Theoret. Chim. Acta (Berl.) 48, 119–125 (1978)

THEORETICA CHIMICA ACTA

An Investigation of the Reliability of the Galerkin–Petrov Method

III. Excited States and Nonlinear Parameters

Karol Jankowski
Institute of Physics, Nicholas Copernicus University, Toruń, Poland

Danuta Rutkowska and Andrzej Rutkowski
Division of Physics, Higher Pedagogical School, Olsztyn, Poland

It is shown that the Galerkin–Petrov method if applied in a controlled way yields reliable results for excited states of the same symmetry classifications as the ground state. Computations are performed for the 2^1S and 3^1S states of He. The problem of optimizing nonlinear parameters of the basis functions by means of the GP method is discussed. A special optimization scheme is suggested and numerically illustrated for some S states of He.

Key words: Bivariational procedures – Method of moments, reliability of ~

1. Introduction

The Galerkin–Petrov (GP) method of approximately solving the Schrödinger equation offers the attractive possibility of considerable simplification of the integral problem which hampers the application of many variational approaches to more complex atoms and molecules. In our recent paper ([1], hereafter referred to as *I*) we have presented a convergence characterization of the GP method by means of quantities describing pairs of subspaces used in the procedure. We have also demonstrated for the ground states of the He [1] and Be [2] atoms the usefulness of our approach for setting up reliable computational schemes.

All applications of the GP method to quantum chemical problems have been concerned with the ground state only. The only attempt of studying excited states was undertaken by Bangudu *et al.* [3] in the case of the quartic oscillator. To get a more complete idea about the applicability of the GP method to quantum chemical problems we would like to consider the problem of determination of excited-states wavefunctions and energy levels in the case of states which belong to the same symmetry classification as the ground state. We have chosen as the object of our study the 2^1S and 3^1S states of the helium atom.

0040-5744/78/0048/0119/$01.40

Let us now proceed to another problem. It is a well known fact that variational methods of determining approximate solutions for excited states of many-electron systems face convergence problems (cf. Ref. [4]). Therefore it is of importance to use sets of basis functions that are well suited for the description of the state under consideration. Standard strategies for obtaining such basis sets involve the introduction of nonlinear parameters into the basis functions and minimization of the proper root of the secular equation with respect to these parameters.

The problem of optimization of nonlinear parameters of the basis functions defining the projective and coordinate subspaces [1] has not been discussed in the literature so far. This task is much more complicated in the case of the GP method than in the variational procedure. This situation is due to the fact that consecutive roots of the non-symmetric secular equation do not disclose the upper bound character in relation to appropriate exact eigenvalues of the Hamiltonian. It seems to us, however, that the optimization problem is not an insurmountable one provided that the optimization procedure involves somehow both subspaces under consideration. The second aim of this paper is to suggest an optimization scheme and to demonstrate its applicability by considering the three lowest ^1S states of the helium atom.

2. Theory

Details needed in applying the GP technique to quantum chemical problems may be found in paper I of this series [1].

Let us denote by E_i'' the GP energy corresponding to the i'th eigenvalue of the Schrödinger equation, and by E_i' its variational counterpart belonging to the approximate wavefunction Φ_i obtained by means of the coordinate basis set [1]. It was shown in I that the following estimate may be given

$$|E_i' - E_i''| \leqslant \|(H - E_i)\delta\Phi_i\| D \tag{2.1}$$

where

$$R \leqslant D \leqslant \sqrt{n}\, R, \tag{2.2}$$

and

$$\delta\Phi_i = \Phi_i - \gamma_i \Psi_i, \quad \gamma_i = (\Psi_i, \Phi_i).$$

Here Ψ_i denotes the exact eigenfunction, and R characterizes the distance between the coordinate and projective subspaces [1].

In papers I and II we have used the relation (2.1) to set up strategies for the reliable determination of wavefunctions and energies, corresponding to the ground state of two- and four-electron systems by means of the GP method. It should be emphasized, however, that this relation holds for all eigenstates of the Hamiltonian including excited states of the same symmetry classification as the ground state. Therefore the methods which proved useful in obtaining reliable results for the ground state should work as well for the excited states. A demonstration of this fact is given in Sect. 3.

We now proceed to the problem of optimizing nonlinear parameters. Let us consider the variational energy obtained for the n-dimensional coordinate basis set. Let us denote this energy by $E_i'(\bar{\eta})$, where $\bar{\eta}$ stands for the set of nonlinear parameters of the basis set. Let us further assume that both the coordinate and projective subspaces depend on the same set of parameters. Hence, the GP energies as well as the indices characterizing the distance between the subspaces are functions of $\bar{\eta}$, i.e., we have $E^{i''}(\bar{\eta})$, $D(\bar{\eta})$ and $R(\bar{\eta})$. Let us denote by $\bar{\eta}_0$ the point in the parameter space corresponding to the minimum of the variational energy. Relation (2.1) may be rewritten as

$$|E_i'(\bar{\eta}_0) - E_i''(\bar{\eta}_0)| \leqslant \|(H - E_i)\delta\Phi_i(\bar{\eta}_0)\| D(\bar{\eta}_0) . \tag{2.3}$$

We further assume that 1) $\|(H - E_i)\delta\Phi_i(\bar{\eta}_0)\| D(\bar{\eta}_0)$ is sufficiently small and 2) the value of this expression is almost constant in the neighbourhood of $\bar{\eta}_0$. If so, the relation (2.3) leads to the conclusion that there exists a minimum of the GP energy and it is situated in the vicinity of $\bar{\eta}_0$.

We can take advantage of this consideration in setting up the GP optimization procedure. In order to be successful one should fulfil the two assumptions. To satisfy the first condition, the coordinate basis set should allow for a relatively good approximation of the exact wavefunction (small $\|(H - E_i)\delta\Phi_i\|$) and the projective basis set should be as close as possible to the coordinate one (small D). To fulfil the second condition, the parametrization scheme should be chosen appropriately to assure the almost-constancy of D. We will demonstrate in Sect. 4 that one can practically satisfy all the demands just mentioned.

3. Excited States of He

Let us introduce the Coolidge–James [5] functions:

$$u(n_i, l_i, m_i; \alpha, \gamma) = (r_1^{n_i} r_2^{l_i} \exp\,(-\alpha r_1 - \gamma r_2) + r_1^{l_i} r_2^{n_i} \exp\,(-\gamma r_1 - \alpha r_2)) r_{12}^{m_i}, \tag{3.1}$$

where n_i, l_i, m_i are non-negative integers and α, γ are positive, real parameters. These functions were also used in the work of Perkins [6]. The first part of this section deals with the calculation of the energy of the 2^1S state by means of a coordinate space generated by the very effective set of Perkin's correlated basis functions. Later on we report the results of our calculations for the 2^1S and 3^1S states using a basis set comprising linear parameters optimized within the framework of the GP method.

3.1. Perkins-Like Basis Set

Our coordinate basis functions are defined by Eq. (3.1) and the following set of (n 1 m) powers.

(100), (010), (110), (020), (001), (101),
(001), (000)*, (100)*, (010)*, (001)*, (120), (3.2)
(201), (021), (110), (101), (011), (111),

The nonlinear parameters $\alpha=2.06$ and $\gamma=0.592$ have been used for all cases without an asterisk, whereas for the remaining functions the parameters $\alpha=2.06$ and $\gamma^*=1.37$ have been employed. This basis set is a part of the very effective Perkins basis. It is obtained from the latter one by deleting all functions with $m_i \geqslant 2$.

We define the projective subspace by means of a configuration interaction basis which has been obtained from the coordinate basis set by making the replacement: $(n\ 1\ m) \rightarrow (n, 1, 2m)$. We have found in I that this procedure leads to pairs of close subspaces.

Results of our He 2^1S calculations are shown in Table 1. The GP energies approach the "exact" non-relativistic energy -2.14597402 [7] as the number of basis functions, n, increases. The variational energies E_2' and E_{2p} obtained for the coordinate and projective subspaces, respectively, are also listed. The results shown in Table 1 are in agreement with the conclusions of our general analysis presented in Sect. 2.

Table 1. GP-energies E'', variational energies E', E_p and R values for the 2^1S state of He in the case of the Perkins-like basis set

n	$-E_2''$	$-E_2'$	$-E_{2p}$	R
4	2.11825	2.11825	2.11825	0
11	2.14572	2.14589[a]	2.14496	3.72
18	2.14579	2.14591	2.14548	1.53

[a] Result of Perkins [6].

3.2. GP-*Optimized Basis Set*

In this calculation we have used the basis sets with nonlinear parameters optimized in Sect. 4 within the framework of the GP method. The coordinate basis sets comprise functions of the form (3.1) for which $m \leqslant 1$ and $n \leqslant 1$. The projective basis sets are obtained by means of the replacement $m \rightarrow 2m$ from the coordinate sets. The nonlinear parameter α has a fixed value $\alpha=2$, whereas the optimized values $\gamma=0.707$ and $\gamma=0.364$ have been taken for treating the states 2^1S and 3^1S respectively. The coordinate basis functions have been grouped and ordered according to the value of the sum $k=1+m+n$. Calculations have been performed for several basis sets comprising each time all groups characterized by k values not exceeding a given integer. The dimensions of the respective subspaces are $n=3$, 6, 10, 15, 21 and 28.

The results for the 2^1S and 3^1S states of the He atom are collected in Table 2. The GP-energies, E_i, for both states exhibit systematic n-convergence towards the "exact" non-relativistic results [7] $E(2^1S) = -2.145974$ and $E(3^1S) = -2.061272$ respectively. Also of interest is the fact that for $n = 15, 21, 28$ in the case of 2^1S and $n = 21, 28$ in the case of 3^1S the GP results are closer to the "exact" energies than the variational energies, E_i, obtained for the coordinate basis sets. The variational energies E_i and E_{ip} reflect the convergence problems mentioned in Sect. 1. This is especially true for the 3^1S state where the results for $n=3$ are useless, and the energy obtained for $n=6$, when correlated basis functions are

Table 2. GP-energies E'', variational energies E', E_p and R values for the 2^1S and 3^1S states of He

State		n					
		3	6	10	15	21	28
	R	1.10	2.28	4.07	5.56	5.74	5.81
2^1S	$-E_2'$	2.128191	2.143193	2.145378	2.145689	2.145855	2.145909
	$-E_{2p}$	2.131156	2.142847	2.144231	2.144806	2.145052	2.145302
	$-E_2''$	2.127817	2.143359	2.144880	2.145822	2.145974	2.145987
	R	1.93	3.36	5.65	9.28	16	38.7
3^1S	$-E_3'$	0.997707	2.060397	2.060536	2.060755	2.060920	2.061038
	$-E_{3p}$	1.718217	2.060465	2.060523	2.060626	2.060684	2.060742
	$-E_3''$	0.525849	2.060417	2.060527	2.060751	2.060966	2.061166

used. E_3', is less accurate than for the uncorrelated projective basis set E_{3p}. However, the general character of the results is the same as in the case of the ground state, as discussed in I. The GP energies obtained for both excited states, together with the variational energies E_1', provide a convincing illustration of the relation (2.1).

4. Optimization of Nonlinear Parameters for S States of He

The fact that the GP procedure involves two basis sets leads to a variety of possibilities of introducing nonlinear parameters which have to be optimized. We

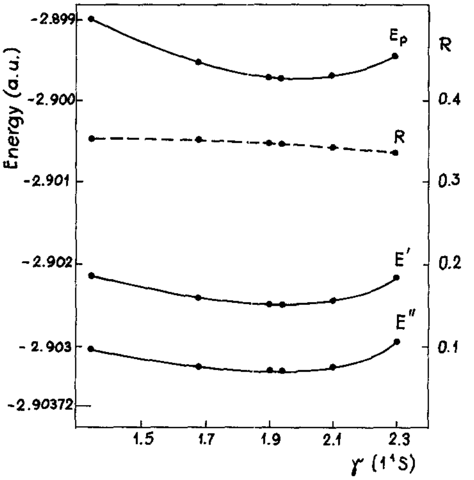

Fig. 1

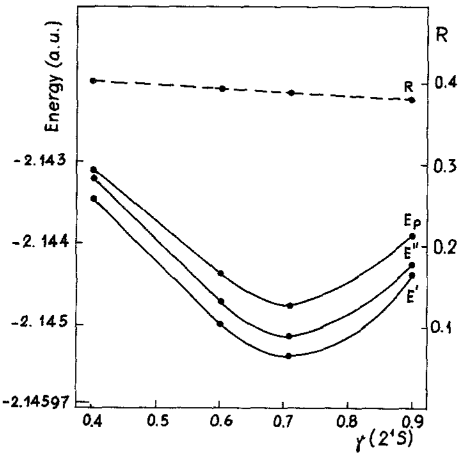

Fig. 2

Fig. 1. GP energy E_1'', variational energies E_1', E_{1p}, and index R as a function of the nonlinear parameter η for the 1^1S state

Fig. 2. GP energy E_2'', variational energies E_2', E_{2p}, and index R as a function of the nonlinear parameter η for the 2^1S state

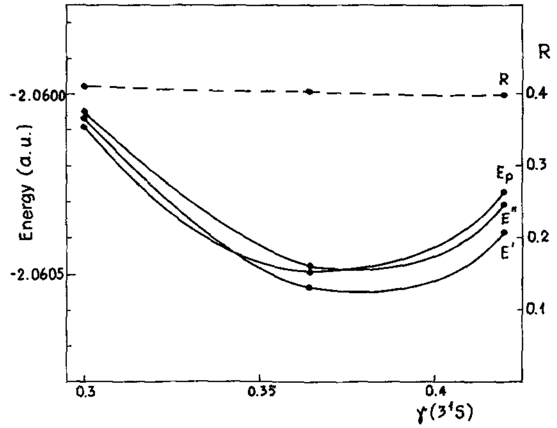

Fig. 3. GP energy E_3'', variational energies E_3', E_{3p}, and index R as a function of the nonlinear parameter η for the 3^1S state

assume that both the projective as well as the coordinate basis sets depend on nonlinear parameters.

Let us define the two basis sets by means of the Coolidge–James functions (3.1). To simplify the discussion we assume a constant value $\alpha=2$ for one of the nonlinear parameters. Now, the coordinate basis sets consist of functions of the form $u(n_i, l_i, m_i; 2, \gamma)$ where $m_i \leqslant 1$ and $n_i \leqslant l_i$.

It is our task to optimize within the framework of the GP method the nonlinear parameter γ for the three lowest S states of He. We tried to make use of the discussion presented in Sect. 2. To fulfil the first condition we have searched for the optimal value in the case of a 10 term coordinate basis set (small $\|(H-E_i)\,\delta\Phi_i\|$). Furthermore, to reduce the value of the R indices the projective basis has been constructed by means of the projection procedure using a 28 term basis set of the form $u(n_i, l_i, 2m_i; 2, \gamma)$. To fulfil partially the second condition we have used the parametrization scheme 3c mentioned above.

The results of our calculations are displayed in Figs. 1–3. We can see that the GP energies possess minima in all cases. Furthermore, the values corresponding to these minima are very close to the values of that parameter corresponding to the minima of the variational energies E_i' and E_{ip} obtained in the case of the coordinate and projective basis sets respectively. Figs. 1 and 2 show that for the 1^1S and 2^1S states the energy curves of E_i'', E_i and E_{ip} vs. γ are almost parallel. The situation is somewhat more complicated in the case of the 3^1S state where the curves intersect. It is interesting that the R values depend only very slightly on the values of the parameters, which may be the reason of our success.

The optimal values of the parameters are:

$$\gamma(1^1S)=1.94, \qquad \gamma(2^1S)=0.707 \quad \text{and} \quad \gamma(3^1\mathrm{S})=0.364.$$

The two latter parameters have been used in our computations reported in Sect. 3.2. The optimal parameter for the ground state also leads to n-convergent GP energies, e.g., we obtained the results -2.90050, -2.90232, -2.90266 and -2.90273 a.u. for $n=6$, 10, 21 and 28 respectively. The result for $n=28$ may be compared with the variational energies -2.90347 and -2.89991 obtained for the coordinate and projective basis sets respectively.

5. Concluding Remarks

We have here illustrated that our strategy for the reliable determination of wavefunctions and energies by means of the GP method works well in the case of excited states of the same symmetry classification as the ground state. The GP energies for the excited states disclosed similar behaviour as has been observed previously [1] for the ground state.

We have also presented a scheme for optimizing nonlinear parameters within the framework of the GP method, and have applied it with success in the case of some He atom S states. We would like to emphasize that our study is only meant as a first sketch which leaves room for many improvements. We hope that the present work will spur other workers to further investigate the crucial nonlinear parameter problem.

Acknowledgment. This work has been sponsored by the Polish Academy of Sciences (Grant No. I-12/3/3).

References

1. Jankowski, K., Rutkowski, A.: Theoret. Chim. Acta (Berl.) **43**, 145 (1976)
2. Janowski, K., Muszyńska, J., Rutkowski, A.: Theoret. Chim. Acta (Berl.), **47**, 275 (1978)
3. Bangudu, E. A., Jankowski, K., Dion, D. R.: Chem. Phys. Letters **19**, 418 (1973)
4. Ermolaev, A. M.: J. Phys. B7, 1611 (1974)
5. Coolidge, A. S., James, H. M.: Phys. Rev. **49**, 676 (1936)
6. Perkins, J. F.: J. Chem. Phys. **39**, 687 (1963)
7. Winkler, P., Porter, R. N.: J. Chem. Phys. **61**, 2038 (1975)
8. Fröhman, A., Hall, G. G.: J. Mol. Spectry. **7**, 410 (1961)

Received July 27, 1977/November 21, 1977