Padé approximants and perturbation theory for screened Coulomb potentials

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By forming the Padé approximants to the energy perturbation series for screened Coulomb potentials, we study the cases of an electron in the Yukawa potential and a representative screened potential of the atom in the form of the Yukawa potential. It is found that the [6,6] and [6,7] Padé approximants to the energy series can account for the energy eigenvalues of various energy eigenstates to a very high accuracy.

I. INTRODUCTION

The screened Coulomb potential of the form[1]

$$V(r) = -\frac{Z}{r}\sum_{k=0}^{\infty} V_k(\lambda r)^k, \tag{1}$$

where λ is the screening parameter, is of great importance in atomic, plasma, and solid-state physics. In particular, the problem of an electron in the Yukawa potential has been studied before by many authors[2-7], employing perturbation theory[3,7], the variational method,[2,6] and actual numerical integration[4,5] of the Schrödinger equation. The results of Rogers *et al.*[5] obtained by numerical techniques are of high accuracy over a wide range of screening parameter.

McEnnan, Kissel, and Pratt[8] have developed an analytic perturbation theory for screened Coulomb potentials and obtained the bound-state energies E in closed form correct to the third order of screening parameter λ. By employing the Hellman-Feynman theorem and the hypervirial theorems[9,10], we[11] have recently shown that one can express the bound-state energies E of screened Coulomb potentials in power series of the screening parameter correct to any order of λ as one wishes. However, Mehta and Patil[12] have pointed out that the energy levels of some screened Coulomb potentials have an asymptotic series in λ and one cannot use the perturbation series expansions to obtain the energy levels to an arbitrary accuracy.

In this paper, we would like to show that the Padé approximant method[13] can be used to calculate the bound-state energies of screened Coulomb potentials to a very high accuracy, in the case of the Yukawa potentials. We show by the actual calculations that the [6,6] and [6,7] Padé approximants to the energy series of the Yukawa potential can be used to obtain the results of Rogers *et al.* obtained from the numerical integration of the Schrödinger equation. In Sec. II we summarize the results of the perturbation theory for screened Coulomb potentials given in a previous paper,[11] and outline the Padé approximant calculation for energy perturbation series. In Sec. III we calculate the energy eigenvalues of an electron in the Yukawa potential as a function of screening parameter for various eigenstates and compare them with those obtained by Rogers *et al.*[5] In Sec. IV we calculate the K- and L-shell binding energies of atoms, assuming that the screened potential of the atom is of the model Yukawa potential. Finally, we present the conclusions in Sec. V.

II. THE PADÉ APPROXIMANTS AND PERTURBATION THEORY FOR SCREENED COULOMB POTENTIALS

The Hamiltonian for the screened Coulomb potential (1) can be written as

$$H = -\frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{r}\frac{d}{dr} + \frac{l(l+1)}{2r^2} + V(r), \tag{2}$$

where l is the orbital angular momentum quantum number. Here we use atomic units $\hbar = e = m_e = 1$, so that distances are measured in the Bohr radius a_0, and energies in units of $2\,RY = 27.212$ eV. By employing the Hellman-Feynman theorem and the hypervirial theorems[9,10], we have obtained, in a previous paper, the following hypervirial relations[11]

$$(E+ZV_1\lambda)\langle r^j\rangle = -1/2\left[\frac{2j+1}{j+1}Z\langle r^{j-1}\rangle + \left(-\frac{jl(l+1)}{j+1} + \tfrac{1}{4}j(j-1)\right)\langle r^{j-2}\rangle + \sum_{k=2}^{\infty}\frac{2j+k+1}{j+1}ZV_k\lambda^k\langle r^{j+k-1}\rangle\right], \quad j \geq -1 \tag{3}$$

where Z can be the charge of the nucleus. Let us assume that the energy E and the expectation values $\langle r^j\rangle$ can be expanded in power series of the screening parameter λ as

$$E_n = \sum_{k=0}^{\infty} E_n^{(k)}\lambda^k, \tag{4}$$

$$\langle r^j\rangle=\sum_{k=0}^{\infty}C_j^{(k)}\lambda^k, \tag{5}$$

where the energy of the unperturbed nth state $E_n^{(0)}=-Z^2/2n^2$ is known, and $C_0^{(k)}=\delta_{0k}$ from the normalization condition. From the Hellman-Feynman theorem, we find immediately[11]

$$kE_n^{(k)}=-Z\sum_{m=0}^{\infty}mV_mC_{m-1}^{(k-m)}. \tag{6}$$

By equating the coefficients of various powers of λ on both sides of (3), we can calculate, with the aid of (4)–(6), the energy coefficients $E_n^{(k)}$ in a hierarchical manner. For example, we get,[11] from the coefficients of λ^0 and λ^1,

$$C_j^{(0)}=\frac{n^2}{Z^2}\left[\frac{2j+1}{j+1}ZC_{j-1}^{(0)}+\left(-\frac{jl(l+1)}{j+1}+\tfrac{1}{4}j(j-1)\right)C_{j-2}^{(0)}\right],\quad j\geq -1$$

$$C_j^{(1)}=0, \tag{7}$$

and

$$E_n^{(0)}=-Z^2/2n^2,\quad E_n^{(1)}=-ZV_1,\quad E_n^{(2)}=-ZV_2C_1^{(0)},\quad E_n^{(3)}=-ZV_3C_2^{(0)}. \tag{8}$$

From the coefficients of λ^2 in (3), we obtain[11]

$$C_j^{(2)}=\frac{n^2}{Z^2}\left[\frac{2j+1}{j+1}C_{j-1}^{(2)}+\left(-\frac{jl(l+1)}{j+1}+\tfrac{1}{4}j(j-1)\right)C_{j-2}^{(2)}+\frac{2j+3}{j+1}ZV_2C_{j+1}^{(0)}\right]+2\frac{n^2}{Z^2}E_n^{(2)}C_j^{(0)},\quad j\geq -1 \tag{9}$$

and

$$E_n^{(4)}=-\tfrac{1}{4}Z(2V_2C_1^{(2)}+3V_3C_2^{(1)}+4V_4C_3^{(0)}). \tag{10}$$

Next, we find[11]

$$C_j^{(3)}=\frac{n^2}{Z^2}\left[\frac{2j+1}{j+1}\,C_{j-1}^{(3)}+\left(-\frac{jl(l+1)}{j+1}+\tfrac{1}{4}j(j-1)\right)C_{j-2}^{(3)}+\frac{2j+3}{j+1}ZV_2C_{j+1}^{(1)}+\frac{2j+5}{j+1}ZV_3C_{j+2}^{(0)}\right]+2\frac{n^2}{Z^2}(E_n^{(2)}C_j^{(1)}+E_n^{(3)}C_j^{(0)}),$$

$$j\geq -1, \tag{11}$$

and

$$E_n^{(5)}=-\tfrac{1}{5}Z(2V_2C_1^{(3)}+3V_3C_2^{(2)}+4V_4C_3^{(1)}+5V_5C_4^{(0)}), \tag{12}$$

and so on. Thus, we can calculate the energy coefficient $E_n^{(k)}$ from the knowledge of $C_j^{(m)}$ and $E_n^{(m)}$ with $m\leq k-2$ in a hierarchical manner.

Though the energy series (4) appears divergent, or, at best, asymptotic for small λ,[11] we can still calculate the bound-state energy E_n to a very high accuracy by forming the Padé approximants to the energy series[13,14]. The $[N, M+1]$ Padé approximant to the energy series (4) is given by

$$E[N,M+1]=E^{(0)}+\lambda E^{(1)}\frac{1+\lambda p_1+\lambda^2p_2+\cdots+\lambda^Mp_M}{1+\lambda q_1+\lambda^2q_2+\cdots+\lambda^Nq_N}$$

$$=E^{(0)}+\lambda E^{(1)}+\lambda^2E^{(2)}+\cdots+\lambda^{M+N+1}E^{(M+N+1)}, \tag{13}$$

TABLE I. Energy eigenvalues as a function of screening parameter for the 1s state in atomic units. Values obtained in Ref. 6 are enclosed in angle brackets.

Screening parameter λ	Our results $E[6,6]$	Our results $E[6,7]$	$E12$	Harris (Ref. 2) (variational)	Rogers *et al.* (Ref. 5) (numerical)
1.15	−0.000 54	−0.000 41	−12 387.5	⟨−0.000 41⟩	
1.10	−0.002 35	−0.002 25	−7 203.91	−0.002 12	
1.05	−0.005 60	−0.005 53	−4 083.73	−0.005 46	
1.00	−0.010 32	−0.010 27	−2 250.89	−0.010 23	−0.010 29
0.90	−0.024 33	−0.024 31	−621.038	−0.024 30	
0.80	−0.044 71	−0.044 70	−146.907	−0.044 70	
0.50	−0.148 12	−0.148 12	−0.601 44	−0.148 12	−0.148 1
0.25	−0.290 92	−0.290 92	−0.291 00	−0.290 92	−0.290 9
0.20	−0.326 81	−0.326 81	−0.326 81	⟨−0.326 81⟩	−0.3268
0.10	−0.407 06	−0.407 06	−0.407 06	⟨−0.407 06⟩	−0.407 1

TABLE II. Energy eigenvalues as a function of screening parameter for the $2s$ and $2p$ states in atomic units. Values obtained in Ref. 2 are enclosed in angle brackets.

Screening parameter λ		Our results $E[6,6]$	Our results $E[6,7]$	$E12$	Lam and Varshni (Ref. 6) (variational)	Rogers *et al.* (Ref. 5) (numerical)
0.30	$2s$	−0.000 17	−0.000 05	−522.098	−0.000 08	
0.25	$2s$	−0.003 41	−0.003 39	−56.026 1	−0.003 36	−0.003 39
0.20	$2s$	−0.012 11	−0.012 11	−3.627 22	−0.012 08	−0.012 11
	$2p$	−0.004 18	−0.004 04	−2.591 10	⟨−0.002 91⟩	−0.004 10
0.10	$2s$	−0.049 93	−0.049 93	−0.050 61	−0.049 93	−0.049 93
	$2p$	−0.046 53	−0.046 53	−0.047 02	⟨−0.048 19⟩	−0.046 54
0.05	$2s$	−0.081 77	−0.081 77	−0.081 77	−0.081 77	−0.081 77
	$2p$	−0.080 74	−0.080 74	−0.080 74		−0.080 74

where the coefficients $q_1, q_2, \ldots, q_N$ and $p_1, p_2, \ldots, p_M$ can be found from a knowledge of $E^{(2)}, E^{(3)}, \ldots, E^{(M+N+1)}$. We confine ourselves to the calculations of the Padé approximants $E[6,6]$ and $E[6,7]$ in this paper. The energy series (4) for the Yukawa potentials may be a Stieltjes series, though it is difficult to prove. If it is a Stieltjes series, the [6,6] and [6,7] Padé approximants then provide the upper and lower bounds[13] to the energy series. To test the applicability of the Padé approximant method on the perturbation theory for screened Coulomb potentials, we calculate the energy eigenvalues of an electron in the Yukawa potential, and the K- and L-shell binding energies of atoms in the next two sections.

III. ENERGY EIGENVALUES OF AN ELECTRON IN THE YUKAWA POTENTIAL

Let us calculate the energy eigenvalues of an electron in the Yukawa potential

$$V(r) = -\frac{1}{r}e^{-\lambda r}, \tag{14}$$

where λ is the screening parameter. This problem has been studied before by many authors.[2-7] Substituting (14) into the hierarchical relations (7)–(12) and so on, we can compute the energy coeffeicients $E^{(k)}$ to arbitrary orders of λ. In turn, we can calculate the [6,6] and [6,7] Padé approximants to the energy series (4). The results of the present calculation are to be compared with those of the variational method[2,6] and the numerical integration[5] of the Schrödinger equation.

The calculated energy values of the [6,6] and [6,7] Padé approximants to the energy series (4) for the Yukawa potential (14) are shown in Tables I–IV. We list also in the tables the energy values $E12$ of the perturbation series (4) correct to the twelfth order of λ for reference. Our calculated values of the bound-state energies are compared with those of Rogers *et al.*,[5] Harris,[2] and Lam and Varshni[6]. The results of $E[6,6]$ and $E[6,7]$ are almost in total agreement with those of Rogers *et al.*[5] from the numerical integration of the Schrödinger equation. It is evi-

TABLE III. Energy eigenvalues as a function of screening parameter for the $3s$, $3p$, and $3d$ states in atomic units. Values obtained in Ref. 2 are enclosed in angle brackets.

Screening parameter λ		Our results $E[6,6]$	Our results $E[6,7]$	$E12$	Lam and Varshni (Ref. 6) (variational)	Rogers *et al.* (Ref. 5) (numerical)
0.12	$3s$	−0.000 74	−0.000 73	−26.973 3	−0.000 72	
0.10	$3s$	−0.003 21	−0.003 21	−2.875 95	−0.003 20	−0.003 21
	$3p$	−0.001 53	−0.001 58	−2.479 27	⟨−0.001 87⟩	−0.001 59
0.08	$3s$	−0.007 78	−0.007 78	−0.191 34	−0.007 77	
	$3p$	−0.006 35	−0.006 33	−0.164 59	⟨−0.006 48⟩	
	$3d$	−0.003 25	−0.003 24	−0.106 07	⟨−0.002 96⟩	
0.05	$3s$	−0.019 35	−0.019 35	−0.019 89	−0.019 35	−0.019 35
	$3p$	−0.018 56	−0.018 56	−0.019 02		−0.018 56
	$3d$	−0.016 92	−0.016 92	−0.017 22		−0.016 92
0.025	$3s$	−0.034 33	−0.034 33	−0.034 33	−0.034 33	−0.034 33
	$3p$	−0.034 08	−0.034 08	−0.034 08		−0.034 08
	$3d$	−0.033 57	−0.033 57	−0.033 57		−0.033 57

TABLE IV. Energy eigenvalues as a function of screening parameter for the $4s$, $4p$, $4d$, and $4f$ states in atomic units.

Screening parameter λ		Our results $E[6,6]$	Our results $E[6,7]$	$E12$	Lam and Varshni (Ref. 6) (variational)	Rogers *et al.* (Ref. 5) (numerical)
0.08	$4s$	−0.000 05	−0.000 01	−79.751 3	−0.0	
0.06	$4s$	−0.001 24	−0.001 24	−2.337 15	−0.001 24	
	$4p$	−0.000 71	−0.000 75	−2.146 63		
0.05	$4s$	−0.003 09	−0.003 09	−0.250 21	−0.003 09	−0.003 09
	$4p$	−0.002 60	−0.002 60	−0.229 58		−0.002 60
	$4d$	−0.001 57	−0.001 58	−0.186 19		−0.001 58
0.025	$4s$	−0.012 50	−0.012 50	−0.012 55	−0.012 50	−0.012 51
	$4p$	−0.012 29	−0.012 29	−0.012 34		−0.012 30
	$4d$	−0.011 87	−0.011 87	−0.011 90		−0.011 87
	$4f$	−0.011 22	−0.011 22	−0.011 22		−0.011 22

dent from Tables I–IV that, for small λ, both the [6,6] and [6,7] Padé approximants yield identical results, and for λ near λ_c, the calculated values of Rogers *et al.*[5] fall between the two bounds provided by $E[6,6]$ and $E[6,7]$. Thus, we can conclude that the [6,6] and [6,7] Padé approximants to the energy series (4) can be employed to determine the energy eigenvalues of an electron in the Yukawa potential.

IV. THE *K*- AND *L*-SHELL BINDING ENERGIES OF ATOMS

As representative example of screened atomic potentials, we consider the Yukawa potential of the form

$$V(r) = -\frac{Z}{r}e^{-\lambda r}, \tag{15}$$

where the screening parameter λ is given by

$$\lambda = \lambda_0 Z^{1/3}, \tag{16}$$

corresponding to the Z dependence of the reciprocal of the Thomas-Fermi radius of the atom.[8] We note that the model potential (15) for screened atomic potentials used here is not entirely realistic, and other physical effects such as relativistic corrections are known to enter. Mehta and Patil[12] have recently evaluated the energy levels of atoms for the screened atomic potential

$$V(r) = -\frac{Z}{r} + \lambda\frac{(Z-1)}{1+\lambda r}, \tag{17}$$

using twice-subtracted dispersion relations. They have claimed that very good fits of experimental values[15] can be obtained with a value of $\lambda_0 = 0.98$.

Substituting (15) and (16) into the hierarchial

TABLE V. Calculated K-shell binding energies E_1 in keV for some values of Z with $\lambda_0 = 0.98$.

Z	Our results $E[6,6]$	Our results $E[6,7]$	$E12$	E_{dis} (Ref. 12)	E_{expt} (Ref. 16)
4	−8.9032(−2)	−8.9032(−2)	−9.7837(−2)		−1.11(−1)
9	−6.7768(−1)	−6.7768(−1)	−6.7774(−1)		−6.85(−1)
14	−1.8703	−1.8703	−1.8703	−1.89	−1.84
19	−3.6884	−3.6884	−3.6884	−3.71	−3.61
24	−6.1429	−6.1429	−6.1429	−6.16	−5.99
29	−9.2404	−9.2404	−9.2404	−9.26	−8.98
34	−1.2986(1)	−1.2986(1)	−1.2986(1)	−1.30(1)	−1.27(1)
39	−1.7382(1)	−1.7382(1)	−1.7382(1)	−1.74(1)	−1.70(1)
44	−2.2432(1)	−2.2432(1)	−2.2432(1)	−2.25(1)	−2.21(1)
49	−2.8137(1)	−2.8137(1)	−2.8137(1)	−2.82(1)	−2.79(1)
54	−3.4500(1)	−3.4500(1)	−3.4500(1)	−3.45(1)	−3.46(1)
59	−4.1523(1)	−4.1523(1)	−4.1523(1)	−4.15(1)	−4.20(1)
64	−4.9205(1)	−4.9205(1)	−4.9205(1)	−4.92(1)	−5.02(1)
69	−5.7549(1)	−5.7549(1)	−5.7549(1)	−5.76(1)	−5.94(1)
74	−6.6555(1)	−6.6555(1)	−6.6555(1)	−6.66(1)	−6.95(1)
79	−7.6224(1)	−7.6224(1)	−7.6224(1)	−7.63(1)	−8.07(1)
84	−8.6557(1)	−8.6557(1)	−8.6557(1)	−8.66(1)	−9.31(1)

TABLE VI. Calculated L-shell binding energies E_{20} in keV for some values of Z with $\lambda_0 = 0.98$.

Z	Our results $E[6,6]$	$E[6,7]$	$E12$	E_{dis} (Ref. 12)	E_{expt} (Ref. 16)
9	−1.4917(−2)	−1.4820(−2)	−3.6792(+1)		−3.1(−2)
14	−1.1066(−1)	−1.1065(−1)	−2.4806	−9.17(−2)	−1.49(−1)
19	−3.1513(−1)	−3.1513(−1)	−6.6738(−1)	−3.42(−1)	−3.77(−1)
24	−6.4100(−1)	−6.4100(−1)	−7.2241(−1)	−7.24(−1)	−6.95(−1)
29	−1.0960	−1.0960	−1.1208	−1.24	−1.10
34	−1.6855	−1.6855	−1.6946	−1.89	−1.65
39	−2.4134	−2.4134	−2.4172	−2.70	−2.37
44	−3.2827	−3.2827	−3.2845	−3.64	−3.22
49	−4.2958	−4.2958	−4.2966	−4.73	−4.24
54	−5.4546	−5.4546	−5.4551	−5.97	−5.45
59	−6.7608	−6.7608	−6.7610	−7.35	−6.83
64	−8.2158	−8.2158	−8.2159	−8.89	−8.38
69	−9.8207	−9.8207	−9.8208	−1.06(1)	−1.01(1)
74	−1.1568	−1.1568(1)	−1.1577(1)	−1.24(1)	−1.21(1)
79	−1.3485(1)	−1.3485(1)	−1.3485(1)	−1.44(1)	−1.43(1)
84	−1.5545(1)	−1.5545(1)	−1.5545(1)	−1.65(1)	−1.69(1)

relations (7)–(12) and so on, we can again calculate the energy coefficients $E^{(k)}$ to arbitrary orders of λ, and evaluate the [6,6] and [6,7] Padé approximants to the energy series E_{nl}. From the example studied in Sec. III, we can infer that the $E[6,6]$ and $E[6,7]$ Padé approximants to (4) will yield energy eigenvalues to a very high accuract. The calculated energy values of $E[6,6]$ and $E[6,7]$ Padé approximants for the K- and L-shell electrons with $\lambda_0 = 0.98$ are shown in Tables V–VII. The energy values $E12$ of the energy series (4) up to the twelfth order in λ are also listed for reference. Our calculated energy values are compared with those of Mehta and Patil[12] and the experiments.[15] As can be seen from Tables V–VII, the nonperturbative method[12] tends to overestimate the energy values of the L-shell electrons. It appears that the agreement between the prediction of the [6,6] and [6,7] Padé approximants to (4) and the experimental values is very satisfactory.

V. CONCLUSIONS

By employing the Hellman-Feynman theorem and the hypervirial theorems[9,10] to screened Coulomb potentials, we have derived, in a previous paper,[11] the hypervirial relations (3). From (3), we can calculate the energy coefficients $E^{(k)}$ to arbitrary orders of λ in a hierarchical manner. The energy series (4) so obtained appears divergent in λ. It is not easy to prove that the energy series (4) is a Stieltjes series in the case of the Yukawa potentials. But, if the energy series (4) were a Stieltjes series, it is well known that the $[N,N]$ and $[N, N+1]$ Padé approximants to the energy $E(\lambda)$ would provide the upper and lower bounds to the energy $E(\lambda)$.

In this paper, we have calculated the [6,6] and [6,7] Padé approximants to the energy series for the cases of an electron in the Yukawa potential and a representative screened potential of the atom in the form of the Yukawa potential. The results of our calculated values $E[6,6]$ and $E[6,7]$ for an electron in the Yukawa potential are almost in total agreement with those of Rogers *et al.*[5] obtained from the numerical integration of the Schrödinger equation. Also, the prediction of the model Yukawa potential for the K- and L-

TABLE VII. Calculated L-shell binding energies E_{21} in keV for some values of Z with $\lambda_0 = 0.98$.

Z	Our results $E[6,6]$	$E[6,7]$	$E12$	E_{expt} (Ref. 16)
9	+1.0428(−3)	+2.9957(−3)	−2.6322(1)	−8.6(−3)
14	−7.3315(−2)	−7.3230(−2)	−1.7680	−9.92(−2)
19	−2.6145(−1)	−2.6144(−1)	−5.1315(−1)	−2.96(−1)
24	−5.7247(−1)	−5.7247(−1)	−6.3015(−1)	−5.84(−1)
29	−1.0136	−1.0136	−1.0313	−9.51(−1)
34	−1.5899	−1.5899	−1.5964	−1.48
39	−2.3052	−2.3052	−2.3079	−2.16
44	−3.1624	−3.1624	−3.1636	−2.99
49	−4.1637	−4.1637	−4.1643	−3.94
54	−5.3112	−5.3112	−5.3115	−5.10
59	−6.6063	−6.6063	−6.6065	−5.96
64	−8.0506	−8.0506	−8.0507	−7.93
69	−9.6451	−9.6451	−9.6451	−9.62
74	−1.1391(1)	−1.1391(1)	−1.1391(1)	−1.15(1)
79	−1.3289(1)	−1.3289(1)	−1.3289(1)	−1.37(1)
84	−1.5340(1)	−1.5340(1)	−1.5340(1)	−1.62(1)

shell binding energies of atoms is in good agreement with the experimental values.[15] We can therefore conclude that the [6,6] and [6,7] Padé approximants to the energy series (4) can be used to determine the energy eigenvalues of the Yukawa potentials to a very high accuracy. Compared with other methods of calculation,[2-7] the present scheme of forming the Padé approximants to the energy series of screened Coulomb potentials appears to be quite simple and straightforward, and therefore it should play an important role in the description of screened Coulomb potentials.

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