

## Variational function of the Padé type — an application to a test system

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**Abstract.** It is shown that a trial function of the Padé type is overwhelmingly superior to a linear variational function (containing the same number of parameters) for hydrogen-like atoms for 'strong perturbations'.

**Keywords.** Variational function; Padé type; trial function.

### 1. Introduction

It has been shown recently (Sane *et al* 1979) that if the so-called "local energy gap" approximation is introduced in the Brillouin-Wigner perturbation series, then the summation of the resulting series yields a form for the wave function which can be recognised as the product of the unperturbed wave function and a rational function of the Padé type. This observation suggests that the incorporation of Padé approximants into trial functions may prove useful for solving the Schrödinger equation by the variational method. Trial functions of this type for a single variable problem are expected to be superior than the ones employing a power series expansion since whereas the latter converges in a circle of radius given by the nearest singularity, the Padé approximants have a much wider domain of convergence (actually the whole of a cut plane in the case of a function possessing branch points) thereby enabling them to simulate functions having singularities much better than a power series. On the other hand, the use of rational functions introduces the somewhat inconvenient nonlinear variational parameters. The assessment of the Padé type variational functions can therefore be best made on *a posteriori* grounds by applying them to some standard problems like the helium atom, anharmonic oscillator, Stark effect and so on. Preliminary investigation of these systems has yielded encouraging trends but in order to clarify the mathematical and physical ideas associated with the use of such functions, it is felt desirable to test them on an idealised problem. In this paper, we report the variational study of the ground state of the hydrogen atom treated as a test system—the trial function being constructed from a rational function of the

[2,2] Padé type. The results for this four-parameter function are then compared with the exact wave function and with a power series trial function having linear variational parameters.

## 2. Formulation of the problem

Let the Hamiltonian  $H$  of a hydrogenic atom with nuclear charge  $(Z + 1)$  be written in atomic units as

$$H = H_0 + V, \quad (1)$$

$$\text{where } H_0 = -\frac{1}{2} \nabla^2 - Z/r, \quad (2)$$

$$\text{and } V = -1/r. \quad (3)$$

Approximations to the wave function for the ground state of (1) will now be obtained using two different types of trial functions. In one case, following the considerations given by Sane *et al* (1979), the trial function is taken as the eigenfunction of  $H_0$  multiplied by a rational function of the Padé type in the variable  $r$ . The specific function chosen has the form

$$\psi_{\text{trial}} = \frac{1 + a_1 r + a_2 r^2}{1 + b_1 r + b_2 r^2} \exp(-Zr). \quad (4)$$

In the other case, the rational function in (4) is replaced by a polynomial in  $r$ , i.e.,

$$\psi_{\text{trial}} = \left( \sum_n A_n r^n \right) \exp(-Zr). \quad (5)$$

It is to be noted that the exponent  $Z$  in both the trial functions is the same as enters  $H_0$  and is therefore kept fixed. It is obvious that if the exponent is allowed to vary, it will tend to  $(Z + 1)$  while the factor multiplying the exponential in (4) and (5) will tend to unity thus yielding the exact ground state wave function  $\exp[-(Z + 1)r]$  of  $H$ . Since the interest here is not to obtain the exact eigenfunction but merely to compare the relative merits of a rational approximation to the wave function with a polynomial approximation, it is necessary not to treat  $Z$  as a variational parameter. This leaves (4) as a four-parameter variational problem with two nonlinear parameters, and (5) as a problem with  $(n - 1)$  linear variational parameters.

## 3. Method

The integrals  $\langle \psi | H | \psi \rangle$  and  $\langle \psi | \psi \rangle$  for the trial function (4) can be expressed in terms of the integrals :

$$I_{p,q} = \int_0^{\infty} \exp(-2Zr) \frac{r^p}{(r + \alpha)^q} dr, \quad (6)$$

which are evaluated by the Gauss-Laguerre method.

As far as (5) is concerned, it has been found computationally more convenient to rewrite the trial function as

$$\psi(r) = \sum_n B_n \phi_n(r) \quad (7)$$

$$\text{where } \phi_n(r) = \exp(-\rho/2) L_n^1(\rho); \quad \rho = 2Zr, \quad (8)$$

where  $L_n^1$  are the associated Laguerre polynomials (Pauling and Wilson 1935). The energy matrix in the  $L_n^1$  basis being tridiagonal, the diagonalisation method described by Biswas *et al* (1971) proves useful.

Since the moments provide a sensitive check for the 'goodness' of a wave function, the calculated quantities include—apart from the energy  $E$ —the expectation values of  $r^n$  with  $n$  ranging from 1 to 6.

#### 4. Results and discussion

Tables 1, 2 and 3 summarise the results obtained with the exact wave function and the wave functions (4) and (7) for  $Z = 1, 2$  and 3 respectively. The four-parameter rational function shows excellent agreement with the exact wave function as far as the calculated quantities are concerned. Indeed the  $\langle r^6 \rangle$  value for  $Z = 1$  is the only quantity which shows a deviation of more than 1% from the exact value. It is, however, of greater interest to compare the wave function (4) with the linear variational functions having different number of parameters. Table 1 shows that for  $Z = 1$ , the nonlinear function is overwhelmingly superior to the linear function having the same number of parameters. One has to include as many as ten terms in the linear function to get a wave function compa-

**Table 1.** Comparison of energy and moments for the exact, the nonlinear and the linear wave functions for  $Z = 1$ . All numbers are in atomic units ( $m = e = \hbar = 1$ ).

Wave function	No. of parameters	Energy	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\langle r^5 \rangle$	$\langle r^6 \rangle$
Exact	0	-2.000000	0.7500	0.7500	0.9375	1.4062	2.4609	4.9219
Nonlinear	4	-1.999994	0.7500	0.7501	0.9376	1.4072	2.4745	5.0524
Linear	4	-1.998508	0.7505	0.7669	1.1390	3.5516	25.761	267.05
„	5	-1.999764	0.7498	0.7538	0.9902	2.0444	10.489	109.55
„	6	-1.999965	0.7499	0.7508	0.9495	1.5699	4.8093	39.753
„	7	-1.999995	0.7500	0.7502	0.9400	1.4440	3.0705	15.062
„	8	-1.999999	0.7500	0.7500	0.9380	1.4143	2.6052	7.5189
„	9	-2.000000	0.7500	0.7500	0.9376	1.4078	2.4926	5.5636
„	10	-2.000000	0.7500	0.7500	0.9375	1.4065	2.4675	5.0664
„	11	-2.000000	0.7500	0.7500	0.9375	1.4063	2.4614	4.9328
„	12	-2.000000	0.7500	0.7500	0.9375	1.4062	2.4610	4.9241
„	13	-2.000000	0.7500	0.7500	0.9375	1.4062	2.4610	4.9222

**Table 2.** Comparison of energy and moments for the exact, the nonlinear and the linear wave functions for  $Z = 2$ . All numbers are in atomic units ( $m = e = \hbar = 1$ ).

Wave function	No. of parameters	Energy	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\langle r^5 \rangle$	$\langle r^6 \rangle$
Exact	0	-4.500000	0.5000	0.3333	0.2778	0.2778	0.3241	0.4321
Nonlinear	4	-4.500000	0.5000	0.3333	0.2778	0.2777	0.3241	0.4324
Linear	4	-4.499975	0.4999	0.3333	0.2781	0.2793	0.3317	0.4755
„	5	-4.499998	0.5000	0.3333	0.2778	0.2779	0.3250	0.4382
„	6	-4.500000	0.5000	0.3333	0.2778	0.2778	0.3242	0.4328
„	7	-4.500000	0.5000	0.3333	0.2778	0.2778	0.3241	0.4321

**Table 3.** Comparison of energy and moments for the exact, the nonlinear and the linear wave functions for  $Z = 3$ . All numbers are in atomic units ( $m = e = \hbar = 1$ ).

Wave function	No. of parameters	Energy	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^3 \rangle$	$\langle r^4 \rangle$	$\langle r^5 \rangle$	$\langle r^6 \rangle$
Exact	0	-8.000000	0.3750	0.1875	0.1172	0.0879	0.0770	0.0770
Nonlinear	4	-8.000000	0.3750	0.1875	0.1172	0.0879	0.0770	0.0770
Linear	4	-8.000000	0.3750	0.1875	0.1172	0.0879	0.0770	0.0770

table to (4), if moments upto  $\langle r^6 \rangle$  are considered. The superiority of the rational function sharply decreases as  $Z$  becomes larger. Thus, for  $Z = 2$ , a six-parameter linear function is comparable to (4) while for  $Z = 3$ , there is no essential difference between the rational function and the polynomial function with the same number of parameters.

It is observed that as  $Z$  increases, the parameters at the energy minimum, in the rational function tend to the following values:  $a_1 \rightarrow -1/2$ ,  $a_2 \rightarrow b_2 \rightarrow 1/12$ , and  $b_1 \rightarrow 1/2$ . In other words, the rational function tends to the [2,2] Padé approximant of  $\exp(-r)$  as  $Z$  increases. Since the 2,2 approximant and the power series expansion of  $\exp(-r)$  are identical as far as the first five terms are concerned it is to be expected that for  $Z = 3$  (where the four parameter linear form is adequate) there should be little difference between the rational function and the polynomial function.

## 5. Conclusion

It is concluded on the basis of this study, that for hydrogen-like atoms a rational function can simulate the true function with much fewer parameters than a polynomial, for 'strong perturbations' (viz.  $Z = 1$ ). This suggests that the incorpo-

ration of Padé approximants in variational wave functions may prove useful in treatment of problems involving strong perturbations, e.g., the ground state of  $H^-$  and helium atom.

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