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EXPERIMENT AND THEORY IN COMPUTATIONS OF THE He ATOM GROUND STATE

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Extensive variational computations are reported for the ground state energy of the nonrelativistic two-electron atom. Several different sets of basis functions were systematically explored, starting with the original scheme of Hylleraas. The most rapid convergence is found with a combination of negative powers and a logarithm of the coordinate $s = r_1 + r_2$. At $N = 3091$ terms we pass the previous best calculation (Korobov's 25 decimal accuracy with $N = 5200$ terms) and we stop at $N = 10257$ with $E = -2.90372$, 43770, 34119, 59831, 11592, 45194, 40444, ...

Previous mathematical analysis sought to link the convergence rate of such calculations to specific analytic properties of the functions involved. The application of that theory to this new experimental data leaves a rather frustrating situation, where we seem able to do little more than invoke vague concepts, such as "flexibility." We conclude that theoretical understanding here lags well behind the power of available computing machinery.

Keywords: Variational calculations; Helium atom; convergence rates.

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1. Introduction

For thousands of years mathematicians have enjoyed competing with one another to compute ever more digits of the number π. Among modern physicists, a close analogy is computation of the ground state energy of the Helium atom, begun 75 years ago by E. A. Hylleraas.[1]

Many have contributed incremental steps in this endeavor, flexing their computational muscle and ingenuity, often trying to use mathematical insight for advantage. The strongest line of theory has been to focus on the analytic properties of the wavefunction, especially following the 1954 work of V. A. Fock[2] which showed a weak logarithmic singularity at the three-particle coalescence.

The recent work of V. I. Korobov[3] stands out for its simplicity and its success. His trial functions use the three scalar coordinates packaged as $e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}$, with many sets of the complex nonlinear parameters α, β, γ selected in a quasirandom manner within specified intervals $A_i \le \alpha_i \le B_i$, etc. With a linear combination of

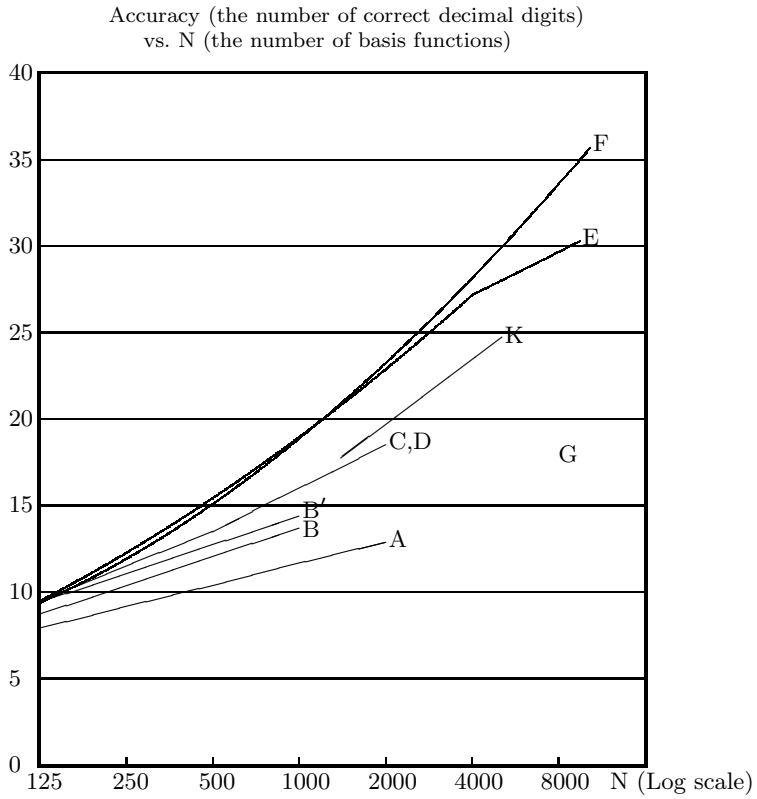

Fig. 1. Comparative convergence rates of different basis sets.

$N = 2200$ terms of this type, grouped into four sets $[A_i, B_i]$, Korobov surpassed the best previous work by three decimals of accuracy in the Helium ground state energy; and more recently he went on to $N = 5200$ and added four more decimal places.

What struck me as surprising in Korobov's work was the fact that it seemed to ignore that earlier "wisdom" about analytic properties of wavefunctions. His basis functions are, analytically, no different from the original Hylleraas basis; yet his computational results appear to converge so much more rapidly. This perception motivated the investigations reported below.

Section 2 presents the new experimental data — systematic variational calculations using a variety of different basis functions that have been suggested over the years: these include negative powers, fractional powers and logarithms of the coordinates. Vastly different rates of convergence are observed, as illustrated in Fig. 1.

Section 3 offers a qualitative discussion and attempts to interpret this wealth of new data. Section 4 is a review, and an attempt to apply, the theoretical approach for understanding, at least semi-quantitatively, the observed convergence rates. We conclude that this state of the theory is far from satisfactory.

Table 1. Energy accuracy — summary data.

ω	N	A-basis	B-basis	B′-basis
9	125	7.9	8.7	9.4
12	252	8.7	10.2	10.7
16	525	10.4	11.7	12.3
21	1078	11.6	13.2	13.9
27	2135	12.8		
ω	N	C-Basis	D-Basis	
7	139	9.5	9.6	
9	249	11.2	11.3	
12	503	13.4	13.5	
16	1049	15.8	16.0	
21	2155	18.3	18.5	
ω	N	E-Basis	E′ -Basis	F-Basis
7	139	9.5	9.8	9.4
9	249	11.7	11.6	11.5
12	503	14.5	14.5	14.3
16	1049	18.2	18.3	18.1
21	2155	22.5		22.4
27	4269	27.2		27.6
34	8093	29.7		33.0

Accuracy = Number of correct decimals

2. Experiments — Data

Several different sets of basis functions were used in the standard variational calculations for the ground state energy of the Hamiltonian (with $Z = 2$),

$$H = -\frac{1}{2}[\bigtriangledown_1^2 + \bigtriangledown_2^2] - Z/r_1 - Z/r_2 + 1/r_{12}\,, \tag{2.1}$$

and they are detailed below in terms of the Hylleraas coordinates,

$$s = r_1 + r_2, \qquad t = r_1 - r_2, \qquad u = r_{12} = |\vec{x}_1 - \vec{x}_2|\,. \tag{2.2}$$

Table 1 presents summary results for the primary bases studied. The Accuracy of any energy value E is defined as $\mathrm{Log}_{10}[E^*/(E^* - E)]$ where E^* is our best estimate of the exact value. Thus, the numerical value of Accuracy tells how many correct decimal places there are in the calculated result. Generally, we see that convergence was found to be more rapid as one progressed through this series, A, B, C, D, E, F. More detailed discussion of the results will be deferred to the following sections.

- Basis A is just the original Hylleraas set:

$$\psi = \sum C_{l,m,n} e^{-ks/2} s^l u^m t^n \tag{2.3a}$$

$$l, m = 0, 1, 2, 3, \ldots, \qquad n = 0, 2, 4, 6, \ldots \tag{2.3b}$$

and we use the order parameter $\omega = l + m + n$ to group the terms. We also designate a calculation of order ω to mean a basis set including all terms with $l + m + n \leq \omega$. The total number of terms, N, grows asymptotically as $\omega^3/12$. This same organizational scheme is used for all the experiments listed below.

- Basis B allows negative powers of s, which were introduced by Kinoshita[4]:

$$e^{-ks/2} s^l (u/s)^m (t/s)^n \tag{2.4}$$

and we can rearrange the terms as

$$e^{-ks/2} s^l (u/s)^{m+n} P_n(t/u)\,, \tag{2.5}$$

using the Legendre polynomials to get the selection rule $\Delta n = 0, \pm 2$. This technique follows the work of Goldman[5] and leads to more efficient use of computer space and time.

- Basis C allows fractional powers of s, which were first introduced by H. M. Schwartz[6]:

$$(1, s^{1/2}) e^{-ks/2} s^l u^m t^n \tag{2.6}$$

which doubles the size N of the basis for each order ω. (The $s^{1/2}$ term is omitted for $\omega = 0$.)

- Basis D uses the logarithm of s, first introduced by Frankowski and Pekeris[7]:

$$(1, \ln(s)) e^{-ks/2} s^l u^m t^n \tag{2.7}$$

(The $\ln(s)$ term is omitted for $\omega = 0, 1$. The values of N shown in Tables 1 and 2 are two units off for bases D and F.)

- Basis E has both negative powers and fractional powers of s.

$$(1, s^{1/2}) e^{-ks/2} s^l (u/s)^m (t/s)^n\,. \tag{2.8}$$

- Basis F has both the logarithm and negative powers of s.

$$(1, \ln(s)) e^{-ks/2} s^l (u/s)^m (t/s)^n\,. \tag{2.9}$$

For each of the basis sets described above, the scale parameter k was varied somewhat to find the lowest energy at each order. For the Table 1 data on Basis A, k varied from 5.0 to 8.2; for Basis B, from 3.8 to 5.9; for Basis C, from 4.7 to 6.6; and for Basis D, from 4.6 to 6.6. For Bases E and F, it was found that the optimum value of k stayed close to 2.0 for the mid-size and larger orders, so k was fixed at this value for all the data shown.

In two cases I replaced the set of functions $e^{-ks/2} s^l$ by the set $e^{-\alpha_l s}$, using Korobov's quasi-random method for selecting the (real) nonlinear parameters α in a single group. The results for these experiments are shown as Bases B′ and E′ in Table 1.

Several variants of these basis sets were also explored briefly but discarded when they appeared less effective, as functions of N, than their counterparts above.

Among these were the use of:

$$\text{Negative powers of } s \text{ and } u\text{: } (u/s)^m(t/u)^n\,, \tag{2.10a}$$

$$\text{Third roots of } s \text{ instead of the square root}\,, \tag{2.10b}$$

$$\text{Two or more powers of } \ln(s)\,, \tag{2.10c}$$

$$\text{The coordinate } r = \sqrt{r_1^2 + r_2^2}\,, \tag{2.10d}$$

$$\text{The coordinate } R = |\vec{x}_1 + \vec{x}_2|. \quad \text{(See the Appendix.)} \tag{2.10e}$$

In Table 2 are the detailed results for the two bases — E and F — that show the most rapid convergence. This table uses a compact format which omits repetition

Table 2. Calculated results with the two best bases.

ω	N	E-basis energies	Ratios	F-basis energies	Ratios
4	43	−2.90372 183		−2.90371 941	
5	67	−2.90372 42300	17.9	−2.90372 415	22.5
6	99	” 43643	11.3	−2.90372 43610	14.2
7	139	43762 2	15.8	” 43758 7	14.0
8	189	43769 759	14.3	43769 382	12.2
9	249	43770 28348	10.5	43770 25283	11.2
10	321	43770 33352	7.32	43770 33068	8.35
11	405	” 34036	9.37	” 34000 4	8.80
12	503	34109 6	8.30	34106 294	8.94
13	615	34118 444	8.63	34118 13633	9.02
14	743	34119 46685	8.79	34119 44847	10.1
15	887	34119 58229	8.06	34119 57846	7.33
16	1049	” 59667	10.4	” 59620	10.0
17	1229	59806	6.32	59797	5.90
18	1429	59828 5	10.5	59827 3	9.38
19	1649	59830 654	5.12	59830 456	5.50
20	1891	59831 06419	9.69	59831 03831	8.89
21	2155	59831 10650	5.08	59831 10381	6.18
22	2443	” 11482	9.14	” 11442	8.22
23	2755	11573 8	5.62	11571 6	7.25
24	3093	11589 997	7.94	11589 408	6.66
25	3457	11592 03902	6.18	11592 08081	8.87
26	3849	11592 36947	5.29	11592 38154	4.79
27	4269	” 43186	4.80	” 44444	11.0
28	4719	44484	2.97	45017 4	3.57
29	5199	44922	2.88	45177 752	13.1
30	5711	45074 35	2.32	45189 95689	3.00
31	6255	45139 97	2.29	45194 02040	14.8
32	6833	45168 66	2.16	45194 29566	2.76
33	7445	45181 95	2.11	” 39521	15.1
34	8093	45188 24	2.06	40182	2.78
35	8777	45191 29	2.02	40420 7	13.5
36	9499	45192 80		40438 342	3.11
37	10259			40444 00495	

Extrapolate: $E^* = -2.90372,\ 43770,\ 34119,\ 59831,\ 11592,\ 45194,\ 40444,\ 6$

of the leading digits. One quantitative measure of the rate of convergence is the Ratio of successive differences and this is also shown in the table.

Technical notes. For these computations, I wrote a set of subroutines for multiple-precision arithmetic (in C), eschewing more professional packages which are available. [My source code is available at the website http://socrates.berkeley.edu/~schwrtz/mppkg.html] The last row of data in Table 2 used 101 decimals of precision and took one week running on an otherwise idle desktop computer equipped with a 300 MHz processor and 320 MB of memory.

3. Experiments — Discussion

Figure 1 provides a visual comparison of the convergence rates for the different variational basis sets (A–F), plotting Accuracy versus the Log of N, the number of basis functions used. I found a number of surprises in these results.

Surprise 1. Basis B (negative powers of s) shows a significant improvement over basis A (the original Hylleraas basis).

Surprise 2. Bases E and F do a great deal better than any of the others. Somehow, the benefits of B and C (or B and D) are cumulative.

Surprise 3. The performance of C and D are nearly identical, as with E and F (until we reach very high orders.)

Surprise 4. The performance of basis E drops off dramatically after $\omega = 27$; but basis F keeps up its rapid convergence, although with marked oscillation, as seen from the Ratios in Table 2.

The surprising performance of Korobov's basis has already been noted: his published results are shown by the line labelled with the letter "K" in Fig. 1.

The fact that Basis C performs a lot better than Basis A was not a surprise, since earlier work[8] had already shown that. Ditto for Basis D.[7] Also, the smallness of the gain shown by basis B′ over B (and by E′ over E) is as expected, based upon the analytic equivalence of exponentials and power series.

While I cannot explain the surprising results, I can readily offer suggestions on how one might interpret them. The virtue of Bases C and D lies in providing more flexibility to the "radial" behavior of the wavefunction (coordinate s); while that of the negative powers lies in providing more flexibility in the "angular" behavior (ratios u/s and t/s). The similarity between C and D (and between E and F) indicates that the precise analytic behavior in the "radial" coordinate is not important — any flexibility will do — until one gets to the very high orders.

This appeal to "flexibility" is just armwaving; it lacks any mathematical foundation. Such appeal to flexibility is also the best way I know to understand the success of Korobov's calculations: his work seems akin to the "adaptive" techniques used in numerical integration, where one puts additional mesh points into any region that shows a slower rate of convergence.

In varying the scale parameter k, I most always found a simple minimum in the

Table 3. Double minimum in $E(k)$ for Basis E at $\omega = 21$.

k	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4
E	10567	10697	10691	10650	10635	10640	10636	10603

These numbers for the energy E follow the first 20 decimal places.

energy. However, in one case — Basis E at $\omega = 21$ — a more complex behavior emerged: see Table 3. While the variation shown here is not very great, this does raise the general question of how effectively one may search for the minimum of a complicated function of many nonlinear parameters. This is a possible source of worry in using Korobov's technique, especially when it comes to error estimation and extrapolation.

4. Theories

The first lesson in analysis of atomic wavefunctions concerns the two-particle cusps: linear behavior as any one of the coordinates r_1, r_2, or r_{12} goes to zero. All of the basis functions studied in this paper are correct in that regard; we are concerned here with what comes next.

Take the Hylleraas expansion (2.3a) and put it into the Schrodinger equation (2.1). Then collect the coefficients of each monomial in s, u, and t and set that equal to zero. Early in this infinite set of algebraic equations for the expansion coefficients $C_{l,m,n}$ one finds the following *inconsistent* equations

$$C_{1,0,0} + ZC_{0,0,0} = 0\,, \tag{4.1a}$$

$$-2C_{1,1,0} + C_{1,0,0} = 0\,, \tag{4.1b}$$

$$4C_{1,1,0} - C_{1,0,0} = 0\,. \tag{4.1c}$$

This contradiction in the Hylleraas basis was discovered by Bartlett, Gibbons and Dunn[9] in 1935 and it led them to consider an alternative expansion: one that involved logarithms of the hyperradius $r = \sqrt{r_1^2 + r_2^2}$. Later, Fock[2] independently developed a systematic expansion of the wavefunction with such terms.

In 1962 this author[10] developed a general theory about the convergence rate of variational calculations, based upon analogy with least-squares fitting of functions and one-dimensional model problems. This line of analysis was expanded by others[11] and in some cases given a more rigorous mathematical basis.[12]

That theoretical work[10] led directly to the idea that the convergence rate in Hylleraas-type calculations for the Helium ground state was controlled by the Fock logarithmic singularity; and the semi-quantitative analysis seemed to fit the available data. It also led to the successful exploitation of the fractional power basis C.[8] Shortly thereafter, Frankowski and Pekeris[7] took logarithmic terms explicitly into their trial functions and this also seemed to confirm the importance of the Fock behavior.

However, when Kinoshita[4] considered the systematic use of negative powers — in the form (2.10a), not (2.4) — he found that there was no contradiction of the

type noted above. I have confirmed that this conclusion holds also for the basis (2.4) used in the current work.

Thus, one might be drawn to believe that the logarithmic singularity is not an intrinsic property of the He atom wavefunction itself but rather results from a particular analysis that relies on the six-dimensional coordinate r. This idea may be dispelled by reading the work of Myers *et al.*,[13] where they take one for a walk around the three-particle coalescence and show that the (finite) discontinuity in the local energy disappears when one includes the full set of terms that accompany the Fock logarithm.

This approach helps us understand some other experimental results. We noted earlier that inclusion of negative powers t/u gave poorer results than t/s. Each of these ratios shows a (finite) discontinuity when one walks around the place where the denominator vanishes — something that the correct wavefunction should not allow. In the case of (t/u) this error occurs along a line, while in the case of (t/s) this error occurs only at a point. A similar situation appears in the work of Goldman,[5] who used a basis of size up to N=8066. His use of the coordinates $r_<, r_>$ led to a very efficient computational scheme, but demonstrates relatively slow convergence. (See the letter "G" in Fig. 1.) This may be attributed to the discontinuity of his basis functions on the 2-dimensional surface $r_1 = r_2$.

4.1. *Fitting the data*

The goal of a good theoretical understanding should be the ability to predict or to explain, *at least semi-quantitatively*, the observed rates of convergence for systematic variational calculations with different basis sets. In my earlier work,[10] the attempt to do this was based upon analogies with one-dimensional model problems, doing least-squares fit with appropriate orthogonal bases to represent functions with various types of singularities:

$$\text{Minimize} \int \rho(x)dx[f(x) - \sum_{i=0}^{n-1} C_i u_i(x)]^2 \,, \tag{4.2a}$$

$$C_i = \int \rho(x)dx f(x)u_i(x) \,, \tag{4.2b}$$

$$\text{Error } \approx (C_n)^2 \,. \tag{4.2c}$$

For one example we find:

$$f(x) = x^\nu \ln x, \qquad \rho(x) = x^\mu \qquad \text{on the interval } (0,1) \,,$$
$$C_n \sim 1/n^{\mu+2\nu+3/2}; \tag{4.3}$$

and an alternative example is:

$$f(x) = x^\nu \ln x, \qquad \rho(x) = x^\mu e^{-x} \qquad \text{on the interval } (0,\infty) \,,$$
$$C_n \sim 1/n^{\mu/2+\nu+1} \,. \tag{4.4}$$

The difference in convergence rates for these two examples may be understood qualitatively as follows. The basis functions $x^n e^{-x}$ peak at $x = n$. Therefore, at higher n these basis functions on the interval $(0, \infty)$ get farther and farther away from the singularity, which is at $x = 0$. One may improve the situation by using basis functions $x^n e^{-kx}$, where k is a scale parameter that may grow as one proceeds to higher orders. I do not have a quantitative theory for this result but it is qualitatively relevant to the current study. (See also Ref. 14.)

In my 1962 work I applied this simple modeling to the He atom problem, identifying the Fock term $r^2 \ln r$ as the dominant singularity which is neglected in conventional Hylleraas coordinates. This led me to predict a convergence rate formula,

$$E(\omega) - E(\omega - 1) \sim \text{const.}/\omega^p \,, \tag{4.5}$$

and I estimated that p should be between 5.5 and 10, due to uncertainties in replacing the real 3-dimensional problem with the one-dimensional model. The then best results with Hylleraas variables (work of Pekeris,[15] up to order 21, using a cleverly orthogonalized basis) fit the convergence rate formula (4.5) with a value of p between 7 and 8. This was good confirmation of the theory. The extended computations reported here (Basis A data in Table 1) fit the convergence rate formula (4.5) with a value of p which varies from 7, at the lower orders, to a value about 12 at the higher orders. This improvement is probably due to my allowing the scale parameter k to vary, which was not done in the earlier work.

Also, in 1962, I introduced the half-powers of coordinate s, explicitly for the purpose of increasing the convergence rate, following this theory. That was successful, with the observed value of p approximately doubled to 14 or 15 at $\omega \leq 8$. The extended computations reported here (Basis C data in Table 1) are fit to values of p which vary from about 16 to 21. Again, this is fairly good confirmation of the theory; and again we acknowledge some improvement by allowing the scale parameter to vary.

Following that earlier theory one would certainly not expect Basis D to converge at the same rate as Basis C – but this is exactly the behavior we have found in the present experiments.

What can I say about the observed convergence rate of Basis B, introducing negative powers into the Hylleraas functions? The data in Table 1 are fit with a value of the exponent p around 13. I do not understand this but will only offer a guess that it may have to do with fitting the complex "angular" behavior around the Fock singularity, which was described in Ref. 13. Maybe this is connected with the difference in convergence rates noted above, in Eqs. (4.3) and (4.4), for the model problems on (0,1) and on (0,∞).

Finally, look at the results for Bases E and F. The data in Tables 1 and 2 are fit with values of the exponent p which grow from the 20's to the 40's in the middle range of ω; at the top end, the data for Basis E drop to around p=25, while the data for Basis F climb to about p=65. I am at a loss to explain these large exponents following the former analysis.

An alternative to the power law convergence rate formula (4.5) is the exponential

rate formula

$$E(\omega) - E(\omega - 1) \sim \text{const.}(\sigma)^{\omega} \,, \tag{4.6}$$

which one could expect from a model fitting problem that involved no singularities at all. For example, expanding e^{-ax} in terms of $x^n e^{-bx}$ would yield the formula (4.6) with $\sigma = (\frac{a-b}{a+b})^2$. If one plots the data for Basis F (Log of increments in E versus ω), it does look close to a straight line; and the smoothed data in Table 2 may be fitted with a value of σ in the range 0.13 - 0.16 for $\omega > 16$. If one looks at the asymptotic behavior of the He wavefunction as r_1 goes to infinity, the behavior in r_2 should be as e^{-Zr_2} with $Z = 2$. The trial functions I used for this basis have the exponential envelope $e^{-k(r_1+r_2)/2}$ with $k = 2$. Using the formula quoted above, this model gives us the parameter σ as $(\frac{2-1}{2+1})^2 = 0.11$. This looks like a fairly good fit to the data; but accepting this explanation would lead us to doubt the relevance of the Fock singularities for the He wavefunction.

Also, I know of no published theoretical attempts to explain the excellent convergence found by Korobov with his highly nonlinear fitting of the trial wavefunction. John Morgan has suggested (in private communication) that Korobov's approach may be likened to the work of fitting the Hydrogen radial wavefunction with a set of gaussians, using "floating exponents".[16] This is plausible, but at present it is just more handwaving about "flexibility".

I conclude that theoretical understanding of the convergence of variational calculations on the two-electron atom is far outstripped by the raw computing power of available machinery.

Some may ask if any of this is really relevant to current issues in physics. One response is to point to high accuracy measurements performed on atomic systems which may check the current theories of fundamental particles and interactions. Recent work[17] aims to determine the fine structure constant to a few parts-per-billion, based upon measurements of the 2^3P_J states in Helium and detailed calculations that rely upon an accurate representation of the atomic wavefunction.

Then, again, all this may be nothing more than an expression of π-envy.

Acknowledgement

I am grateful to John D. Morgan III for several very helpful discussions.

Appendix: Integrals

Integrals of the following type were needed in the calculations reported here:

$$\int_0^\infty ds e^{-s} s^p (\ln(s))^q \,. \tag{A.1}$$

There is a simple recursion formula on the index p; and for the minimum values of p I used a particular technique of numerical integration. (See Ref. 18.) First change

variables, $s = exp(y)$; then use the simple rule,

$$\int_{-\infty}^{\infty} f(y)dy \approx h \sum_{n=-\infty}^{\infty} f(nh)\,. \tag{A.2}$$

The summation is truncated when terms are smaller than the desired accuracy; and the answer converges exponentially as the interval h is decreased.

For the two-electron atom, one can evaluate the most conventional integrals from the formula,[19]

$$\int \frac{d^3x_1}{4\pi} \int \frac{d^3x_2}{4\pi} \frac{e^{-ar_1}}{r_1} \frac{e^{-br_2}}{r_2} \frac{e^{-cr_{12}}}{r_{12}} = \frac{1}{(a+b)(b+c)(c+a)}\,, \tag{A.3}$$

and derivatives of this simple result with respect to the parameters a, b, c.

In exploring more complicated functions, I was able to find another simple formula for the following integral, which involves $R = |\vec{x}_1 + \vec{x}_2|$,

$$\int \frac{d^3x_1}{4\pi} \int \frac{d^3x_2}{4\pi} \frac{e^{-ar_1}}{r_1} \frac{e^{-br_2}}{r_2} \frac{e^{-cr_{12}}}{r_{12}} \frac{e^{-dR}}{R}$$
$$= \frac{1}{(a^2+b^2-2c^2-2d^2)} \ln \frac{(a+b+2c)(a+b+2d)}{2(a+c+d)(b+c+d)}\,. \tag{A.4}$$

To derive this, insert the Laplacian operators into the middle of the integral and let them work both ways. It appears that one could almost deduce these results (A.3) and (A.4) purely by arguments of analyticity and symmetry. Consider, for example, how the integral behaves as $r_1 \to \infty$: by counting powers one sees the nature of the singularity as $(a + c)$, or $(a + c + d)$, goes to zero.

As noted earlier, using this variable R in the He trial wavefunction did not produce good results — as one might expect since it introduces a spurious cusp when the two electrons are on opposite sides of the nucleus. I have, nevertheless, recorded the above information here in case it might be useful to others.

The result (A.4) can be generalized with $R = |\mu\vec{x}_1 + \nu\vec{x}_2|$.

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