

## Spline Algorithms for the Hartree–Fock Equation for the Helium Ground State

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Spline algorithms are evaluated for the non-linear, integro-differential equation describing the Hartree–Fock approximation for the He  $1s^2\ ^1S$  ground state. The error in the energy decreases as  $h^{2K-2}$ , where  $h$  is a grid parameter and  $K$  is the order of the spline. It is shown that for higher order splines, the method is fast and accurate, and contrary to the conclusion reached by Altenberger-Siczek and Gilbert, that spline methods are suitable for SCF atomic structure calculations. Accuracy and timing studies are presented as well as comparisons with other accurate procedures. © 1990 Academic Press, Inc.

### 1. INTRODUCTION

The radial equation for an electron in a coulomb potential along with the Hartree–Fock equation for the  $1s^2\ ^1S$  ground state of helium, are frequently used test cases for computational procedures. Both are second-order differential equations with two-point boundary conditions that are eigenvalue problems. The latter is also a non-linear, integro-differential equation, usually solved by the iterative self-consistent field (SCF) method and introduces a number of problems not encountered in the radial equation.

In 1976, Altenberger-Siczek and Gilbert [1] reported results from a study of the Hartree–Fock equation for helium using a cubic  $B$ -spline basis. In earlier work, the effectiveness of cardinal splines had been investigated [2, 3]. Unlike cardinal splines that are non-zero between the selected grid points (or knots), the  $B$ -spline representation has “finite support” and is non-zero over a set of  $K$  intervals, where  $K$  is the order of the spline. (For a discussion of splines and their representation see Refs. [4, 5]). The  $B$ -spline representation was argued to be preferable over the cardinal spline basis for several reasons. Matrices representing a local potential are banded within the  $B$ -spline representation whereas those for cardinal splines are dense. Furthermore, test calculations showed that the error with cardinal splines was much larger than the error for  $B$ -splines with the same grid.

Using the cubic  $B$ -spline basis for which  $K=4$ , Altenberger-Siczek and Gilbert performed the error analysis experimentally using meshes equally spaced in the  $\log r$  variable. They concluded that the error was roughly proportional to  $N^{-6}$ , where the number of mesh points is  $N+1$ , for meshes with less than 21 points. By

extrapolation, they found that 40 mesh points would be required to reduce the relative error  $\delta E/E$  to  $10^{-8}$  and nearly 200 points would be needed to reduce the error to  $10^{-12}$ . According to their analysis, 2058  $N^4$  arithmetic operations are needed to compute the standard supermatrix for the Hartree-Fock operators ( $O(N^6)$  for cardinal splines). This was deemed prohibitively expensive and an SCF iteration used instead. During each SCF iteration cycle, the two electron integrals must be recalculated requiring 512  $N^2$  operations in their scheme.

Based on the above discussions as well as their accuracy and timing studies, they came to the critical conclusion that spline bases are not suitable for SCF calculations.

In 1979, Roothaan and Soukup [6] reported accurate stable results for the  $1s^2$  ground state of  $H^-$ , He,  $Li^+$ , and  $Be^{+2}$  using methods closer to the traditional approach [7, 8]. The range of integration was partitioned into three regions—origin, central, and tail. Near the origin and in the tail region, accurate analytic expansions were devised which represented the solution to high accuracy. The central region was then solved numerically. The error was reported of the order  $h^{10}$ .

In 1989, Godefroid *et al.* [9] proposed another method, based on an accurate approximation of a variational calculation. The basis functions now are Lagrange functions which, like cardinal splines, are non-zero between the mesh points, but unlike splines are continuous functions over the range of approximation rather than piecewise polynomials. By selecting the  $N$  mesh-points to be the zero's of the Laguerre polynomial of degree  $N$ , the kinetic energy integrals can be evaluated exactly in a trivial fashion. Similarly, the nuclear potential integral can be evaluated exactly and, for the hydrogen equation, some remarkably accurate results were obtained with only  $N=10$  mesh points. In effect, their results essentially are exact with respect to a finite basis. They also studied the accuracy of the method for the ground state of He and  $H^-$ . However, unless an exact integration of the two-body integrals is introduced, we shall see later that their accuracy no longer increases rapidly as the number of mesh points increases (recall that slow convergence was one of the charges made against the  $B$ -spline basis method by Altenberger-Siczek and Gilbert [1]).

The early tests with the  $B$ -splines were restricted to the relatively low order, cubic splines. Since then, general spline algorithms have become available [5] and calculations with higher-order splines can be performed as readily as with cubic splines. Johnson *et al.* [10] have used  $B$ -splines extensively in perturbation theory calculations. Splines have also been evaluated by Froese Fischer and Idrees [12] for the solution of continuum problems, where the differential equations are linear. In this paper, the spline procedures are re-evaluated for the non-linear Hartree-Fock equation and a new procedure analyzed for evaluating the two-electron integrals. Timing studies and error analyses are reported and compared with the previous methods.

## 2. THE HARTREE-FOCK EQUATION AND ITS SOLUTION

The Hartree-Fock equation for the radial function,  $P_{1s}(r)$ , of the  $1s$  orbital defining the  $1s^2$  ground state of a two-electron system, with nuclear charge  $Z$ , is the solution of the boundary value problem (Froese Fischer, Ref. [7])

$$\left( \frac{d^2}{dr^2} + \frac{2}{r} (Z - Y^0(1s, 1s; r)) - \varepsilon \right) P_{1s}(r) = 0, \quad (1)$$

$$P_{1s}(r) = 0 \quad \text{and} \quad P'_{1s}(r) \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty.$$

The function,  $Y^0(1s, 1s; r)$ , represents the screening of the nucleus by the other electron and is defined as

$$Y^0(1s, 1s; r) = \int_0^r P_{1s}^2(s) ds + \int_r^\infty \frac{r}{s} P_{1s}^2(s) ds. \quad (2)$$

Note that the presence of the  $Y^0$  term makes the problem a non-linear, integro-differential equation of eigenvalue type. This problem is usually solved iteratively by the self-consistent field method as follows [8]:

- Let an initial estimate of  $P_{1s}(r)$  to be a hydrogenic function
- until converged
  - Compute  $Y^0$  using the current estimate of  $P_{1s}(r)$ .
  - Solve the linear differential equation for a new estimate of  $P_{1s}(r)$ .

A spline approximation over an interval  $[a, b]$ , is a piecewise polynomial approximation of degree  $K-1$ , for which the function and all derivatives up to degree  $K-2$  are continuous. The subintervals are defined by a grid or set of knots. In a  $B$ -spline approach, the radial function is represented as a linear combination of spline basis functions,  $B_i(r)$ ,  $i=0, \dots, N+K-2$  for an interval  $[0, r_{\max}]$ ,  $N$  representing the number of subintervals. Applying the boundary conditions eliminates the first and last basis function. Thus

$$P_{1s}(r) \approx \tilde{P}_{1s}(r) = \sum_1^{N+K-3} c_i B_i(r). \quad (3)$$

The Galerkin method [11] of solving the general differential equation  $\mathcal{L}P_{1s}(r) = 0$ , requires that

$$\int_0^\infty B_j(r) \mathcal{L} \tilde{P}_{1s}(r) dr = 0, \quad j = 1, \dots, N+K-3.$$

This condition leads to the generalized eigenvalue problem,

$$(\mathbf{A} - \varepsilon \mathbf{B})\mathbf{c} = 0,$$

where  $\mathbf{A} = (a_{ij})$ , and  $\mathbf{B} = (b_{ij})$  are symmetric matrices of dimension  $M = N + K - 3$ , with

$$a_{ij} = \int_0^\infty B_i(r) \left( \frac{d^2}{dr^2} + \frac{2}{r} (Z - Y^0(1s, 1s; r)) \right) B_j(r) dr$$

$$b_{ij} = \int_0^\infty B_i(r) B_j(r) dr,$$

and  $\tilde{\epsilon}$  is an approximation to an eigenvalue of the differential equation. Because of the piecewise polynomial nature of the  $B$ -spline, the evaluation of the matrix elements reduces to a sum of integrals over those intervals where both  $B_i(r)$  and  $B_j(r)$  are non-zero. Gaussian quadrature using  $K$  points was used for each interval.

Only one eigenvector is required, and since the estimates of  $\mathbf{c}$  improve as the SCF iterations proceed, inverse iteration was used along with the Rayleigh-quotient [8] to find the approximation to the eigenvalue, namely  $\tilde{\epsilon}$  and the associated eigenvector. The LINPACK routines [13], DGBFA and DGBSL for banded structures, were used to solve the system of equations.

To solve the differential equation numerically by the spline method, the range  $(0, \infty)$  must be divided into a set of subintervals, over  $[0, r_{\max}]$ , with  $\tilde{P}_{1s}(r) = 0$  for  $r > r_{\max}$ . Earlier numerical procedures used a grid, which required special series expansions near the origin [7]. One of the advantages of spline procedures is that the grid can easily change from one region to another. We used an exponential grid (sometimes also called a logarithmic grid because the grid points are equally spaced in the  $\log(r)$  variable) along with an equally spaced grid near the origin. In order to generate the complete spline basis, points of multiplicity  $K$  are introduced at the end-points of the range. The one dimensional grid was defined in terms of a step parameter,  $h = 2^{-m}$  as follows:

$$\begin{aligned} Z * r_i &= 0 && \text{for } i = 1, \dots, K \\ &= (i - K)h && \text{for } i = K + 1, K + 2, \dots, K + 2^m \\ &= r_{i-1} * (1 + h) && \text{for } i = K + 2^m + 1, \dots, N + K \\ &= r_{N+K} && \text{for } i = N + K + 1, \dots, N + 2K - 1. \end{aligned}$$

Because of the iterative nature of the SCF method, additional features could be added to the algorithm such as the automatic adjustment of  $r_{\max} = r_{MX}$ ,  $MX \leq N + K$ . As long as the initial range was sufficiently large,  $MX$  could be reduced to eliminate the negligible "tail" of the expansion of Eq. (3) which, in turn, reduces the size of the matrix that needs to be considered in the eigenvalue problem. The criterion used for range reduction was  $|c_{N+K-1}| \leq 10^{-13}$ .

Similarly, if the last two coefficients in the expansion were too large, namely their sum of absolute values was  $> 10^{-10}$ , the value of  $MX$  was increased. In this manner, the range of the solution was allowed to adapt to the solution and the

requested level of accuracy, eliminating the possibility of an erroneous or inefficient choice of  $r_{\max}$ .

The changes in the function  $Y^0$  from one iteration to the next are such that the sequence of eigenvalues oscillate about the converged, self-consistent value. In order to speed the convergence, a weighting parameter  $\omega$  (or accelerating parameter) was introduced so that

$$\tilde{P}^{\text{next}} = (1 - \omega)\tilde{P}^{\text{computed}} + \omega\tilde{P}^{\text{previous}}.$$

Since it is convenient to assume that  $\tilde{P}$  is normalized,  $\tilde{P}^{\text{next}}$  was normalized. The algorithm for damping or relaxing the oscillations was the same as the one used successfully for many years by MCHF [7, 8].

### 3. SOLVING FOR FUNCTIONS $Y^k$

The presence of the  $Y^0(1s, 1s; r)$  function in Eq. (1) makes the problem non-linear. This function is a special case of a more general integral entering into two-electron Slater integrals, namely,

$$Y^k(nl, n'l'; r) = \int_0^r \left(\frac{s}{r}\right)^k P_{nl}(s) P_{n'l'}(s) ds + \int_r^\infty \left(\frac{r}{s}\right)^{k+1} P_{nl}(s) P_{n'l'}(s) ds. \quad (4)$$

Several approaches can be taken to determining  $Y^k$ . One would be to evaluate the integrals for those values of  $r$  needed for the Gaussian quadrature calculation of the matrix elements  $a_{ij}$ . Such integrations were done in the continuum calculations but lead to lengthy procedures [11]. More typically, the  $Y^k$  functions are determined from differential equations. When finite differences were used, it was customary [7] to integrate first-order differential equations outward for the first term of Eq. (4) and inward for the  $Y^k$  function. But this pair of equations can be combined into a single second-order differential equation,

$$\frac{d^2}{dr^2} Y^k(r) = \frac{k(k+1)}{r^2} Y^k(r) - \frac{2k+1}{r} P_{nl}(r) P_{n'l'}(r), \quad (5)$$

with boundary conditions

$$Y^k(0) = 0,$$

$$\frac{d}{dr} Y^k(r) = \frac{-k}{r} Y^k(r) \quad \text{as } r \rightarrow \infty,$$

and solved by the spline Galerkin method, in the same way as the equation for  $P_{1s}(r)$ . This leads to a banded linear system of equations for the expansion of  $Y^k(r)$ . The last equation in this system arises from applying the boundary condition at  $r = r_{MX}$ .

TABLE I  
 Values of  $F^0(1s, 1s)$  Obtained Using the Spline Galerkin Method  
 for a Series of Values of  $K$  and  $h$

K	h=1/2	h=1/4	h=1/8
3	1.2495956407295	1.2499697638865	1.2499980392691
4	1.2499723357051	1.2499994968798	1.2499999904072
5	1.2500001146424	1.2499999930235	1.249999999597
6	1.2499980586619	1.249999997814	1.249999999998
7	1.2500009176233	1.2500000000754	1.250000000000
8	1.2500024217236	1.249999997972	1.250000000000
9	1.2499932020168	1.2500000003663	1.250000000000
10	1.2500094438748	1.249999996700	1.250000000000
11	1.2499913532449	1.249999999725	1.250000000000
12	1.2500045106909	1.2500000005390	1.250000000000
13	1.2500012611142	1.249999991367	1.250000000000
14	1.2499933959515	1.2500000007486	1.250000000000
15	1.2500099891306	1.249999997904	1.250000000000

*Note.* The exact value of this integral for  $Z = 2$  and a hydrogenic  $P_{1s}(r)$  in 1.25.

The accuracy of this procedure was tested by computing the Slater integral

$$F^0(1s, 1s) = \int_0^\infty \left(\frac{1}{r}\right) Y^0(1s, 1s; r) P_{1s}^2(r) dr$$

using a hydrogenic function  $P_{1s}$ , for which the integral is known to be exactly 1.25 when  $Z = 2$ . Table I shows values of this integral for a range of parameters  $h$  and  $K$ . Note that for  $h = \frac{1}{2}$ , the best accuracy is achieved for  $K = 5$ , that the accuracy does not improve with the higher values of  $K$ . For  $h = \frac{1}{8}$ , an exact result is obtained for  $K = 7$ , and almost exact for  $K = 6$ .

## 4. ACCURACY AND TIMING STUDIES

The calculations in this paper are restricted to the Helium ground state where  $Z = 2$ .

The procedures outlined above depend on a number of parameters. The parameter  $r_{\max}$  depends, in general, on the eigenfunction and the accuracy to which the function is to be represented. For a higher eigenstate, the wave functions extend further to infinity, and  $r_{\max}$  needs to be larger. For the ground state, and the cutoff criterion of  $10^{-12}$ ,  $r_{\max}$  was found to be in the neighborhood of 22.

There are two other fundamental parameters of the calculation. One is the step-size parameter  $h$  and the other is the order  $K$ . Ideally, one would like to find that combination of parameters for which a given accuracy can be obtained in the least amount of CPU time. Such a criterion ignores the role of memory which could be a critical resource but, as in the studies mentioned earlier, the evaluation of an algorithm is usually based on arithmetic operations or CPU time. In order to gain an understanding of the interplay of step-size and order, timing studies have been performed for all combinations of  $h = 2^{-m}$ ,  $m = 0$  to 5, and  $K = 3$  to 15.

For the helium ground state, the total energy of the system is

$$E = 2I(1s) + F^0(1s, 1s),$$

where

$$I(1s) = -(1/2) \int_0^\infty P_{1s}(r) \left( \frac{d^2}{dr^2} + \frac{2Z}{r} \right) P_{1s}(r) dr.$$

The first term in this expression is part of the kinetic energy operator, say  $T$ ; the rest together with the Slater integral,  $F^0$ , represent the potential energy,  $V$ . For an exact variational calculation and a complete basis, the virial theorem states that

$$V/T = -2.$$

Because in this case the exact energy is not known, the value of  $2 + V/T$  was used as a measure of the error in the calculation. Table II reports the results for  $h = \frac{1}{2}$  and  $h = \frac{1}{8}$ .

The error versus the execution time is plotted in Fig. 1 for a number of different combinations of the parameters. Each curve is for a constant value of  $h$  and a range of  $K$  values from 3 to 15. For the least amount of CPU time, the leftmost curve with the lowest degree of accuracy is the one with  $h = \frac{1}{4}$ , but as the accuracy increases, the  $h = \frac{1}{8}$  curve is the leftmost one, representing the least amount of CPU time. The other two curves are for  $h = \frac{1}{16}$  and  $h = \frac{1}{32}$ . Each curve becomes essentially "flat" in the region where the finite precision of the floating point arithmetic becomes a limiting factor. The best accuracy seems to be just under 13 significant digits. From Fig. 1, we can see that the optimum parameters to achieve this

TABLE II  
Hartree-Fock Results for Different Parameters,  $K$  and  $M = N + K - 1$ ,  
Using the Spline Galerkin Method

h	K	M	Energy	V	T	$2 + V/T$	
1/2	3	25	-2.8614677389529	-5.7221730299525	2.8607052909996	-2.67(-04)	
	4	26	-2.8616792915868	-5.7233563243103	2.8616770327235	-7.89(-07)	
	5	27	-2.8616799885673	-5.7233599772565	2.8616799886891	4.26(-11)	
	6	28	-2.8616799954178	-5.7233599910755	2.8616799956577	8.38(-11)	
	7	29	-2.8616799956240	-5.7233599912265	2.8616799956024	-7.53(-12)	
	8	30	-2.8616799955421	-5.7233599911527	2.8616799956106	2.39(-11)	
	9	31	-2.8616799955979	-5.7233599912091	2.8616799956113	4.69(-12)	
	10	32	-2.8616799957999	-5.7233599914109	2.8616799956110	-6.60(-11)	
	11	33	-2.8616799953127	-5.7233599909233	2.8616799956106	1.04(-10)	
	12	34	-2.8616799958695	-5.7233599914816	2.8616799956122	-8.99(-11)	
	13	35	-2.8616799955650	-5.7233599911771	2.8616799956121	1.65(-11)	
	14	36	-2.8616799953831	-5.7233599909952	2.8616799956121	8.01(-11)	
	15	37	-2.8616799960339	-5.7233599916460	2.8616799956121	-1.47(-10)	
	1/8	3	43	-2.8616663245256	-5.7232844124722	2.8616180879466	-1.69(-05)
		4	44	-2.8616799825485	-5.7233599248684	2.8616799423199	-1.41(-08)
5		45	-2.8616799955797	-5.7233599912031	2.8616799956234	1.53(-11)	
6		46	-2.8616799956110	-5.7233599912233	2.8616799956124	4.74(-13)	
7		48	-2.8616799956113	-5.7233599912235	2.8616799956122	3.18(-13)	
8		49	-2.8616799956113	-5.7233599912235	2.8616799956122	3.02(-13)	
9		50	-2.8616799956114	-5.7233599912236	2.8616799956122	2.63(-13)	
10		51	-2.8616799956114	-5.7233599912235	2.8616799956122	2.87(-13)	
11		53	-2.8616799956114	-5.7233599912236	2.8616799956122	2.79(-13)	
12		54	-2.8616799956114	-5.7233599912236	2.8616799956122	2.78(-13)	
13		55	-2.8616799956114	-5.7233599912236	2.8616799956122	2.72(-13)	
14		56	-2.8616799956114	-5.7233599912236	2.8616799956122	2.81(-13)	
15		57	-2.8616799956115	-5.7233599912236	2.8616799956122	2.56(-13)	

*Note.* Included is the total energy (in au.), the potential energy  $V$ , the kinetic energy  $T$ , and  $2 + V/T$ , which is a measure of the error. The notation n.nnn (-mm) is used to represent  $n.nnn \times 10^{-mm}$ .



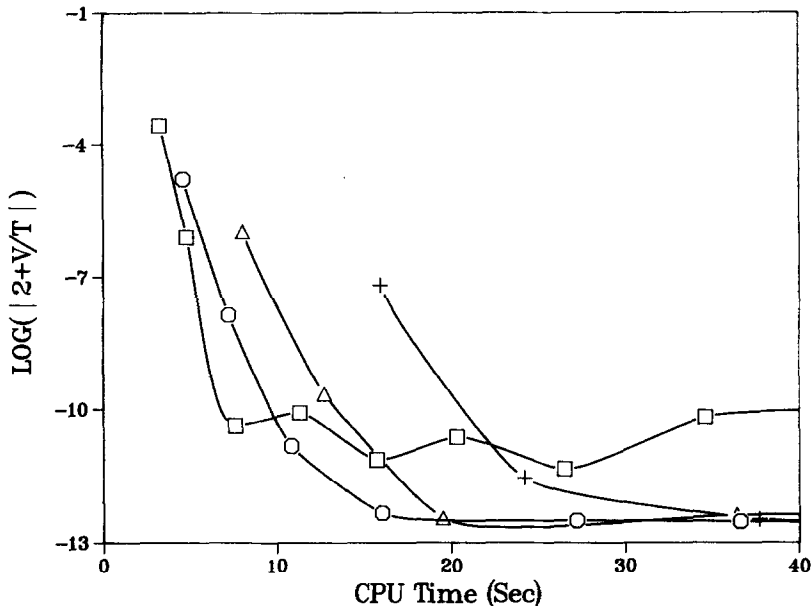


FIG. 1. Plot showing the dependence of  $\log_{10} |2 + V/T|$  versus the CPU time for a series of calculations for all possible combinations of  $h = 2^{-m}$ ,  $m = 2, \dots, 5$ , and  $K = 3, \dots, 15$ . The curves are for constant  $h$  with the topmost point on the left being on the curve with  $h = \frac{1}{2}$ , the next curve being  $h = \frac{1}{4}$ , etc.

accuracy in the minimum amount of CPU time are  $h = \frac{1}{8}$  and  $k = 6$ . Table II shows that this calculation required 46 basis functions and that the error is  $5.2 \times 10^{-13}$ , just slightly smaller than the error of  $7.0 \times 10^{-13}$  derived from the values reported by Roothaan and Soukup [6] who used 251 integration points. Our total energy is slightly higher than their value; they applied the analytic tail correction at  $r_{\max} = 20$ .

Figure 1 also shows that the accuracy increases very rapidly at first as  $K$  increases and then stabilizes. Analysis of the early portion of the data, where rounding errors are negligible, show that the asymptotic behavior of the error in both the virial theorem and the energy is  $\mathcal{O}(h^{2K-2})$ . (The error in the energy was computed as the difference with the energy obtained from the optimum parameters.) Thus, the higher the  $K$  value, the more rapidly the error decreases as  $h$  decreases.

Godefroid *et al.*'s method [9], on the other hand, converges much more slowly as the number of mesh points increase when approximate, but rapid integration procedures are used for the electrostatic interaction. Ideally, the two methods should be compared on the basis of accuracy versus CPU time, since their procedure was designed specifically to minimize the time required for evaluating matrix elements. Such information is not available. Instead, Hartree-Fock results are presented for 10, 30, and 70 mesh points. To facilitate a comparison, Fig. 2 shows the dependence of the accuracy of our method on the number of basis functions,  $N + K - 1$ , for  $h = 1$  and  $h = \frac{1}{2}$ , and the same range of  $K$  values as in Fig. 1. There

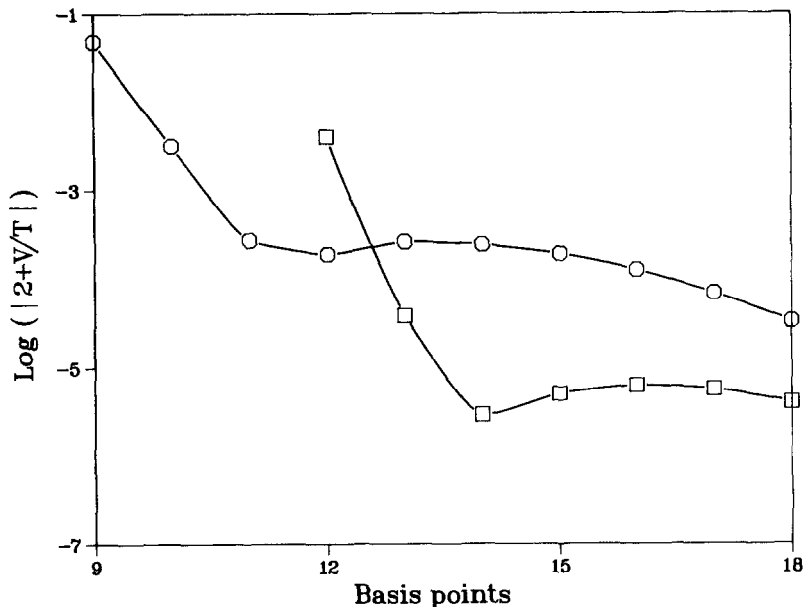


FIG. 2. Plot showing the dependence of  $\log_{10} |2 + V/T|$  versus the number of basis spline for a series of calculations, with  $K = 3, \dots, 15$ . The topmost curve is for  $h = 1$  with nine intervals; the second for  $h = \frac{1}{2}$  with 10 intervals.

were  $N = 9$  and  $N = 10$  intervals in the range of approximation for the two curves respectively.

Figure 2, shows that the absolute error is already less than  $10^{-5}$  when the number of basis functions is equal to 13. The smallest error reported by Godefroid *et al.* was  $14 \times 10^{-4}$ ,  $6 \times 10^{-4}$ , and  $2 \times 10^{-4}$  for  $N = 10, 30$ , and  $70$ , respectively. On the other hand, with an "exact"  $Y_0(1s, 1s; r)$  function and an optimum value of  $h$ , their error in  $V/T$  is  $1.5 \times 10^{-7}$  with only 10 mesh points.

These studies, as well as the earlier spline investigations, show that the critical step in the Hartree-Fock calculation is the evaluation of the  $Y^k$  functions arising from the Slater integrals in the energy expression.

## 5. CONCLUSIONS

On the basis of studies using the cubic spline ( $K = 4$ ), Altenberger-Siczek and Gilbert concluded that the spline approach was not suitable for Hartree-Fock atomic structure calculations and that the desired degree of accuracy could not be achieved with sufficient speed. In this paper we have shown that, by going to higher degree splines, a high degree of accuracy can be achieved with a relatively small basis set. Our studies show that, for a grid that is linear near the origin and

exponential at larger values, the optimum choice of parameters are  $h = \frac{1}{8}$  and  $K = 6$  requiring 46 basis functions with  $r_{\max} = 22$ .

The present calculations were performed on a SUN 3/160 with a floating point accelerator. Issues of vectorization or concurrency were not considered. For the more complex multiconfiguration Hartree-Fock calculations these will be important issues. In particular, the spline routines [5] will need to be redesigned to permit more efficient vectorization. The present codes tend to have vector length of  $K$ ; a better organization would be one where vectors are of length  $N$  or  $N + K$ .

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