Highly accurate eigenvalues for the distorted Coulomb potential

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We consider the eigenvalue problem for the radial Schrödinger equation with potentials of the form $V(r)=S(r)/r+R(r)$ where $S(r)$ and $R(r)$ are well behaved functions which tend to some (not necessarily equal) constants when $r\to 0$ and $r\to\infty$. Formulas (14.4.5)–(14.4.8) of Abramowitz and Stegun [*Handbook of Mathematical Functions*, 8th ed. (Dover, New York, 1972)], corresponding to the pure Coulomb case, are here generalized for this distorted case. We also present a complete procedure for the numerical solution of the problem. Our procedure is robust, very economic and particularly suited for very large n. Numerical illustrations for n up to 2000 are given.

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I. INTRODUCTION

There is not a unique way to solve numerically the radial Schrödinger equation

$$y''=\left(\frac{l(l+1)}{r^2}+V(r)-E\right)y, \quad r>0. \tag{1.1}$$

Instead, a large variety of algorithms is available and the choice of one algorithm or another depends on the characteristics of the problem. When the orbital quantum number l equals zero, $V(r)$ is a well behaved, nonsingular function and when the involved range of energies is low lying (as it is when the ground state and a few excited states are searched for) any standard algorithm for solving ordinary differential equations (Runge-Kutta or Numerov, for example) is perhaps satisfactory. However, when high lying bound states or resonance states are investigated, special techniques should be chosen to adequately account for the oscillatory character of the solution. For such a case methods based on the exponential fitting or on the piecewise perturbation technique [1] are among the best candidates for use. In other situations, for example when $V(r)$ is a succession of hills and valleys (e.g., Coffey-Evans potential [2]) or when $V(r)$ exhibits a violent variation around the origin [Lenard-Jones (12,6) [3]] some additional care is required.

In this paper we are concerned with the case when $V(r)$ behaves as a Coulomb potential both around the origin and in the asymptotic range but not necessarily with the same electric charge in the two regions. There is no drastic restriction on how $V(r)$ behaves in between. We thus cover a wide variety of physical problems, to mention only phenomena related to the total or partial screening or to the superposition of electric and nuclear effects. All such effects become tractable with high accuracy and, most important, our procedure is particularly suited for the case of very large n's, as it is for the Rydberg states [4].

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II. FORMULATION OF THE PROBLEM

As said, we are concerned with potentials of the form

$$V(r)=\frac{S(r)}{r}+R(r), \tag{2.1}$$

where $S(r)$ and $R(r)$ are well behaved functions such that

$$\lim_{r\to 0}S(r)=S_0, \quad \lim_{r\to\infty}S(r)=S_{as},$$
$$\lim_{r\to 0}R(r)=R_0, \quad \lim_{r\to\infty}R(r)=R_{as}, \tag{2.2}$$

where S_0, S_{as}, R_0, and R_{as} are constants. In atomic physics S_0 might be seen as $-2Z_0$ and S_{as} as $-2Z_{as}$ where Z_0 is the nuclear charge and Z_{as} the ion charge. Specifically, it is assumed that around the origin $S(r)$ and $R(r)$ can be written in polynomial form

$$S(r)=\sum_{m=0}^{M}S_m r^m, \quad R(r)=\sum_{m=0}^{M-1}R_m r^m, \quad 0\leqslant r\leqslant r_0 \tag{2.3}$$

and that some r_{as} does exist such that

$$V_{as}(r)=\frac{S_{as}}{r}+R_{as} \tag{2.4}$$

is a good approximation of $V(r)$ for all $r>r_{as}$.

As also said, we are interested in the accurate computation of the eigenvalues E_{nl} of Eq. (1.1) for this potential, with uniform accuracy vs the principal quantum number n. The procedure which will be described allows computing the associated normalized eigenfunctions as well.

We locate the eigenenergies by shooting. The half axis $r>0$ is first cut at some large $r_{\max}>r_{as}$ and a matching point r_{match} is fixed somewhere on $I=(0,r_{\max}]$. For each test value of E the equation is integrated from the two ends up to r_{match} to generate the so-called miss distance corresponding to that E. A new value of E, hopely closer to the required eigenvalue, is calculated in terms of the miss distance and the procedure is repeated as many times as necessary to bring the

miss-distance at the round-off level. The shooting procedure is described in many books, e.g., Ref. [1,3].

Two specific issues have to be examined adequately.

(1) The equation is singular at the origin and therefore the numerical integration around the origin should be carried out by a procedure which explicitly accounts for this fact. Since, on the other hand, the effect of the singularity progressively dies out when r is increased, the integration interval I has to be split into two subintervals, a narrow subinterval around the origin, $I_1=(0,r_0]$, and the remaining $I_2=(r_0,r_{\max}]$. The algorithm to be used on I_1 should be consistent with the singular nature of the equation while the algorithm to be used on I_2 should be chosen on the basis of a different condition.

(2) The condition to be fulfilled by the algorithm for I_2 is mainly dictated by another characteristic of the problem, namely, that I_2 is typically a very long interval. For example, in the classical hydrogen atom case [$S(r)=-2$ and $R(r)=0$] the energy levels are $E_{nl}=1/(n+l+1)^2$. [Note in passing that, due to the scale adopted in Eq. (1.1), the energy levels are twice their values in the usual atomic units.] To compute numerically $E_{1999,0}$ for this innocent looking problem $r_{\max}$ should be taken such that $V(r_{\max})>E_{1999,0}$, i.e., $r_{\max}>8\times10^6$. As a consequence, the method to be used on such a broad I_2 should be of a type which enables producing highly accurate results at unusually big steps, with widths of several thousands or so. This is not at all the case with the standard methods for differential equations but, fortunately, this condition was the easiest to fulfil. In fact, the piecewise perturbation method, originally formulated in Ref. [1], was recently reexamined and a high order version was constructed [5,6]. The method can work without difficulty with big steps, produces very accurate results and, more than this, its accuracy stays the same no matter how big the energy is. This is the method we choose for I_2.

Therefore, the problem of I_1 is the one which requires a detailed investigation, and in this paper we chose placing it on the central focus. A first question to be answered is where should r_0 be located and what algorithm has to be chosen for I_1?

The position of r_0 results as a compromise of two opposite tendencies. If we take r_0 so close to the origin that only the centrifugal component matters, then the regular solution on I_1 (this is the only solution we are interested in) is simply $y(r)=r^{l+1}$; the Coulomb term introduces components with higher exponents. The point is that when we start to advance the solution on I_2, then for a while the solution is still dominated by such a form of the solution and if the method chosen for I_2 would be a classical method (Runge-Kutta or Numerov, for example) the width of the steps will be dictated by how good such a shape of the solution can be approximated by a low degree polynomial. This is obviously a poor approximation and therefore the resulting steps will be too small for making the integration efficient. For some related investigation see Ref. [7]. A similar situation is taking place with the piecewise perturbation algorithm too because here the starting approximation is that of $l(l+1)/r^2+V(r)$ through a step function. A way to increase the value of r_0 consists of taking a better approximation around the origin and one possibility is to take just the regular Coulomb function F_l for y. (For a numerical procedure to calculate the Coulomb functions, see Ref. [8].) However, this is equivalent to fully disregarding the other components in $S(r)$ and $R(r)$ and in many cases this may be a too severe simplification.

In short, if the usual ways are only considered, then a too small r_0 is convenient for I_1 but it creates difficulties on I_2 while the opposite is true if r_0 is enlarged. An escape from this situation consists in developing a new procedure for I_1 which compactly accounts for both the singularity of the equation and the structure (2.3) of $S(r)$ and $R(r)$. Such a procedure is worked out in the next section.

III. AN ACCURATE SOLUTION ON I_1

The Coulomb wave equation

$$w''=\left[\frac{l(l+1)}{x^2}+\frac{2\eta}{x}-1\right]w \tag{3.1}$$

admits two linear independent solutions, one regular F_l and one singular G_l. Formulas (14.4.5)–(14.48) in [9] allow writing F_l and its derivative in terms of the spherical Bessel functions. The expansion of F_l reads

$$F_l(\eta,x)=1\times3\times5\times\cdots\times(2l+1)C_l(\eta)x \times\sum_{k=l}^{\infty}b_k(\pi/2x)^{1/2}J_{k+1/2}(x), \tag{3.2}$$

with $b_l=1$, $b_{l+1}=(2l+3)\eta/(l+1)$,

$$C_l(\eta)=2^l e^{-\pi\eta/2}|\Gamma(l+1+i\eta)|/\Gamma(2l+2),$$

and

$$b_k=\frac{2k+1}{k(k+1)-l(l+1)} \times\left(2\eta b_{k-1}-\frac{(k-1)(k-2)-l(l+1)}{2k-3}b_{k-2}\right), \qquad k>l+1. \tag{3.3}$$

We want to generalize this formula in a way to be convenient for our purpose. Upon using Eq. (2.3) and denoting $V_0=S_0$, $V_1=S_1+R_0$, $\ldots$, $V_M=S_M+R_{M-1}$, Eq. (1.1) becomes

$$y''=\left[\frac{l(l+1)}{r^2}+\sum_{m=0}^{M}V_m r^{m-1}-E\right]y \tag{3.4}$$

and, with the change of the variable $x=\sqrt{E}\,r$, and of the function $w(x)=y(r)$, it reads

$$w''=\left[\frac{l(l+1)}{x^2}+\sum_{m=0}^{M}v_m x^{m-1}-1\right]w, \tag{3.5}$$

where $v_m=V_m/E^{(m+1)/2}$. The Coulomb wave equation is the particular case of the latter for $v_0=2\eta$ and $v_m=0$, $m=1,2,\ldots,M$.

In dealing with the present generalization we prefer to work with the set of functions $\xi(Z)$, $\eta_s(Z)$, $s=0,1,2,\ldots$ (see Appendix) instead of the Bessel functions. There are two reasons for it: (i) this set is at the basis of the whole formalism of the piecewise perturbation method we use on I_2 and (ii) the simple differentiation properties of these functions make the manipulations simplier. As a matter of fact, these functions are related to the spherical Bessel functions

$$\xi(-x^2)=(\pi/2x)^{1/2}J_{-1/2}(x),$$
$$\eta_s(-x^2)=(\pi/2)^{1/2}x^{-(s+1/2)}J_{s+1/2}(x),\quad s=0,1,2,\ldots \tag{3.6}$$

and therefore Eq. (3.2) reads $F_l(\eta,x)=\beta\phi(x)$, where

$$\phi(x)=x\sum_{s=0}^{\infty} g_s^0(x)\,\eta_{l+s}(-x^2),\quad g_s^0(x)=b_{l+s}x^{l+s} \tag{3.7}$$

and β is a constant, viz, $\beta=1\times3\times5\cdots(2l+1)C_l(\eta)$.

We are interested in the expression of $\phi(x)$ for the distorted Coulomb wave equation (3.5). The results are as follows:

The regular solution of Eq. (3.5) is

$$\phi(x)=x\sum_{s=0}^{\infty} g_s(x)\,\eta_{l+s}(-x^2),\quad g_s(x)=\sum_{j=0}^{\infty} g_{s,j}x^{l+s+j}. \tag{3.8}$$

The coefficients $g_{s,j}$ are

$$g_{0,0}=1,\quad g_{0,j}=0,\quad j=1,2,3,\ldots,$$
$$g_{1,j}=\frac{(2l+3)v_j}{(j+1)(2l+j+2)},\quad j=0,1,2,\ldots,$$
$$g_{s,j}=\frac{2l+2s+1}{(s+j)(2l+s+j+1)}\left[\sum_{p=0}^{P} g_{s-1,j-p}v_p-\frac{(s-j-2)(2l+s-j-1)}{2l+2s-3}g_{s-2,j}\right]$$
$$s=2,3,\ldots,\ j=0,1,2,\ldots. \tag{3.9}$$

Its derivative with respect to x is

$$\phi'(x)=\sum_{s=0}^{\infty}\sum_{j=0}^{\infty} g_{s,j}[-(l+s-j)\,\eta_{l+s}(-x^2)+\eta_{l+s-1}(-x^2)]x^{l+s+j}, \tag{3.10}$$

where $P=\min\{j,M\}$.

Since Eq. (3.5) comes from the original equation through an E dependent scaling it is clear that $\phi(x)$ and $\phi'(x)$ will depend on E both implicitly (through x) and explicitly (through v_m). The latter is reflected in the E dependence of $g_{s,j}$.

We have the additional result that the first derivative of $\phi(x)$ and of $\phi'(x)$ with respect to E [let them be denoted as $\phi_E(x)$ and $\phi'_E(x)$, respectively] can be expressed as

$$\phi_E(x)=\frac{1}{2E}\left[x\phi'(x)+\sum_{s=0}^{\infty}\sum_{j=0}^{\infty} x^{l+s+j+1}w_{s,j}\,\eta_{l+s}(-x^2)\right], \tag{3.11}$$

$$\phi'_E(x)=\frac{1}{2E}\left[x\phi''(x)+\sum_{s=0}^{\infty}\sum_{j=0}^{\infty} x^{l+s+j}w_{s,j}[-(l+s-j)\,\eta_{l+s}(-x^2)+\eta_{l+s-1}(-x^2)]\right], \tag{3.12}$$

where $w_{0,j}=0$, $w_{1,j}=-(j+1)g_{1,j}$, $j=0,1,2,\ldots$, and

$$w_{s,j}=\frac{2l+2s+1}{(s+j)(2l+s+j+1)}\left[\sum_{p=0}^{P}(w_{s-1,j-p}-(p+1)\times g_{s-1,j-p})v_p-\frac{(s-j-2)(2l+s-j-1)}{2l+2s-3}w_{s-2,j}\right],$$
$$s=2,3,\ldots,\ j=0,1,2,\ldots. \tag{3.13}$$

For a numerical evaluation $\phi''(x)$ is replaced by the right-hand side (RHS) of Eq. (3.5) with ϕ for w.

Remarks.

(1) As expected, in the particular case $v_0=2\eta$ and $v_m=0$, $m=1,2\ldots$ formulas (3.8) and (3.10) reduce to the formulas (14.4.5–8) in Ref. [9] except, of course, for the constant factor β.

(2) Conversion of these values, obtained in the x variable, to the values to be used in the original r variable is: $y(r)=\phi(x)$, $y'(r)=\sqrt{E}\,\phi'(x)$, $y_E(r)=\phi_E(x)$, $y'_E(r)=\sqrt{E}\,\phi'_E(x)$.

(3) The values of y_E and y'_E are useful for calculating the integral of y^2 on I_1. As shown in Ref. [10] the following formula exists:

$$\int_0^{r_0} y^2(r)dr=y'(r_0)y_E(r_0)-y'_E(r_0)y(r_0). \tag{3.14}$$

They are also used in the process of forming the derivative of the miss-distance with respect to E which, at its turn, is necessary to locate the eigenvalues by a Newton-Raphson procedure.

(4) The standard formulas cannot accomodate the case $E=0$; indeed, since $x=\sqrt{E}\,r$, Eq. (3.1) cannot be defined. With the new formulas this difficulty is easily circumvented because we can conveniently shift the input V_1 and E, $V_1^{\text{new}}=V_1+\Delta$, $E^{\text{new}}=E+\Delta$, say, and then take $x=\sqrt{E^{\text{new}}}\,r$.

(5) The above formulas directly apply to the case of E positive. When E is negative, $x=i\sqrt{-E}\,r$ and $v_m=i^{-(m+1)}V_m/(-E)^{(m+1)/2}$, and it is readily verified from Eq. (3.9) that $g_{s,j}$ is either real or purely imaginary depending of whether $s+j$ is even or odd. It follows that for $E<0$ one can avoid complex arithmetic by setting $x=\sqrt{-E}\,r$, $v_m=V_m/(-E)^{(m+1)/2}$, and by inserting at some appropriate places a minus sign in Eq. (3.8) and (3.9).

Proof. The idea consists in constructing the two sides of Eq. (3.5) separately and then identifying the like terms.

With the expression (3.8) for $\phi(x)$ the first derivative is

$$\phi'(x)=\sum_{s=0}^{\infty}\left[g_s(x)\,\eta_{l+s}(-x^2)+xg_s'(x)\,\eta_{l+s}(x^2)+xg_s\frac{d}{dx}\,\eta_{l+s}(-x^2)\right]. \tag{3.15}$$

Since

$$\frac{d}{dx}\,\eta_{l+s}(-x^2)=\frac{d}{d(-x^2)}\,\eta_{l+s}(-x^2)\frac{d(-x^2)}{dx}=-x\,\eta_{l+s+1}(-x^2), \tag{3.16}$$

see Eq. (A9), and

$$-x^2\,\eta_{l+s+1}(-x^2)=\eta_{l+s-1}(-x^2)-(2l+2s+1)\times\eta_{l+s}(-x^2), \tag{3.17}$$

see Eq. (A4), Eq. (3.15) becomes

$$\phi'(x)=\sum_{s=0}^{\infty}\{[-2(l+s)g_s(x)+xg_s'(x)]\,\eta_{l+s}(-x^2)+g_s(x)\,\eta_{l+s-1}(-x^2)\}. \tag{3.18}$$

We differentiate this once again and use the same procedure as before, with the result

$$\phi''(x)=\sum_{s=0}^{\infty}\left[\left(xg_s''(x)-4(l+s)g_s'(x)+2(l+s)\times(2l+2s+1)\frac{g_s(x)}{x}\right)\eta_{l+s}(-x^2)+\left[2g_s'(x)-(4l+4s-1)\frac{g_s(x)}{x}\right]\eta_{l+s-1}(-x^2)+\frac{g_s(x)}{x}\,\eta_{l+s-2}(-x^2)\right]. \tag{3.19}$$

For the RHS we have in order

$$[\text{RHS of Eq. (3.19)}]=\left(\frac{l(l+1)}{x^2}+\sum_{m=0}^{M}v_mx^{m-1}-1\right)\phi(x)=\sum_{s=0}^{\infty}\left[\left(\frac{l(l+1)}{x}+\sum_{m=0}^{M}v_mx^m\right)\times g_s(x)\,\eta_{l+s}(-x^2)-xg_s(x)\,\eta_{l+s}(-x^2)\right]. \tag{3.20}$$

We replace the last $\eta_{l+s}(-x^2)$ by its expression in terms of $\eta_{l+s-1}(-x^2)$ and $\eta_{l+s-2}(-x^2)$,

$$\eta_{l+s}(-x^2)=-\frac{1}{x^2}[\,\eta_{l+s-2}(-x^2)-(2l+2s-1)\times\eta_{l+s-1}(-x^2)], \tag{3.21}$$

so that

$$[\text{RHS of Eq. (3.19)}]=\sum_{s=0}^{\infty}\left[\left(\frac{l(l+1)}{x}+\sum_{m=0}^{M}v_mx^m\right)g_s(x)\,\eta_{l+s}(-x^2)-(2l+2s-1)\frac{g_s(x)}{x}\,\eta_{l+s}(-x^2)+\frac{g_s(x)}{x}\,\eta_{l+s-2}(-x^2)\right]. \tag{3.22}$$

We now consider the equation $\phi''=\text{RHS}$ [i.e., Eq. (3.5] with ϕ for w) and identify the terms with the same label for η. The terms with η_{l+s-2} cancel out while from the others we get

$$2g_0'(x)-(4l-1)\frac{g_0(x)}{x}=-(2l-1)\frac{g_0(x)}{x} \tag{3.23}$$

from $\eta_{l-1}(-x^2)$ (Note: η_{-1} which appears when $l=0$ means formally ξ.),

$$xg_0''(x)-4lg_0'(x)+2l(2l+1)\frac{g_0(x)}{x}+2g_1'(x)-(4l+3)\times\frac{g_1(x)}{x}=\left(\frac{l(l+1)}{x}+\sum_{m=0}^{M}v_mx^m\right)g_1(x), \tag{3.24}$$

from $\eta_l(-x^2)$, and

$$xg_p''(x)-4(l+p)g_p'(x)+2(l+p)(2l+2p+1)\frac{g_p(x)}{x}+2g_{p+1}'(x)-(4l+4p+3)\frac{g_{p+1}(x)}{x}=\left(\frac{l(l+1)}{x}+\sum_{m=0}^{M}v_mx^m\right)g_p(x), \tag{3.25}$$

from $\eta_{l+p}(-x^2)$, $p=1,2,\ldots$. Finally we introduce the series (3.8) for the g_s, take $g_{0,0}=1$ and identify the coefficients of the like powers in each of the last three equations to just obtain Eq. (3.9). The expression (3.10) for ϕ' results by substituting the series (3.8) into Eq. (3.18). To derive the formula for ϕ_E we take into account that x depends of E through the relationship $x=\sqrt{E}\,r$ and use

$$\phi_E=\phi'(x)\frac{\partial x}{\partial E}+\frac{\partial\phi}{\partial E}. \tag{3.26}$$

With ϕ as in Eq. (3.8) we have

$$\frac{\partial\phi}{\partial E}=\sum_{j=0}^{\infty}\sum_{s=0}^{\infty}\frac{dg_{s,j}}{dE}x^{l+s+j+1}\,\eta_{l+s}(-x^2) \tag{3.27}$$

so that, upon noticing that $\partial x/\partial E = x/2E$ and upon denoting $dg_{s,j}/dE = 2Ew_{s,j}$ we get formula (3.13). The formulas to be satisfied by the $w_{s,j}$'s result by just differentiating Eqs. (3.9) for the $g_{s,j}$'s. The formula for ϕ'_E is obtained in the same way. The proof is thus completed. □

The forms (3.8) and (3.10) for the solution of Eq. (3.5) are of a type which would alternatively result if the piecewise perturbation technique were used with $\overline{V}(x) = l(l+1)/x^2$ as the reference potential and with $\Delta V(x) = \Sigma_{m=0}^{M} v_m x^{m-1}$ as the perturbation, in a Schrödinger equation with the unit value for the energy. An examination from this perspective enables drawing some qualitative estimation on the accuracy to be expected from the above formulas. First, the series over s and j are infinite but in practice they must be cut off somewhere. What about the accuracy for one and the same cut? As in any perturbation procedure with a finite number of corrections included, the answer depends on how small or big is the perturbation with respect to the reference potential. One general conclusion is that, insomuch as the reference potential dies out quickly with x, but this is not necessarily the case for the perturbation, the formulas are expected to be particularly efficient only in the vicinity of the origin. The actual extension of this interval depends on the specific features of the problem to be solved. If $l=0$, for example, the relative importance of the perturbation is big even at small x and therefore the interval is necessarily very narrow. Moreover, the larger and larger $|v_0|$ the smaller and smaller is the interval. Another expectation is that, for fixed $\Delta V(x)$, the efficiency of these formulas will increase with l or, alternatively, they will be convenient on a larger and larger interval.

Technically, these tendencies appear under the form of a slower and slower convergence of the series when x is increased. We are aware that an additional extension of the range of x may be achieved provided the so called acceleration procedures were used when summing the series. However, the success of each acceleration procedure (see, e.g., Ref. [11]) depends on the specific characteristics of the series. We did some tests by using the procedures of Wynn, of Levin, and a hybrid of them. There were cases when some of the three gave good results but the number of such cases was small. This indicates that in general the behavior of the series for which the mentioned procedures work does not fit the behavior of our series.

Another question refers to the energy dependence of the accuracy. In fact, Eq. (3.5) is an energy dependent scaling of Eq. (3.4) we actually have to solve, and therefore for each and the same input l and $V(r)$ the comparative magnitude of the reference and perturbation potential in the x variable is necessarily E dependent. This suggests that a really energy independent treatment will be achieved only if the perturbation technique will be applied directly on the original equation, not on its energy dependent representation. This is possible in principle but in practice some technical inconveniences appear. The most severe is that the expressions of successive orders of the perturbation will contain increasingly complicated expressions with logarithmic functions. By using MATHEMATICA we were unable to obtain more than two orders of perturbation. We also mention that a perturbation procedure applied directly on the original equation is described in Sec. 3.7 of Ref. [1]. However, that procedure remains energy dependent because there the reference potential is $\overline{V}(r) = l(l+1)/r^2$ but the perturbation is the whole $V(r) - E$.

In our computations the upper end of I_1 was set as

$$r_0 = \min\left\{\frac{12(l+1)}{l+21}, \frac{10(l+5)}{|S_0|}\right\}, \tag{3.28}$$

an empirical formula which disregards the energy dependence. On I_1 defined in this way we tested the accuracy of the new formulas for various values of l between 0 and 25, $|S_0|$ between 2 and 200, E between $-|S_0|^2/4(l+1)^2$ and $|S_0|^2/4(l+1)^2$, and for various shapes for the distorsion. With s and j limited up to 50 and 25, respectively, the relative error in y and in y' was typically of 10^{-14} except in the vicinity of the zeros of these functions. The accuracy of the procedure described in Sec. 3.7 of Ref. [1] was often good as well, but a systematic deterioration of the accuracy (of two or three orders of magnitude) was observed at the ends of the energy interval. The coefficients $S_0, S_1, \ldots, S_M$ and $R_0, R_1, \ldots, R_{M-1}$ were computed by first developing $S(r)$ and $R(r)$ over shifted Legendre polynomials and then reconverting these expansions in powers of r.

IV. A SHORT DESCRIPTION OF THE PROGRAM

In essence, the program consists of an adaptation of the program described in Refs. [5,6] for the eigenvalue problem associated to the regular Sturm-Liouville equation. In that program the Sturm-Liouville equation is first converted to a regular Schrödinger form and it is the latter which is actually solved. In other words, that program solves the Schrödinger equation only when the interval is of the I_2 type. We then had to enlarge it in a way to accept the interval I_1 as well and also to add a procedure which allows convenient selection of the subinterval of I_2 to be used in the range of interest for E. The user has to provide as input a suitably large value for $r_{\max}$ and the program constructs the partition of $I_2 = (r_0, r_{\max}]$ in terms of the tolerance tol also given on input. If $r_1, r_2, \ldots, r_{k_{\max}} = r_{\max}$ are the mesh points of the partition, the matching point of the forward and backward solutions is selected as that r_k for which $l(l+1)/r_k^2 + V(r_k)$ is minimal. For each test value of E in the iteration procedure for the calculation of the eigenvalues, a current lower limit for $r_{\max}$ is taken. This current value, call it $r'_{\max}$, is given as the lowest mesh point for which the condition

$$Q = \int_{r_t}^{r_k} \sqrt{\frac{l(l+1)}{r^2} + V_{as}(r) - E}\; dr > 25 \tag{4.1}$$

is fulfilled, where r_t is the rightmost turning point for that E. This condition is consistent with the usual WKB arguments (see, e.g., Ref. [12]) as it ensures that taking the RHS boundary condition simply as

$$y'(r'_{\max}) = -\sqrt{\frac{l(l+1)}{r'^{\,2}_{\max}} + V_{as}(r'_{\max}) - E}\; y(r'_{\max}) \tag{4.2}$$

is safe for double precision calculations. For that E only the current $I'_2 = (r_0, r'_{\max}]$ is actually involved.

The method used on I_2' is a highly accurate piecewise perturbation method in the *CP* form. On each interval $[r_k, r_{k+1}]$ with the width $h = r_{k+1} - r_k$ the Schrödinger equation for a generic $V(r)$

$$y'' = [V(r) - E]y \tag{4.3}$$

and its derivative with respect to E,

$$y_E'' = [V(r) - E]y_E - y, \tag{4.4}$$

are considered. Of course, the generic $V(r)$ is in our case the whole sum $l(l+1)/r^2 + V(r)$.

The algorithm links the y, y' and their first derivatives with respect to E, vectors $y(r) = (y(r), y'(r))$ and $y_E(r) = (y_E(r), y_E'(r))$, at the two ends of the interval. The solution is propagated forwards or backwards according to the following matrix equations:

$$\begin{aligned} \boldsymbol{y}(r_{k+1}) &= \boldsymbol{T}^f(h)\boldsymbol{y}(r_k), \\ \boldsymbol{y}_E(r_{k+1}) &= \boldsymbol{T}_E^f(h)\boldsymbol{y}(r_k) + \boldsymbol{T}^f(h)\boldsymbol{y}_E(r_k), \\ \boldsymbol{y}(r_k) &= \boldsymbol{T}^b(h)\boldsymbol{y}(r_{k+1}), \\ \boldsymbol{y}_E(r_k) &= \boldsymbol{T}_E^b(h)\boldsymbol{y}(r_{k+1}) + \boldsymbol{T}^b(h)\boldsymbol{y}_E(r_{k+1}), \end{aligned} \tag{4.5}$$

respectively, where $\boldsymbol{T}^f$, $\boldsymbol{T}_E^f$, $\boldsymbol{T}^b$, and $\boldsymbol{T}_E^b$ are 2×2 matrices,

$$\begin{aligned} \boldsymbol{T}^f(h) &= \begin{bmatrix} u(h) & v(h) \\ u'(h) & v'(h) \end{bmatrix}, \\ \boldsymbol{T}_E^f(h) &= \begin{bmatrix} u_E(h) & v_E(h) \\ u_E'(h) & v_E'(h) \end{bmatrix}, \end{aligned} \tag{4.6}$$

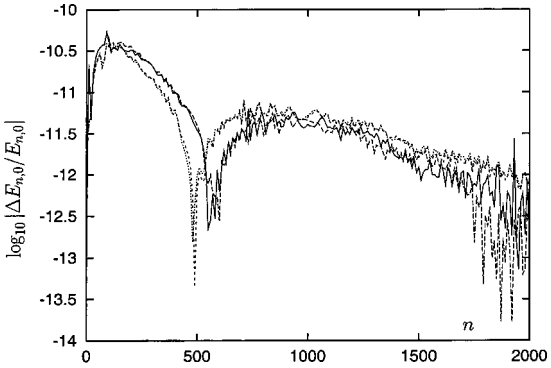

FIG. 1. The n dependence of the relative error in eigenvalues for four cases: (a) $l=0$, $Z=1$ (solid); (b) $l=0$, $Z=100$ (broken); (c) $l=20$, $Z=1$ (dotted); (d) $l=20$, $Z=100$ (dashed).

$$\begin{aligned} \boldsymbol{T}^b(h) &= \begin{bmatrix} v'(h) & -v(h) \\ -u'(h) & u(h) \end{bmatrix}, \\ \boldsymbol{T}_E^b(h) &= \begin{bmatrix} v_E'(h) & -v_E(h) \\ -u_E'(h) & u_E(h) \end{bmatrix}. \end{aligned} \tag{4.7}$$

The expressions of $u(h)$, $u'(h)$, $v(h)$, $v'(h)$, $u_E(h)$, $u_E'(h)$, $v_E(h)$, and $v_E'(h)$ are given in Ref. [5].

The program produces the eigenvalues and the eigenfunctions under different options. The user may ask for these data either in a preset energy range $[E_{\min}, E_{\max}]$ or in a preset range of labels $[n_{\min}, n_{\max}]$. The program also gives an estimated value of the error.

V. NUMERICAL ILLUSTRATIONS AND CONCLUSIONS

We take the following four cases.

(1) Pure attractive Coulomb potential $V(r) = -2Z/r$,

TABLE I. The first eleven and the last three bound state levels for the Hulthén potential, for three values of l. The parameters of the potential are $Z=50$ and $\lambda=0.025$. The data for $l=0$ are given according to the format of the output and blanks are used to separate the figures which, according to the error evaluation of the program, are correct. This evaluation is fully confirmed independently, i.e., by the deviations of the computed levels from the exact ones. For the other l's only the correct figures (in the above sense) are written. Numbers in brackets represent powers of 10.

	$l=0$		$l=5$		$l=10$	
n	E_{nl}	dev	n	E_{nl}	n	E_{nl}
0	−2498.7501562499 724	−0.3 [−10]	0	−68.1985069764	0	−19.42433530452
1	−623.750624999 5449	−0.5 [−09]	1	−49.7765019879	1	−16.1278839619
2	−276.529184027 0629	−0.7 [−09]	2	−37.820937644	2	−13.5635796169
3	−155.00249999 90256	−0.1 [−08]	3	−29.625291530	3	−11.5300024482
4	−98.75390624 87254	−0.1 [−08]	4	−23.764062901	4	−9.8905446167
5	−68.20006944 32761	−0.1 [−08]	5	−19.428501384	5	−8.5499045662
6	−49.778064412 3505	−0.9 [−09]	6	−16.132049498	6	−7.4399576882
7	−37.822499999 3734	−0.6 [−09]	7	−13.5677444066	7	−6.5109602329
8	−29.626853780 4022	−0.5 [−09]	8	−11.5341662475	8	−5.7259039790
9	−23.765624999 6776	−0.3 [−09]	9	−9.8947071396	9	−5.05679485664
10	−19.430063274 5708	−0.2 [−09]	10	−8.5540654812	10	−4.48214107892
60	−0.00326865258 12	0.1 [−11]	54	−0.00626012849	48	−0.00926096971
61	−0.000989203954 9	0.6 [−12]	55	−0.00269155996	49	−0.00444878383
62	−0.000037832262 7	0.1 [−12]	56	−0.000553923280	50	−0.001188166259

TABLE II. A set of bound state levels E_{nl} from the Hulthén partially screening potential. The parameters of the potential are $Z_0=50$, $Z_{as}=1$, $\lambda=0.025$. Numbers in brackets represent powers of 10.

n	$l=0$	$l=5$	$l=10$
0	−0.24987751531249 [+04]	−0.682234257245 [+02]	−0.1944907169591 [+02]
1	−0.623775612499 [+03]	−0.498013801077 [+02]	−0.161525484209 [+02]
2	−0.276554155902 [+03]	−0.37845768882 [+02]	−0.135881658647 [+02]
10	−0.19454685083 [+02]	−0.85782960477 [+01]	−0.450587380624 [+01]
11	−0.16158160999 [+02]	−0.746824376356 [+01]	−0.400881870174 [+01]
12	−0.13593777352 [+02]	−0.653913412087 [+01]	−0.357632424414 [+01]
50	−0.13362188273 [+00]	−0.4975916339 [−01]	−0.1067645345 [−01]
51	−0.11265757533 [+00]	−0.3912666814 [−01]	−0.7608426770 [−02]
52	−0.9403357799 [−01]	−0.3017823140 [−01]	−0.5621004447 [−02]
100	−0.3743860458 [−03]	−0.3056329551 [−03]	−0.24725724477 [−03]
101	−0.3602719091 [−03]	−0.29519803028 [−03]	−0.23964578233 [−03]
102	−0.3469430529 [−03]	−0.28528961739 [−03]	−0.23238111697 [−03]

$Z>0$ and various l. Exact energy levels: $E_{nl}=-Z^2/(n+l+1)^2$, $n=0,1,2,\ldots$.

(2) Hulthén screening potential

$$V(r)=-2ZV_H(r,\lambda),\quad Z>0,\quad V_H(r,\lambda)=\frac{\lambda e^{-\lambda r}}{1-e^{-\lambda r}}, \tag{5.1}$$

and various l. Exact eigenvalues are only known for $l=0$, viz. $E_{n0}=-[2Z-(n+1)\lambda]^2/4(n+1)^2$, $n=0,1,\ldots,$ $n_{\max}=\lfloor\sqrt{2Z/\lambda}\rfloor-1$, see Ref. [13].

(3) Partially screening Hulthén potential

$$V(r)=-2Z_0V_H(r,\lambda)-2Z_{as}\left(\frac{1}{r}-V_H(r,\lambda)\right),$$
$$Z_0>0,\ Z_{as}>0. \tag{5.2}$$

This behaves as a pure Coulomb potential with charge Z_0 for small r and as a pure Coulomb potential with charge Z_{as} at large r.

(4) Partially screening exponential-cosine potential. With

$$V_{ec}(r,\lambda,\mu)=\frac{1}{r}e^{-\lambda r}\cos(\mu r),$$

see, e.g., Ref. [14], this reads

$$V(r)=-2Z_0\,V_{ec}(r,\lambda,\mu)-2Z_{as}\left(\frac{1}{r}-V_{ec}(r,\lambda,\mu)\right). \tag{5.3}$$

In all cases we ask for a tolerance $\mathrm{tol}=10^{-8}$.

Problem (1) is considered with the aim of offering a first insight on the practical features of our approach. We take four, perhaps extreme situations: (a) $l=0$, $Z=1$; (b) $l=0$, $Z=100$; (c) $l=20$, $Z=1$; (d) $l=20$, $Z=100$; and ask for the evaluation of E_{nl} up to $n=2000$. The values of the input $r_{\max}$ and of the output r_0 and number of steps on I_2 are in order (a) 10^7, 1.09, 1008; (b) 2.10^5, 0.025, 1268; (c) 10^7, 12.0, 1004; (d) 3.10^5, 1.025, 1242. On Fig. 1 the decimal logarithm of the relative error, $\log_{10}|(E_{nl}-E_{nl}^{\mathrm{comp}})/E_{nl}|$ is displayed vs n. It is seen that the number of correct significant figures is at least 10 in all cases and that there is some tendency to increase by one unit when n is big. The result is remarkable in so much that the very magnitude of

TABLE III. A set of boundstate levels E_{nl} from the exponential cosine partially screened Coulomb potential. The parameters of the potential are $Z_0=50$, $Z_{as}=1$, $\lambda=\mu=0.025$. Numbers in brackets represent powers of 10.

n	$l=0$	$l=5$	$l=10$
0	−0.24975500006120 [+04]	−0.6699477512707 [+02]	−0.1821445124040 [+02]
1	−0.622550008557 [+03]	−0.485711749449 [+02]	−0.149165994843 [+02]
2	−0.275327819864 [+03]	−0.36613972923 [+02]	−0.123512992294 [+02]
10	−0.18218254864 [+02]	−0.73435721558 [+01]	−0.328994328401 [+01]
11	−0.14921061074 [+02]	−0.623594367131 [+01]	−0.280069798073 [+01]
12	−0.12356453704 [+02]	−0.5310240385481 [+01]	−0.237751777759 [+01]
50	−0.1531833374 [−02]	−0.1028479562 [−02]	−0.699631 [−03]
51	−0.14172138790 [−02]	−0.9650369650 [−03]	−0.663808 [−03]
52	−0.1315138619 [−02]	−0.907333058 [−03]	−0.630684 [−03]
100	−0.17450705849 [−03]	−0.1512989287 [−03]	−0.1293940 [−03]
101	−0.16998420260 [−03]	−0.1476427349 [−03]	−0.1264983 [−03]
102	−0.16563500787 [−03]	−0.1441175462 [−03]	−0.1236987 [−03]

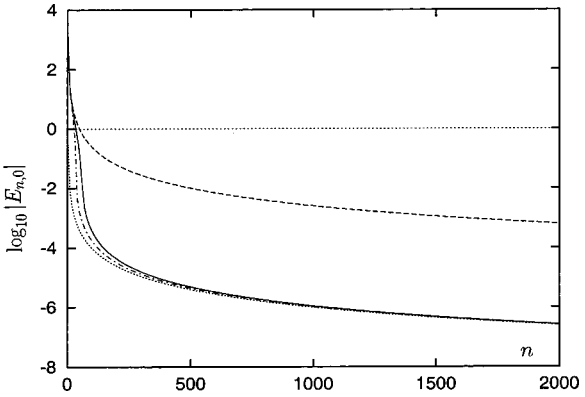

FIG. 2. The screening effect for eigenvalues: pure Coulomb potential with charge $Z_0=50$ (broken), $Z_{as}=1$ (dashed) and two partial screening potentials, Hulthen (solid) and exponential-cosine (dash-and-dots).

the energy level decreases when n is increased. In cases (a) and (b), for example, $E_{2000,0}$ is by six orders of magnitude lower than the ground state energy. It is also seen that all four curves are well packed together in spite of the fact that the parameters of these cases are so different. This is a direct indication that the stepsize selection rule works properly. Finally, the number of steps is extremely small.

To tackle problem 2 with our program, the expression of the Hulthén potential should be first brought to the form (2.3). It can be easily verified that $V_H(r,\lambda)=R(r)/r$ where $R(r)=e^{-\lambda r/2}/\eta_0[(\lambda r)^2/4]$. With this problem we consider two issues. The first is to check for the accuracy of the error estimation of our program. Since the exact eigenenergies are known for $l=0$, in Table I we present our output for this case and place a blank after the figure which, according to the program error evaluation, may be altered by ± 1. We separately list the very difference between the exact and our eigenvalues to conclude that the prediction is convincingly confirmed. The second issue is to make available accurate numerical eigenvalues for cases where there is no analytic form ($l=5$ and $l=10$). Such data may be used as references when checking for the performance of other programs.

The results for problems (3) and (4) are collected in Tables II and III and on Fig. 2. Only the correct figures are mentioned for the eigenvalues. It is again seen that although the eigenvalues vary with six or seven orders of magnitude the number of exact significant figures exceeds eight in Table II. The situation is comparatively worse in Table III. Yet, the absolute error is well within tol for all cases. On Fig. 2 we illustrate the physical feature of problems (3) and (4) for $l=0$. Each of the two potentials has a pure Coulomb potential at the limits. Then the low lying energy levels have to be close to the ones for $-2Z_0/r$ while when n is increased they have to gradually approach those of $-2Z_{as}/r$. We plot $\log_{10}|E_{n0}|$ for the two limiting Coulomb potentials and for the two partially screening potentials. The graphs just confirm the expectation.

We conclude that the approach developed in this paper is highly accurate, robust and safe. Its capacity of producing highly accurate results at high values of n is perhaps unparalleled by any other approach.

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APPENDIX

Functions $\xi(Z)$, $\eta_0(Z)$, $\eta_1(Z)$, . . . , were originally introduced in Sec. 3.4 of Ref. [1] and denoted there as $\overline{\xi}(Z)$, $\overline{\eta}_0(Z)$, $\overline{\eta}_1(Z)$, ... They are defined as follows. The functions $\xi(Z)$ and $\eta_0(Z)$ are generated first by the formulas:

$$\xi(Z)=\begin{cases}\cos(|Z|^{1/2}) & \text{if } Z<0,\\ \cosh(Z^{1/2}) & \text{if } Z\geqslant 0,\end{cases} \tag{A1}$$

$$\eta_0(Z)=\begin{cases}\sin(|Z|^{1/2})/|Z|^{1/2} & \text{if } Z<0\\ 1 \quad \text{if } Z=0 & \\ \sinh(Z^{1/2})/Z^{1/2} & \text{if } Z>0,\end{cases} \tag{A2}$$

while $\eta_s(Z)$ with $s>0$ are further generated by recurrence

$$\eta_1(Z)=[\xi(Z)-\eta_0(Z)]/Z, \tag{A3}$$

$$\eta_s(Z)=[\eta_{s-2}(Z)-(2s-1)\eta_{s-1}(Z)]/Z,\ s=2,3,4,\ldots \tag{A4}$$

if $Z\neq 0$, and by following values at $Z=0$:

$$\eta_s(0)=1/(2s+1)!!,\ s=1,2,3,4,\ldots . \tag{A5}$$

These functions satisfy the following properties.

(i) Power series:

$$\eta_s(Z)=2^s\sum_{q=0}^{\infty} g_{sq}Z^q/(2q+2s+1)! \tag{A6}$$

with

$$g_{sq}=\begin{cases}1 \quad \text{if } s=0,\\ (q+1)(q+2)\ldots(q+s) \quad \text{if } s>0.\end{cases} \tag{A7}$$

(ii) Behavior at large $|Z|$:

$$\eta_s(Z)\simeq\begin{cases}\xi(Z)/Z^{(s+1)/2} & \text{for odd } s,\\ \eta_0(Z)/Z^{s/2} & \text{for even } s.\end{cases} \tag{A8}$$

(iii) Differentiation with respect to Z:

$$\xi'(Z)=\frac{1}{2}\eta_0(Z) \quad \text{and} \quad \eta_s'(Z)=\frac{1}{2}\eta_{s+1}(Z),$$

$$s=0,1,2,\ldots . \tag{A9}$$

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