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Convergent perturbation studies in screened coulomb potential systems: a high precision numerical algorithm via Laguerre basis set

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In this work, a high precision algorithm is developed to determine the discrete spectrum of screened coulomb potential systems. The algorithm is mainly based upon the use of the perturbation of a hydrogen-like operator by a bounded operator. The Laguerre basis set expansion is employed in the procedure to obtain the operator inversion. Although a functional analytic analysis of errors and proof of convergence theorem are still lacking, it appears, numerically, that the method rapidly converges for bounded screened coulomb potential. Extremely accurate numerical results for the bound-state energies, in the case of Yukawa potential, are presented for illustrative purposes.

Key words: Screened coulomb potentials—Perturbation theory—Yukawa potential

1. Introduction

Perturbation theory is frequently used in many branches of physical and engineering sciences. For treating several problems, it is possible to model a system so that a parameter, say ε, whose small real values are interesting in many circumstances naturally arises. Hence the problem generally becomes analytically solvable by expanding all ε-dependent entities in powers of ε. Depending on the functional behaviour of the equations with respect to ε, such series may or may not converge. There are notable references which give concrete ideas on perturbation theory, especially in the case of linear operators [1-5].

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Screened coulomb potentials are of considerable importance in the mathematical modelling and understanding of the physical phenomena of many quantum chemical and quantum electrodynamic systems. Various works on the spectral investigation of these systems may be cited [6–16]. There is a general tendency in the perturbative treatment of the problems to use the screening parameter, say γ, as a natural perturbation parameter, except in Smith's work [17] and in our previous work [18]. Even if the total potential operator is bounded in the whole co-ordinate space and has a finite norm, the individual operators appearing in the expansion of potential with respect to powers of γ are generally not bounded. hence the expansion of the Hamiltonian of the system in powers of γ presents a divergent expansion. The divergency of the resulting perturbative series of energy and wave function is therefore not surprising on the contrary it must be expected. To cure divergent perturbational results Padé approximants can be employed [19–22].

If a series approximated by Padé approximants is of Stieltjes type, one can benefit from certain well-known theorems on the convergence of certain sequences in the Padé table and on the uniqueness of their limits [23]. Such a treatment was realized for the Yukawa case, and it was conjectured that the form of the γ-series expansion was Stieltjes. Results for bound-state energies accurate to five digits were given by means of this argument [24]. However, in a very recent paper, by using multiple precision arithmetic to prevent error accumulations in the construction of the Padé table, it has been shown that the perturbation series in powers of γ for 1s, 2s and 2p energy levels are not Stieltjes [25]. Indeed, it is very difficult to prove whether a series is Stieltjes or not unless an amenable integral representation of its coefficients is available. Generally, numerical implementation of the positiveness of the determinants of first few upper left square blocks in the determinental representation of Padé approximants may not be sufficient to satisfy the general determinental conditions for Stieltjes series. Furthermore, the sensitivity of the Padé table to error accumulations prevents one from increasing the order of Padé approximants arbitrarily, so that very high precision arithmetic should be used. In [25], results accurate to 20 digits for almost the entire regime of the screening parameter, in the cases of 1s, 2s and 2p states were presented. There is, however, a considerable loss of accuracy for high screening values in the 2p state.

All these discussions imply that the use of the naturally arising perturbation parameter, γ, is not suitable for the spectral investigation of screened coulomb potential systems. This motivates us to insert a superfluous parameter, say ε, into a convenient place in the operational form of the Hamiltonian. In our previous work [18], the first paper of this series, certain analytical evaluations up to third-order perturbative energies have been realized for the Yukawa case. In this work, we shall deal with central field screened coulomb potential systems and shall develop an algorithm for numerical implementation of the method to any desired order of perturbation.

To obtain our original problem, the superfluous parameter, ε, is replaced by unity after the construction of the perturbative series. This kind of perturbation technique is generally known as Neumann perturbation theory [26]. If the operator multiplied by ε is bounded, or if its unboundedness is less than the unperturbed operator, the perturbation theory of linear operators dictates that ε-power series converging in a non-empty circle around the origin of ε-complex plane can be constructed. In particular, if the convergence radii of the series exceed unity then we can represent energy and wave function of the system without any trouble by putting $\varepsilon = 1$. Although we shall not give a systematic investigation of the convergence radii of perturbative series, numerical results will be presented which support their convergence.

In the frame of these introductory remarks, this paper contains five sections. In Sect. 2, a detailed presentation of our formalism is given. Section 3 covers the discussion on the role of an effective charge parameter inserted into the scheme for the acceleration of convergence. The fourth section includes the interpretation of numerical results and certain discussions about the convergence properties of the algorithm. The last section involves the conclusions, motivations for future applications and also the standardization and generalization of the proposed technique.

2. Formulation of the algorithm

Let us consider the following Schrödinger equation:

$$-\tfrac{1}{2}\nabla^2\Psi - \frac{1}{r}\,V(\gamma \boldsymbol{x})\Psi = E\Psi, \qquad \Psi \in \mathscr{H} \tag{2.1}$$

where $\mathscr{H}$ is the Hilbert space of the problem, $\boldsymbol{x}$ stands for position vector, and r denotes the radial variable in spherical co-ordinates. In the equation, γ characterizes the screening of the central force field by other electrically charged particles. It is clear that the amplitude of the screening may depend on the direction. We shall, however, omit the angle-dependence of the potential, V, for the sake of dealing with a system which can be investigated via ordinary differential equations. That is, we assume

$$V = V(\gamma r). \tag{2.2}$$

In fact, angle-dependency does not make important changes in the systematic construction of the perturbational algorithm, only an extra expansion is needed over spherical harmonics. However, the investigation of this rather generalized case is left for future studies, and, after the separation of variables, the radial form of (2.1) is taken as

$$-\frac{1}{2}\frac{d^2\Psi}{dr^2} - \frac{1}{r}\frac{d\Psi}{dr} + \left[\frac{1}{2}\,l(l+1)\frac{1}{r^2} - \frac{1}{r}\,V(\gamma r)\right]\Psi = E\Psi, \tag{2.3}$$

where l $(=0, 1, 2, \ldots)$ characterizes the angular dependence of the system in a global sense, and now, Ψ is solely a function of r. The accompanying boundary conditions of (2.3) are the regularity, the continuity and the appropriately vanishing behaviour of Ψ as $r \to \infty$. Since our problem is defined on the Hilbert space, or more specifically, on the space of the square integrable functions, the limitation of square integrability of the ptoential, V, will result in certain advantages, especially on the convergence nature of our algorithm. Moreover, we assume that $V(0)=1$. This specification does not create any loss of generality due to the fact that a scaling transformation on r transforms any case, except $V(0)=0$ to $\mathrm{V}(0)=1$. The case where $V(0)=0$ removes the coulombic nature of the potential in the vicinity of the origin, that is, when $r \rightarrow 0$. We, therefore, assume that $V(0) \neq 0$ in order to avoid this undesired case.

By inserting the superfluous perturbation parameter, ε, the equation (2.3) takes the form

$$-\frac{1}{2} \frac{d^2 F}{d r^2}-\frac{1}{r} \frac{d F}{d r}+\left[\frac{1}{2} l(l+1) \frac{1}{r^2}-\frac{1}{r}\right] F+\varepsilon \frac{1-V(\gamma r)}{r} F=\nu F. \tag{2.4}$$

It is, therefore, evident that we can obtain the solution of (2.3) in terms of F and ν by letting $\varepsilon=1$, thus

$$\Psi(r)=F(r, \varepsilon)|_{\varepsilon=1} \tag{2.5}$$

$$E=\nu(\varepsilon)|_{\varepsilon=1}. \tag{2.6}$$

The Hamiltonian of (2.4), which is self-adjoint provided that ε remains on the real axis of ϵ-complex plane, is formally written as

$$H=H_0+\varepsilon H_1, \tag{2.7}$$

where

$$H_0=-\frac{1}{2} \frac{d^2}{d r^2}-\frac{1}{r} \frac{d}{d r}+\frac{1}{2} l(l+1) \frac{1}{r^2}-\frac{1}{r} \tag{2.8}$$

and

$$H_1=\frac{1}{r}[1-V(\gamma r)]. \tag{2.9}$$

One can observe that H has a discrete spectrum located on the negative real axis. In addition, its continuous spectrum covers the entire positive real axis in the ν-complex plane. The Hamiltonian for hydrogen atom, H_0, possesses the same type of spectrum as H, except in the number of discrete states. Indeed, H_0 has a countably infinite number of discrete spectral points, whereas, as a result of the existence of screening, H has only a finite number of discrete states. Hence, as long as ϵ changes from zero to unity, almost all of the discrete spectral points, except a finite number of low-lying ones, have to merge into the continuous spectrum. The number of surviving states is completely determined by the value of γ. Of course, the difference in the number of states between H and H_0 implies that a slowing down of convergence may be expected when γ is close to a critical value where the discrete state under consideration does not survive anymore.

Now, we can develop a perturbative scheme based on the standard Rayleigh–Schrödinger perturbation technique [2]. Let us consider the expansion of the energy and wave function

$$\nu = \sum_{j=0}^{\infty} \varepsilon^j \nu_j \tag{2.10a}$$

$$F = \sum_{j=0}^{\infty} \varepsilon^j F_j(r). \tag{2.10b}$$

If we use these expressions in (2.4),

$$(H_0 + \varepsilon H_1)F = \nu F, \tag{2.11}$$

and equate the coefficients of various powers of ε on both sides of equality, we arrive at the recursion

$$(H_0 - \nu_0 I)F_j = (\nu_1 I - H_1)F_{j-1} + \sum_{k=0}^{j-2} \nu_{j-k} F_k; \qquad j \geq 2 \tag{2.12}$$

with the initial equations

$$(H_0 - \nu_0 I)F_0 = 0 \tag{2.13}$$

$$(H_0 - \nu_0 I)F_1 = (\nu_1 I - H_1)F_0 \tag{2.14}$$

for the evaluation of ν_j and F_j, where I stands for the unit operator of the operator space to which H_0 and H_1 belong.

By making the co-ordinate transformation,

$$x = 2r/(n+l+1), \tag{2.15}$$

the solution of the eigenvalue problem of the hydrogenic case,

$$H_0 u_n = \lambda_n u_n, \tag{2.16}$$

is obtained where the discrete eigenfunctions and eigenvalues are

$$u_n = \frac{2}{(n+l+1)^2}\left[\frac{n!}{(n+2l+1)!}\right]^{1/2} x^l e^{-x/2} L_n^{2l+1}(x) \tag{2.17}$$

$$\lambda_n = -1/[2(n+l+1)^2]; \qquad l, n = 0, 1, 2, \ldots \tag{2.18}$$

$L_n^m(x)$ is the associated Laguerre function. Therefore, we can show that the solution of (2.13) is

$$\nu_0 = \lambda_n \tag{2.19}$$

$$F_0 = u_n. \tag{2.20}$$

The structure of H_0 necessitates using r^2 as a weight function in the scalar products of the Hilbert space. The set of u_n's is an ortho-normal set under the weight r^2. Since a global normalization is always possible after obtaining the eigenfunctions, we can assume, without any loss of generality, that the normalization condition

$$\langle F_j, F_0 \rangle = \delta_{0j}; \qquad j = 0, 1, 2, \ldots \tag{2.21}$$

where ket and bra notation implies the scalar product and δ_{kj} is Kronecker's delta, holds. This removes any arbitrariness from the solutions of the F_j's.

The self-adjointness of the operator $(H_0 - \nu_0 I)$ implies that the homogeneous solution and the right-hand side must be orthogonal both in (2.14) and in (2.12). Thus, in conjunction with (2.21), we obtain the relations

$$\nu_1 = \langle F_0, H_1 F_0 \rangle = \langle u_n, H_1 u_n \rangle \tag{2.22}$$

$$\sum_{k=0}^{j-2} \nu_{j-k} \langle F_0, F_k \rangle - \langle F_0, H_1 F_{j-1} \rangle = 0 \rightarrow \nu_j = \langle u_n, H_1 F_{j-1} \rangle; \quad j \geq 2 \tag{2.23}$$

to determine the coefficients of the energy series (2.10a). Here, the last equation involves (2.22) for $j = 1$, and it is not problematic to evaluate ν_1. However, in the cases where $j > 1$, first of all we have to find F_j in order to obtain ν_{j+1}. This can be accomplished through the inversion of the operator $(H_0 - \nu_0 I)$ on the complementary space of its null space spanned by u_n's. F_j's can then be obtained from (2.12) and (2.14). Therefore, we should solve the inversion problem

$$(H_0 - \nu_0 I) f = g \tag{2.24}$$

where it is assumed that

$$\langle u_n, f \rangle = \langle u_n, g \rangle = 0. \tag{2.25}$$

If $\mathcal{F}$ denotes the inverse of $(H_0 - \nu_0 I)$, the solution will be expressed in the form

$$f = \mathcal{F} g. \tag{2.26}$$

A frequently used technique for finding $\mathcal{F}$ is the utilization of the spectral decomposition of H_0. This is possible, provided that the eigenfunction set of H_0 is complete. However, the spectral structure of H_0 implies that the decomposition of H_0 into projection operators, which project a given function into a specified eigenspace of H_0, can be expressed as an infinite sum over a countably infinite set of discrete eigenfunctions, in addition to an infinite sum over an uncountable infinite set of eigendistributions corresponding to the continuous spectrum. The analytical treatment of such sums creates many technical problems and necessitates the evaluation of certain integrals over confluent hypergeometric functions. However, since the spectral series converge very slowly, certain operators cannot be approximated by finite truncations. It is therefore preferable to seek an appropriate way of dealing with an operator which has solely discrete spectra with a complete eigenfunction set. This has been realized in our previous work [18], and Eq. (2.24) was converted to

$$[T - (n + l + 1) I] \tilde{f} = g \tag{2.27}$$

where

$$T = -x \frac{d^2}{dx^2} - 2 \frac{d}{dx} + l(l+1) \frac{1}{x} + \tfrac{1}{4} x, \tag{2.28}$$

$$\tilde{f} = f[(n+l+1)x/2], \qquad \tilde{g} = \tfrac{1}{2}(n+l+1)^2 x g[(n+l+1)x/2]. \tag{2.29}$$

The operator T is a very well-known operator, which arises in the theory of Laguerre polynomials, and has only a discrete spectrum with a complete set of eigenfunctions. Thus

$$\left.\begin{aligned} &T\phi_m=(m+l+1)\phi_m \\ &\phi_m=\left[\frac{m!}{(m+2l+1)!}\right]^{1/2} e^{-x/2}x^l L_m^{2l+1}(x) \\ &\langle\phi_m,\phi_n\rangle=\int_0^\infty \phi_m\phi_n x\,dx=\delta_{mn}, \end{aligned}\right\} \tag{2.30}$$

and $\tilde{f}$ can be represented by the linear combination of ϕ_i's, that is,

$$\tilde{f}=\sum_{i=0}^{\infty}\tilde{f}_i\phi_i(x). \tag{2.31}$$

Therefore, the inverse of $[T-(n+l+1)I]$, say $\mathscr{L}$, is established such that

$$\tilde{f}=\mathscr{L}\tilde{g}=\sum_{\substack{m=0\\ m\neq n}}^{\infty}\frac{1}{m-n}\,\phi_m\langle\phi_m,\tilde{g}\rangle. \tag{2.32}$$

Here, the relation between $\mathscr{L}$ and $\mathscr{F}$ is

$$\mathscr{F}g=\tfrac{1}{2}(n+l+1)^2\mathscr{L}(xg) \tag{2.33}$$

in terms of x. Finally, we show, from (2.12), that the coefficients, F_j, of the wave function (2.10b) for $j\geq 1$ can be evaluated by the recursive formula

$$F_j(x)=\tfrac{1}{2}(n+l+1)^2\sum_{k=0}^{j-1}\nu_{j-k}\mathscr{L}(xF_k)-(n+l+1)\mathscr{L}\{[1-V(\tilde{\gamma}x)]F_{j-1}\}, \tag{2.34}$$

where we have written $\tilde{\gamma}$ for $(n+l+1)\gamma/2$.

Summation formulae for Laguerre functions and their products may be employed, in the case of some specific potentials, to obtain solutions in terms of elementary or special functions of mathematical analysis. Indeed, in the case of the Yukawa potential, where

$$V(\gamma r)=e^{-\gamma r}, \tag{2.35}$$

analytical evaluations up to third-order perturbative contributions were accomplished in the first paper of this series [18]. However, the analytical evaluations are not essentially necessary except for checking purposes and mathematical elegance. A more reasonable way is to develop an appropriate and readily accessible numerical algorithm in order to calculate F_j.and ν_j up to any desired order of perturbation. So we choose the M-dimensional subspace, say $\mathscr{S}$, spanned by ϕ_j such that $\{\phi_j\colon n-m_1<j\leq n+m_2,\ m_1+m_2=M\}$. M is called the truncation order for the matrix representations of the related entities. It is possible to write

$$\mathscr{S}=\mathscr{C}+\mathscr{N}, \tag{2.36}$$

where $\mathcal{N}$ is the one-dimensional subspace spanned by ϕ_n, i.e. the null space of the operator $[T-(n+l+1)I]$, and the $(M-1)$ dimensional space $\mathcal{C}$ stands for its complement. If we consider the vector representation of F_j and denote its projection into S by f_j, it is readily shown that

$$f_j \in \begin{cases} \mathcal{C}, & j>0 \\ \mathcal{N}, & j=0 \end{cases} \tag{2.37}$$

where f_j is now a vector of order $(M-1)$ if $j>0$, and a scalar if $j=0$. Furthermore, if we denote the matrix representations of $[1-V(\tilde{\gamma}x)]$, $\mathcal{L}$ and x on $\mathcal{C}$ by $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{X}$ respectively, and the projections of $x\phi_n$ and $(n+l+1)[1-V(\tilde{\gamma}x)]\phi_n$ into $\mathcal{C}$ by the vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ respectively, one can conclude that

$$f_j \cong \sum_{k=1}^{j-1} \mu_{j-k}\boldsymbol{BX}f_k + \mu_j\boldsymbol{Bu} - \boldsymbol{BA}f_{j-1}; \qquad j\geq 2 \tag{2.38}$$

$$f_1 \cong \mu_1\boldsymbol{Bu} - \boldsymbol{Bv} \tag{2.39}$$

where

$$\mu_j = \tfrac{1}{2}(n+l+1)^2\nu_j. \tag{2.40}$$

We can finally reproduce, from (2.22) and (2.23), the coefficients of the energy series after some intermediate algebra as follows:

$$\mu_j \cong \tfrac{1}{4}(n+l+1)^2\boldsymbol{v}^T f_{j-1} \tag{2.41}$$

$$\mu_1 = \tfrac{1}{4}(n+l+1)^2\int_0^\infty \phi_n^2[1-V(\tilde{\gamma}x)]x\,dx. \tag{2.42}$$

It should be noticed that the $(M-1)\times(M-1)$ matrices in (2.38) are symmetrical, and $\boldsymbol{B}$ and $\boldsymbol{X}$ are diagonal and tridiagonal matrices respectively. Consequently, μ_j's and f_j's can be recursively approximated up to a prescribed j value, say N, which is named as the order of perturbation. By treating with sufficiently large values of M and N is possible to get highly accurate numerical results.

3. Use of the effective charge parameter

In our formulation we used H_0 as the Hamiltonian for the unperturbed hydrogen atom, and H_1 as the perturbing operator. Since there is no adjustable parameter in the structure of either H_0 or H_1, it is not possible to affect the convergence rate of the perturbative series. Had there been a flexibility to adjust the comparative norm of H_1 with respect to H_0, the desired accurate results could have been obtained by expending less effort. For this purpose, we insert a dummy parameter into the operational form of the problem and hence replace H_0 and H_1 by

$$\tilde{H}_0 = H_0 + (1-\zeta)/r \tag{3.1}$$

$$\tilde{H}_1 = H_1 - (1-\zeta)/r. \tag{3.2}$$

Here, ζ plays the same role as the atomic charge parameter of hydrogen-like systems, so it may be called the effective charge parameter. Even though it looks as if the insertion of ζ destroys the boundedness of H_1 when $r=0$, the normed character of H_1 does not alter due to the existence of the weight r^2. On the other hand, since the ζ-contributions of $\tilde{H}_0$ and $\tilde{H}_1$ cancel each other out in the evaluation of the perturbation series at $\varepsilon=1$, we have to point out that there is no real effect on the differential equation and on the limits of the series. There is, however, no effect for the case where both truncation size M and the order of perturbation N go to infinity. For finite values of M, ζ-dependence of the limits of perturbation series becomes more important and more prominent, especially as γ approaches its critical value, say γ_{cr}. This is due to the sensitivity of truncation errors to ζ and the slowing down of convergence for high screening. Here, ζ can be interpreted as an artificial screening factor which may, at least in part, share the role of γ. We can therefore expect the value of ζ to start from unity when γ is zero, and to decrease as γ increases to γ_{cr}. However, the choice of best ζ, which makes the perturbational series under consideration stable, is not a very easy task. If one carefully studies Tables 1-10, in which numerical results are presented, it is apparent that values smaller than a half have not been used for ζ to avoid possible error accumulations in the calculation of elements of the matrix A, particularly where the truncation order M is quite large.

Although there are such problematic aspects of using an effective charge parameter, we can conclude that ζ can be employed to accelerate the convergence of the series. Indeed, if γ is not nearly zero and if M is sufficiently large, it is always possible to find a ζ value different from unity such that the desired accurate results for energy can be obtained by selecting an order of perturbation which is less than when $\zeta=1$. Furthermore, one can test the accuracy of the limit of the perturbational series by slightly increasing the size of truncation, M, or systematically changing the value of ζ. Finally, we should also notice that upon transforming variable x to x/ζ, H_0 and H_1 are unaltered in form so that it is unnecessary to modify the formulation in Sect. 2.

4. Discussions and numerical applications for Yukawa potential systems

For numerical purposes, primarily, the matrices $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{X}$ can be constructed. Since the elements of the diagonal matrix $\boldsymbol{B}$ and of the tridiagonal matrix $\boldsymbol{X}$ can be analytically determined by using certain properties of Laguerre polynomials, there is no difficulty in constructing them. On the other hand, if we consider the full matrix $\boldsymbol{A}$, the definition of which is

$$A_{mn}=\int_0^{\infty}\phi_m(x)Q(x)\phi_n(x)x\,dx \tag{4.1}$$

where we have $Q(x)=[1-V(\tilde{\gamma}x)]$, it is possible to attain a recursion relationship to calculate its elements. By using the expression of ϕ_n in Eq. (2.30) and the recurrence formulae for the Laguerre polynomials [27] we obtain the relationship

$$\phi_n=\frac{1}{2(n+l+1)}\{x\phi_n+[(n+1)(n+2l+2)]^{1/2}\phi_{n+1}+[n(n+2l+1)]^{1/2}\phi_{n-1}\}. \tag{4.2}$$

Table 1. The comparison of cumulative perturbational energy eigenvalues for 1s state

γ	M	N	ζ	Our results	Vrscay 1986 [25]
0.1	30	22	1.0	−0.407 058 030 613 403 156 754 507 070 361	−0.407 058 030 613 403 156 75
0.2	35	29	0.95	−0.326 808 511 369 193 384 882 495 419 282	−0.326 808 511 369 193 384 88
0.3	40	38	0.9	−0.257 638 586 303 054 148 878 964 069 306	−0.257 638 586 303 054 148 88
0.4	45	51	0.85	−0.198 376 083 361 850 216 608 413 859 926	−0.198 376 083 361 850 216 61
0.5	50	67	0.8	−0.148 117 021 889 932 616 711 758 220 725	−0.148 117 021 889 932 616 71
0.6	55	136	0.85	−0.106 135 907 505 814 193 000 738 693 811	−0.106 135 907 505 814 193 00
0.7	55	239	0.9	−0.071 833 555 904 512 213 040 262 126 802	−0.071 833 555 904 512 213 04
0.8	60	415	1.0	−0.044 704 304 497 359 663 200 348 766 240	−0.044 704 304 497 359 663 20
0.9	60	550	0.85	−0.024 314 193 827 502 054 887 384 151	−0.024 314 193 827 502 054 89
1.0	60	600	0.7	−0.010 285 789 990 017 696 804 8	−0.010 285 789 990 017 696 80
1.1	60	650	0.5	−0.002 287 244 234 053	−0.002 287 244 234 053 485 46

Table 2. The comparison of cumulative perturbational energy eigenvalues for 2s state

γ	M	N	ζ	Our results	Vrscay 1986 [25]
0.01	30	12	1.0	−0.115 293 285 167 994 256 222 045 516 170	−0.115 293 285 167 994 256 22
0.02	30	13	0.99	−0.106 148 320 244 695 503 250 708 341 186	−0.106 148 320 244 695 503 25
0.03	30	16	0.98	−0.097 531 786 134 660 862 770 039 060 920	−0.097 531 786 134 660 862 77
0.04	35	19	0.97	−0.089 414 634 185 159 188 415 714 621 025	−0.089 414 634 185 159 188 42
0.05	40	24	0.96	−0.081 771 195 795 253 124 173 489 413 770	−0.081 771 195 795 253 124 17
0.06	40	29	0.95	−0.074 578 534 412 709 709 694 885 171 159	−0.074 578 534 412 709 709 69
0.07	45	35	0.935	−0.067 815 959 981 462 181 222 810 363 311	−0.067 815 959 981 462 181 22
0.08	45	38	0.92	−0.061 464 656 212 300 385 911 466 251 113	−0.061 464 656 212 300 358 91
0.09	50	45	0.9	−0.055 507 388 553 290 736 394 798 978 074	−0.055 507 388 553 290 736 39
0.10	50	47	0.875	−0.049 928 271 331 918 889 234 996 681 037	−0.049 928 271 331 918 889 23
0.15	50	108	0.825	−0.027 222 190 725 688 518 250 187 267 589	−0.027 222 190 725 688 518 25
0.20	55	252	0.775	−0.012 107 865 195 440 464 385 855 372 408	−0.012 107 865 195 440 464 39
0.25	60	700	0.7	−0.003 395 906 283 239 307 796 442 264	−0.003 395 906 283 239 307 80
0.30	60	700	0.5	−0.000 091 602 444	−0.000 091 602 443 891 899 01

Table 3. The comparison of cumulative perturbational energy eigenvalues for 2p state

γ	N	ζ	Our results	Vrscay 1986 [25]
0.01	12	1.0	−0.115 245 224 090 564 185 894 783 216 336	−0.115 245 224 090 564 185 89
0.02	13	0.99	−0.105 963 398 179 939 904 755 731 028 037	−0.105 963 398 179 939 904 76
0.03	16	0.975	−0.097 131 366 795 691 310 671 783 889 214	−0.097 131 366 795 691 310 67
0.04	19	0.96	−0.088 729 373 582 879 526 287 939 141 468	−0.088 729 373 582 879 526 29
0.05	21	0.95	−0.080 740 387 037 784 609 712 102 743 610	−0.080 740 387 037 784 609 71
0.06	24	0.925	−0.073 149 619 385 860 625 023 805 418 421	−0.073 149 619 385 860 625 02
0.07	29	0.9	−0.065 944 176 996 156 573 384 560 516 652	−0.065 944 176 996 156 573 38
0.08	31	0.875	−0.059 112 804 787 031 234 635 692 332 928	−0.059 112 804 787 031 234 64
0.09	35	0.85	−0.052 645 701 331 584 274 463 576 906 198	−0.052 645 701 331 584 274 46
0.10	38	0.825	−0.046 534 390 486 724 608 386 600 840 395	−0.046 534 390 486 724 608 39
0.15	104	0.75	−0.021 104 888 927 736 242 916 943 382 961	−0.021 104 888 927 736 242 92
0.20	600	0.675	−0.004 101 646 530 784 090 388 446 610 214	−0.004 101 646 53

Table 4. Cumulative perturbational energy eigenvalues for 3s state

γ	N	ζ	Energy
0.01	17	1.0	−0.046 198 857 799 033 191 519 298 258 968
0.02	22	0.95	−0.038 020 014 393 017 364 134 542 111 478
0.03	30	0.9	−0.030 886 083 779 974 481 232 731 547 628
0.04	34	0.85	−0.024 692 267 257 683 267 057 858 319 277
0.05	47	0.8	−0.019 352 554 814 752 342 295 397 996 789
0.06	59	0.75	−0.014 794 157 295 178 504 997 929 579 983
0.07	65	0.725	−0.010 953 922 474 898 051 105 461 938 169
0.08	109	0.7	−0.007 775 877 038 957 710 092 639 379 433
0.09	205	0.725	−0.005 209 440 420 383 781 109 197 435 239
0.10	400	0.75	−0.003 208 046 744 690 258 718 213 516 792

Table 5. Cumulative perturbational energy eigenvalues for 3p state

γ	N	ζ	Energy
0.01	17	1.0	−0.046 153 104 829 162 287 315 273 878 682
0.02	22	0.95	−0.037 852 389 200 223 176 326 568 017 591
0.03	30	0.9	−0.030 540 967 584 512 981 172 892 758 929
0.04	38	0.85	−0.024 132 353 610 390 802 462 032 068 924
0.05	47	0.8	−0.018 557 751 883 405 996 604 893 993 884
0.06	60	0.75	−0.013 761 345 303 506 408 408 115 349 158
0.07	77	0.725	−0.009 697 593 751 970 732 639 176 727 847
0.08	137	0.7	−0.006 329 995 439 268 113 269 338 178 286
0.09	300	0.7	−0.003 631 543 813 637 522 782 845 891 872
0.10	650	0.675	−0.001 589 001 525 867 560 267 558 634 940

Table 6. Cumulative perturbational energy eigenvalues for 3d state

γ	N	ζ	Energy
0.01	17	1.0	−0.046 061 454 160 659 627 138 130 277 717
0.02	25	0.95	−0.037 515 127 700 686 930 313 438 432 490
0.03	30	0.9	−0.029 841 829 666 598 187 704 128 300 102
0.04	40	0.85	−0.022 987 856 759 885 760 676 935 559 909
0.05	45	0.8	−0.016 915 570 569 815 842 886 114 758 244
0.06	60	0.75	−0.011 601 829 474 162 576 042 503 968 775
0.07	105	0.7	−0.007 039 878 805 433 782 543 374 296 726
0.08	235	0.65	−0.003 248 360 428 751 993 572 467 525 047

Multiplying by ϕ_m and reusing this identity to express $x\phi_m$ in terms of ϕ_{m-1}, ϕ_m and ϕ_{m+1} we obtain the two-dimensional recursion relationship

$$\begin{aligned}2(n-m)\phi_m\phi_n=&[(n+1)(n+2l+1)]^{1/2}\phi_m\phi_{n+1}+[n(n+2l+1)]^{1/2}\phi_m\phi_{n-1}\\&-[(m+1)(m+2l+2)]^{1/2}\phi_{m+1}\phi_n-[m(m+2l+1)]^{1/2}\phi_{m-1}\phi_n.\end{aligned} \tag{4.3}$$

Table 7. Cumulative perturbational energy eigenvalues for 4s state

γ	N	ζ	Energy
0.01	25	1.0	−0.022 356 120 521 237 134 526 537 480 368
0.02	29	0.9	−0.015 379 266 427 896 141 378 328 766 000
0.025	37	0.85	−0.012 503 238 318 007 071 505 739 698 432
0.03	50	0.8	−0.009 992 038 197 871 687 950 471 313 673
0.04	72	0.75	−0.005 958 084 497 576 461 475 241 796 902
0.05	163	0.7	−0.003 091 659 900 161 321 484 658 950 292
0.06	550	0.7	−0.001 236 719 097 035 032 773 917 445 475

Table 8. Cumulative perturbational energy eigenvalues for 4p state

γ	N	ζ	Energy
0.01	25	1.0	−0.022 313 420 741 967 189 431 061 748 014
0.02	30	0.9	−0.015 233 805 356 103 025 211 040 276 736
0.025	40	0.85	−0.012 294 320 436 313 933 670 168 893 845
0.03	50	0.8	−0.009 716 695 159 602 488 892 977 681 790
0.04	80	0.75	−0.005 556 019 078 689 840 613 671 502 405
0.05	205	0.7	−0.002 598 058 852 571 853 965 261 191 255
0.06	650	0.625	−0.000 729 172 766 636 200 572 968 574

Table 9. Cumulative perturbational energy eigenvalues for 4d state

γ	N	ζ	Energy
0.01	25	1.0	−0.022 227 792 489 804 398 453 786 853 194
0.02	30	0.9	−0.014 940 057 467 644 185 894 004 256 442
0.025	40	0.85	−0.011 870 448 936 190 599 940 851 142 013
0.03	50	0.8	−0.009 155 162 858 705 684 411 207 666 945
0.04	85	0.7	−0.004 727 823 602 939 955 013 950 318 353
0.05	280	0.65	−0.001 580 871 626 871 004 952 883 948 070

Table 10. Cumulative perturbational energy eigenvalues for 4f state

γ	N	ζ	Energy
0.005	16	1.0	−0.026 468 096 084 105 162 944 667 005 790
0.010	24	1.0	−0.022 098 770 463 802 567 552 796 834 984
0.015	23	0.95	−0.018 113 729 630 539 752 961 409 742 799
0.020	30	0.9	−0.014 491 978 017 490 743 686 655 396 720
0.025	40	0.85	−0.011 218 210 790 350 454 862 863 561 467
0.030	45	0.8	−0.008 282 152 466 779 632 959 281 124 005
0.035	63	0.75	−0.005 678 737 573 824 696 847 170 265 471
0.040	115	0.7	−0.003 409 544 912 277 651 176 630 332 167
0.045	260	0.65	−0.001 487 359 743 334 720 048 551 730 070

Hence, we conclude that

$$A_{m+1,n}=[(m+1)(m+2l+2)]^{-1/2}\{[(n+1)(n+2l+2)]^{1/2}A_{m,n+1}$$
$$+[n(n+2l+1)]^{1/2}A_{m,n-1}$$
$$-[m(m+2l+1)]^{1/2}A_{m-1,n}+2(m-n)A_{mn}\}; \qquad m, n=0, 1, 2, \ldots. \tag{4.4}$$

This implies that all rows of the matrix can be recursively obtained from its first row. It should also be noted that this property does not depend on the explicit form of the algebraic operator $Q(x)$. That is, a knowledge of only $2M$ integrals over $Q(x)$ is sufficient to progress through the presented algorithm for any screened coulomb potential. Depending on the analytical structure of the potential, these integrals can be performed analytically or numerically.

Now to take a particular case, consider the Yukawa potential for which

$$V(\gamma r)=e^{-\gamma r}. \tag{4.5}$$

In this case, one can analytically evaluate all elements of the matrix $\boldsymbol{A}$. However, in the computational sense, this causes a considerable increase in execution time. It is, therefore, preferable to employ the recurrence relationship (4.4).

Numerical results in the case of Yukawa poential systems are presented for 1s, 2s, 3s, 4s; 2p, 3p, 4p; 3d, 4d and 4f states in Tables 1–10. Table 1 contains the results for 1s state. The screening parameter γ, in the first column, has been varied over a great portion of its domain between zero and γ_{cr}. The size of truncation M, the perturbation order N, and the value of the effective charge parameter ζ have been given in the second, third and fourth columns respectively. The last two columns are devoted to the presentation of our results corresponding to γ, M, N and ζ and also to Vrscay's results corresponding to γ, for comparison. For all values of γ from zero to one, extremely accurate results are obtained. However, as γ approaches γ_{cr}, the present method starts to lose its efficiency. This may possibly be due to the structure of ϕ_n-functions. Hence it is necessary to utilize high-order perturbations such as 650 for large screening parameters. In fact, it is well known that most of the methods used in such problems, where a composite spectrum appears, fail in the close neighbourhood of γ_{cr}.

In the other tables, almost the same kind of presentation is used. In all states, results are obtained by systematically increasing γ. However, tables may not involve all values in the close vicinity of γ_{cr}. M has been given only in Tables 1 and 2, and only Tables 1–3 (for 1s, 2s and 2p states) include a comparison with literature values, since there are no highly accurate results for other states to the authors' knowledge. We have to admit that our algorithm cannot achieve the power of Vrscay's method, which is mainly based on continued fractions and Padé approximations, for relatively high values of γ for 1s and 2s states. However, in our method a decreasing accuracy is not observed for excited states.

A VAX-780 is employed for numerical calculations, and programmes are executed in quadruple precision. If we recall the fact that in Vrscay's work a multiple precision arithmetic was used, and the accuracy of the results obtained was compared in each approximating step, the validity of the present algorithm becomes clearer. To give a rough idea about the time consumption we can say that a hundred-step perturbation with a size of truncation of approximately 40 consumes one CPU minute. To control numerical instabilities due to error accumulations, ζ and M are appropriately chosen. M can be estimated by comparing results with our previous analytical ones, setting ζ equal to one, and is considered to be sufficient whenever there is no discrepancy between both results. For a large variety of γ in all states, it is observed that a truncation size of 30–40 and an order of perturbation of 100–150 are sufficient to obtain the desired accuracy.

The software is written in a machine-independent manner. It may, however, be improved by taking certain precautions for the unnecessary time and memory consumption. Work on the standardization of the algorithm and the removal of the slow convergence problem around the critical value of the screening parameter is under consideration.

5. Conclusions and remarks

In this work, we have presented a rapidly convergent perturbation algorithm for radially screened coulomb potential systems. The numerical results presented for the Yukawa case are the most accurate results for almost all states except a certain narrow γ-domain around the critical value of the screening parameter in 1s and 2s states, where the results given by Vrscay [25] are better. The method needs to be modified to speed up its slow convergence when γ approaches γ_{cr}. Investigations to modify the basis set for relatively large γ values are continuing.

The algorithm presented in this work is sufficiently general in its structure, except for the limitation of the square integrability of $V(\gamma r)$. It can be extended to such screened coulomb potentials by altering the input data of the matrix $\boldsymbol{A}$. A functional analytical treatment of the algorithm will reveal its convergence properties and will possibly enable us to evaluate error estimates for a prescribed perturbation order and truncation size.

The next step after the achievement of the items given in the previous paragraphs will be the generalization of this algorithm to angle-dependent potentials. Then it is very likely that we shall have a powerful tool to enter the realm of atoms and molecules. In other words, the investigation of atomic systems in the framework of these kind of approaches is our future goal. It is, however, clear that difficulties arising from the multi-dimensionality of the systems and the singular structure of the potential will create many problems. Once we have the detailed analysis of angle-dependent screened coulomb potential systems, we shall possibly be sufficiently encouraged to deal with these troublesome problems.

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