Variational Perturbation Method Based on the Principle of Moments

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A simple practical variational perturbation method based on the approximate calculation of the moments of the resolvent operator is developed. The method has been applied to the $(1S)^2S$ state of the helium atom. The trial wave functions have been expanded in terms of naturally spaced groups of Hylleraas functions up to 95 terms. The 95 term trial function gives an upper bound of -2.903724305 atomic units to the ground-state energy. Other numerical results have been compared with the 21st-order perturbation energies of Midtdal and other previous calculations. It is found that comparable results can be obtained by the present simple calculation.

1. INTRODUCTION

A NUMBER of authors[1,2] have successfully applied the method of moments to various quantum-mechanical systems. In this method one calculates the moments $(0|H^n|0)$. Here, H is a physical Hamiltonian, n takes on integer values, and $|0)$ is a given approximate ground-state wave function of H. It is well known that, in general, only a limited number of moments exists. The success of the method depends on a good choice of $|0)$.

In Sec. 2, a systematic method of constructing a good approximate ground-state wave function is given. It is based on the construction of the moments of the resolvent operator $1/(H-a)$. No attempt has been made to calculate these moments exactly. In Sec. 3, a variational approach is given, where these moments are calculated with respect to a finite number of basis functions of the helium atom. The method is applied to the ground state of the helium atom in Sec. 4. The basis used is the well-known set of Hylleraas functions. Results are given in Table I for trial functions expanded in terms of naturally spaced groups of Hylleraas functions. Our best result differs from the best nonrelativistic calculations of Pekeris[3] only in the ninth significant figure. Direct comparison with the 20-term expansion calculation of Herzberg[4] is given in Tables II and III and Sec. 5. Direct comparison with the 70- and 95-term expansion, 21st-order perturbation calculation of Midtdal[5] is given in Table IV and Sec. 6. The comparisons showed only minor differences, often in the ninth figure in the energies.

Our numerical calculation was carried out with a 16-digit double-precision floating-point arithmetic program at the Western Data Processing Center by an IBM system 360 computer. The main part of the calculation involves the inversion of one matrix. The average time for a set of calculations with 95 terms is less than 1 min.

[1] F. R. Halpern, Phys. Rev. **107**, 1145 (1957); **111**, 1 (1958); Ann. Phys. (N. Y.) **7**, 146 (1959); **7**, 154 (1959); Richard J. Drachman, Phys. Rev. **125**, 1758 (1966).
[2] Chi-Yu Hu, Phys. Rev. **152**, 1116 (1966).
[3] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[4] J. F. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).
[5] John Midtdal, Phys. Rev. **138**, A1010 (1965).

2. RESOLVENT OPERATOR AND METHOD OF MOMENTS

In the following sections, only the ground state of the physical system represented by the Hamiltonian H is considered. The parameter a that appears in the resolvent operator $1/(H-a)$ is chosen to be an upper bound to the ground-state energy. It should lie closer to the ground state than the first excited state. Assume $|0)$ is some known function not orthogonal to the ground-state wave function of H. One can formally write down the expansion of $|0)$ in terms of the eigenfunctions of H; we have

$$|0) = \sum_{n=0}^{\infty} \langle n|0\rangle |n\rangle, \tag{1}$$

$$H|n\rangle = E_n|n\rangle. \tag{2}$$

Let

$$|XN) = \left(\frac{1}{H-a}\right)^N |0), \tag{3}$$

$$\bar{\epsilon}_N = C_N{}^2 (XN|H|XN),$$

where C_N is the normalization constant of $|XN)$. It follows from Eqs. (1)–(3) that

$$|XN) = \sum_{n=0}^{\infty} \frac{\langle n|0\rangle}{(E_n-a)^N} |n\rangle. \tag{4}$$

Since $E_0 < a < E_1 < E_2 < \cdots$, and $|E_0-a| < |E_1-a| < |E_2-a| < \cdots$, we have

$$\lim_{N\to\infty} C_N|XN) \to |0\rangle,$$

and

$$\lim_{N\to\infty} \bar{\epsilon}_N \to E_0. \tag{5}$$

The successive $|XN)$ can be obtained by solving the inhomogeneous equations

$$(H-a)|XN) = |XN-1), \tag{6}$$

where $N = 1, 2, 3, \cdots$, and $|X_0) = |0)$.

The convergence can be made very fast by choosing the parameter a so that

$$|E_0-a| \ll |E_1-a| < |E_2-a| < \cdots. \tag{7}$$

TABLE I. The energies ϵ_{0U} and ϵ_{0L} (in a.u.) for different a and different number of basis functions in the trial function.

| | $a=-2.85$ | | $a=-2.90$ | | |
M	ϵ_{0U}	ϵ_{0L}	ϵ_{0U}	ϵ_{0L}	k
3	−2.89122948157	−2.89122950254	−2.89122948176	−2.89122948176[a]	3.64
7	−2.90342460676	−2.90342501008	−2.90342461108	−2.90342461118	3.65
13	−2.90364041122	−2.90364151364	−2.90364043524	−2.90364043555	3.80
22	−2.90371383242	−2.90371618985	−2.90371389995	−2.90371390063	4.10
34	−2.90372086685	−2.90372380940	−2.90372095845	−2.90372095929	4.20
50	−2.90372356239	−2.90372795325	−2.90372370027	−2.90372370153	4.45
70	−2.90372393179	−2.90372945910	−2.90372410501	−2.90372410659	4.62
95	−2.90372408039	−2.90373139058	−2.90372430535	−2.90372430743	4.86

[a] In this case −2.90 is a lower bound to ϵ_0, Eq. (17) gives an upper bound (Refs. 7, 8) also. Thus, this ϵ_{0L} is replaced by the iterative solution ϵ_0.

Convergence can be further accelerated by the application of the method of moments.[2] Sufficient accuracy can be obtained with a maximum $N=2$, from which three moments follow. They are, using Eq. (6) and the Hermitian property of H,

$$\lambda_1 = (X2\,|\,H-a\,|\,X2) = (X2\,|\,X1),$$
$$\lambda_2 = (X2\,|\,(H-a)^2\,|\,X2) = (X2\,|\,0) = (X1\,|\,X1),$$
$$\lambda_3 = (X2\,|\,(H-a)^3\,|\,X2) = (X1\,|\,0). \tag{8}$$

The method of moments[6] then gives the upper bound for the ground-state energy,

$$E_{0u} = a + \{\tfrac{1}{2}\alpha - [(\tfrac{1}{2}\alpha)^2 - \beta]^{1/2}\}, \tag{9}$$

$$\alpha = \frac{\lambda_3 - \lambda_1\lambda_2}{\lambda_2 - \lambda_1^2},$$

$$\beta = \frac{\lambda_1\lambda_3 - \lambda_2^2}{\lambda_2 - \lambda_1^2}.$$

A lower bound[7] to the ground-state energy also follows from the three moments

$$t_1 = (0\,|\,\frac{1}{H-a}\,|\,0) = (X1\,|\,0),$$

$$t_2 = (0\,|\,\left(\frac{1}{H-a}\right)^2\,|\,0) = (X1\,|\,X1),$$

$$t_3 = (0\,|\,\left(\frac{1}{H-a}\right)^3\,|\,0) = (X2\,|\,X1). \tag{10}$$

We have[8]

$$E_{0L} = a + 1/\{\tfrac{1}{2}\gamma - [(\tfrac{1}{2}\gamma)^2 - \delta]^{1/2}\},$$

$$\gamma = \frac{t_3 - t_1 t_2}{t_2 - t_1^2},$$

$$\delta = \frac{t_1 t_3 - t_2^2}{t_2 - t_1^2}. \tag{11}$$

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[6] See Sec. 6 of Ref. 2.

[7] A lower bound is obtained only when a is an upper bound.

[8] Eq. (11) holds only when a is an upper bound. If a is a lower bound, the sign of the square root must be changed, so that an upper bound is obtained.

Let a be a rough upper bound, and let us formally expand the variational wave functions of the method of moment in terms of the eigenfunctions of H. It becomes immediately evident that Eqs. (9) and (11) give, respectively, an upper and a lower bound to the ground-state energy.

Where Eq. (5) gives the exact solution E_0, Eqs. (9) and (11) only give approximate solutions. The closer a is to E_0, the better are the solutions. In this sense, the results of Eqs. (9) and (11) for a given parameter a are similar to that obtained by a perturbation expansion of some finite order.

3. VARIATIONAL SOLUTION OF METHOD OF MOMENTS

In this work, the solutions of Eq. (6) are obtained by a variational method, using the functionals

$$F(X^t N) = -(X^t N\,|\,H-a\,|\,X^t N) + 2(X^t N\,|\,\bar{X}N - 1),$$
$$N = 1, 2, 3, \cdots. \tag{12}$$

$|X^t N)$ denotes the trial function to be varied. $|\bar{X}N-1)$ is the given stationary solution of the preceding step. The stationary solution is given by

$$(H-a)\,|\,\bar{X}N) = |\bar{X}N-1), \tag{13}$$
and

$$F(\bar{X}N) = (\bar{X}N\,|\,H-a\,|\,\bar{X}N), \quad N=1, 2, 3, \cdots. \tag{14}$$

Apart from a normalization factor, Eq. (14) gives the expectation value of the energy with respect to the stationary solution $|\bar{X}N)$. Thus, the solution of the inhomogeneous Eq. (13) with a variational function is equivalent to a variational principle for the energy. The corresponding iterative solution

$$\lim_{N \to \infty} C_N^2 (\bar{X}N\,|\,H\,|\,\bar{X}N) = \epsilon_0 \tag{15}$$

gives the variational energy ϵ_0, which is an upper bound to the ground-state energy E_0 of Eq. (5).

$$\epsilon_{0U} = a + \tfrac{1}{2}\bar{\alpha} - [(\tfrac{1}{2}\bar{\alpha})^2 - \bar{\beta}]^{1/2} \tag{16}$$
and

$$\epsilon_{0L} = a + 1/\{\tfrac{1}{2}\bar{\gamma} - [(\tfrac{1}{2}\bar{\gamma})^2 - \bar{\delta}]^{1/2}\} \tag{17}$$

give an upper and a lower bound to ϵ_0, respectively, where $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$, and $\bar{\delta}$ are obtained by replacing $|X2)$ and $|X1)$ in Eqs. (8) and (10) by $|\bar{X}2)$ and $|\bar{X}1)$, respectively.

TABLE II. Coefficients of the basis functions in the trial function given by Eq. (20).

	$a=-2.85$	$N=2$ $a=-2.90$	Iterative solution	Variational solution of Ref. 4
$\mathfrak{N}_N$	1.36763805	1.36686923	1.36686585	1.36686946
X_1	0.41712694	0.41705457	0.41705424	0.417070598
X_2	0.20807147	0.20834547	0.20834659	0.208366354
X_3	−0.00506005	−0.00521615	−0.00521674	−0.005234824
X_4	0.04883101	0.04906824	0.04906917	0.049090025
X_5	−0.15710834	−0.15722820	−0.15722869	−0.157224213
X_6	0.08216212	0.08234822	0.08234904	0.082327506
X_7	−0.12606388	−0.12587023	−0.12586942	−0.125878664
X_8	0.04762219	0.04766263	0.04766279	0.047677478
X_9	0.04092988	0.04080728	0.04080676	0.040706923
X_{10}	0.03235878	0.03196670	0.03196515	0.031908952
X_{11}	−0.00940086	−0.00949011	−0.00949045	−0.009497449
X_{12}	0.00050815	0.00051220	0.00051221	0.000512301
X_{13}	−0.00923434	−0.00923318	−0.00923317	−0.009229647
X_{14}	0.00070772	0.00070697	0.00070697	0.000706572
X_{15}	−0.00724933	−0.00725712	−0.00725715	−0.007251378
X_{16}	0.00212429	0.00228608	0.00228674	0.002303423
X_{17}	0.00134178	0.00136561	0.00136570	0.001366454
X_{18}	0.00150531	0.00159031	0.00159066	0.001605489
X_{19}	0.00062089	0.00066703	0.00066722	0.000758737

4. APPLICATION TO HELIUM ATOM

The Hamiltonian of the system under consideration is

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-2/r_1-2/r_2+1/r_{12}. \quad (18)$$

The Hamiltonian and all the energies are expressed in atomic units. $|0\rangle$ is chosen to be the hydrogenic wave function $(k^3/8\pi)e^{-(1/2)k(r_1+r_2)}$. k is regarded as a variational parameter. The trial wave functions are expanded in terms of the well-known Hylleraas functions.

$$|X^tN\rangle=e^{-(1/2)ks}\sum_{i=1}^{M} C_{iN}S^l t^m u^n, \quad (19)$$

where $S=r_1+r_2$, $t=r_1-r_2$, $u=r_{12}$,

$$l=0, 1, 2, \cdots,$$
$$m=0, 2, 4, \cdots,$$
$$n=0, 1, 2, \cdots,$$

and M is the total number of terms taken in the variational calculation.

In this section emphasis is placed on the systematic behavior of ϵ_{0U} and ϵ_{0L} with different values of a and different M. The energies are monotonic functions of the parameter a $(E_0<a<E_1)$. Only two values, $a=-2.85$ and -2.90, are listed in Table I. M takes the values 3, 7, 13, 22, 34, 50, 70, and 95. They correspond to the expansions with a maximum sum of $l+m+n$ equal to 1, 2, 3, 4, 5, 6, 7, and 8, respectively.

At $a=-2.85$, the upper bounds ϵ_{0U} and the lower bounds ϵ_{0L} agree up to the fifth or sixth figure. When $a=-2.90$, they agree up to the ninth figure. These imply that the convergence of this method is satisfactorily fast (since for $a=-2.90$, $\epsilon_{0U}=\epsilon_0=\epsilon_{0L}$ for the first nine figures).

Our best value for the ground-state energy obtained with a 95-term trial function is -2.903724305. Scherr, Sander, and Knight[9] obtained the value -2.90372433 in their 13th-order perturbation calculation with a somewhat different 100-term expansion. The best known nonrelativistic value for the ground-state energy is -2.903724375, obtained by Pekeris with his 1078-term trial function.[3] Our 95 Hylleraas terms are used only for convenience, not for best result; yet the energy differs only in the ninth figure from the best calculations known.

5. COMPARISON WITH THE 20 BASIS FUNCTIONS VARIATIONAL SOLUTION OF HART AND HERZBERG

In order to examine the convergence of $|XN\rangle$ with increasing N, Tables II and III list the details of the wave functions $|X2\rangle$ for $a=-2.85$ and -2.90, as well as the iterative solution and the energies of the 20 terms trial function used in Ref. 4.

TABLE III. The energies ϵ_{0U}, ϵ_{0L}, and ϵ_0 (in a.u.) obtained with the 20-term trial function given by Eq. (20).

$a=-2.85$		$a=-2.90$	
ϵ_{0U}	ϵ_{0L}	ϵ_{0U}	ϵ_{0L}
−2.90371770802	−2.9037192324	−2.90371775300	−2.90371775344
	ϵ_0 −2.90371775300		ϵ_0 of Ref. 4 −2.9037179

[9] C. W. Scherr, F. C. Sanders, and R. E. Knight, Rev. Mod. Phys. **35**, 436 (1963).

TABLE IV. Energies (in a.u.) for the 70- and 95-term trial functions with $k=4$.

M	$a=-2.85$		$a=-2.90$		21st-order perturbation energies of Ref. 5
	ϵ_{0U}	ϵ_{0L}	ϵ_{0U}	ϵ_{0L}	
70	-2.90372369834	-2.90372574208	-2.90372376288	-2.90372376347	-2.9037237628
95	-2.90372402909	-2.90372607174	-2.90372409251	-2.90372409309	-2.9037240926

By putting $k=3.87$ as in Ref. 4, we calculated the normalized functions

$$C_N|\bar{X}N) = \mathfrak{N}_N \exp-\tfrac{1}{2}ks[1+X_{1N}u+X_{2N}t^2+X_{3N}s$$
$$+X_{4N}s^2+X_{5N}u^2+X_{6N}su+X_{7N}t^2u$$
$$+X_{8N}u^3+X_{9N}t^2u^2+X_{10N}st^2+X_{11N}s^3$$
$$+X_{12N}t^2u^4+X_{13N}u^4+X_{14N}u^5+X_{15N}t^2u^3$$
$$+X_{16N}s^2t^2+X_{17N}s^4+X_{18N}st^2u+X_{19N}t^4]. \quad (20)$$

The coefficients $\mathfrak{N}_N$, X_{1N}, X_{2N}, $\cdots$, X_{19N} for $N=2$, $a=-2.85$ and -2.90, are listed in the second and the third columns of Table II, respectively. The fourth column contains the iterative solutions which are correct to the seventh digit. These iterative solutions are obtained at $N=8$, 12, and 18 for $a=-2.90$, -2.85, and -2.75, respectively. The last column lists the variational solutions of Ref. 4. At $a=-2.85$, ϵ_{0U} and ϵ_{0L} differ in the seventh figure. The corresponding coefficients for the wave function differ from the iterative solution in the fourth or fifth figures. At $a=-2.90$, ϵ_{0U} and ϵ_{0L} differ in the 11th figure, where the corresponding coefficients for the wave function differ from the iterative solution in the sixth or seventh figures. The ϵ_{0U} agrees with the iterative value ϵ_0 up to the 12th figure. Our ϵ_0 differs from the calculation of Ref. 4 in the eighth figure; the corresponding coefficients of the wave functions differ in the fifth or sixth figures. Inasmuch as they have detected an uncertainty in their energy calculation of 1 part in 10^7, the agreements between our calculations are satisfactory.

6. COMPARISON WITH THE 21ST-ORDER PERTURBATION ENERGIES OF MIDTDAL

Our 70- and 95-term variational functions are identical to that used by Midtdal in his 21st-order perturbation calculation. However, the energies listed in Table I have been minimized with respect to k. The energies listed in Table IV are obtained by setting $k=4$ as in Midtdal's calculation.

Our best upper bounds differ only in the 12th and the 11th figures from the corresponding values of Ref. 5.

7. CONCLUSION

It is not our purpose to carry out any higher-dimensional calculations, although there is no essential difficulty. Since approximate solutions of Eq. (5) without resorting to a finite-order expansion are possible, we have contented ourselves with a maximum expansion of 95 terms.

It is, however, very clear from Secs. 4–6 that this method is indeed as effective as it is simple. The calculation involves the inversion of just one matrix.

The fast convergence of this method is clear from Sec. 2. For most quantum-mechanical systems, it is not hard to find a parameter a such that the condition of Eq. (7) is satisfied. A first try of a can be obtained from a rough variational calculation, i.e., the value -2.85 (or even -2.75) used in Secs. 4–6. The upper bound obtained by this method, with convenient roundoff, can be taken as the parameter a for a second try, i.e., the value -2.90 used in Secs. 4–6. The accuracy of the calculation is assured by the degree of agreement between ϵ_{0U} and ϵ_{0L}.