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An Investigation of the Reliability of the Galerkin-Petrov Method

II. Ground-State of the Beryllium Atom

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The Galerkin-Petrov method is applied to the determination of the ground state energy of the beryllium atom. The basis set of the coordinate subspace consists of correlated wavefunctions of the combined configuration-interaction-Hylleraas type. The basis set of the projective subspace is of the configuration-interaction type. The usefulness of a previously proposed way of characterization of pairs of subspaces has been further confirmed. Experience in constructing close pairs of subspaces gathered in the case of two-electron systems is used for the larger system. Two methods for constructing pairs of subspaces are used in the calculations.

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

1. Introduction

The method of moments, as proposed by Szondy [1, 2] more than a decade ago, represents an interesting alternative to the variational procedure of obtaining good approximations to the eigensolutions of the Schrödinger equation. This method offers the attractive possibility of considerable simplifications of the integral computations which hamper the application of the variational method to more complicated atoms and molecules. Very promising seems to be a special realization of the method of moments, known as the Galerkin-Petrov (GP) method [3]. Despite the very accurate results obtained in many cases, some workers arrived at rather pessimistic conclusions about the reliability of the GP method [4, 5]. In our recent paper ([6], hereafter referred to as Paper I) we have proposed a strategy for the reliable determination of wavefunctions and energy levels of many-electron systems by means of the GP method. It was found that the accuracy of the results

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may be related to an index describing the "distance" between the coordinate and projective subspaces used in the formulation of the method. The applicability of the method was demonstrated for the two-electron atom.

In the present paper we apply the method of Paper I to the determination of the approximate wavefunction and energy for the ground state of the beryllium atom. The basis set of the coordinate subspace consists of correlated wavefunctions of the combined configuration-interaction-Hylleraas (CI-HY) type. The projective basis, in turn, is of the configuration interaction type chosen according to our method. The motivation of this study is to demonstrate the usefulness of the strategy proposed in Paper I in the case of a four-electron system for which, unlike the two-electron one, all simplifications pertinent to the GP method can be fully exposed. On the other hand, all mathematical difficulties involved in introducing r_{ij}-dependent terms into the basis set of the projection subspace for atoms with an arbitrary number of electrons occur in the beryllium atom. Thus the present calculation is a test of the general applicability of the theoretical and computational method developed. Another purpose of this work is to show that experience in the construction of close pairs of subspaces gathered in the case of two-electron systems can be utilized for larger systems. In the next section we present some details of the method of calculation and specify the form of the basis functions used. In order to get a better insight into the simplifications inherent in the GP method, we compare (Sect. 2.2) the types of integrals which arise in our scheme with the integrals of the variational method using the CI-HY basis. In Sect. 3 we will present the results of calculations using two projective basis sets. The first one is constructed according to a rule described in Sect. 2.1. In order to reduce the distance between the projective and coordinate subspaces a second basis set obtained by means of a projection procedure has been used.

2. Method of Calculation

The essential idea of the GP method when applied to the Schrödinger equation has been presented in Paper I. For completeness, however, we include a very brief outline of this method in our discussion.

Let us choose the basis sets $\{\varphi_i\}_{i=1}^n$ and $\{\chi_i\}_{i=1}^n$ defining the coordinate and projective subspaces respectively. The approximate wavefunctions may be written

$$\Phi = \sum_{i=1}^{n} c_i \varphi_i \tag{1}$$

where the coefficients c_i are determined from the set of equations [6]

$$(M^{-1}H - EI)C = 0 \tag{2}$$

where the matrices H and M, defined by the elements $H_{ki} = (\chi_k, H\varphi_i)$ and $M_{ik} = (\chi_k, \varphi_i)$, represent the Hamiltonian and mixed overlap matrices respectively. We use the notation E'' for the lowest eigenvalue of the nonsymmetrical problem (2).

It has been shown in Paper I that the results of the GP method, as well as their reliability, depend on the choice of pairs of subspaces involved. It is convenient to characterize the distance between the subspaces in terms of the index R defined as

$$R=\Big(\sum_{i}(1-M_i^2)M_i^{-2}\Big)^{1/2}. \tag{3}$$

where the M_i numbers may be obtained by diagonalizing the matrix

$$\tilde{V}=\Delta_{\Phi}^{-1/2}M^{+}\Delta_{\chi}^{-1}M\Delta_{\varphi}^{-1/2}. \tag{4}$$

where Δ_Φ and Δ_χ are metric matrices of the basis sets $\{\varphi_i\}$ and $\{\chi_i\}$ respectively, i.e. $(\Delta_\varphi)_{ik}=(\varphi_i, \varphi_k)$: $(\Delta_\chi)_{ik}=(\chi_i, \chi_k)$.

It was shown in Paper I that to obtain reliable results one should choose the coordinate and projective subspaces in a way that the R-value be as small as possible. Moreover, in order to ensure the n-convergence of the energy the basis sets should be constructed in a manner that the increase of the R index would be sufficiently slow when n increases.

2.1. Basis Sets

The basis set of the coordinate subspace consists of the combined configuration-interaction-Hylleraas (CI-HY) functions defined by Sims and Hagstrom [7] in their study of the ground state of the beryllium atom. These four-particle functions may be written in the form

$$\varphi_k=O(L^2)O_A\Big(X_1 r_{ij}^{\nu k}\prod_{s=1}^{4}\psi_{ks}(r_s)\Big). \tag{5}$$

In (4), $O(L^2)$ is an orbital momentum projection operator [8] and O_A is the well known antisymmetrization operator. Also, X_1 is a spin function of the form

$$X_1=\tfrac{1}{2}(\alpha_1\beta_2-\beta_1\alpha_2)(\alpha_3\beta_4-\beta_3\alpha_4)$$

corresponding to the eigenvalues $S=S_z=0$ of the spin angular momentum. In (5) $\psi_{ks}(r)$ refers to a basis orbital in the configuration considered. The orbital basis consists of STO's of the general form

$$\psi(r)=\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}}\,r^{n-1}\,e^{-\zeta r}\,Y_{l,m}(\theta,\varphi) \tag{6}$$

where $Y_{l,m}$ denotes a normalized spherical harmonics.

In the present study we restricted the coordinate basis set to the first 15 members of the set used by Sims and Hagstrom [7]:

$$\begin{array}{lll}
(1)\ 1s2s''^2, & (2)\ 1s^2 2p''^2, & (3)\ 1s^2 2s''^2 r_{12},\\
(4)\ 1s^2 2p''^2 r_{12}, & (5)\ 2s1s2s''^2, & (6)\ 1s^2 2s''^2 r_{23},\\
(7)\ 1s^2 1s'' 2s'' r_{23}, & (8)\ 1s^2 2s''^2 r_{34}, & (9)\ 3s1s2s''^2,\\
(10)\ 1s^2 1s'' 2s'', & (11)\ 1s^2 2s''^2 r_{12}^2, & (12)\ 2s^2 2s''^2,\\
(13)\ 2s1s2p''^2, & (14)\ 1s^2 6s'' 2s'', & (15)\ 1s^2 5s'' 2s''.
\end{array} \tag{7}$$

The notation of Sims and Hagstrom [7] has been used. The nonlinear parameters $\zeta_s=3.6847$, $\zeta_{s''}=0.9562$, $\zeta_p=6.2$, $\zeta_{p''}=1.1$, were used.

Let us further define the projective basis. It includes functions of the pure configuration- interaction type i.e. it may consist only of the subset of functions defined by (5) for which $v_k=0$. We include into the projective basis all uncorrelated functions ($v_k=0$) listed in (7). To supplement this set we utilized an observation made in the case of two-electron systems. In Sects. 4.1 and 4.2 of Paper I we have demonstrated that one can get small R values if each basis function of the coordinate subspace depending on r_{12} has a counterpart in the projective subspace depending on r_{12}^2. It is a well known fact that due to the relation

$$r_{ij}^2=r_i^2+r_j^2-(8\pi/3)r_ir_j\sum_{m=-1}^{1}Y_{1m}^*(\theta_i,\varphi_i)Y_{1m}(\theta_j,\varphi_j) \tag{8}$$

functions comprising even powers of r_{ij} are equivalent to configuration interaction functions. As an illustration of the general procedure we consider the function (3) from the set (7). We have by (6) and (8)

$$1s^22s''^2r_{12}=[1s^2r_{12}]2s''^2 \longrightarrow \{3s1s2s''^2,\ 1s3s2s''^2,\ 2p'^22s''^2\} \tag{9}$$

The first two functions in the latter set are linearly dependent. Furthermore, the first function is already included in the projective basis, because it is an uncorrelated member of the set (7) (function (9)). Hence, we can use only the third function of the set in (9)

$$1s^22s''^2r_{12} \longrightarrow 2p'^22s''^2.$$

The same reasoning applied to the functions (3), (4), (6), (7), (8) and (11) of the coordinate basis leads to the projective basis functions $2p^22s''^2$, $2p^22p''^2$, $1s2p3p''2s''$, $1s2p2p''2s''$, $1s^23p''^2$, $3p^22s''^2$ respectively. Hence, a basis set consisting of 15 members is found.

However, in order to apply the projection procedure for obtaining the projective subspace, we increase the number of the set just mentioned. As the program for evaluating the integrals was not adopted to handle d and f orbitals, which we expect to be very effective in our procedure, we had to add configurations of the angular structure similar to the existing ones. The following configurations were used:

(16) $5s1s2s''^2$
(20) $1s^23s2s''$
(24) $1s^24s''^2$
(28) $1s4p2p''2s''$
(32) $1s3p5p''2s''$
(17) $1s^24s''2s''$
(21) $3s1s1s''2s''$
(25) $4p2p2s''^2$
(29) $1s^24p''2p''$
(33) $1s5p3p''2s''$
(18) $5s1s1s''2s''$
(22) $3s1s3s''2s''$
(26) $4p2p2p''^2$
(30) $5p3p2s''^2$
(34) $1s^25p''3p''$.
(19) $3s1s4s''2s''$
(23) $3s^22s''^2$
(27) $1s2p4p''2s''$
(31) $5p3p2p''^2$

2.2. *Integral Treatment*

Before proceeding to details of the integral treatment, let us compare the types of integrals which arise in our GP scheme with the integrals of the variational method using the CI-HY basis. The integrals arising in the latter approach can be written in the general form [9]

$$I = \int \Omega_1(\mathbf{r}_1)\Omega_2(\mathbf{r}_2)\Omega_3(\mathbf{r}_3)\Omega_4(\mathbf{r}_4)\tilde{R}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3\, d\mathbf{r}_4 \qquad (10)$$

where $\tilde{R}$ is an operator of one of the following forms:

$$\text{(a) } r_{12}^{s}, \quad \text{(b) } r_{12}^{s} r_{13}^{t}, \quad \text{(c) } r_{12}^{s} r_{23}^{t} r_{13}^{u}, \quad \text{(d) } r_{12}^{s} r_{13}^{t} r_{14}^{u}, \quad \text{(e) } r_{12}^{s} r_{23}^{t} r_{34}^{u}. \qquad (11)$$

The operator (a) gives rise to two-electron integrals, whereas the operators (b) and (c) lead to three-electron integrals. Finally, the operators (d) and (e) give rise to four-electron integrals. There have been several papers dealing with the problem of evaluation of the integrals depending explicitly on the interelectronic coordinates. For references to the rich literature in this field we refer to the papers of Sims and Hagstrom [9]. Some interesting procedures have been recently proposed by Muszyńska [10, 11]. The most effective methods of handling the integrals (10) are based on an expansion of the r_{ij} variables in a Fourier-Legendre series. The basic integrals arising in this approach are listed in [9]. An analysis of the expressions for the integrals (10), when various $\tilde{R}$'s are used, indicate that the computational difficulties rapidly increase when proceeding from the two-electron integrals to the three- and four-electron ones. The most simple cases represent the two-electron integral and the integral involving the operator (b) of (11). The evaluation of the second type of three-electron integrals, i.e. (c), is considerably more complicated.

The types of integrals which have to be evaluated in the case of the GP method for the basis sets discussed above represent a subset of the integrals arising in the variational approach using the CI-HY basis. One can easily see that all integrals which arise in our approach have either the form of a two-electron integral with the operator (11a) or a three-electron integral with the operator (11b). As was already stated these integrals represent the most simple cases from the numerical point of view.

An irreducible tensor operator formalism applied to the expansion of r_{ij} into Fourier-Legendre series allows for a straightforward separation of the integration over angular and radial coordinates. In effect all the many-electron integrals have been represented as linear combinations of products of certain spherical coefficients W_{oi} and radial integrals I_{oi} [10, 11]. The I_{oi} radial integrals may be expressed by means of auxiliary integrals W, V and A. The problem of evaluation of the V and W auxiliary integrals was discussed by many authors [10–15] and very accurately by Sims and Hagstrom [9]. It seems to be reasonable to compute the auxiliary integrals V and W only once and to store them in a computer peripheral memory for use in computing the radial integrals. A recursive computational scheme of the tabulation of V and W has been given by Sims and Hagstrom [9]. However, when one of the parameters either in V or in W is negative, numerical tests showed a considerable loss of precision due to substruction. A numerically stable computational procedure for the V integrals was already given in the work [9]. In turn, the W integrals are calculated via the series formula proposed by one of the present authors [11]. To reduce the round-off errors, the program for calculation of W is written in such a way that the smallest terms are summed first.

3. Results and Discussion

The results obtained in the case of the basis sets described above are displayed in Table 1. For a given dimension n, of the subspaces involved the coordinate basis set consists of the n first members of the set (7). The basis sets of the respective projective subspaces comprise the n first members of the set defined in Sect. 2.1. Although we are mainly interested in the GP energies, the variational energies E' and E_p obtained for the coordinate and projective subspaces respectively are also set out. The former results are taken from the work of Sims and Hagstrom [7]. The last column of Table 1 shows the R-values for each pair of subspaces. We see from the table that the GP energy, E'', decreases from -14.59688 to -14.65714 as we go from $n=2$ to $n=15$. These results should be compared with the estimate of the "exact" non-relativistic energy $E=-14.6669$ [16] and the Hartree-Fock energy $E_{\mathrm{HF}}=-14.57302$ (all energies in the present paper are given in atomic units). It is interesting to note that in the case $n=15$ the GP results yield 90 percent of the correlation energy, $E_{\mathrm{corr}}=E-E_{\mathrm{HF}}$. Starting from $n=6$ the results for E'' exhibit systematic n-convergence. The small perturbation in the monotonous decrease of the GP energy observed in the case $n=6$ can be explained by the sharp increase of the R value when proceeding from $n=5$ to $n=6$. Comparison of columns two, three and four reveals that for $n \geqslant 5$ the values of E'' are in the range bounded by their variational counterparts E' and E_p. In all cases, however, the GP-energies are considerably closer to the variational results for the correlated basic set, E'.

The last column of Table 1 shows that our method of constructing pairs of close projective and coordinate subspaces proved to be effective. All the R-values are

Table 1. GP-energies (E''), variational energies (E', E_p) and R-values for the ground state of Be

n	$-E''$	$-E'^{a}$	$-E_p$	R
2	14.59688	14.59688	14.59688	0
3	14.63122	14.62296	14.61696	1.606
4	14.63412	14.62513	14.61867	2.408
5	14.63461	14.63928	14.61868	1.898
6	14.63457	14.63928	14.61890	7.477
7	14.63982	14.64528	14.61968	17.201
8	14.64085	14.64829	14.62225	17.339
9	14.64636	14.65104	14.63148	17.257
10	14.64643	14.65373	14.63169	8.801
11	14.64801	14.65803	14.63329	8.901
12	14.65426	14.66007	14.64495	8.866
13	14.65432	14.66147	14.64495	8.708
14	14.65494	14.66164	14.64527	5.329
15	14.65714	14.66173	14.64720	2.366

[a] Results of Sims and Hagstrom [7].

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

	$n=13$		$n=15$	
m	$-E''$	R	$-E''$	R
13	14.65432	8.71	—	—
15	14.65697	1.46	14.65714	2.37
19	14.65782	1.41	14.65807	1.46
24	14.65844	1.36	14.65869	1.40
29	14.65882	1.00	14.65909	1.05
34	14.65900	0.79	14.65926	0.81

small and, except for the case mentioned above, change rather smoothly when n changes. Notice that the changes of R could be still smoothed out by a proper change of nonlinear parameters.

Another possibility of constructing "close" pairs of projective and coordinate subspaces represents the projection procedure described in Paper I. In this method the basis functions of the n-dimensional projective subspace are obtained by projecting individual basis functions onto a given m-dimensional subspace ($m \geqslant n$). The basis of the latter subspace has been described in Sect. 2.1. In Table 2 we present the GP energies obtained for two choices of the coordinate subspace ($n=13$, 15) and various dimensions of the subspaces used in the projection procedure. The case $n=m$ corresponds to the direct GP approach discussed in the first part of this section. We can see from the table that for a given n the increase of m results in a systematic decrease of R. This behaviour causes an improvement of the GP energies. Comparison of the results for $n=13$ and $n=15$ reveals that in the case of similar R values the latter are always lower than the former. The results of Table 2 compare well with the energies obtained in Paper I for the two electron case. As we have already mentioned above our choice of the m-dimensional subspace does not seem to be optimal. It could be improved by adding configurations comprising d and f type orbitals.

4. Concluding Remarks

In this paper we have demonstrated that our strategy for the reliable determination of wavefunctions and energies of many-electron systems by means of the GP method works well in the case of the Be atom for which all the drastic simplifications inherent in the method can be fully used. We have also shown that some experience in the construction of close pairs of subspaces gained in the case of two-electron atoms may be useful when considering larger systems. The results presented above confirm our previous conclusion that the GP method, if applied in a controlled way, leads to reliable results.

In the present paper the basis functions of the coordinate subspace are taken from the work of Sims and Hagstrom [7]. We have done this purposely to get the possibility of comparison of our results with the variational ones. It is important, however, for the prospective quantum chemical applications of the GP method, to have a scheme of determination of nonlinear parameters. This problem will be treated in a forthcoming paper.

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