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An Investigation of the Reliability of the Galerkin-Petrov Method with a Special Study of the Helium Atom Ground State

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A convergence characterization of the Galerkin-Petrov method by means of quantities characterizing pairs of subspaces is presented. The usefulness of our approach for setting up reliable computational schemes is demonstrated for the He atom ground state. Several methods of constructing pairs of subspaces for use in quantum chemistry are suggested.

Key words: Bivariational procedures - Method of moments, reliability and convergence characterization of

1. Introduction

Almost all the attempts of getting good approximations to the Schrödinger equation for use in quantum chemistry are based on the standard Ritz variational method. However, the application of this method to more complicated many-electron systems is impeded by the serious difficulties in the evaluation of the integrals. This fact necessitates the imposition of severe restrictions on the basis sets employed, which often results in the rejection of classes of functions leading to quickly convergent expansions of the wave function, as for example explicitly correlated functions.

To alleviate the integral problem some non-standard procedures have been devised, among which the method of moments as discussed by Szondy (for references, see [1]) deserves special attention.

The most promising, however, seems to be a special realization of the method of moments, known as the Galerkin-Petrov GP method of obtaining approximate solutions of operator equations [2]. This approach preserves some of the advantages of the Ritz method, e.g., it allows for an algebraic expression of the problem and eigenfunctions. The GP method

has already been applied both to the ground [3–5] and excited states [4] of certain quantum mechanical systems.

Despite the very accurate results obtained in many cases (see e.g. [4]), some workers arrived at rather pessimistic conclusions about the reliability of the GP method. They have demonstrated that calculations may fail, partly or completely [3, 5], due to a sort of imbalance between the two subspaces used in the GP method. In order to understand the kind of trouble involved, as well as to provide a basis for developing reliable computational schemes based on the GP method, one of the present authors [6] developed a method of description of pairs of finite-dimensional subspaces of the Hilbert space. It is hoped that by applying the proposed method, one should be able to choose, in a systematic way, those pairs of subspaces used in the GP method which lead to reliable results.

The object of this paper is twofold, a) to provide a convergence characterization of the GP eigenvalues by means of quantities used in our description of pairs of subspaces; b) to demonstrate the usefulness of our approach for setting up reliable computational schemes. For the latter aim we have chosen the helium atom and the types of basis functions used by Schwartz in his pioneering paper on the GP method [3]. This has been done intentionally, because all workers criticizing the reliability of the GP method refer to the difficulties met by Schwartz. It seems that our analysis allows us to avoid such troubles.

In the course of our work special attention has been paid to the n-convergence characterization of the GP method. By applying the result of our general analysis, we were able to present two systematic ways of selecting pairs of subspaces leading to reliable results with proper n-convergence properties.

2. The GP Method, and the Description of Pairs of Finite-Dimensional Subspaces

The essential idea of the GP method when applied to the Schrödinger equation

$$(H - E)\Psi = 0 \tag{2.1}$$

consists of the following. Let F_n and G_n be two n-dimensional subspaces of the Hilbert space under consideration, which will be called the coordinate and projective subspaces respectively. Let P and Q be the projection operators onto F_n and G_n. The approximation Φ to Ψ is assumed to be an element of the coordinate subspace, i.e. $P\Phi = \Phi$. It is determined by the requirement

$$Q(H - E'')\Phi = 0 \tag{2.2}$$

Let us choose the basis sets $\{\phi_i\}_{i=1}^n$ and $\{x_i\}_{i=1}^n$ in F_n and G_n respectively. The approximate eigenfunctions may then be written

$$\Phi = \sum_{i=1}^{n} c_i \phi_i, \tag{2.3}$$

where the coefficients c_i are determined from the representation of (2.2):

$$(H - EM)\boldsymbol{c} = 0, \tag{2.4}$$

where H and M are matrices with the elements $H_{ki} = (\chi_k, H\phi_i)$, $M_{ki} = (\chi_k, \phi_i)$ and c represents a column matrix representing the coefficients c_i corresponding to the eigenvalue E. In the following we shall call M the mixed overlap matrix. Eq. (2.4) represents a set of secular equations which may be considered a counterpart of the Ritz variational procedure. The two methods become identical in the case $F_n = G_n$.

The results of the GP method, as well as their reliability, depend on the choice of the pairs of subspaces involved. For this reason any application of this method should be accompanied by a careful analysis of this pair. Recently [6] one of the authors proposed a method for characterizing pairs of finite dimensional subspaces which is expected to be helpful in making the proper selection of coordinate and projective spaces leading to reliable realizations of the GP method.

The method makes essential use of the operator

$$V = PQP. \tag{2.5}$$

Let us denote by $\{v_i\}_{i=1}^n$ the set of orthogonal eigenvectors of V corresponding to the eigenvalues M_i^2, $i = 1, 2, \ldots, n$. This set provides a special basis for the space F_n. We can easily define a corresponding basis set in G_n. Let s be the number of non-zero M_i-values. We can define s functions

$$u_i = M_i^{-1} Q v_i \qquad (i = 1, 2, \ldots, s). \tag{2.6}$$

This set should be augmented by $(n - s)$ orthogonal functions of G_n which are, in addition, orthogonalized to the members of the set $\{u_i\}_{i=1}^s$. The two orthonormal basis sets $\{v_i\}_{i=1}^n$ and $\{u_i\}_{i=1}^n$ satisfy the relation

$$(u_i, v_i) = M_i \delta_{ij} \qquad (i, j = 1, 2, \ldots, n). \tag{2.7}$$

Both the M_i numbers as well as the v_i and u_i functions have several interesting properties which have been discussed in [6]. It has also been shown that the set of M_i numbers provides means for characterizing pairs of finite dimensional subspaces. Many indices for the characterization of the "proximity" of two subspaces may be defined by means of the M_i numbers [6]. The problem which of them are the best from the practical point of view seems to be still open. In Sect. 3, for example, a new index manifested itself in the course of the convergence analysis.

3. A Convergence Characterization of the Eigenvalues

Let us recall that calculations by means of the GP method are usually performed by taking for the coordinate-space-basis elaborate functions which are capable of fitting the exact eigenfunction very accurately. The projective basis $\{\chi_i\}$ may not have this property, but it should lead to relatively simple integrals.

Let us define the set $\{\Phi_i\}_{i=1}^n$ of orthonormal functions which diagonalizes the standard energy matrix $\tilde{H}(\tilde{H}_{ij} = (\phi_i, H\phi_j))$ in the coordinate space F_n, i.e. $\Phi_i = \Sigma_{j=1}^n a_{ij}\phi_j$ are approximations to the eigenfunctions of (2.1) obtained by the Ritz variational method. The approximate eigenvalue corresponding to Φ_i is denoted by E_i'. It is a well-known fact that, if $n \to \infty$, then $E_i' \to E_i$ (E_i = the exact eigenvalue) from above, i.e. $E_i' - E_i \geqslant 0$.

Let us assume that all M_i numbers for the considered pair of subspaces, F_n and G_n, are different from zero, $M_i \neq 0$. It is then possible to define in G_n a set $\{\Gamma_i\}_{i=1}^n$, $\Gamma_i = \sum_{j=1}^n b_{ij}\chi_j$, with the property

$$(\Gamma_j, \Phi_k) = \delta_{jk}. \tag{3.1}$$

Let us make the observation that these orthogonality relations are invariant with respect to any simultaneous unitary transformation of the basis sets $\{\Phi_i\}$ and $\{\Gamma_i\}$, i.e.

$$(\Gamma'_i, \Phi'_k) = \delta_{ik}, \tag{3.2}$$

where

$$\Gamma'_i = \sum_l U_{il}\Gamma_l, \qquad \Phi'_i = \sum_i U_{il}\Phi_i. \tag{3.3}$$

The proof of (3.2) is straightforward:

$$(\Gamma'_i, \Phi'_k) = \sum_{l,m} U^*_{il}U_{km}(\Gamma_l, \Phi_m) = \sum_l U^*_{il}U_{kl} = \delta_{ik}.$$

We may further write

$$\Gamma_i = \Phi_i + \Delta\Gamma_i. \tag{3.4}$$

From (3.2) and the orthogonality of the Φ_i's, we have

$$(\delta\Gamma_k, \Phi_i) = 0 \qquad (i, k = 1, 2, \ldots, n), \tag{3.5}$$

i.e. $\delta\Gamma_k$ is orthogonal to the whole subspace F_n.

We use the notation E''_i for the eigenvalues obtained by means of the GP method.

In order to get an insight into the convergence properties of the approximate eigenvalues one considers the difference $|E_i - E''_i|$, which may be given the following estimate:

$$|E_i - E''_i| \leqslant (E'_i - E_i) + |E''_i - E'_i|. \tag{3.6}$$

As we have already mentioned, the first term of the right-hand side sum tends to zero as the dimension of the coordinate space increases. Therefore, the convergence properties of E''_i are essentially determined by the second term of (3.6).

We shall now prove that this term fulfils the inequality

$$|E''_i - E'_i| \leqslant \sum_{k=1}^n |(\delta\Gamma_k, (H - E_i)\delta\Phi_i)|, \tag{3.7}$$

where

$$\delta\Phi_i = \Phi_i - \gamma_i\Psi_i, \qquad \gamma_i = (\Psi_i, \Phi_i) \tag{3.8}$$

and Ψ_k is the exact eigenfunction of (2.1).

Proof. Let us consider the eigenvalue problem equivalent to (2.4)

$$(\boldsymbol{H}'' - E''\boldsymbol{I})\boldsymbol{c}'' = 0,$$

where $H''_{ik} = (\Gamma_i, H\Phi_i)$. It is obtained from (2.4) by taking proper linear combination of the equations involved. The eigenvalues E are now denoted by E''.

The use of (3.5) and the definition of Φ_i enables us to write

$$H''_{ik} = \begin{cases} (\delta\Gamma_i, H\Phi_k), & \text{if } i \neq k \\ (\Phi_i + \delta\Gamma_i, H\Phi_i), & \text{if } i = k. \end{cases} \tag{3.9}$$

We now apply the Gerschgorin theorem [7] for the localization of the eigenvalues of $\boldsymbol{H}''$ (see Appendix) and obtain

$$|E''_i - H''_{ii}| \leqslant \sum_{k \neq i} |H''_{ki}|. \tag{3.10}$$

According to (3.9) we have further

$$|E''_i - H''_{ii}| = |E''_i - E'_i - (\delta\Gamma_i, H\Phi_i)|, \tag{3.11}$$

and

$$|E''_i - E'_i| \leqslant \sum_k |(\delta\Gamma_k, H\Phi_i)|. \tag{3.12}$$

Since $\Phi_i = \gamma_i\Phi_i + \delta\Phi_i$, one obtains

$$(\delta\Gamma_k, H\Phi_i) = \gamma_i E_i(\delta\Gamma_k, \Psi_i) + (\delta\Gamma_k, H\delta\Phi_i) = E_i(\delta\Gamma_k, \Phi_i) + (\delta\Gamma_k, (H - E_i)\delta\Phi_i). \tag{3.13}$$

By combining (3.13) and (3.5) we may write

$$(\delta\Gamma_k, H\Phi_i) = (\delta\Gamma_k, (H - E_i)\delta\Phi_i). \tag{3.14}$$

Substitution of (3.14) into (3.12) concludes our proof.

We now turn to the inequality (3.7). Use of the Schwarz inequality enables one to write

$$|E''_i - E'_i| \leqslant \|(H - E_i)\delta\Phi_i\| \cdot D, \tag{3.15}$$

where

$$D = \sum_k \|\delta\Gamma_k\|. \tag{3.15a}$$

This relation provides a convergence characterization of the eigenvalues of the GP method. The last sum may be considered as a measure of the closeness of the coordinate and projection spaces, because it vanishes if two spaces are identical. Unfortunately, this type of measure is of no use for the GP method, because in order to construct $\delta\Gamma_k$ one has to perform a Ritz type calculation in the coordinate space.

It seems to use that one can obtain an idea about the magnitude of $\Sigma_k \|\delta\Gamma_k\|$ from the analysis of $(\Sigma_k \|\delta\Gamma_k\|^2)^{1/2}$.

The latter sum is invariant with respect to a simultaneous unitary transformation of the $\{\Phi_i\}$ and $\{\chi_i\}$ basis sets, i.e.

$$\sum_k \|\delta\Gamma'_k\|^2 = \sum_k \|\delta\Gamma_k\|^2, \tag{3.16}$$

where $\delta\Gamma'_k = \Gamma'_k - \Phi'_k$, and Γ'_k, Φ'_k are defined by (3.3). Now,

$$\delta\Gamma'_k = \sum_l U_{kl}\delta\Gamma_l \tag{3.17}$$

and

$$\sum_k \|\delta\Gamma'_k\|^2 = \sum_k \sum_{l,m} U^*_{kl}U_{km}\|\delta\Gamma_k\|^2 = \sum_l \|\delta\Gamma_l\|^2$$

which proves Eq. (3.16).

We next consider the unitary matrix which transforms the $\{\Phi_i\}$ basis into the $\{v_i\}$ basis defined in Sect. 2. This transformation, when applied to $\{\Gamma_i\}$, gives rise to a new set $\{U_i\}_{i=1}^n$ with the property

$$(U_i, v_k) = \delta_{ik} \qquad (i, k = 1, 2, \ldots, n). \tag{3.18}$$

The functions U_i are not normalized.

Bearing in mind that the $\{v_i\}$ and $\{u_i\}$ basis sets which fulfil Eq. (2.7) are unique for a given pair of subspaces, and using Eq. (3.18), one gets

$$u_i = N_i U_i,$$

where N_i is a normalization constant. One easily finds that $N_i = M_i^{-1}$.

Now, $\delta\Gamma'_i = M_i^{-1}u_i - v_i$, $\|\delta\Gamma'_i\|^2 = (1 - M_i^2)M_i^{-2}$. With this in hand, we have by Eq. (3.16)

$$R \equiv \left(\sum_i \|\delta\Gamma_i\|^2\right)^{1/2} = \left(\sum_i (1 - M_i^2)M_i^{-2}\right)^{1/2}. \tag{3.19}$$

The quantity R is specified in terms of the M_i numbers discussed in Sect. 2. The value of R is zero if two subspaces are identical (all $M_i = 1$) and tends to infinity in case the two subspaces involved comprise parts orthogonal to the other subspace (some $M_i = 0$). Hence R may be considered as an index for the characterization of the proximity of the coordinate and projective spaces. It is obvious that R does not provide so much information like sets of several or all M_i numbers.

From the well-known relation

$$\left(\sum_{i=1}^n a_i^2\right)^{1/2} \leqslant \sum_{i=1}^n |a_i| \leqslant \left(n \sum_{i=1}^n a_i^2\right)^{1/2}$$

we have by (3.15) and (3.19)

$$R \leqslant D \leqslant \sqrt{n}R. \tag{3.20}$$

Unfortunately it is rather difficult to obtain more precise bounds to D either in terms of R or other functions of the M_i numbers.

An analysis of the inequality (3.15) when combined with the rough estimates of D given by (3.20) allows us to grasp an idea about the convergence characterization of the GP method. It follows from the properties of the Ritz procedure, that if n increases the norm of $(H - E_i)\delta\Phi_i$ decreases. Therefore in order to ensure the reduction of the bounds to $|E'' - E_i|$ with increasing n, it is necessary that the increase of the D value

is sufficiently slow. The best situation is, of course, when D is almost constant. Relation (3.20) says, that in the case of finite dimensional subspaces, one can avoid significant changes of the D values by choosing the coordination and projective subspaces in such a way that the R values do not change considerably. Futhermore, an inspection of (3.15) reveals that in the case of a given coordinate space, i.e. for fixed $\|(H - E_i)\delta\Phi_i\|$, one can improve the accuracy by choosing the projective space which minimizes D. We expect that this requirement could be fulfilled by minimizing the R numbers.

4. Numerical Examples for the Ground State of the Helium Atom

In this work the GP method is applied in the calculation of energy for the helium atom in its ground state.

For reasons that have been mentioned in the Introduction, we have chosen the basis sets of the coordinate F_n and projective G_n spaces in a way similar to that of the paper of Schwartz [3].

We consider the following sets of basis functions:

(A) Hylleraas basis:

(A') $e^{-\alpha s} s^l u^m t^{2n}$, with $s = r_1 + r_2, t = r_1 - r_2, u = r_{12}$. (4.1)

(A'') As in (A') with the restriction to odd m's. (4.2)

(B) Correlation factor basis:

(B') $e^{-\alpha s} s^l u^{2m} t^{2n}(1 + \beta u)$ (4.3a)

(B'') $e^{-\alpha s} s^l t^{2n}(1 + \beta u)$ (4.3b)

(C) Configuration interaction basis:

(C') $e^{-\alpha s} s^l u^{2m} t^{2n}$ (only even powers of u) (4.4a)

(C'') $e^{-\alpha s} s^l t^{2n}$ (4.4b)

The basis functions will be grouped and ordered according to the value of the sum $l + m + 2n$. We report the results of several series of computations. In all cases discussed below, basis sets of the coordinate subspace used in consecutive computations differ by such groups. This convention has determined the dimensions of the secular problems in all cases, e.g., in the case of the basis set A' we have $n = 3, 7, 13$ respectively.

At the beginning of each calculation the sets of basis functions $\{\chi_i\}_{i=1}^n$ and $\{\Phi_i\}_{i=1}^n$ were chosen. For these sets we performed the computations of the following quantities: a) the M_i numbers, and the R index, b) the energy value E'' using the GP method, c) the variational energies E' and E_p within the framework of the Ritz method for the basis functions of the coordinate and projective spaces respectively.

The M_i numbers were obtained by diagonalizing the matrix representation of the operator (2.5) for the basis sets of F_n and G_n [5]

$$\tilde{V} = \Delta_\phi^{-1/2} M^+ \Delta_\chi^{-1} M \Delta_\phi^{-1/2}, \tag{4.5}$$

M denotes the mixed overlap matrix used in Eq. (2.4), Δ_ϕ and Δ_χ are metric matrices of the basis sets $\{\phi_i\}$ and $\{\chi_i\}$ respectively, i.e. $(\Delta_\phi)_{ik} = (\phi_i, \phi_k)$, $(\Delta_\chi)_{ik} = (\chi_i, \chi_k)$. E'' was obtained as the lowest eigenvalue of the non-symmetrical eigenvalue problem (2.5), which has been further transformed to the form

$$(M^{-1}H - E)c = 0. \tag{4.6}$$

The eigenvalues of this problem have been obtained by means of the QR algorithm [7].

The variational energies E' and E_p are useful as criteria of the accuracies attainable in the coordinate and projective subspaces respectively. They have been obtained as eigenvalues of the symmetrical problems

$$(H_\phi - E\Delta_\phi)c = 0 \qquad \text{and} \qquad (H_\chi - E\Delta_\chi)c = 0, \tag{4.7}$$

where H_ϕ and H_χ are matrix representations of the Hamiltonian in the $\{\phi\}$ and $\{\chi\}$ basis sets respectively. All energies are reported in atomic units. The exact energy of the helium-atom ground state is $E = -2.903724$. The computations were preformed on an ODRA-1204 computer with a precision of ten digits.

4.1. The (A', C')-Type Pairs of Subspaces

The A', C'-type pairs of subspaces, with $\alpha = 1.85$, were extensively used by Schwartz [3] in his (1, 3) case. They led to very erratic results and were used to support objections concerning the reliability of the GP method (see, e.g. [10]). Our computations confirmed the behaviour found by this author. A general property of the basis sets used by Schwartz is that they are characterized by very large values of the R index given by (3.20). There are even cases when $R = \infty$, e.g. for $n = 3$, if the coordinate and projective bases are

$$e^{-\alpha s}\{1, s, u\}, \tag{4.8}$$

and

$$e^{-\alpha s}\{1, s, s^2\} \tag{4.8a}$$

respectively, the M_i numbers are (0, 1, 1).

We tried to see whether it is possible to get reliable results using basis sets of the form A' and C'.

It turned out that for a fixed coordinate basis one can select the projective basis set for which R is relatively small. This is also true for the case $n = 3$. For example, the projective basis

$$e^{-\alpha s}\{1, s, u^2\} \tag{4.8b}$$

corresponds to the M_i numbers (0.874, 1, 1) and $R = 0.56$. The GP energy $E'' = -2.89096$ in close to the Ritz energy $E' = -2.89113$. The variational result for the projective space is $E_p = -2.87809$,

A similar situation was found for $n = 7$. It was also possible to find projective spaces leading to reasonable R values. The smallest value of this index, $R = 5.65$, was found for

$$e^{-\alpha s}\{1, s, s^2, u^2, t^2, su^2, u^2t^2\}. \tag{4.9}$$

For this case $E'' = -2.90253$, whereas the variational results for the F_n and G_n subspaces were $E' = -2.90340$ and $E_p = -2.89598$ respectively. The M_i numbers are (0.176, 0.773, 1, 1, 1, 1, 1).

The values of R may be minimized not only by proper choices of the basis sets. It is also possible to make use of the non-linear parameter α in the $\{\chi_i\}$ set. For example, in the case of the basis set (4.9) we obtained for $\alpha = 2.1$ the value $R = 5.3$ and the very good energy value $E'' = -2.90333$. It should however be mentioned that such behaviour has been observed only for relatively small R values.

In order to get an idea about the n-convergence in the case of the $(A'C')$-type pairs, let us perform the calculations for $n = 13$. In most cases the R indices were very large and the energies very poor. But it was possible to make selections similar to those in (4.8b) and (4.9), e.g., let us take the projective space obtained from (4.9); by adding the following functions

$$e^{-\alpha s}\{s^3, st^2, t^4, s^2u^2, u^4, su^2t^2\}. \tag{4.9a}$$

The results are: $R = 59, E'' = -2.89229, E' = -2.90363, E_p = -2.89867$. The M_i numbers are (0.017, 0.118, 0.687, 0.972, 0.987, 1, 1, 1, 1, 1, 1, 1, 1). We see that the energy E'' became worse than for $n = 7$. Such behaviour was typical for the $(A'C')$ pairs. The reason for it is the specific structure of the projective space which with increasing n differs more and more from the coordinate one. This fact is manifested by a sharp increase of R.

Let us have another look at the projective spaces (4.8b), (4.9) and (4.9) + (4.9a) leading to relatively small R's. They may be obtained from their coordinate counterparts by the following replacements: $u \to u^2, (u, su) \to (u^2t^2, su^2)$, and $(u, su, s^2u, ut^2, u^3) \to (t^4, su^2t^2, s^2u^2, u^2t^2, u^4)$. We can see that with increasing n functions comprising low odd powers of u are replaced by functions comprising increasingly higher powers of that variable. Therefore the distance between the two subspaces increases quickly when n increases.

4.2. A Special Matching Procedure

It turned out to be possible to improve the situation just mentioned. This can be done by removing functions comprising even powers of u from the coordinate basis set, i.e. by using the set A''. The projective set is still defined by the set C'. Now, one can describe the replacements as

$$e^{-\alpha s}s^l u^{2m+1}t^{2n} \to e^{-\alpha s}s^l u^{2m+2}t^{2n}. \tag{4.10}$$

In the present case, an increase of n causes substitutions of functions comprising odd powers of u by functions with even powers of u, obtained by enlarging the odd ones by one. Therefore, there are no reasons for such a fast increase of the distance between subspaces as in Sect. 4.1. In order to diminish the distance between F_n and G_n we have rescaled the projective basis functions involved in the replacement (4.10) to obtain maximum overlap integrals between the functions paired in (4.10). This requirement is fulfilled for

$$\alpha' = \alpha(1 + a/(1 + 2m + 2n + 4)), \qquad \text{where } a = 1 \tag{4.11}$$

To obtain an idea about the distance of the subspaces we found the M_i numbers and R indices for various n's. The properties of the first are displayed by the following set obtained for $n = 11$ (0.684, 0.874, 0.918, 0.991, 1.000, 1, 1, 1, 1, 1, 1). We see that the discussed method of matching subspaces results in M_i''s that are rather close to unity. The R indices for various dimensions are collected in Table 1, together with the energies obtained. The first quantities are unexpectedly low even for large n-values. The GP energies are close to the exact one. The results exhibit systematic n-convergence.

Table 1. R, $M_{\min}$ and approximate energies for the $A''B'$-type pairs of subspaces

		n				
a		3	6	11	17	26
1	R	0.6	0.9	1.3	1.8	2.3
	$M_{\min}$	0.874	0.770	0.684	0.613	0.554
	$-E'$	2.89113	2.90281	2.90341	2.90358	2.90364
	$-E_p$	2.87809	2.89574	2.89837	2.89989	2.90082
	$-E''$	2.89096	2.90098	2.90248	2.90296	2.90321
	$\lvert E'' - E' \rvert$	0.00017	0.00183	0.00093	0.00062	0.00043
0.8	R	0.2	0.3	0.5	0.7	1.0
	$M_{\min}$	0.976	0.962	0.937	0.902	0.858
	$-E'$	2.89113	2.90281	2.90341	2.90358	2.90364
	$-E''$	2.88976	2.90127	2.90264	2.90305	2.90326
	$\lvert E'' - E' \rvert$	0.00137	0.00154	0.00077	0.00053	0.00038

We attempted to diminish the R indices still more. We managed to do this by taking values of the parameter a in (4.11) different from unity. For the cases $n = 3$ and $n = 6$ minimum R was obtained for $a = 0.8$. We used this value for the whole series. The results are listed in the lower part of Table 1. The R's are now about half the previous ones, and the convergence properties of E'' became still better.

We would like to emphasize the fact that all the results presented in Table 1 are in agreement with the conclusions of the general analysis presented in Sect. 3.

4.3 A Projection Procedure for Obtaining the Projective Subspace

In the previous part of this paper we demonstrated how by means of maximizing the overlap integrals of individual pairs of functions it is possible to obtain a considerable reduction of the R indices. We would now like to suggest a systematic procedure for constructing close pairs of subspaces.

We start by fixing the $\{\phi_i\}_{i=1}^n$ basis of the coordinate subspace. Next, we select a set of functions $\{\eta_i\}_{i=1}^m$ with $m \geqslant n$. The ith member χ_i of the basis of the projective basis is then obtained by projecting the function ϕ_i onto the subspace spanned by $\{\eta_i\}$ [9], i.e.

$$\chi_i = P_\eta \phi_i = \sum_{k,l} (\Delta_\eta^{-1})_{kl} (\eta_l, \phi_i) \eta_k, \tag{4.12}$$

where P_η denotes the projection operator associated with the manifold $\{\phi_i\}$ and Δ_ϕ is the metric matrix of $\{\phi_i\}$. The secular equation for the present case may be written in the form

$$(M^T\Delta_\eta^{-1}H - E''M^T\Delta_\eta^{-1}M)c = 0. \tag{4.13}$$

We used the sets A' and C' for $\{\phi_i\}$ and $\{\eta_i\}$ respectively.

Table 2. Numerical results for the projection method of generation of the projective basis

		m						
n		5	8	14	20	30	40	$-E'$
	R	0.40	0.23	0.16	0.12	0.09	0.08	
	$M_{\min}$	0.930	0.974	0.988	0.993	0.996	0.997	
3	$-E_p$	2.87870	2.88359	2.88605	2.88743	2.88830	2.88887	2.89113
	$-E''$	2.88966	2.88998	2.89029	2.89049	2.89063	2.89072	
	$\lvert E'' - E'\rvert$	0.00147	0.00115	0.00084	0.00064	0.00050	0.00041	
	R		[a]	0.86	0.58	0.43	0.34	
	$M_{\min}$		~0	0.771	0.877	0.925	0.950	
7	$-E_p$		2.89647	2.89868	2.89991	2.90072	2.90127	2.90341
	$-E''$		2.89352	2.90278	2.90297	2.90308	2.90315	
	$\lvert E'' - E'\rvert$		0.00989	0.00063	0.00043	0.00033	0.00026	
	R			[a]	57	1.6	1.1	
	$M_{\min}$			~0	0.018	0.574	0.712	
13	$-E_p$			2.89887	2.90015	2.90094	2.90148	2.90364
	$-E''$			2.90990	2.89728	2.90348	2.90351	
	$\lvert E'' - E'\rvert$			0.00626	0.00636	0.00016	0.00013	
	$-E_\eta$	2.89376	2.89648	2.89890	2.90023	2.90105	2.90156	

[a] A very large number computed with a significant numerical error.

The results are collected in Table 2. We can see that for $m > n + 1$ the R indices are small and decrease considerably when m increases. The M_i numbers are close to unity, e.g. for $n = 13, m = 30$ we have

$$(0.574, 0.846, 0.977, 0.996, 0.999, 1, 1, 1, 1, 1, 1). \tag{4.14}$$

The GP energies, E'', together with the variational results E' provide a convincing illustration of the relation (3.15). We can see from that table that for a given n (i.e. fixed value of $\|(H - E)\delta\Phi_i\|$) the energy E'' improves as m increases (i.e. R and $\Sigma_i \|\delta\Gamma_i\|$ decreases). On the other hand, for increasing n's, when choosing m-values giving rise to R-indices of comparative magnitude, a clear-cut n-convergence may be observed. In order to get an energetical characterization of the manifold spanned by $\{\eta_i\}_{i=1}^m$, we computed the Ritz variational energies E for various m's. The results are presented in the lowest row of Table 2. We see that in the cae of small R's the GP results are considerably closer to the exact energy than the respective E values.

4.4. The (B', C')-Type Pairs of Subspaces

In this case we take the basis of F_n in the form (4.3a) comprising a common correlation factor $(1 + \beta u)$, whereas the G_n subspace is of the configuration interaction type. These bases have been used by Schwartz [3], $\alpha = 1.85$, $\beta = 0.5$, and led to reliable results. The energy values disclosed correct n-convergence and were close to their variational counterparts E'. This behaviour becomes clear when the M_i numbers are taken into account, e.g., for $n = 14$ we obtained the set

$$(0.933, 0.956, 0.959, 0.972, 0.980, 0.984, 0.990, 0.998, 0.999, 1.000,$$
$$1.000, 1.000, 1.000, 1.000). \tag{4.15}$$

The R-values resulting from our computations were small and changed slowly. Table 3 summarizes the results of the calculations. It lists, for different n-values, the R-indices, the minimum M_i value, $M_{\min}$, the GP energy E'', and the variational energies E', E_p. The differences $|E'' - E'|$, which have been analysed in Sect. 3, are also presented.

Table 3. Numerical results for the $B'C'$-type pair of subspaces

	n			
	5	8	14	20
R	0.4	0.5	0.7	0.8
$M_{\min}$	0.957	0.945	0.933	0.922
$-E'$	2.90164	2.90267	2.90324	2.90347
$-E_p$	2.89376	2.89648	2.89890	2.90023
$-E''$	2.90613	2.90460	2.90421	2.90402
$\|E'' - E'\|$	0.00449	0.00193	0.00097	0.00055

The results collected in Table 3 support the conclusions of the discussion presented in Sect. 3. The subspaces under discussion are close in the sense of the R-index characteristics. Moreover, the way in which the coordinate basis functions are obtained from the projective ones allows for enlarging the dimensions of the problem without considerable increase of R or decrease of $M_{\min}$. Such behaviour has never been found for the basis sets discussed in Sect. 4.1.

It seems to us that pairs of subspaces defined by basis sets constructed in such a way that the members of one of them are obtained from their counterparts of the second by multiplication by a correlation factor should lead to small R-indices, and therefore, may be useful in the formulation of reliable GP schemes.

4.5. The (B'', C'')-Type of Subspaces

In order to support the latter conjecture, we performed the computations for the case in which the coordinate space is defined by the set B'', whereas the projective one is defined by the set C'', which consists of totally uncorrelated (i.e. comprising no u

variables) functions, The set B'' involves functions used in the standard correlation factor method [8]. We performed the calculations for two choices of the coordinate space which differ by the value of β in the correlation factor. This was caused by the fact that for $\beta = 0.5$ the coordinate space is very ineffective in representing the exact wavefunction. This situation has changed for $\beta = 0.29$. This value of the parameter has been obtained by minimizing E' for $n = 6$.

The M_i numbers disclosed a behaviour similar to that obtained for $n = 12$:

$$(0.929, 0.945, 0.966, 0.981, 0.985, 0.991, 0.993, 0.995, 0.997, 0.998, 0.999, 0.999) \quad \alpha = 1.85, \beta = 0.5 \tag{4.16a}$$

$$(0.959, 0.966, 0.979, 0.988, 0.992, 0.995, 0.996, 0.998, 0.998, 0.999, 0.999, 9.999) \quad \alpha = 1.85, \beta = 0.29 \tag{4.16b}$$

One can see that these two sets exhibit the same behaviour as in the case of the set (4.15). The same is true of the R-indices and of the minimal M_i values which are listed in Table 4. The results of the energy calculations are also collected in this table. The energies obtained for $\beta = 0.5$ are rather poor. This is caused by the fact that both sets involved lead to very slow convergence of the expansion of the ground state wavefunctions. We are in a situation where $\|(H - E)\delta\Phi_i\|$ of (3.15) is almost constant. Because R increased considerably along the series, one is, due to the inequality (3.15), not surprised to find a slight deterioration of E''. The results for $\beta = 0.29$ behave quite differently. Although the R indices are only slightly lower than in the previous case a considerable improvement of E'' as well as n-convergence has been obtained. This is obviously due to the fact that the coordinate basis set is much better suited for the approximation of the gound state wavefunction than in the previous case.

Table 4. Numerical results for the $B''C'$-type pair of subspaces

β		n				
		4	9	12	16	20
0.5	R	0.4	0.6	0.7	0.8	0.9
	$M_{\min}$	0.959	0.939	0.929	0.921	0.916
	$-E'$	2.89685	2.89696	2.89700	2.89701	2.89702
	$-E_p$	2.87781	2.87843	2.87867	2.87879	2.87886
	$-E''$	2.91419	2.91433	2.91440	2.91443	2.91445
	$\lvert E'' - E' \rvert$	0.01734	0.01737	0.01740	0.01742	0.01743
0.29	R	0.3	0.4	0.5	0.6	0.7
	$M_{\min}$	0.978	0.965	0.959	0.953	0.947
	$-E'$	2.90193	2.90222	2.90232	2.90236	2.90239
	$-E_p$	2.87781	2.87843	2.87867	2.87879	2.87886
	$-E''$	2.90248	2.90283	2.90303	2.90310	2.90314
	$\lvert E'' - E' \rvert$	0.00055	0.00061	0.00071	0.00074	0.00075

These results, together with those obtained in Sect. 4.4, seem to indicate that the use of coordinate basis sets with correlation factors provides a possibility for constructing subspaces well suited for setting up reliable GP schemes.

5. Concluding Remarks

In this paper we have presented a convergence characterization for the energy values obtained within the framework of the Galerkin–Petrov method. It was found that the accuracy of the results may be related to the index R defined by means of the M_i numbers [5], which characterizes in a detailed way the distance between two n-dimensional subspaces of the Hilbert space.

It has been extensively demonstrated for the helium-atom ground state that reliable results for the energy can be obtained if proper attention is paid to the choice of the pair of subspaces involved. Such choices can be made in systematic ways. We presented three methods leading to proper pairs of subspaces and showed that for these the GP method is reliable.

Our approach allowed for an understanding of the sort of trouble met by Schwartz [3], and provided a method of avoiding it from the very beginning.

The present method may be applied to systems containing more than two electrons. This can be realized, for example, by taking the subspace used in the combined configuration-interaction-Hylleraas-type approach CI-HY (see, e.g. [11]) to be the coordinate subspace. The projective subspace is then defined by a configuration-interaction-type basis set chosen according to our method. Such approach reduces drastically the numerical difficulties met by the variational calculation within the CI-HY basis. The latter method involves five types of two-, three-, and four-electron r_{ij} integrals (according to the classification of Sims and Hagstrom [12]). The full application of our procedure involves only the two most simple types of two- and three-electron r_{ij} integrals (types 1 and 2 of Fig. 1 in [12]). A practical realization of this idea is now in progress in our group.

We hope that the present work will strengthen the confidence in the reliability of the GP method.

Appendix: Discussion of the Relation (3.10)

Gerschgorin's theorem makes only the statement that E_i'' lies in one of the Gerschgorin's circles. Its placement in the circle embracing H_{ii} is ensured if, in the left-hand eigenvector c^+ of H'', i.e. $c(H'' - EI) = 0$, the inequality $|c_k^+| \leqslant |c_i^+|$ is fulfilled for all $k \neq i$. We have then, for $\Theta = \Sigma_k c_k^+ \Gamma_k$,

$$(\Theta, H\Phi_i) = \sum_k c_k^+ H_{ki}'' = E'' c_i^+ \qquad \text{and} \qquad c_i^+(E_i'' - H_{ii}) = \sum_{k \neq i} c_k^+ H_{ki}''.$$

Hence,

$$|E_i'' - H_{ii}''| \leqslant \sum_{k \neq i} \frac{|c_k^+|}{|c_i^+|} |H_{ki}| \leqslant \sum_k |H_{ki}|,$$

which leads to (3.9). The condition $|c_k^+| \leqslant |c_i^+|$ is fulfilled for all non-pathological choices of the coordinate and projective spaces.

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