Asymptotically exact expression for the energies of the $^3S^e$ Rydberg series in a two-electron system

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The $1sns\,^3S^e$ Rydberg series in a two-electron system with the charge of the nucleus, $Z \approx 1$, is treated by means of the quantum-defect theory. Comparison with configuration interaction calculations suggests that the quantum-defect expression for the energy levels becomes asymptotically exact as $Z \to 1$. This provides an analytic description of the disappearance of the $1sns\,^3S^e$ bound states when Z approaches the critical value of 1.

I. INTRODUCTION

Critical phenomena, i.e., the question of when and how a given physical system undergoes a change in its properties, is a question which, for a nontrivial system, is often difficult to answer. In quantum mechanics, one such example is the disappearance of bound states of a two-electron system, when the charge Z of the nucleus in the Hamiltonian

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

becomes less than a certain critical value. The ground-state eigenvalue $E(Z)$ of this Hamiltonian and its properties as function of parameter Z have been studied for a long time. It was rigorously proved by Kato [1] that $E(Z)$ is an analytic function of Z. It could be expected that the change in the physical properties of the ground state, i.e., its disappearance as a bound state for a certain $Z = Z_{\text{crit}}$ is to be accompanied by the singularity which $E(Z)$ has at the point $Z = Z_{\text{crit}}$.

The position of this singularity can, in principle, be located by studying coefficients of the perturbation series in powers of $1/Z$. This has been done using different methods [2–5] such as the ratio test (i.e., the numerical analysis of the sequence constructed from the ratio of two subsequent coefficients of the perturbation series), or using Pade analysis of the perturbation expansion.

In the paper of Baker *et al.* [6], the authors performed high-precision calculations of the 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 $Z_{\text{crit}} \approx 0.911\,029$ as the position of the singular point of $E(Z)$ for the ground state. These authors also resolved a long-standing controversy by proving that it is exactly at the singular point $Z = Z_{\text{crit}}$ that the ground state ceases to be a bound state. Their value of the critical point has been subsequently refined [7–9].

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 [2,10]. In Refs. [11,12], a dispersion relation for $E(Z)$ has been proposed and verified by means of a complex rotation calculation.

As far as excited states and their properties 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 $Z = 1$ [6]. The authors of Ref. [6] computed the first 26 coefficients of the perturbation expansion in powers of $1/Z$ for the $1s2s\,^3S^e$ state and performed the same analysis as that for the ground state. These results were not conclusive since only a relatively small number of the perturbation coefficients were analyzed.

In the present paper an analytic model is proposed, which describes the $1sns\,^3S^e$ Rydberg series for Z sufficiently close to 1. Configuration interaction calculations performed separately suggest that as $Z \to 1$, the energies the analytic model predicts for the levels of the Rydberg $1sns\,^3S^e$ series become increasingly accurate, thus providing exact analytic expressions describing the triplet states of a two-electron system as $Z \to 1$.

II. THEORY

A simple model of a Rydberg state of a two-electron system with a nucleus of charge Z is a particle moving in a combination of Coulomb and short-range potentials,

$$V(r) = V_{\text{sr}}(r) - \frac{z}{r}, \qquad (2)$$

where $z = Z - 1$ and $V_{\text{sr}}(r)$ is a short-range interaction. We present below arguments showing that despite its simplicity, this model provides an asymptotically exact description of the Rydberg series of a two-electron system with its nuclear charge $Z \to 1$.

The physical situation of a combination of short-range and Coulomb potentials is described naturally in terms of the quantum-defect (QD) approach [13]. The position of the T matrix poles in QD theory is given by the solutions of the following equation in the complex k plane [14]:

$$M(k^2) = -2z\,\tau(k), \qquad (3)$$

where the function $M(k^2)$ could be found, in principle, if the logarithmic derivative of the radial wave function is known at some point where any inner short-range interaction disap-

pears and only the Coulomb potential is present. The function $\tau(k)$ can be expressed in terms of known special functions [15],

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

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

The key point in the standard development of the QD procedure is the observation that $M(k^2)$ is an analytic function of k^2. This generally follows from the analycity of the solutions of a differential equation as functions of a given parameter, provided the initial conditions do not depend upon this parameter. From the same general statement, it follows that the function $M(k^2,z)$ is also an analytic function of z. As we shall see, this fact can be usefully exploited in describing the behavior of the levels of the Rydberg series as the charge of the nucleus $Z\rightarrow1$.

Introducing variables $k=i\kappa$ and $u=z/\kappa$, expanding the left-hand side of Eq. (3) in powers of z, and using known properties of the digamma function [15], Eq. (3) can be rewritten as

$$M_0(k^2)+zM_1(k^2)+ \ldots$$
$$=-2z\left(\ln z-\ln u+\pi\cot\pi u+\frac{1}{2u}+\Psi(u)\right), \quad (5)$$

where $M_i(k^2)$ are all analytic functions of k^2. To track z dependences it is more convenient to recast Eq. (5) in a slightly different form,

$$\frac{\beta(k^2,z)}{z}-\ln z=-\ln u+\pi\cot\pi u+\frac{1}{2u}+\Psi(u), \quad (6)$$

with $\beta(k^2,z)=-M(k^2,z)/2$ being an analytic function of both arguments. We shall be interested in the solutions of Eq. (6) for which $u\rightarrow C$, where C is a positive constant, when $z\rightarrow0$. As we shall see, for $z\rightarrow0$ such solutions describe the Rydberg series $1sns$ of a two-electron atom.

For $z\rightarrow0$, the left-hand side of Eq. (6) is unbound, and the only possibility of satisfying Eq. (6) is for $u=n+\epsilon(z)$, and thus $\kappa=z/(n+\epsilon)$, where $\epsilon\rightarrow0$ when $z\rightarrow0$. This gives the Rydberg formula with the following explicit expression for ϵ:

$$\epsilon=\frac{\pi z}{\beta(z)-z\ln z}. \quad (7)$$

This equation is obtained in the assumption that z is so small that all the terms decaying faster than first power of z (when $z\rightarrow0$) can be neglected when solving Eq. (6). In particular, it implies that only the first two terms of the z expansion of the function $\beta(z)$ should be preserved. Thus, $\beta(z)$ can be represented as

$$\beta(z)\approx\beta_0+\beta_1z, \quad (8)$$

where β_0, β_1 are both independent of energy (accounting for their energy dependence introduces terms of higher order in z).

Recalling that parameter z in our model is $z=Z-1$, where Z is the charge of the nucleus, one obtains the following tentative expression for the energy levels of the $1sns$ Rydberg series for $Z\rightarrow1$:

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

with $n=1,2,\ldots$, and

$$\epsilon=\frac{\pi(Z-1)}{\beta(Z)-(Z-1)\ln(Z-1)}. \quad (10)$$

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

$$\beta(Z)=\beta_0+\beta_1(Z-1)+\cdots. \quad (11)$$

When deriving Eqs. (9) and (10), it is assumed that apart from the Coulomb potential, only short-range interactions are present. Strictly speaking, this is not the case for a Rydberg state of a real two-electron system, since there is also a polarization interaction due to the polarizability of the core.

The presence of such a polarization interaction does not affect Eqs. (9) and (10). Indeed, when deriving these equations we used the analycity of the functions M_0 and M_1 in Eq. (5) as functions of k^2 and retained only the leading constant terms of the corresponding expansions. When a polarization potential is present, the functions M_0 and M_1 in Eq. (5) are no longer analytic functions of k^2, but can still be represented as a power series in κ, $M_i(k)=a_0+a_1\kappa+\cdots$ (where $k=i\kappa$). Accounting of the terms of higher order than the linear term introduces terms of higher order than $Z-1$. Since $\kappa\approx Z-1$, accounting for the linear term only rescales the $Z-1$ coefficient (β_1) in Eq. (11). We therefore recover Eqs. (9) and (10), even in the presence of the polarization interaction.

One may expect that Eqs. (9) and (10) provide an adequate description of a two-electron system, given that the charge of the nucleus Z is close enough to 1. Indeed, on physical grounds it is clear that the state of a two-electron system with $Z\approx1$ is spatially extended (quantitative illustration of this statement is given in the following section). Such systems are natural candidates for the quantum-defect theory. However, the numerical calculations described in the following section strongly suggest that Eqs. (9) and (10) are more than just a good approximation. The numerical evidence suggests that these formulas actually give the leading terms of the asymptotic behavior of the exact energy when $Z\rightarrow1$.

Further discussion of this premise is postponed for the presentation of the details of the numerical calculations.

III. CI METHOD

To numerically compute the energies of a two-electron system with $Z\approx1$, the configuration interaction (CI) method

was employed [16]. Only a brief description of the numerical procedure is given here since the details closely follow that of two-electron CI calculations (with model potentials) of the $^1S^e$ ground state and lowest $^1P^o$ excited state of the group II atoms [17].

The nonrelativistic atomic wave function with good L and S quantum numbers ($|\Psi;LS\rangle$) is taken to be a linear combination of antisymmetrized states created by multiplying two single-particle electron orbitals with the usual Clebsch-Gordan coupling coefficients;

$$|\Psi;LS\rangle = \sum_{i,j} c_{i,j}\mathcal{A}\langle\ell_i m_i \ell_j m_j|LM_L\rangle$$
$$\times \left\langle\frac{1}{2}\mu_i\frac{1}{2}\mu_j\bigg|SM_S\right\rangle\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2), \quad (12)$$

where the radial form of the single-particle orbitals $\phi_j(\mathbf{r})$ was constructed from a Laguerre-type orbital (LTO) basis. The method for computing the LTO radial basis functions, as well as the details of numerically computing the matrix elements have been discussed elsewhere [18]. The Hamiltonian of Eq. (1) was diagonalized in a purely LTO basis, since the dimension of such a basis can be made arbitrarily large without any linear dependence problems arising. Two series of CI calculations were performed to ensure convergence, with the lowest energy of the two being reported.

The smaller $L_{max}=2$ calculation included $40s$, $20p$, and $20d$ single-particle states (with L_{max} denoting the maximum angular momentum of the single-particle orbitals, and the total number of configurations included, $N_{CI}=1240$). The Laguerre exponent for all of the s, p, and d LTOs was set to $\lambda=0.2$ to represent the two-electron states located at large distances from the nucleus.

The larger $L_{max}=10$ calculation included $35s$ orbitals with 20 orbitals for each of the other partial waves, with $N_{CI}=1955$. The Laguerre exponents of single-particle states for each partial wave were fixed at $\lambda=0.5$, providing an improved basis for the more tightly bound states.

With these two contrasting LTO basis sets, no optimization of λ for each partial wave for each $1sns\,^3S^e$ state for each Z was required. Since the partial-wave convergence for two-electron $^3S^e$ states in a CI-type expansion is faster that that of the $^1S^e$ series [19], no extrapolations to account for the $L_{max}\to\infty$ partial waves were required.

IV. RESULTS

Once the energies of the few low-lying Rydberg levels of $^3S^e$ symmetry for a sequence of Z values in the vicinity of $Z\approx1$ were obtained from the CI calculations, the next task was to use the energy of the lowest $1s2s\,^3S^e$ state to determine the parameters β_0, β_1 in Eq. (10). The exact function $\beta(Z)$ was determined using Eqs. (9) and (10) and the computed energies of the lowest $^3S^e$ level. The results are presented in Table I (fourth column).

The second and third columns represent successive approximations to the first two terms of the series in Eq. (11). These approximations have been defined as follows. For the

TABLE I. Sequences $\beta_0(Z)$ and $\beta_1(Z)$, calculated value of $\beta(Z)$, and approximation given by Eq. (13) for different values of Z.

Z	$\beta_0(Z)$	$\beta_1(Z)$	$\beta(Z)$	Eq. (13)
1.05	0.8745	3.1300	1.02808	1.025
1.10	0.8777	3.1639	1.18458	1.180
1.15	0.8843	3.2309	1.34278	1.335
1.20	0.8947	3.3089	1.50433	1.490
1.25	0.9092	3.3891	1.66978	1.645

sequence Z_i of Z values, the sequence $\beta_1(Z)=[\beta(Z_i)-\beta(Z_{i-1})]/(Z_i-Z_{i-1})$, has been formed. The limit of this sequence when $Z\to1$ is equal to the coefficient β_1 in Eq. (11). The third column of Table I shows that $\beta_1(Z)$ is nearly constant. From this a number of conclusions can be drawn. First, this confirms the overall validity of Eqs. (9)–(11). Further, it signifies that for the Z values considered here, higher-order terms (in powers of $Z-1$) are insignificant. Finally, near constancy of $\beta_1(Z)$ allows accurate determination of the coefficient β_1 in Eq. (8) by extrapolating values of $\beta_1(Z)$ given in Table I to $Z=1$. The value for β_1 obtained as a result of such extrapolation was $\beta_1\approx3.10$. Having determined β_1, the sequence $\beta_0(Z)$ defined as $\beta_0(Z)=\beta(Z)-\beta_1(Z)(Z-1)$ has been formed. The results from the Table I (second column) show that $\beta_0(Z)$ is an almost constant function, which can thus be reliably extrapolated to $Z=1$, giving $\beta_0\approx0.87$. Thus the ''exact'' function $\beta(Z)$ is approximately given by

$$\beta(Z)\approx0.87+3.10(Z-1). \quad (13)$$

That this approximation accurately represents the exact $\beta(Z)$ can be seen from Table I (columns four and five), where the exact $\beta(Z)$ as well as the results given by the approximation in Eq. (13) are presented. Even for Z as large as 1.3, the error remains at about 1%.

Besides the lowest $^3S^e$ level, the energies of the next few members of the Rydberg series have been computed. The results for the quantum defects for these levels [determined using Eq. (9)] are presented in Table II. Quantum defects predicted by Eq. (10) with $\beta(Z)$ given by Eq. (13) are also shown. Not all the entries in Table II are filled since the higher-lying members of the Rydberg series are difficult to

TABLE II. Quantum defects for the first few levels of $^3S^e$ symmetry for Z values close to 1.

| Level | Z | | | | | |
	1.05	1.10	1.15	1.20	1.25	1.30
1	0.1333	0.2220	0.2895	0.3440	0.3895	0.4283
2	0.1351	0.2252	0.2942	0.3497	0.3960	0.4355
3		0.2262	0.2953	0.3511	0.3977	0.4374
4			0.2964	0.3517	0.3984	0.4381
5				0.3557	0.3987	0.4385
6						0.4395
Eqs. (13,10)	0.1337	0.2228	0.2909	0.3468	0.3944	0.4361

TABLE III. Quantity $E+Z^2/2$, computed and given by QD formula (9) for the first few levels of $^3S^e$ symmetry for Z values close to 1.

CI	QD	CI	QD
$Z=1.05$		$Z=1.1$	
-0.0009731	-0.0009725	-0.0033481	-0.0033441
-0.0002741	-0.0002745	-0.0010097	-0.0010120
-0.0001088	-0.0001272	-0.0004803	-0.0004814
	-0.0000731	-0.0002676	-0.0002803
	-0.0000474	-0.0000699	-0.0001833
	-0.0000332		-0.0001291
	-0.0000245		-0.0000958
$Z=1.15$		$Z=1.2$	
-0.0067648	-0.0067502	-0.0110712	-0.0110265
-0.0021373	-0.0021434	-0.0036221	-0.0036315
-0.0010359	-0.0010387	-0.0017808	-0.0017855
-0.0006094	-0.0006110	-0.0010560	-0.0010585
-0.0003830	-0.0004018	-0.0006972	-0.0006995
-0.0001483	-0.0002842	-0.0004608	-0.0004965
	-0.0002116	-0.0001818	-0.0003705
$Z=1.25$		$Z=1.3$	
-0.0161854	-0.0160731	-0.0220579	-0.0218196
-0.0054430	-0.0054509	-0.0075861	-0.0075827
-0.0027068	-0.0027122	-0.0038084	-0.0038113
-0.0016153	-0.0016182	-0.0022845	-0.0022867
-0.0010721	-0.0010739	-0.0015214	-0.0015227
-0.0007586	-0.0007642	-0.0010851	-0.0010863
-0.0005007	-0.0005715	-0.0007961	-0.0008138

TABLE IV. Two-electron energies computed and given by QD formula (9) for the first few levels of $^3S^e$ symmetry for Z close to 1. Energies given in units of hartree.

E_{CI}	E_{QD}	E_{CI}	E_{QD}
$Z=1.05$		$Z=1.1$	
-0.552223140	-0.552222538	-0.608348079	-0.608344125
-0.551524187	-0.551524561	-0.606009713	-0.606012004
-0.551358841	-0.551377290	-0.605480382	-0.605481407
	-0.551323153	-0.605267629	-0.605280399
	-0.551297429		-0.605183303
	-0.551283225		-0.605129123
	-0.551274563		-0.605095844
$Z=1.15$		$Z=1.2$	
-0.668014878	-0.668000300	-0.731071242	-0.731026545
-0.663387381	-0.663393460	-0.723622187	-0.723631507
-0.662285996	-0.662288737	-0.721780862	-0.721785570
-0.661859451	-0.661861002	-0.721056094	-0.721058511
-0.661633088	-0.661651867	-0.720697255	-0.720699594
	-0.661534261	-0.720460834	-0.720496505
	-0.661461633	-0.720181872	-0.720370541
$Z=1.25$		$Z=1.3$	
-0.797435430	-0.797323106	-0.867057915	-0.866819670
-0.786693047	-0.786700934	-0.852586126	-0.852582724
-0.783956865	-0.783962277	-0.848808463	-0.848811387
-0.782865319	-0.782868299	-0.847284580	-0.847286712
-0.782322156	-0.782323915	-0.846521415	-0.846522786
-0.782008663	-0.782014286	-0.846085178	-0.846086346
-0.781750768	-0.781821543	-0.845796105	-0.845813810

treat computationally, especially for Z very close to 1. The energies for which the error in the CI calculations became significant were omitted.

Two important observations follow from the data presented in Table II. First, the predicted quantum defects agree closely with the calculated values. Second, the computed quantum defects for the different levels for a given Z reveal remarkable constancy, thus confirming the overall validity of the quantum-defect description for the Rydberg series of $1sns\,^3S^e$ when $Z \to 1$.

Tables III and IV present results for the energies both computed and predicted by the QD Eqs. (9), (10), and (13) of the first few levels of $1sns\,^3S^e$ Rydberg series for different Z-values. The energies in Table III are given relative to the threshold, i.e., are presented as $E+Z^2/2$. The overall agreement between the numerically calculated and predicted values is generally of the order of 1% or better. As expected, the agreement deteriorates for the higher-lying members of the Rydberg series, as the CI calculated energies are inherently less accurate than the CI calculated lower-lying state energies.

Primarily for reference purposes, we give in Table IV the full energies of the $1sns\,^3S^e$ states, both numerically calculated and those predicted by Eqs. (9), (10), and (13). Agreement is again excellent, but keep in mind that for Z very close to 1, the energy is largely dominated by the first term of Eq. (9). The true level of accuracy that the QD approach

gives should be judged by Table III. Taking into account possible numerical inaccuracies in the computed energies for the high-lying states and the fact that Eqs. (9), (10), and (13) only require two free parameters, the overall agreement of the present model is quite acceptable.

V. CONCLUSION

The comparison of the energies calculated numerically using the configuration-interaction method and those predicted by Eqs. (9), (10), and (13) strongly advocates the claim that these formulas provide not just a good physical approximation, but also describe the leading asymptotic behavior of the energies of $1sns\,^3S^e$ levels as $Z \to 1$. The constancy of quantum defects for different members of the Rydberg series and the accuracy with which the quantum defect is reproduced by the two-parameter theory constitutes a consistent picture.

For the excited states of a two-electron system, it has been suggested that $Z_{\text{crit}}=1$ exactly [6]. This implies that the bound states of the $1snl\,^3S^e$ Rydberg series cease to exist at $Z=1$. Equations (9), (10), and (13) are consistent with this view, presenting an asymptotically exact (as $Z \to 1$) description of the $^3S^e$ two-electron system. This exactness of the quantum-defect description could be due to the fact that the other channels of a two-electron system, neglected in the present single-channel approach, give contributions decaying for $Z \to 1$ faster than the right-hand side of Eq. (9). By the

same reasoning, it is quite possible that these channels, neglected in the present formulation, could introduce singular terms (i.e., exponentially decaying as $Z \to 1$) whose singularity at $Z \to 1$ would be more complicated than the simple logarithmic singularity given by Eqs. (9), (10), and (13).

A closely related but more complicated question regards the analytic structure of the exact energies of a two-electron atom in the vicinity of Z_{crit}. This has been studied extensively for the $^1S^e$ ground state of a two-electron system. The point at which the bound state ceases to exist, $Z_{crit} \approx 0.911\,028\,225$, is an essential singularity having a very complicated nature [6]. The approach in the present paper indicates that exact energies of the $^3S^e$ Rydberg series have singular points at $Z = 1$. The nature of these singular points (in the sense of a theory of analytic functions) cannot be studied by means of the present method. As mentioned above, the contributions to the energy due to the channels neglected in the present treatment,though being small compared to the leading term when $Z \to 1$, could introduce more complicated singularity than that given by Eqs. (9), (10), and (13).

The simple properties of the singly excited $^3S^e$ levels considered in the present paper are due to their hydrogenic character. The $^1S^e$ levels could also be similarly considered, given modifications involving the presence of a bound state (and noting that correlations play a predominant role in the formation of the $^1S^e$ ground state H^-). This and issues regarding states with nonzero angular momenta will be investigated separately.

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