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An asymptotic series solution to the Schrödinger equation for a model potential

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Abstract. Using the method of Frobenius, the attempt to find a closed-form solution to the Schrödinger equation for a model potential $V(r) = -Ze^2/\sqrt{r^2+a^2}$ is described. Inspection of the series solution in the asymptotic region suggests a substitution of a *four term* recurrence relation by a *two* term relation in order to extract explicit solutions that approach to those obtained for the hydrogen atom as $a \to 0$ smoothly. The resulting approximate solutions are compared with numerical ones and shown to provide a good basis set for high Rydberg states.

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1 Introduction

In previous studies [1,2], we have developed the inverse Born-Oppenheimer approximation (IBOA) as providing a new set of basis to perform *ab initio* calculations. By the IBOA, a molecule in high Rydberg states can be approximated as a Rydberg electron-ion system where in the zeroth order description the Rydberg electron and the parent ion can be treated separately. One natural basis for the Rydberg electron is the usual hydrogen basis. However, as we have pointed out in a previous paper [2], the singularity of the pure Coulomb potential causes divergence problems when applying it to low-l Rydberg states. To remedy this difficulty and at the same time to preserve the simplicity of the above-mentioned picture, we proposed a model potential of the form

$$V(r) = \frac{-Ze^2}{\sqrt{r^2+a^2}} \tag{1.1}$$

where the parameter a is of about the size of nuclear motion. This potential arises from an expansion, other than the usual von Neumann expansion, of the Coulombic interactions between the Rydberg electron and the ion [2]. Using this model potential, one can avoid the divergence problems because the potential has no singularity as $r \to 0$. Besides, this model potential exhibits the same long-range Coulombic tail as $r \to \infty$ and serves as a better choice to represent the true short-range behavior of a molecular system.

Initiating from different motivation, the model potential of equation (1.1) (soft-Coulomb potential) has been extensively used in the numerical simulation of the dynamical response of an atomic system in strong radiation fields [3–9], in the calculation of high harmonic generation and multiphoton ionization [10–13], and in the pseudopotential modeling of electronic structure of solids and surfaces [14,15]. Recently, Liu and Clark [16] and Clark [17] reported a family of closed-form solutions to the Schrödinger equation for the model potential in 1D and 3D cases, respectively. In their method, the known function form of the eigenvalues is fixed and "quantization" is performed to the suitable parameter a so that the physical boundary conditions can be satisfied. This procedure has been used to generate the Sturmian functions for hydrogen atom [18] and might be referred as the "pre-quantization" method. However, one should notice that only a subset of the solutions to a Sturmian equation can be obtained in this method and thus the general properties of complete sets can not be guaranteed. For example, they obtained only eigenvalues with integer quantum defects but could not find the global weight function over which all eigenfunctions of a given n are orthogonal [16,17].

In this paper, we will use the Frobenius series to represent the wavefunction and use the method of Frobenius to solve the equation. The question when the method of Frobenius will work is assured by the Fuchs's theorem [19,20], which states that at least one series solution can be obtained if the series is expanded at an ordinary point or at worst a regular singular point. By standard methods, one can find only implicit solutions from which the energy spectrum can not be obtained and the expansion coefficients become apparently infinite as $a \to 0$. Therefore, an assumption is proposed to extract explicit solutions that approach to those obtained for the hydrogen atom

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as $a \to 0$ smoothly. To justify the validity of this assumption, a numerical analysis is performed and the numerical results are compared with the series ones. It is found that the series solutions show good agreement with almost all the energy eigenvalues except for low n states.

2 Solutions by the Frobenius series expansion

The radial part equation for the model potential is

$$\frac{\mathrm{d}^2R}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}+\left[-\alpha^2+\frac{\beta}{\sqrt{r^2+a^2}}-\frac{l\,(l+1)}{r^2}\right]R=0 \tag{2.1}$$

where

$$\alpha=\sqrt{\frac{2m}{\hbar^2}\,(-E)} \tag{2.2}$$

and

$$\beta=\frac{2m}{\hbar^2}Ze^2. \tag{2.3}$$

Substituting

$$R\,(r)=r^l\chi\,(r)\,, \tag{2.4}$$

into equation (2.1), we have

$$\frac{\mathrm{d}^2\chi}{\mathrm{d}r^2}+\frac{2l+2}{r}\frac{\mathrm{d}\chi}{\mathrm{d}r}+\left[-\alpha^2+\frac{\beta}{\sqrt{r^2+a^2}}\right]\chi=0. \tag{2.5}$$

Letting $\rho=\sqrt{r^2+a^2}$ yields

$$\left(1-\frac{a^2}{\rho^2}\right)\frac{\mathrm{d}^2\chi}{\mathrm{d}\rho^2}+\left(\frac{2l+2}{\rho}+\frac{a^2}{\rho^3}\right)\frac{\mathrm{d}\chi}{\mathrm{d}\rho}+\left[-\alpha^2+\frac{\beta}{\rho}\right]\chi=0. \tag{2.6}$$

Making the substitution

$$\chi\,(\rho)=\mathrm{e}^{-\alpha\rho}f\,(\rho)\,, \tag{2.7}$$

we find

$$\begin{aligned}\left(1-\frac{a^2}{\rho^2}\right)\frac{\mathrm{d}^2f}{\mathrm{d}\rho^2}+\left(-2\alpha+\frac{2l+2}{\rho}+\frac{2\alpha a^2}{\rho^2}+\frac{a^2}{\rho^3}\right)\frac{\mathrm{d}f}{\mathrm{d}\rho}\\+\left[\frac{\beta-\alpha\,(2l+2)}{\rho}-\frac{\alpha^2a^2}{\rho^2}-\frac{\alpha a^2}{\rho^3}\right]f=0.\end{aligned} \tag{2.8}$$

Noticing that the point $\rho=0$ is a regular singular point, we apply the Frobenius series

$$f\,(\rho)=\rho^\lambda\sum_k b_k\rho^k, \tag{2.9}$$

where λ is the indicial index to be determined. The recurrence formula for the coefficients is then given by

$$\begin{aligned}a^2\,(k+\lambda+3)\,(k+\lambda+1)\,b_{k+3}=\alpha a^2\,(2k+2\lambda+3)\,b_{k+2}\\+\left[(k+\lambda+1)\,(k+\lambda+2l+2)-\alpha^2a^2\right]b_{k+1}\\+\left[\beta-2\alpha\,(k+\lambda+l+1)\right]b_k\end{aligned} \tag{2.10}$$

where $k=-3,-2,-1,...$

If $a=0$, equation (2.10) becomes

$$(k+\lambda+1)(k+\lambda+2l+2)b_{k+1}=[2\alpha(k+\lambda+l+1)-\beta]b_k. \tag{2.11}$$

The indicial equation of equation (2.11) is

$$\lambda\,(\lambda+2l+1)=0, \tag{2.12}$$

yielding $\lambda=0$ or $\lambda=-(2l+1)$. The series corresponds to the hydrogenic case with quantized energy $E_n=-1/2n^2$ (au), where $n=\overline{k}+l+1$ if the series terminates as a polynomial of the $\overline{k}$-th degree.

On the other hand, if $a\neq0$, for $k=-3$, equation (2.10) gives

$$a^2\lambda\,(\lambda-2)\,b_0=0 \tag{2.13}$$

yielding $\lambda=0$ or $\lambda=2$. For $\lambda=0$, we have

$$b_1=\alpha b_0 \tag{2.14}$$

$$b_3=\alpha b_2+\frac{\beta-\alpha^3a^2}{3a^2}b_0 \tag{2.15}$$

and so on, while for $\lambda=2$, equation (2.10) leads to

$$b_1=\alpha b_0 \tag{2.16}$$

$$b_2=\left(\frac{\alpha^2}{2}+\frac{2l+3}{4a^2}\right)b_0 \tag{2.17}$$

and

$$b_3=\left(\frac{\alpha^3}{6}+\frac{\alpha\,(2l+3)}{4a^2}+\frac{\beta}{15a^2}\right)b_0. \tag{2.18}$$

Continuing this procedure we can determine b_4, b_5, b_6, ... and the attempted series solution is achieved. However, the series represents only an implicit solution because the eigenvalues have not yet been determined.

From the above discussions, one can see that it is impossible to connect the solutions from the case of $a\neq0$ to the case of $a=0$ by simply letting $a\to0$ because the parameter a always appears in the denominators. To make this connection possible and to obtain the required energy spectrum, we notice that for large $k+l$ the recurrence formula (Eq. (2.10)) becomes

$$a^2\left(k^2b_{k+3}-2\alpha kb_{k+2}\right)=k^2b_{k+1}-2\alpha kb_k. \tag{2.19}$$

Restated, in the asymptotic region the series defined by equation (2.10) looks like a combination of two series with the same term ratios. This inspection from equation (2.19) suggests that the *four term* recurrence relation can be reduced to a *two term* relation

$$\begin{aligned}\left[(k+\lambda+1)\,(k+\lambda+2l+2)-\alpha^2a^2\right]b_{k+1}\\=\left[2\alpha\,(k+\lambda+l+1)-\beta\right]b_k.\end{aligned} \tag{2.20}$$

for the large $k+l$ limit. The series defined by equation (2.20) behaves as $\mathrm{e}^{+2\alpha r}$ and thus must be terminated.

Table 1. Comparison of the numerical (N) and analytical (A) eigenvalues of the model potential for $Z = 1$ and $a = 1$.

n	l=0 (N)	l=0 (A)	l=1 (N)	l=1 (A)	l=2 (N)	l=2 (A)	l=3 (N)	l=3 (A)	l=4 (N)	l=4 (A)
1	-0,2749	-0,3229								
2	-0,0927	-0,1175	-0,1130	-0,1185						
3	-0,0455	-0,0548	-0,0521	-0,0548	-0,0544	-0,0549				
4	-0,0269	-0,0311	-0,0298	-0,0311	-0,0308	-0,0311	-0,0311	-0,0311		
5	-0,0177	-0,0200	-0,0192	-0,0200	-0,0198	-0,0200	-0,0199	-0,0200	-0,0200	-0,0200
6	-0,0126	-0,0139	-0,0135	-0,0139	-0,0138	-0,0139	-0,0138	-0,0139	-0,0139	-0,0139
7	-0,0094	-0,0102	-0,0099	-0,0102	-0,0101	-0,0102	-0,0102	-0,0102	-0,0102	-0,0102
8	-0,0072	-0,0078	-0,0076	-0,0078	-0,0078	-0,0078	-0,0078	-0,0078	-0,0078	-0,0078
9	-0,0058	-0,0062	-0,0060	-0,0062	-0,0061	-0,0062	-0,0062	-0,0062	-0,0062	-0,0062
10	-0,0047	-0,0050	-0,0049	-0,0050	-0,0050	-0,0050	-0,0050	-0,0050	-0,0050	-0,0050
11	-0,0039	-0,0041	-0,0041	-0,0041	-0,0041	-0,0041	-0,0041	-0,0041	-0,0041	-0,0041
12	-0,0033	-0,0035	-0,0034	-0,0035	-0,0035	-0,0035	-0,0035	-0,0035	-0,0035	-0,0035
13	-0,0028	-0,0030	-0,0029	-0,0030	-0,0029	-0,0030	-0,0030	-0,0030	-0,0030	-0,0030
14	-0,0024	-0,0026	-0,0025	-0,0026	-0,0025	-0,0026	-0,0025	-0,0026	-0,0026	-0,0026
15	-0,0021	-0,0022	-0,0022	-0,0022	-0,0022	-0,0022	-0,0022	-0,0022	-0,0022	-0,0022
16	-0,0019	-0,0020	-0,0019	-0,0020	-0,0019	-0,0020	-0,0020	-0,0020	-0,0020	-0,0020
17	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017	-0,0017
18	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015	-0,0015
19	-0,0013	-0,0014	-0,0014	-0,0014	-0,0014	-0,0014	-0,0014	-0,0014	-0,0014	-0,0014
20	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012	-0,0012

For a definite $b_{\overline{k}+1}$ to be vanished, we obtain (in atomic units)

$$E_n = -\frac{1}{2\left(n - \delta_l\left(E_n, a\right)\right)^2} \tag{2.21}$$

and

$$\delta_l\left(E, a\right) = -\lambda. \tag{2.22}$$

Notice that equation (2.21) is equivalent to the general Rydberg formula observed in experiments and $\delta_l\left(E_n, a\right)$ is the quantum defect. Therefore, we assume that the series defined by equation (2.20) represents an approximate solution to equation (2.10). In the asymptotically large k domain this assumption can be satisfied if the indicial index λ can be determined by requiring the ratios b_{k+1}/b_k inferred from equations (2.10, 2.20) to be the same; that is,

$$\frac{\alpha\left(2k + 2\lambda - 1\right)}{\left(k + \lambda + 1\right)\left(k + \lambda - 1\right)} = \frac{2\alpha\left(k + \lambda + l + 1\right) - \beta}{\left(k + \lambda + 1\right)\left(k + \lambda + 2l + 2\right) - \alpha^2 a^2}\,. \tag{2.23}$$

From equation (2.23), only the fractional part of λ can be determined (λ is the quantum defect with a minus sign) and we then find

$$\lambda = \frac{\alpha\left(2l + 3\right) + 2\beta + 2\alpha^3 a^2 - \sqrt{\Delta}}{2\left[\alpha\left(2l + 3\right) + \beta\right]} \mathrm{mod}\left(1\right), \tag{2.24}$$

where

$$\Delta = \left[\alpha(2l+3) + 2\beta + 2\alpha^3 a^2\right]^2 - 12\alpha^3 a^2\left[\alpha(2l + 3) + \beta\right]. \tag{2.25}$$

By making use of equations (2.24, 2.25), we can easily show the important characteristics found in the quantum defect theory; that is, $\delta_l\left(E, a\right) \to 0$ as $a \to 0$, and $\delta_l\left(E, a\right)$ decreases as l increases. Therefore, it is indeed proved that the above approach is consistent with the quantum defect theory.

From equation (2.20) we obtain

$$b_1 = \frac{2\alpha\left(\lambda + l + 1\right) - \beta}{\left(\lambda + 1\right)\left(\lambda + 2l + 2\right) - \alpha^2 a^2} b_0 \tag{2.26a}$$

$$b_2 = \frac{2\alpha\left(\lambda + l + 2\right) - \beta}{\left(\lambda + 2\right)\left(\lambda + 2l + 3\right) - \alpha^2 a^2} b_1 \tag{2.26b}$$

$$b_3 = \frac{2\alpha\left(\lambda + l + 3\right) - \beta}{\left(\lambda + 3\right)\left(\lambda + 2l + 4\right) - \alpha^2 a^2} b_2 \tag{2.26c}$$

and so on. The general form of the series is thus given by

$$f\left(\rho\right) = b_0\rho^{-\delta_l} + b_1\rho^{1-\delta_l} + b_2\rho^{2-\delta_l} + ... + b_{\overline{k}}\rho^{\overline{k}-\delta_l}, \tag{2.27}$$

which can be reduced to the hydrogen case as $a \to 0$. It is obvious that using this wavefunction one can avoid the divergence problems in calculating relevant matrix elements compared to using the hydrogen one.

Although physically preferred, it should be noted that the assumption of reducing the *four term* recurrence relation to the *two term* relation seems accidental. It has not been clear yet from the above analysis as to what to the extent the assumption holds. Therefore, we shall perform a numerical analysis to compare the energy spectrum obtained by the series method with the resulting ones. We use the Runge-Kutta 4th order method with the finest resolution of 10^{-3} to solve equation (2.1). Table 1 shows comparison between the series and the numerical results for $Z = 1$ and $a = 1$. One can see in Table 1 that almost all the energy eigenvalues can be obtained by using the above simple analytical solutions except for low n states. For example, for np states, the numerical and the series results are the same as $n \geq 17$ and for ng states, they are the same as $n \geq 5$. The general agreement between the analytical and the numerical results has been verified and shown to be extended to other nl states. Therefore, we conclude that we have obtained an approximate analytical solution to equation (2.1) for high Rydberg states.

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