

## Hypervirial perturbation theory for eigenenergies for two types of atomic potentials

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**Abstract.** Eigenenergies are calculated for the potentials  $V_1(r) = -(a/r)[1 + (1 + br)e^{-2br}]$  and  $V_2(r) = -(v/r)[1 - \lambda r(1 - Z^{-1})(1 + \lambda r)^{-1}]$ , using renormalized series technique. Accurate results produced here for various eigenstates agree with those available in the literature.

**Keywords.** Schrödinger equation; two types of potentials; eigenenergies.

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### 1. Introduction

In quantum mechanics calculation of the eigenvalues of the Schrödinger equation is a very important task. These eigenvalues can be obtained analytically for a few potentials, e.g., for the Coulomb potential, the Morse potential, the square-well potential and the harmonic oscillator. On the contrary large majority of potentials belong to a class of quantum-mechanical potentials which cannot be solved exactly in general, such as the potentials given by equations (2, 3). There is a wide range of approaches, such as variational techniques, the Padé approximant method, the finite difference method and perturbations schemes, to calculate the energy eigenvalues of the Schrödinger equation.

In the present work we apply the hypervirial perturbation theory to study the discrete spectra of Schrödinger equation of the form

$$\left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l}{2}(l+1)r^{-2} + V_L(r) \right] \Psi(r) = E\Psi(r), \quad L = 1, 2. \quad (1)$$

We use atomic units ( $m = \hbar = 1$ ). Two examples dealt with and for which there are several comparable studies [1–6] in the atomic physics literature are given by

$$V_1(r) = -\frac{a}{r}[1 + (1 + br)e^{-2br}] \quad (2)$$

with appropriate values of  $a$  and  $b$ ,  $V_1(r)$  represents the potential experienced by the second electron in a helium atom, due to the nucleus and the first electron. Besides its importance for the helium problem, the potential  $V_1(r)$  is of special interest being the prototype of more general potentials used in atomic problems [7]. The potential (2) has been studied by many workers [1–3] who have computed its bound state energies, using different numerical techniques.

The second example is the screened Coulomb potential of the form

$$V_2(r) = -\frac{v}{r}[1 - \lambda r(1 - Z^{-1})(1 + \lambda r)^{-1}]. \quad (3)$$

The problem of the screened Coulomb potential is of great importance in all atomic phenomena involving electronic transitions because these potentials are known to adequately describe the effective interaction in many-body atomic phenomena. The potential (3) has been studied by many workers using different types of numerical techniques [4–6]. In the atomic physics application the coupling constant  $v$  and the screening parameter  $\lambda$  for the non-Coulombic factor are given by  $v = \alpha Z$ ,  $\lambda = \lambda_0 \alpha Z^{1/3}$ ,  $\lambda_0 = 0.98$ , where  $\alpha = 1/137.037$  is the fine-structure constant and  $Z$  is the atomic number. The potential (3) is almost Coulombic everywhere for it is like  $-v/r$  for small  $r$  and like  $-v/Zr$  for large  $r$ .

In the present paper we shall treat the potentials (2 and 3) in the context of renormalized series technique based on the hypervirial theorem and a renormalization parameter  $\beta$ . This technique has previously been used to treat many potentials such as Yukawa, Hulthen potential and other screened Coulomb potentials [8].

## 2. The hypervirial method and recurrence relations for potential $V_1(r)$

To calculate the eigenvalues for the Schrödinger equation with the potential (2) using hypervirial perturbation theory, it is necessary to write the potential (2) in terms of the perturbation parameter  $\lambda$  as

$$V_1(r) = -\frac{a}{r} - a\left(r^{-1} + \frac{\lambda}{2}\right)e^{-\lambda r}, \quad b = \frac{\lambda}{2}. \quad (4)$$

The central idea of this is to expand the potential function  $e^{-\lambda r}$  in a Taylor series around  $r = 0$ , and solve the resulting approximate problem by hypervirial perturbation theory. The expansion of  $V_1(r)$  can be written as

$$V_1(r) = -\frac{a}{r} - a\left[\sum_{m=0}^{\infty} \frac{(-\lambda)^m r^{m-1}}{m!} + \frac{\lambda}{2} \sum_{m=0}^{\infty} \frac{(-\lambda)^m r^m}{m!}\right], \quad (5)$$

$$\equiv -\frac{a}{r} - a\left[\sum_{m=0}^{\infty} \frac{(-\lambda)^m}{m!} r^{m-1} + \frac{1}{2} \sum_{m=0}^{\infty} \frac{(-)^m (\lambda)^{m+1}}{m!} r^m\right]. \quad (6)$$

If we change summation limit of the first term in (6), we obtain

$$V_1(r) = -\frac{2a}{r} - a\left[\sum_{m=1}^{\infty} \frac{(-\lambda)^m}{m!} r^{m-1} + \frac{1}{2} \sum_{m=0}^{\infty} \frac{(-)^m (\lambda)^{m+1}}{m!} r^m\right]. \quad (7)$$

To improve the convergence properties of perturbation series we rearrange terms in the expanded potential (7). To illustrate this technique it is necessary to write the potential appearing in (7) in renormalized form

$$V_1(r) = -2a[\mu + \lambda\beta]r^{-1} - a\left[\sum_{m=1}^{\infty} \frac{(-\lambda)^m}{m!} r^{m-1} + \frac{1}{2} \sum_{m=0}^{\infty} \frac{(-)^m (\lambda)^{m+1}}{m!} r^m\right] \quad (8)$$

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where  $\mu = 1 - \beta\lambda$ . Let us assume that the energy  $E$  and the expectation  $\langle r^N \rangle$  can be expanded in power series of the perturbation parameter  $\lambda$  as

$$E = \sum E(I)\lambda^I, \quad (9)$$

$$\langle r^N \rangle = \sum H(N, M)\lambda^M. \quad (10)$$

If we use the perturbation expansions given by (9) and (10) in the hypervirial relation given by [8] in the form

$$2E(N+1)\langle r^N \rangle = \sum V_m(2N+2+m)\langle r^{N+m} \rangle - \frac{N}{2}(N^2-1)\langle r^{N-2} \rangle, \quad (11)$$

we obtain the following recurrence relation after some algebra

$$\begin{aligned} (2N+2)\sum_0^M E(I)H(N, M-I) &= N[l(l+1) - \frac{1}{4}(N^2-1)]H(N-2, M) \\ &- 2a[2N+1][\mu H(N-1, M) + \beta H(N-1, M-1)] \\ &+ V_{m1}[2N+m+1]H(N+m-1, M-m) \\ &+ V_{m2}[2N+2+m]H(N+m, M-m-1). \end{aligned} \quad (12)$$

The coefficients  $V_{m1}$  and  $V_{m2}$  can be written as

$$V_{m1} = -a \sum_{m=1}^{\infty} \frac{(-)^m}{m!}, \quad (13)$$

$$V_{m2} = -\frac{a}{2} \sum_{m=0}^{\infty} \frac{(-)^m}{m!}. \quad (14)$$

We have expanded the potential coefficients (13) and (14) to the limit in which any term beyond that limit makes no difference to our calculations. For the present calculations this limit was reached for ( $m = 16$ ). The two coefficients (13 and 14) in general alternate in sign and the coefficients decrease with increasing  $m$ .

Applying the Hellmann–Feynman theorem in the form

$$\frac{\partial E}{\partial \lambda} = \left\langle \frac{\partial V}{\partial \lambda} \right\rangle \quad (15)$$

we obtain a recurrence relation for the energy coefficients of the form

$$\begin{aligned} (M+1)E(M+1) &= -2a\beta H(-1, M) + mV_{m1}H(m-1, M-m+1) \\ &+ [m+1]V_{m2}H(m, M-m) \end{aligned} \quad (16)$$

where the energy of the unperturbed  $n$ th state is

$$E(0) = -\frac{a^2\mu^2}{n^2}. \quad (17)$$

The recurrence relations (12) and (16) can be used to calculate the energy coefficients from a knowledge of  $H(0, 0) = 1$  and  $E(0)$ .

### 3. The hypervirial method and recurrence relations for potential $V_2(r)$

In this section we calculate the bound state energies of the screened Coulomb potential  $V_2(r)$  for different eigenstates, by applying the hypervirial and Hellmann–Feynman theorems to calculate perturbatively the bound state energy levels without using perturbed wavefunctions, the potential  $V_2(r)$  may be written in the form

$$V_2(r) = -\frac{v}{r} + \lambda v(1 - Z^{-1})(1 + \lambda r)^{-1}. \quad (18)$$

The potential (18) can be expanded as

$$= -\frac{v}{r} - v(1 - Z^{-1}) \sum_{m=0}^{\infty} (-\lambda)^{m+1} r^m. \quad (19)$$

The potential (19) can be expressed in renormalized form

$$V(r) = -v[\mu + \lambda\beta]r^{-1} - v(1 - Z^{-1}) \sum_{m=0}^{\infty} (-\lambda)^{m+1} r^m \quad \mu = 1 - \lambda\beta \quad (20)$$

If we use the hypervirial relation (11) as in the previous section together with perturbation expansions given by (9) and (10) for potential (20) leading to the following recurrence relation

$$\begin{aligned} (2N + 2) \sum_0^M E(l)H(N, M - l) &= N[l(l + 1) - \frac{1}{4}(N^2 - 1)]H(N - 2, M) \\ &- v[2N + 1][\mu H(N - 1, M) + \beta H(N - 1, M - 1)] \\ &+ V_m[2N + m + 2]H(N + m, M - m - 1) \end{aligned} \quad (21)$$

where

$$V_m = -v(1 - Z^{-1}) \sum_{m=0}^{\infty} (-\lambda)^{m+1} \quad (22)$$

If we apply the Hellmann–Feynman theorem which is given by (15) and use the energy and the expectation value  $\langle r^N \rangle$  series as given by (9) and (10) we obtain the following recurrence relation

$$(M + 1)E(M + 1) = -\beta H(-1, M) + [m + 1] V_m H(m, M - m). \quad (23)$$

The recurrence relations (21) and (23) with unperturbed energy  $E(0) = -v^2 \mu^2 / 2n^2$  and initial condition  $H(0, 0) = 1$  can be used to evaluate the energy coefficients  $E(M)$ .

### 4. Numerical results and discussion

In the present work we show how the renormalized series technique can be used for solving the eigenvalue problem. Our technique has been tested for the Schrödinger equation involving two types of atomic potentials. This technique has been shown to be very effective and more accurate than other methods which have been used to handle the same calculations [1–6]. We have calculated energy levels for potentials (2) and (3), for several eigenstates, different values of  $\lambda$  and over a wide range of values of an atomic number  $Z$ .

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**Table 1.** Eigenvalues of the potential  $V_1(r)$ , for several states and different values of the perturbation parameter  $\lambda$ . The empty spaces mean that the corresponding eigenvalues cannot be reached by our technique.

S	$-E_{nl/a^2}$			
	$\lambda = 0.010$	$\lambda = 0.015$	$\lambda = 0.018$	$\lambda = 0.020$
1s	1.990000506306924	1.985001719575	1.982002982696	1.98000410184407
2s	0.490007282474012	0.485025075092	0.482043856739	0.48006064920319
3s	0.212259757166784	0.207354504983	0.204456932941	0.20254999056173
4s	0.115125251146804	0.110457274703	0.107830352762	0.10617901123446
5s	0.070331611296376	0.066279398685	0.06442855	0.063592
6s	0.046323898496	0.04388		
7s	0.0324852			
2p	0.490005179368098	0.485017794813	0.482031082486	0.48004294593839
3p	0.212254715472863	0.207336473486	0.204424654765	0.20250464670232
4p	0.115115441929899	0.110420433374	0.107762271451	0.10608116832868
5p	0.070314330389804	0.066209366162	0.06429074	0.06338
6p	0.04629474917	0.04374		
7p	0.0324354			
3d	0.212244709229763	0.207300827916	0.204360999606	0.20241537041801
4d	0.115095975575826	0.110347620894	0.107628061997	0.1058886351467
5d	0.070280041156948	0.066071034235	0.06401954	0.062967
6d	0.04623692646	0.043467		
7d	0.0323367			
4f	0.115067156077349	0.110240576818	0.107431630061	0.10560771699417
5f	0.070229288635185	0.065867869543	0.06362375	0.062369
6f	0.046151382507	0.043063		
7f	0.032191			
6h	0.0460395458168	0.042546		
7h	0.03200107	0.03		
8h	0.0241			

  

$\lambda$	$-E_{nl/a^2}$			
	1s	2s	2p	3s
0.025	1.975008062303	0.475120894718	0.475085416748	0.19789232491473
0.030	1.970014020431	0.470213255371	0.470150337166	0.19343652031976
0.035	1.965022406241	0.465345779041	0.465243213018	0.18924939238
0.040	1.960033660542	0.460527177763	0.460369961841	0.18541468
0.045	1.955048235217	0.455766900334	0.455536956196	0.182044
0.050	1.950066593503	0.451075221633	0.450751076828	0.17931
0.055	1.945089210289	0.446463354484	0.446019778919	0.1775
0.060	1.940116572432	0.441943592771	0.441351176185	0.176
0.065	1.935149179084	0.4375294994	0.43675415007	
0.070	1.930187542037	0.433236162	0.4322384959	
0.075	1.925232186087	0.42908056	0.427815128	
0.080	1.920283649421	0.4250822	0.42349639	
0.085	1.915342484017	0.42164	0.4192965	
0.090	1.910409256077	0.41765	0.415233	
0.095	1.905484546482	0.4143	0.41133	
0.100	1.900568951274	0.41119	0.40759	
0.150	1.852057405331			
0.200	1.80525132			
0.250	1.76114			
0.300	1.7213			
0.400	1.67			

In table 1, we present the eigenvalues for the potential  $V_1(r)$  for different values of  $\lambda$  and different state numbers. The renormalized series provides extremely accurate eigenvalues at low  $\lambda$ . But, at larger values of  $\lambda$  and higher excited states, the accuracy

**Table 2.** Bound-state energies (in keV) for the potential  $V_2(r)$  for the states (1s, 2s, 2p, 3s, 3p, 3d). The values of the renormalization parameter  $\beta$  are given.  $M$  is the order of the perturbation expansion with which we obtain convergence.

Z	$-E_{1s}$	M	$-\beta$	$-E_{2s}$	M	$-\beta$	$-E_{2p}$	M	$-\beta$
4	0.13523	12	1.2	0.0138	40	26	0.0123	10	2.6
9	0.766002	14	1	0.0828	48	18	0.0697	16	2.5
14	1.993278	16	1	0.2448	54	15	0.2142	17	2.4
19	3.8419428	17	0.9	0.5172	60	14	0.4674	18	2.2
24	6.3241426	16	0.8	0.9107	70	14	0.8411	19	2.1
29	9.44728452	17	0.7	1.4324	73	13	1.3428	18	1.9
34	13.21643035	16	0.6	2.0873	74	12	1.9779	19	1.9
39	17.635292381	16	0.5	2.87934	75	11	2.7503	20	1.8
44	22.706727619	18	0.5	3.81148	75	10	3.6631	19	1.7
49	28.4330136113	40	0.4	4.88617	80	10	4.7187	17	1.6
54	34.81601545815	39	0.3	6.10552	70	8	5.91934	18	1.4
59	41.857292885107	28	0.2	7.47117	65	7	7.26647	18	1.2
64	49.558172935606	28	0.2	8.98457	70	7	8.76162	18	0.9
69	57.919800654238	32	0	10.64701	62	6	10.406027	17	0.9
74	66.9431758274224	34	0	12.45959	69	6	12.200809	16	0.8
79	76.6291802637234	34	0	14.42328	44	4	14.1469203	17	0.7
84	86.9785985081688	31	0	16.53894	43	4	16.2452164	16	0.7
89	97.9921338756381	28	0	18.80734	38	3	18.4964652	16	0.6
94	109.670421069675	20	0	21.229208	16	0	20.9013591	15	0.6
100	124.562645734566	21	0	24.338872	15	0	23.99092361	16	0.5
110	151.514471031952	20	0	30.0173678	16	0	29.63648765	15	0.5
120	181.133721056460	17	0	36.3189465	16	0	35.905799803	16	0.4

  

Z	$-E_{3s}$	M	$-\beta$	$-E_{3p}$	M	$-\beta$	$-E_{3d}$	M	$-\beta$
14	0.0476	12	1.8	0.0381	11	1.5	0.0228	14	1.4
19	0.1049	12	1.4	0.0876	14	1.4	0.0576	12	1.2
24	0.19477	15	1.3	0.16832	16	1.2	0.12033	12	0.8
29	0.32191	16	1.3	0.28526	14	1.1	0.217001	14	0.8
34	0.49007	16	1.2	0.44249	16	1.1	0.352318	16	0.8
39	0.70223	16	1.2	0.64317	15	1.1	0.529913	14	0.6
44	0.96083	15	1.1	0.88987	16	1.1	0.752687	14	0.6
49	1.26792	16	1.1	1.184772	16	0.9	1.023009	14	0.6
54	1.625248	17	0.9	1.529661	16	0.8	1.342859	12	0.5
59	2.034299	14	0.8	1.926106	15	0.7	1.7139192	12	0.5
64	2.4963937	16	0.7	2.3754626	16	0.7	2.1376324	15	0.5
69	3.0126824	16	0.6	2.8789179	17	0.7	2.6152581	14	0.5
74	3.5841909	14	0.6	3.4375239	17	0.5	3.1479033	14	0.5
79	4.2118361	15	0.5	4.0522190	15	0.5	3.7365502	15	0.5
84	4.8964437	15	0.4	4.7238464	14	0.4	4.3820766	16	0.5
89	5.6387619	15	0.5	5.4531682	16	0.5	5.08527290	14	0.4
94	6.4394719	12	0.5	6.24087711	14	0.5	5.84685424	14	0.3
100	7.47827502	14	0.5	7.26408595	14	0.5	6.83873299	14	0.3
110	9.401082478	14	0.5	9.160952213	15	0.5	8.68350120	15	0.3
120	11.56665076	17	0.4	11.30067818	15	0.5	10.77134969	13	0.3

decreases, exactly as in our previous renormalized series calculations [8]. The accuracy of our results in general is better than that of previous studies [1–3].

Our confidence in the accuracy of our results comes from the checks, the agreement between our results and with those results produced by using finite difference technique [9]. Also by two separate computations for some eigenstates with slightly increasing or decreasing the value of the renormalization parameter  $\beta$ , yielded eigenenergy agreeing to all digits.

In table 2, we list the energy of states (1s, 2s, 2p, 3s, 3p, 3d), for different values of  $Z$  ( $4 \leq Z \leq 120$ ). For a given shell the results improve with increasing  $Z$ , and this behavior is clear from our listed results. The degree of agreement between our results and those arising from other methods [4–6] is good, but for  $Z > 84$  numerical results are not reported. We state that the renormalized series technique work equally for  $\lambda = \lambda_0$  and  $\lambda = \lambda_0 \alpha Z^{1/3}$  as perturbation parameter; we used two values of  $\lambda$  to verify the accuracy of renormalized series.

For comparison with the results available in literature [1–6], the energy in table 1 is given as  $-E_{nl/a^2}$ . Also using other parameters such as  $\nu = \alpha Z$ ,  $\lambda = \lambda_0 \alpha Z^{1/3}$  in our calculations and listed energies  $E_{nl}$  in keV in table 2 we obtain the relation

$$\begin{aligned} \text{Energy} &= [2 \times 13.6047][1000\alpha^2]^{-1} E \text{ keV} \\ &= 510.969E \text{ keV.} \end{aligned} \tag{24}$$

## References

- [1] R Sever and C Tezcan, *Phys. Rev.* **A36**, 1045 (1987)
- [2] R Sever and C Tezcan, *Phys. Rev.* **A37**, 3158 (1988)
- [3] Y P Varshni, *Phys. Rev.* **A38**, 1595 (1988)
- [4] C H Mehta and S H Patil, *Phys. Rev.* **A17**, 34 (1978)
- [5] R L Hall, *Phys. Rev.* **A32**, 14 (1985)
- [6] R Roychoudhury, B Roy and Y P Varshni, *Phys. Rev.* **A38**, 3944 (1988)
- [7] A Hibbert, *Adv. At. Mol. Phys.* **18**, 309 (1982)
- [8] M R M Witwit, *J. Phys.* **A24**, 4535 (1991)
- [9] M R M Witwit, *J. Phys.* **A25**, 503 (1992)