in the energy spectrum of highly excited Rydberg states. The energy spectra of the  $s$ ,  $p$ , and  $d$  highly excited Rydberg states of a rubidium atom have been measured by different groups. However, there is a discrepancy between the reported data concerning the energy levels of highly excited  $s$  and  $d$  states of Rb. We address this issue by performing accurate calculations of  $\text{Rb}(ns, np, nd)$  energy levels using the parametric one-electron valence potential [Marinescu, Sadeghpour, and Dalgarno, *Phys. Rev. A* **49**, 982 (1994)] with spin-orbit coupling. We compare results with reference data from the National Institute of Standards and Technology and from available experiments. This enables us to recommend energy levels of highly excited Rydberg states of Rb that can be used as reference values.

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**I. INTRODUCTION AND MOTIVATION**

The rapid development of advanced experimental techniques has enabled increasingly accurate measurements of highly excited Rydberg states [1–9]. The detailed experimental data require better theoretical models in order to verify the results. Some spectroscopic parameters may be calculated, e.g., by applying the semiclassical approach [10,11], the numerical Coulomb approximation [12], or single-electron model potentials [13–15]. Therefore, the parallel development of theory and experiment is essential. Rydberg atoms continue to be a subject of numerous investigations due to their exaggerated properties, forming exotic Rydberg molecules, long-range dipolar interactions, a Rydberg blockade, and Rydberg optics [1–8,16–27].

In this work, we investigate highly excited  $s$ ,  $p$ , and  $d$  Rydberg states of a rubidium atom with principal quantum numbers ranging from  $n = 30$  to 60. The many-body problem can be reduced to the problem of one electron in the field of a frozen core, whose interaction with the valence electron is represented by a modified Coulomb potential. Our main goal is to find out how accurately the atomic energies of Rydberg states can be obtained based on the model potential reported by Marinescu, Sadeghpour, and Dalgarno [13] in comparison with available experimental data. This potential is the six-parametric single-electron model potential describing the motion of the valence electron in the presence of an alkali-metal ionic core. It was initially developed to calculate the dynamic multipole polarizabilities at imaginary frequencies and van der Waals interactions of alkali-metal atoms [13]. Moreover, the spin-orbit coupling effect is explicitly included. The method of our calculations is variational. It involves a basis set consisting of Slater-type functions. We use Hartree atomic units and we assume  $1 \text{ a.u.} = 219474.6313708 \text{ cm}^{-1}$  [28].

The energy levels for one electron in a modified Coulomb potential are given by the Rydberg formula [29] (in a.u.),

$$E_n = -\frac{Z^2}{2(n^*)^2} = -\frac{Z^2}{2(n-\delta)^2}, \quad (1)$$

where  $n^*$  is the effective principal quantum number and  $Z = 1$  for a neutral atom. The correction,  $\delta$ , to the principal quantum number,  $n$ , is known as the quantum defect. The energies (1) are with respect to a zero value for the (core)<sup>1</sup> $S_0$  level [29].

**II. VARIATIONAL PRINCIPLE FOR EXCITED STATES**

The valence electron in the field of an alkali-metal core can be represented by the following Hamiltonian (in a.u.):

$$\hat{H} = -\frac{1}{2}\Delta + V_l(r) + V_{LS}(r), \quad (2)$$

where  $V_l(r)$  is a model potential developed by Marinescu *et al.* [13] given by

$$V_l(r) = -\frac{Z_l(r)}{r} + V_{\text{pol}}. \quad (3)$$

The radial charge  $Z_l(r)$  is in the form

$$Z_l(r) = 1 + (\mathcal{Z} - 1)e^{-a_1 r} - r(a_3 + a_4 r)e^{-a_2 r}, \quad (4)$$

where  $\mathcal{Z}$  is the nuclear charge of atom. The polarization potential  $V_{\text{pol}}$  in (3) describes the core polarization:

$$V_{\text{pol}} = -\frac{\alpha_c}{2r^4}(1 - e^{-(r/r_c)^6}), \quad (5)$$

where  $\alpha_c$  is the static dipole polarizability of the ionic core, whereas  $r_c$  is the cutoff parameter. The values of six parameters appearing in (4) and (5) for the angular momentum  $l$  are taken from Ref. [13].

The spin-orbit interaction potential  $V_{LS}$  in Hamiltonian (2) is (in a.u.)

$$V_{LS}(r) = \frac{\alpha^2}{2} \left( \frac{1}{r} \frac{dV_l(r)}{dr} \right) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (6)$$

with fine-structure constant  $\alpha = 1/c = 0.0072973525698$  [28]. For a given orbital angular momentum quantum number

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$l > 0$ , the potential (6) for two possible values of total angular momentum quantum number  $j = l \pm s$  has the opposite sign and as usual  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}\psi = (1/2)[j(j+1) - l(l+1) - s(s+1)]\psi$  (here atomic units are used), where  $s = 1/2$ . Thus the spin-orbit coupling leads to the splitting of each energy level into two levels.

We have applied the Ritz method to solve the time-independent Schrödinger equation. The wave function is represented in a basis set consisting of 500 Slater-type orbitals (STOs) of angular momentum  $l = 0$  (for the  $s$  states),  $l = 1$  (for the  $p$  states),  $l = 2$  (for the  $d$  states), and  $m = 0$ . The radial parts of STOs are as follows:

$$\varphi_j = r^{b-1} e^{-\beta_j r}, \quad (7)$$

where  $b$  and  $\beta_j$  are the variational parameters (whose optimization is described in the next paragraph). The full angular functions are the spherical harmonics. The linear expansion of basis functions leads to the generalized matrix eigenvalue equation

$$\mathbf{HC} = \mathbf{E}\mathbf{SC}. \quad (8)$$

The  $\mathbf{H}$  and  $\mathbf{S}$  matrices are Hamiltonian and overlap matrices, respectively. The cumbersome part of calculating  $H_{ij}$  is the matrix element of the polarization term,  $\langle r^{b-1} e^{-\beta_j r} | V_{\text{pol}} | r^{b-1} e^{-\beta_j r} \rangle$ , because of the existence of  $(-r^6)$  in the exponent of  $V_{\text{pol}}$ . A simple analytical solution of that matrix element does not exist. However, by applying

MATHEMATICA [30] one can obtain

$$\begin{aligned} & \langle r^{b-1} e^{-\beta_j r} | r^\zeta e^{-(r/r_c)^\delta} | r^{b-1} e^{-\beta_j r} \rangle \\ &= \frac{1}{720} r_c^{2b+\zeta} \left[ 120 r_c \Gamma(\gamma_1) {}_1F_5 \left( \gamma_1; \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{5}{6}; z \right) \right. \\ & \quad \left. - 120 r_c^2 \beta_{ij} \Gamma(\gamma_2) {}_1F_5 \left( \gamma_2; \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{5}{6}, \frac{7}{6}; z \right) \right] \end{aligned}$$

TABLE I. The low- and high-lying atomic energy levels of Rb( $ns$ ) states. Presented results of Kuhn [35], Li *et al.* [2], Ferguson and Dunn [37], and Liberman and Pinard [38] have been calculated based on (1). The results of Johansson (taken from Ref. [34]) have been converted to  $E_n = E(5s^2S - ns^2S) - E_I$ , where  $E_I$  is the ionization energy (taken from Ref. [34]). Notation of  $(-x)$  denotes  $\times 10^{-x}$ .

$n$	$-E$ (a.u.)			This work
	Ref. [34]	Ref. [35]	Ref. [34]	
5	0.153507	0.153467		0.153433
6	0.617762(-1)	0.617306(-1)		0.617539(-1)
7	0.336229(-1)	0.336276(-1)		0.336177(-1)
8	0.211596(-1)			0.211580(-1)
9	0.145428(-1)			0.145422(-1)
10	0.106093(-1)			0.106091(-1)
11	0.808107(-2)			0.808098(-2)
12	0.636018(-2)			0.636000(-2)
	Ref. [2]	Ref. [37]	Ref. [38]	This work
30	0.692597(-3)			0.692426(-3)
31	0.643784(-3)			0.643631(-3)
32	0.599955(-3)			0.599817(-3)
33	0.560454(-3)		0.561906(-3)	0.560329(-3)
34	0.524729(-3)		0.526045(-3)	0.524616(-3)
35	0.492315(-3)		0.493511(-3)	0.492212(-3)
36	0.462814(-3)		0.464470(-3)	0.462720(-3)
37	0.435887(-3)	0.393636(-3)	0.437401(-3)	0.435802(-3)
38	0.411244(-3)	0.371428(-3)	0.412157(-3)	0.411165(-3)
39	0.388633(-3)	0.352167(-3)	0.390780(-3)	0.388561(-3)
40	0.367836(-3)	0.334885(-3)	0.368810(-3)	0.367770(-3)
41	0.348666(-3)	0.317561(-3)	0.349934(-3)	0.348605(-3)
42	0.330956(-3)	0.303033(-3)	0.331445(-3)	0.330889(-3)
43	0.314562(-3)	0.288369(-3)	0.316284(-3)	0.314509(-3)
44	0.299356(-3)	0.275777(-3)	0.300513(-3)	0.299308(-3)
45	0.285227(-3)	0.262062(-3)	0.286029(-3)	0.285182(-3)
46	0.272075(-3)	0.251137(-3)	0.272822(-3)	0.272033(-3)
47	0.259812(-3)	0.240143(-3)	0.260153(-3)	0.259773(-3)
48	0.248360(-3)	0.229264(-3)	0.249234(-3)	0.248324(-3)
49	0.237649(-3)	0.221048(-3)	0.237947(-3)	0.237615(-3)
50	0.227616(-3)	0.210993(-3)	0.228090(-3)	0.227584(-3)
51	0.218206(-3)	0.202748(-3)	0.218468(-3)	0.218175(-3)
52	0.209367(-3)	0.194746(-3)		0.209338(-3)
53	0.201054(-3)	0.187789(-3)		0.201027(-3)
54	0.193227(-3)	0.180032(-3)		0.193202(-3)
55	0.185848(-3)			0.185824(-3)
56	0.178884(-3)			0.178862(-3)
57	0.172304(-3)			0.172283(-3)
58	0.166081(-3)			0.166060(-3)
59	0.160189(-3)			0.160169(-3)
60	0.154605(-3)			0.154589(-3)

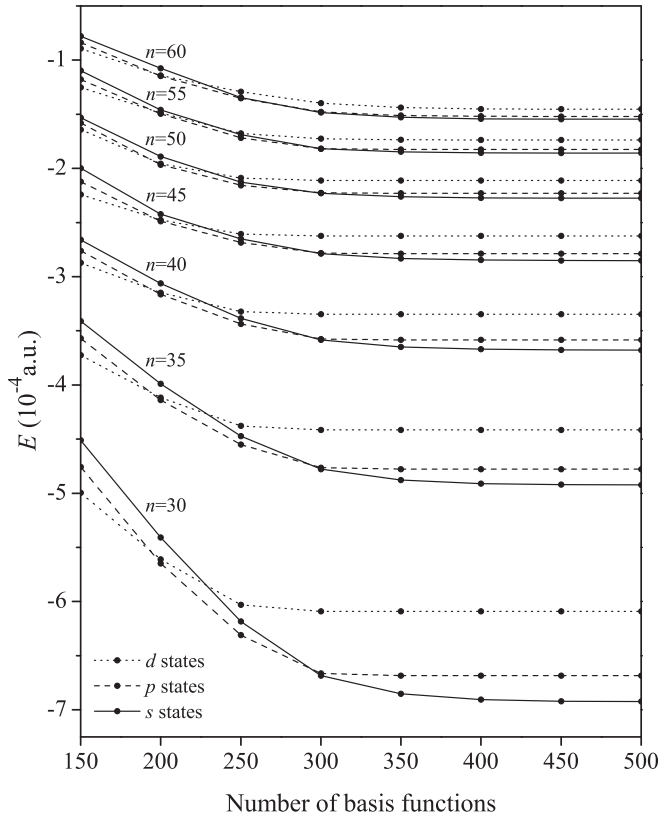


FIG. 1. Convergence of the energy computations (without spin-orbit interaction) of selected states ( $ns$ ,  $np$ , and  $nd$  series for  $n = 30, 35, \dots, 60$ ) with respect to the size of the basis set.

$$\begin{aligned}
 &+ 60r_c^3 \beta_{ij}^2 \Gamma(\gamma_3) {}_1F_5\left(\gamma_3; \frac{1}{2}, \frac{2}{3}, \frac{5}{6}, \frac{7}{6}, \frac{4}{3}; z\right) \\
 &- 20r_c^4 \beta_{ij}^3 \Gamma(\gamma_4) {}_1F_5\left(\gamma_4; \frac{2}{3}, \frac{5}{6}, \frac{7}{6}, \frac{4}{3}, \frac{3}{2}; z\right) \\
 &+ 5r_c^5 \beta_{ij}^4 \Gamma(\gamma_5) {}_1F_5\left(\gamma_5; \frac{5}{6}, \frac{7}{6}, \frac{4}{3}, \frac{3}{2}, \frac{5}{3}; z\right) \\
 &- r_c^6 \beta_{ij}^5 \Gamma(\gamma_6) {}_1F_5\left(\gamma_6; \frac{7}{6}, \frac{4}{3}, \frac{5}{2}, \frac{11}{3}, \frac{5}{6}; z\right), \quad (9)
 \end{aligned}$$

where  $\zeta = -4$  for  $V_{\text{pol}}$  [see Eq. (5)];  $\beta_{ij} = \beta_i + \beta_j$ ;  $\gamma_k = (k + 2b + \zeta)/6$ ,  $k = 1, 2, \dots, 6$ ;  $z = (r_c \beta_{ij}/6)^6$ ;  $\Gamma$  is the Euler gamma function; and  ${}_pF_q$  is the generalized hypergeometric function given by

$${}_pF_q(a_1, \dots, a_p; c_1, \dots, c_q; z) = \sum_{k=0}^{\infty} \frac{(a_1)_k \cdots (a_p)_k}{(c_1)_k \cdots (c_q)_k} \frac{z^k}{k!}, \quad (10)$$

where  $(x)_k = x(x+1)\cdots(x+k-1)$ . This series converges quickly for  $z < 0$ , but for large values of  $z$ , which in our

TABLE II. The low- and high-lying atomic energy levels of Rb( $np$ ) states. Presented results of Kuhn [35], Li *et al.* [2] and Liberman and Pinard [38] have been calculated based on (1). The results of Johansson (taken from Ref. [34]) and Kratz [39] have been converted to  $E_n = E(5s^2S - np^2P_j) - E_I$ , where  $E_I$  is the ionization energy (taken from Ref. [34] and Ref. [39], respectively). Notation of  $(-x)$  denotes  $\times 10^{-x}$ .

$n$	$-E$ (a.u.)						
	Ref. [34]		Ref. [35]		This work <sup>a</sup>	This work	
	$j = 1/2$	$j = 3/2$	$j = 1/2$	$j = 3/2$	$j = 1/2, 3/2$	$j = 1/2$	$j = 3/2$
5	0.961927(-1)	0.951101(-1)	0.961834(-1)	0.950959(-1)	0.956523(-1)	0.964604(-1)	0.952803(-1)
6	0.454528(-1)	0.450996(-1)	0.454443(-1)	0.450631(-1)	0.452771(-1)	0.455364(-1)	0.451573(-1)
7	0.266809(-1)	0.265211(-1)	0.266806(-1)	0.265210(-1)	0.266013(-1)	0.267181(-1)	0.265472(-1)
8	0.175686(-1)	0.174827(-1)			0.175265(-1)	0.175891(-1)	0.174976(-1)
9	0.124475(-1)	0.123961(-1)			0.124222(-1)	0.124596(-1)	0.124049(-1)
10	0.928107(-2)	0.924777(-2)			0.926486(-2)	0.928894(-2)	0.925370(-2)
11	0.718653(-2)	0.716388(-2)			0.717557(-2)	0.719199(-2)	0.716796(-2)
	Ref. [2]		Ref. [39]	Ref. [38]	This work <sup>a</sup>	This work	
	$j = 1/2$	$j = 3/2$	$j = 1/2, 3/2$	$j = 1/2, 3/2$	$j = 1/2, 3/2$	$j = 1/2$	$j = 3/2$
30	0.668687(-3)	0.668042(-3)	0.668414(-3)	0.668429(-3)	0.668362(-3)	0.668829(-3)	0.668145(-3)
31	0.622336(-3)	0.621756(-3)	0.621894(-3)		0.622044(-3)	0.622463(-3)	0.621849(-3)
32	0.580642(-3)	0.580120(-3)	0.580432(-3)	0.580831(-3)	0.580379(-3)	0.580757(-3)	0.580203(-3)
33	0.543002(-3)	0.542530(-3)	0.542705(-3)	0.542816(-3)	0.542764(-3)	0.543106(-3)	0.542605(-3)
34	0.508907(-3)	0.508478(-3)	0.508578(-3)	0.508739(-3)	0.508691(-3)	0.509001(-3)	0.508547(-3)
35	0.477925(-3)	0.477535(-3)	0.477732(-3)	0.478068(-3)	0.477729(-3)	0.478011(-3)	0.477598(-3)
36	0.449689(-3)	0.449333(-3)	0.449482(-3)	0.449820(-3)	0.449510(-3)	0.449768(-3)	0.449390(-3)
37	0.423883(-3)	0.423557(-3)	0.423739(-3)	0.424003(-3)	0.423719(-3)	0.423955(-3)	0.423609(-3)
38	0.400237(-3)	0.399938(-3)	0.400137(-3)	0.400347(-3)	0.400086(-3)	0.400303(-3)	0.399986(-3)
39	0.378515(-3)	0.378240(-3)	0.378176(-3)	0.378409(-3)	0.378377(-3)	0.378576(-3)	0.378284(-3)
40	0.358515(-3)	0.358261(-3)	0.358219(-3)	0.358417(-3)	0.358387(-3)	0.358571(-3)	0.358302(-3)
41	0.340059(-3)	0.339825(-3)	0.339811(-3)	0.340146(-3)	0.339941(-3)	0.340111(-3)	0.339862(-3)
42	0.322993(-3)	0.322776(-3)	0.322634(-3)	0.322909(-3)	0.322883(-3)	0.323040(-3)	0.322810(-3)
43	0.307179(-3)	0.306978(-3)	0.306869(-3)	0.307102(-3)	0.307078(-3)	0.307224(-3)	0.307010(-3)
44	0.292500(-3)	0.292313(-3)	0.292198(-3)	0.292428(-3)	0.292405(-3)	0.292541(-3)	0.292343(-3)
45	0.278847(-3)	0.278674(-3)	0.278665(-3)	0.278913(-3)	0.278760(-3)	0.278886(-3)	0.278701(-3)
46	0.266129(-3)	0.265967(-3)	0.265908(-3)	0.266190(-3)	0.266048(-3)	0.266165(-3)	0.265993(-3)
47	0.254262(-3)	0.254111(-3)	0.254016(-3)	0.254319(-3)	0.254186(-3)	0.254295(-3)	0.254135(-3)
48	0.243171(-3)	0.243029(-3)	0.242989(-3)	0.243224(-3)	0.243100(-3)	0.243202(-3)	0.243052(-3)
49	0.232790(-3)	0.232658(-3)	0.232692(-3)	0.232941(-3)	0.232723(-3)	0.232819(-3)	0.232679(-3)
50	0.223060(-3)	0.222936(-3)	0.223033(-3)	0.223296(-3)	0.222997(-3)	0.223088(-3)	0.222956(-3)
51	0.213928(-3)	0.213811(-3)	0.213874(-3)	0.214149(-3)	0.213869(-3)	0.213953(-3)	0.213830(-3)
52	0.205345(-3)	0.205235(-3)	0.205035(-3)		0.205289(-3)	0.205369(-3)	0.205252(-3)
53	0.197268(-3)	0.197165(-3)	0.197016(-3)		0.197216(-3)	0.197291(-3)	0.197181(-3)
54	0.189659(-3)	0.189562(-3)	0.189680(-3)		0.189610(-3)	0.189681(-3)	0.189577(-3)
55	0.182482(-3)	0.182390(-3)	0.182299(-3)	0.182308(-3)	0.182435(-3)	0.182502(-3)	0.182404(-3)
56	0.175704(-3)	0.175617(-3)	0.175647(-3)		0.175660(-3)	0.175723(-3)	0.175631(-3)
57	0.169298(-3)	0.169215(-3)	0.169313(-3)		0.169256(-3)	0.169316(-3)	0.169229(-3)
58	0.163235(-3)	0.163157(-3)	0.163345(-3)		0.163196(-3)	0.163252(-3)	0.163170(-3)
59	0.157492(-3)	0.157418(-3)	0.157513(-3)		0.157456(-3)	0.157509(-3)	0.157432(-3)
60	0.152047(-3)	0.151977(-3)	0.152227(-3)	0.152233(-3)	0.152013(-3)	0.152062(-3)	0.151989(-3)

<sup>a</sup>The spin-orbit coupling is not included.

case is equal to  $[r_c(\beta_i + \beta_j)/6]^6$ , the series converges slowly and the numerator becomes extremely large. Therefore, those matrix elements of the polarization term where  $z$  is large have been carried out by numerical integration using the composite (extended) Simpson's rule [31]. The analogous procedure has been used for terms containing  $\exp[-(r/r_c)^6]$  in  $\langle r^{b-1} e^{-\beta_i r} | V_{LS} | r^{b-1} e^{-\beta_j r} \rangle$ .

Let us explain how we have optimized the nonlinear variational parameters  $b, \{\beta_j\}_{j=1, \dots, 500}$ . The Hamiltonian matrix is now  $500 \times 500$ , whose eigenvalues are sorted in ascending order. Let us denote these eigenvalues by  $\{\bar{E}_k\}_{k=1, 2, \dots, 500}$ . Based on the Hylleraas-Undheim and MacDonald linear variational theorem [32,33], we know that  $\{\bar{E}_k > E_k^{\text{exact}}\}_{k=1, 2, \dots, 500}$ . Each one of the 500 eigenvalues of the Hamiltonian matrix is a

TABLE III. The low- and high-lying atomic energy levels of Rb(*nd*) states. Presented results of Kuhn [35], Kato and Stoicheff [36], Li *et al.* [2], Ferguson and Dunn [37], and Harvey and Stoicheff [40] have been calculated based on (1). The results of Johansson (taken from Ref. [34]) have been converted to  $E_n = E(5s^2S - nd^2D_j) - E_I$ , where  $E_I$  is the ionization energy (taken from Ref. [34]). Notation of  $(-x)$  denotes  $\times 10^{-x}$ .

$-E$ (a.u.)								
<i>n</i>	Ref. [34]		Ref. [35]		Ref. [36]	This work <sup>a</sup>	This work	
	<i>j</i> = 3/2	<i>j</i> = 5/2	<i>j</i> = 3/2	<i>j</i> = 5/2	<i>j</i> = 3/2,5/2	<i>j</i> = 3/2,5/2	<i>j</i> = 3/2	<i>j</i> = 5/2
4	0.653178(-1)	0.653158(-1)		0.653058(-1)	0.653058(-1)	0.653185(-1)	0.654154(-1)	0.652553(-1)
5	0.364064(-1)	0.363929(-1)	0.364048(-1)	0.363852(-1)	0.364048(-1)	0.363977(-1)	0.364518(-1)	0.363624(-1)
6	0.227985(-1)	0.227881(-1)		0.228285(-1)	0.227896(-1)	0.227954(-1)	0.228242(-1)	0.227766(-1)
7	0.155403(-1)	0.155334(-1)		0.155526(-1)	0.155362(-1)	0.155393(-1)	0.155559(-1)	0.155284(-1)
8	0.112513(-1)	0.112467(-1)			0.112489(-1)	0.112511(-1)	0.112615(-1)	0.112443(-1)
9	0.851559(-2)	0.851242(-2)			0.851476(-2)	0.851567(-2)	0.852255(-2)	0.851118(-2)
10	0.666683(-2)	0.666456(-2)			0.666552(-2)	0.666688(-2)	0.667166(-2)	0.666375(-2)
11					0.535927(-2)	0.535994(-2)	0.536339(-2)	0.535768(-2)
	Ref. [2]		Ref. [37]		Ref. [40]	This work <sup>a</sup>	This work	
	<i>j</i> = 3/2	<i>j</i> = 5/2	<i>j</i> = 3/2,5/2		<i>j</i> = 3/2,5/2	<i>j</i> = 3/2,5/2	<i>j</i> = 3/2	<i>j</i> = 5/2
30	0.609033(-3)	0.608964(-3)			0.610423(-3)	0.609045(-3)	0.609178(-3)	0.608958(-3)
31	0.568649(-3)	0.568587(-3)			0.569902(-3)	0.568661(-3)	0.568781(-3)	0.568582(-3)
32	0.532153(-3)	0.532097(-3)			0.532937(-3) <sup>b</sup>	0.532164(-3)	0.532272(-3)	0.532092(-3)
33	0.499061(-3)	0.499010(-3)			0.500404(-3) <sup>b</sup>	0.499070(-3)	0.499169(-3)	0.499006(-3)
34	0.468962(-3)	0.468916(-3)			0.469896(-3) <sup>b</sup>	0.468971(-3)	0.469061(-3)	0.468912(-3)
35	0.441506(-3)	0.441464(-3)			0.442885(-3) <sup>b</sup>	0.441514(-3)	0.441596(-3)	0.441460(-3)
36	0.416393(-3)	0.416354(-3)			0.417414(-3) <sup>b</sup>	0.416400(-3)	0.416475(-3)	0.416350(-3)
37	0.393362(-3)	0.393327(-3)			0.394521(-3) <sup>b</sup>	0.393369(-3)	0.393438(-3)	0.393324(-3)
38	0.372191(-3)	0.372158(-3)			0.373257(-3) <sup>b</sup>	0.372197(-3)	0.372261(-3)	0.372156(-3)
39	0.352684(-3)	0.352654(-3)	0.388604(-3)		0.353667(-3) <sup>b</sup>	0.352690(-3)	0.352749(-3)	0.352651(-3)
40	0.334672(-3)	0.334644(-3)	0.367411(-3)		0.335753(-3) <sup>b</sup>	0.334677(-3)	0.334731(-3)	0.334641(-3)
41	0.318005(-3)	0.317979(-3)	0.348642(-3)		0.319006(-3) <sup>b</sup>	0.318009(-3)	0.318060(-3)	0.317976(-3)
42	0.302552(-3)	0.302528(-3)	0.330763(-3)		0.303481(-3) <sup>b</sup>	0.302557(-3)	0.302603(-3)	0.302526(-3)
43	0.288199(-3)	0.288177(-3)	0.315015(-3)		0.289202(-3) <sup>b</sup>	0.288203(-3)	0.288247(-3)	0.288175(-3)
44	0.274844(-3)	0.274823(-3)	0.299044(-3)		0.275648(-3)	0.274848(-3)	0.274888(-3)	0.274821(-3)
45	0.262396(-3)	0.262377(-3)	0.285210(-3)		0.263266(-3)	0.262400(-3)	0.262437(-3)	0.262375(-3)
46	0.250775(-3)	0.250757(-3)	0.272059(-3)		0.251475(-3)	0.250778(-3)	0.250814(-3)	0.250755(-3)
47	0.239909(-3)	0.239892(-3)	0.260153(-3)		0.240775(-3)	0.239912(-3)	0.239945(-3)	0.239891(-3)
48	0.229734(-3)	0.229718(-3)	0.248790(-3)		0.230348(-3)	0.229737(-3)	0.229768(-3)	0.229717(-3)
49	0.220194(-3)	0.220179(-3)	0.228285(-3)		0.220121(-3)	0.220196(-3)	0.220225(-3)	0.220177(-3)
50	0.211235(-3)	0.211221(-3)	0.218285(-3)		0.211950(-3)	0.211238(-3)	0.211265(-3)	0.211220(-3)
51	0.202812(-3)	0.202799(-3)	0.209613(-3)		0.202666(-3)	0.202815(-3)	0.202840(-3)	0.202798(-3)
52	0.194883(-3)	0.194871(-3)	0.201448(-3)		0.194746(-3)	0.194886(-3)	0.194910(-3)	0.194870(-3)
53	0.187410(-3)	0.187399(-3)			0.186774(-3)	0.187413(-3)	0.187435(-3)	0.187398(-3)
54	0.180359(-3)	0.180348(-3)			0.180717(-3)	0.180361(-3)	0.180383(-3)	0.180347(-3)
55	0.173699(-3)	0.173688(-3)			0.174037(-3)	0.173701(-3)	0.173721(-3)	0.173687(-3)
56	0.167400(-3)	0.167390(-3)			0.168336(-3)	0.167402(-3)	0.167421(-3)	0.167390(-3)
57	0.161438(-3)	0.161429(-3)			0.162911(-3)	0.161441(-3)	0.161459(-3)	0.161429(-3)
58	0.155789(-3)	0.155781(-3)			0.157185(-3)	0.155794(-3)	0.155811(-3)	0.155783(-3)
59	0.150432(-3)	0.150423(-3)			0.151756(-3)	0.150441(-3)	0.150459(-3)	0.150431(-3)
60	0.145346(-3)	0.145338(-3)			0.146603(-3)	0.145359(-3)	0.145376(-3)	0.145350(-3)

<sup>a</sup>The spin-orbit coupling is not included.

<sup>b</sup>References [38,40].

function of the nonlinear basis set parameters  $b, \{\beta_j\}_{j=1,2,\dots,500}$ . Therefore, in the calculations of the upper bound to the  $k$ th exact eigenvalue of Rb atom, we have searched for the optimal nonlinear basis-set parameters for which the  $k$ th eigenvalue of the Hamiltonian matrix gets the lowest value. To minimize the number of the nonlinear variational parameters, we have used the constraint (known as even-tempered basis functions)  $\beta_j = \beta_0 \epsilon^{j-1}$ ,  $j = 1, 2, \dots, 500$ , where the two optimized parameters are  $\beta_0$  and  $\epsilon$ .

The calculations have been done in quadruple precision. The convergence of eigenenergies with basis size is presented in Fig. 1. When the number of basis functions increases, the eigenvalues stabilize. For all considered states, the convergence is satisfied. Moreover, to demonstrate the quality of our results, we have performed calculations for low-lying energy levels for Rb atom. Tables I, II, and III show comparisons our results with those by Johansson (taken from Ref. [34]), Kuhn [35], and Kato and Stoicheff [36]. Although the basis set has been optimized for the highly excited Rydberg states, the agreement with experiment is remarkable.

### III. RESULTS FOR THE HIGHLY EXCITED RYDBERG STATES OF A RUBIDIUM ATOM

The results of  $ns$ ,  $np$ , and  $nd$  series for  $n = 30, 31, \dots, 60$  are presented in Tables I, II, and III. They are compared with the available data from the experiment. The results of the  $s$  states are shown together with those by Ferguson and Dunn [37], Liberman and Pinard [38], and Li *et al.* [2]. Ferguson and Dunn applied the space-charge-limited thermionic triode to detect the highly excited  $s$  and  $d$  states. Based on their own measurements, they extracted the effective principal quantum numbers  $n^*$ . In turn, Liberman and Pinard used the field ionization method for the detection of the high-lying  $s$ ,  $p$ , and  $d$  states. Unfortunately, the numbers  $n^*$ , which they presented, were not obtained from their own measurements, but were recalled without any reference. The more recent millimeter-wave measurements carried out by Li *et al.* allowed them to extract the quantum defects for  $s$ ,  $p$ , and  $d$  series. In all cases, the values of energies, which are shown in Table I, are obtained using formula (1). One can see that our results for the  $s$  states are significantly different from those by Ferguson and Dunn [37], but they are in very good agreement with the results of Liberman and Pinard [38] and especially of Li *et al.* [2].

The results for the  $p$  states are compared (in addition to those for Liberman and Pinard [38] and for Li *et al.* [2]) with experimental data of Kratz [39]. In Ref. [39], he measured transitions from the  $5s^2S$  level to the excited  $np^2P$  levels and also the ionization energy,  $E_I = 0.153\,507\,3$  a.u. Thus the energy levels of Kratz, shown in Table II, have been determined from  $E_n = E(5s^2S - np^2P) - E_I$ . The agreement is excellent. We note that by taking the spin-orbit interaction into consideration, the agreement with observations is improved. In the worst case, the relative difference between our results and the results of Li *et al.* [2], defined as  $\delta_E \equiv (E_n - E_n^{\text{Li}})/E_n^{\text{Li}}$ , is  $\delta_E \approx 2 \times 10^{-4}$ .

Table III includes the results of the  $d$  states obtained by Ferguson and Dunn [37], Li *et al.* [2], and Harvey and Stoicheff

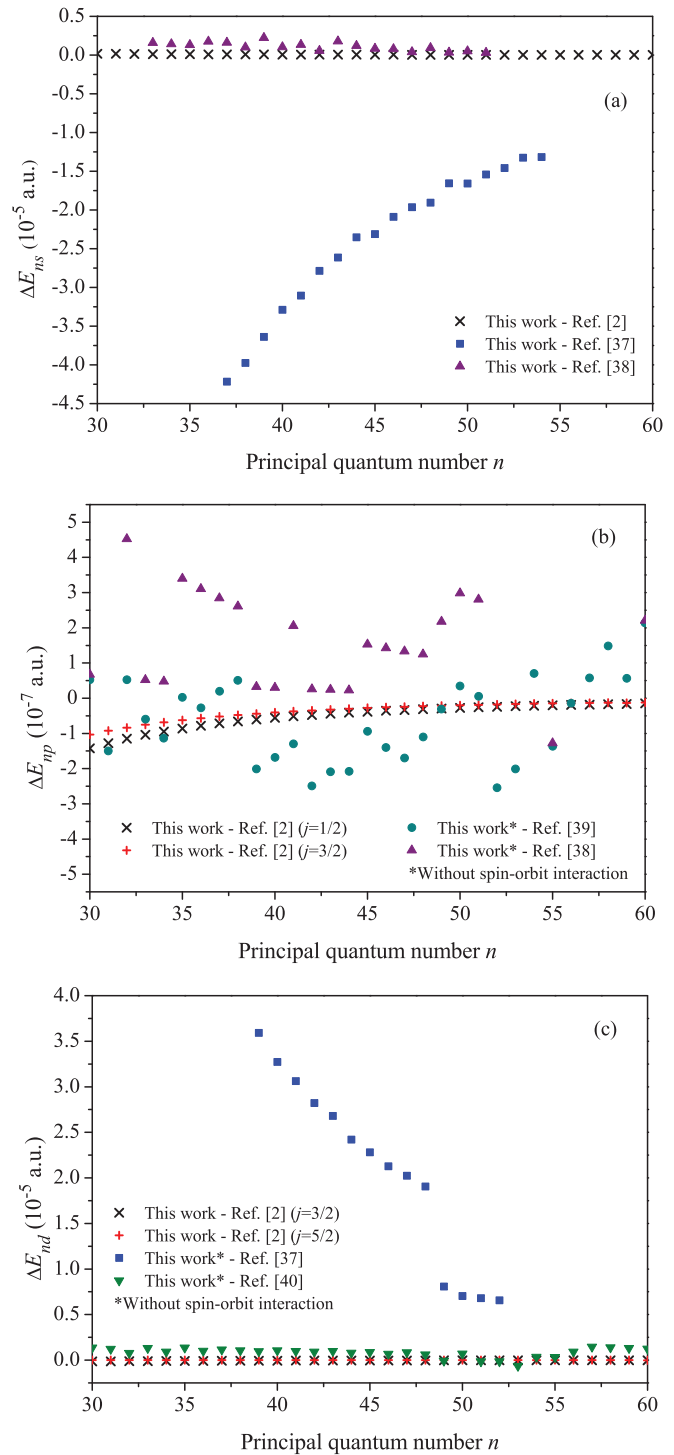


FIG. 2. (Color online) Energy level residuals (the difference between current and previously published results) with principal quantum number for (a) Rb( $ns$ ), (b) Rb( $np$ ), and (c) Rb( $nd$ ) states.

[40]. The latter presented the quantum numbers  $n^*$  calculated on the basis of their own experiment for  $n > 54$  and using data from Ref. [41] for  $n \leq 54$ . The present energies are very similar to those by Li *et al.* [2] and by Harvey and Stoicheff [40], but again they differ from the experimental data of Ferguson and Dunn [37]. Figures 2(a), 2(b), and 2(c) show the energy level residuals for  $ns$ ,  $np$ , and  $nd$  series,



respectively. It is clear that our results are in excellent agreement with the observation of Ref. [2] for Rb( $ns$ ,  $np$ , and  $nd$ ) states.

#### IV. CONCLUDING REMARKS

We have investigated the  $s$ ,  $p$ , and  $d$  highly excited Rydberg states of a rubidium atom with the parametric model potential, developed to represent the motion of the valence electron in the field of a closed alkali-metal positive-ion core [13] and with the spin-orbit interaction potential. The atomic energy levels obtained with the Ritz variational method are in strong agreement with the results of Kratz [39], Harvey and Stoicheff [40], Liberman and Pinard [38], and especially Li *et al.* [2]. The report of Sansonetti from NIST [34] gives as a reference for the  $s$  and  $d$  Rydberg states of Rb the results of Ferguson and Dunn [37]. Our calculations show that the experimental measurements carried out by them are not accurate enough to

be used as reference values since they differ from the results for the  $s$  Rydberg states presented by Liberman and Pinard [38] and for the  $d$  Rydberg states presented by Harvey and Stoicheff [40] as well as for the  $s$  and  $d$  Rydberg states presented by Li *et al.* [2], in very good agreement with our computational results. The fact that the energy levels we obtained also agree very well with the spectrum of the  $p$  Rydberg states as measured by Kratz and accepted by Sansonetti in the report [34] indicates that our calculations can be benchmarked to determine which set of measurements may be used as reference data.

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- [1] S. F. Dyubko, M. N. Efimenko, V. A. Efremov, and S. V. Podnos, *Quantum Electron.* **25**, 914 (1995).
- [2] W. Li, I. Mourachko, M. W. Noel, and T. F. Gallagher, *Phys. Rev. A* **67**, 052502 (2003).
- [3] J. Han, Y. Jamil, D. V. L. Norum, P. J. Tanner, and T. F. Gallagher, *Phys. Rev. A* **74**, 054502 (2006).
- [4] A. K. Mohapatra, T. R. Jackson, and C. S. Adams, *Phys. Rev. Lett.* **98**, 113003 (2007).
- [5] B. Sanguinetti, H. O. Majeed, M. L. Jones, and B. T. H. Varcoe, *J. Phys. B* **42**, 165004 (2009).
- [6] L. A. M. Johnson, H. O. Majeed, B. Sanguinetti, Th. Becker, and B. T. H. Varcoe, *New J. Phys.* **12**, 063028 (2010).
- [7] J. Tallant, D. Booth, and J. P. Shaffer, *Phys. Rev. A* **82**, 063406 (2010).
- [8] M. J. Piotrowicz, C. MacCormick, A. Kowalczyk, S. Bergamini, I. I. Beterov, and E. A. Yakshina, *New J. Phys.* **13**, 093012 (2011).
- [9] A. Nadeem and S. U. Haq, *Phys. Rev. A* **83**, 063404 (2011).
- [10] L. G. D'yachkov and P. M. Pankratov, *J. Phys. B* **27**, 461 (1994).
- [11] B. Kaulakys, *J. Phys. B* **28**, 4963 (1995).
- [12] M. L. Zimmerman, M. G. Littman, M. M. Kash, and D. Kleppner, *Phys. Rev. A* **20**, 2251 (1979).
- [13] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, *Phys. Rev. A* **49**, 982 (1994).
- [14] C. E. Theodosiou, *Phys. Rev. A* **30**, 2881 (1984).
- [15] F. Robicheaux and J. Shaw, *Phys. Rev. A* **56**, 278 (1997).
- [16] D. Jaksch, J. I. Cirac, P. Zoller, S. L. Rolston, R. Côté, and M. D. Lukin, *Phys. Rev. Lett.* **85**, 2208 (2000).
- [17] C. H. Greene, A. S. Dickinson, and H. R. Sadeghpour, *Phys. Rev. Lett.* **85**, 2458 (2000).
- [18] M. D. Lukin, M. Fleischhauer, R. Côté, L. M. Duan, D. Jaksch, J. I. Cirac, and P. Zoller, *Phys. Rev. Lett.* **87**, 037901 (2001).
- [19] J. R. Brandenberger, C. A. Regal, R. O. Jung, and M. C. Yakes, *Phys. Rev. A* **65**, 042510 (2002).
- [20] D. Tong, S. M. Farooqi, J. Stanojevic, S. Krishnan, Y. P. Zhang, R. Côté, E. E. Eyler, and P. L. Gould, *Phys. Rev. Lett.* **93**, 063001 (2004).
- [21] I. I. Ryabtsev, D. B. Tretyakov, and I. I. Beterov, *J. Phys. B* **38**, S421 (2005).
- [22] T. Vogt, M. Viteau, J. Zhao, A. Chotia, D. Comparat, and P. Pillet, *Phys. Rev. Lett.* **97**, 083003 (2006).
- [23] K. Afrousheh, P. Bohloulou-Zanjani, J. A. Petrus, and J. D. D. Martin, *Phys. Rev. A* **74**, 062712 (2006).
- [24] V. Bendowsky, B. Butscher, J. Nipper, J. P. Shaffer, R. Löw, and T. Pfau, *Nature (London)* **458**, 1005 (2009).
- [25] H. Kübler, J. P. Shaffer, T. Baluktian, R. Löw, and T. Pfau, *Nat. Photon.* **4**, 112 (2010).
- [26] W. Li, T. Pohl, J. M. Rost, S. T. Rittenhouse, H. R. Sadeghpour, J. Nipper, B. Butscher, J. B. Balewski, V. Bendkowsky, R. Löw, and T. Pfau, *Science* **334**, 1110 (2011).
- [27] T. Peyronel, O. Firstenberg, Q.-Y. Liang, S. Hofferberth, A. V. Gorshkov, T. Pohl, M. D. Lukin, and V. Vuletić, *Nature (London)* **488**, 57 (2012).
- [28] <http://physics.nist.gov/cuu/Constants/index.html>
- [29] G. W. F. Drake, *Atomic, Molecular, & Optical Physics Handbook* (AIP, New York, 1996).
- [30] <http://www.wolfram.com/mathematica>
- [31] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes in Fortran 90*, 2nd ed. (Cambridge University Press, Cambridge, 1996).
- [32] E. A. Hylleraas and B. Undheim, *Z. Phys.* **65**, 759 (1930).
- [33] J. K. L. MacDonald, *Phys. Rev.* **43**, 830 (1933).
- [34] J. E. Sansonetti, *J. Phys. Chem. Ref. Data* **35**, 301 (2006).
- [35] H. G. Kuhn, *Atomic Spectra*, 2nd ed. (Longmans, Green and Co. Ltd., London and Harlow, 1969).
- [36] Y. Kato and B. P. Stoicheff, *J. Opt. Soc. Am.* **66**, 490 (1976).
- [37] A. I. Ferguson and M. H. Dunn, *Opt. Commun.* **23**, 227 (1977).
- [38] S. Liberman and J. Pinard, *Phys. Rev. A* **20**, 507 (1979).
- [39] H. R. Kratz, *Phys. Rev.* **75**, 1844 (1949).
- [40] K. C. Harvey and B. P. Stoicheff, *Phys. Rev. Lett.* **38**, 537 (1977).
- [41] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U.S. GPO, Washington, DC, 1952), Vol. II.