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The expansion of hydrogen states in Gaussian orbitals

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Abstract. The convergence properties of Gaussian orbitals are studied by considering a very simple system, the hydrogen atom. We have variationally optimized even-tempered basis sets containing up to 60 s functions for the ground state and the first excited S state of the hydrogen atom, to an accuracy of $10^{-15}E_\mathrm{h}$. In addition, we have freely optimized the exponents in basis sets containing up to 12 Gaussians. We have studied the convergence of the total energy, the kinetic energy, the extent of the atom as measured by r^2, and the Fermi-contact interaction at the nucleus in these basis sets as well as in basis sets augmented with additional diffuse or steep functions.

Keywords: Basis-set convergence – Gaussian orbitals – Gaussian expansions – Even-tempered basis sets – Hydrogen atom

1 Introduction

In most applications of quantum chemistry, the atomic orbitals are expanded in a finite set of Gaussian-type orbitals (GTOs), fixed on the atomic nuclei. The GTOs were introduced by Boys in the 1950s [1], so as to avoid the difficult integrations associated with Slater-type orbitals (STOs) [2]. Since the shape of GTOs is less suited to the description of molecular electronic structure than the shape of STOs, many more GTOs than STOs are needed to achieve the same accuracy in the calculations. This is particularly true for regions close to the atomic nuclei and in the outer-valence region of the molecules. At the nuclei, the GTOs have no cusp, making it difficult to calculate accurately properties that depend on the density in the vicinity of or at the nuclei – for example, hyperfine coupling constants and indirect nuclear spin–spin coupling constants. Far away from the nuclei, in the asymptotic region, the GTOs decay too quickly, making the accurate description of properties such as quadrupole moments and dipole polarizabilities problematic.

Over the years, many standard basis sets of GTOs have been introduced. Indeed, the large number of GTO basis sets developed is in itself an indication of the difficulties associated with their construction and it has turned out to be impossible to develop a single, universal set of GTOs suitable for the calculation of the different properties of molecular systems [3, 4]. Instead, families of basis sets have been proposed, in which the parent basis is extended with special functions, depending on the requirements on the calculations. For example, for the calculation of polarizabilities and spin–spin coupling constants, diffuse and steep functions are added, respectively, according to certain recipes.

The performance of GTO basis sets, with and without additional functions, has been carefully benchmarked by extensive calculations on molecular systems, comparing either with experimental data or in some cases with calculations in which the atomic orbitals are represented numerically on a spatial grid. Detailed studies of the energy convergence of GTOs for several small molecules have also recently been published [5, 6, 7].

In this paper, we investigate the performance of the GTOs on the simplest of all systems: the hydrogen atom. The obvious advantage of this system is that the exact solutions are known, making it particularly easy to measure the quality of the calculations. Although properties related to chemical bonding and to the polarization of the atomic charge in a molecular system cannot be studied in this manner, the hydrogen atom nevertheless offers us a unique opportunity to study the GTO description of many one-electron properties, such as the density at the nucleus and in the outer-valence region. In addition, the convergence of GTOs in the hydrogen system has previously been studied theoretically [8].

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2 Computational details

All calculations were carried out using Mathematica, which allows the use of arbitrary precision in the calculations. To achieve the necessary precision in our results, the calculations – in particular, the diagonalizations – were carried out using 70-digit precision.

3 Basis-set optimization

In our calculations, we determined the exponents α_i of the GTOs

$$G_i(\mathbf{r}) = \exp\left(-\alpha_i r^2\right) \tag{1}$$

by energy minimization. The minimization was carried out in two different manners. In the even-tempered basis sets [9, 10], the exponents form a geometrical series

$$\alpha_i = \alpha\beta^{i-1} \qquad i = 1, 2, \ldots, N , \tag{2}$$

with $N \leq 60$. In addition, we constructed fully optimized basis sets, where all exponents $\alpha_1, \alpha_2, \ldots \alpha_N$ were optimized independently.

The two-dimensional optimization of the even-tempered basis sets is a rather simple task – in particular, for the electronic ground state, for which multiple solutions were observed only in a few cases. The values of α and β as functions of the number of basis functions, N, optimized for the ground state are plotted on a logarithmic scale in Fig. 1. By contrast, for the first excited state, the number of local minima appears to be proportional to the number of atomic orbitals (AOs) N, making the optimization of the basis set more difficult than for the ground-state – see Fig. 2, where the value of α at the different local minima is plotted. With two exceptions, the global minimum corresponds to the solution with the largest value of α.

The full optimization of basis sets with no constraints on the exponents is more difficult than the optimization of even-tempered basis sets, at least for basis sets containing more than ten AOs. The problems arise chiefly because it is difficult to provide a good starting point for the optimization. For small N, we used the exponents of the even-tempered basis sets as our starting guess; for large N, it became necessary to determine the initial exponents by extrapolation from the smaller, fully optimized sets. Combined with the large number of conjugate-gradient iterations needed for convergence, these problems restricted the size of the fully optimized basis sets to 12 for all states. The exponents of the fully optimized basis sets are plotted for the ground state in Fig. 3 together with the exponents of the corresponding even-tempered basis sets. A similar plot for the exponents of both basis sets optimized for the first excited state can be found in Fig. 4.

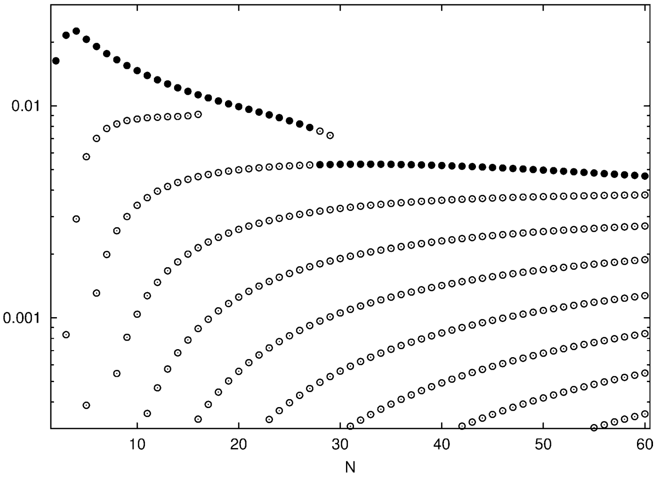

Fig. 2. Logarithmic plot of α as a function of N, optimized for the first excited state. Only solutions where $\alpha > 3.0 \times 10^{-4}$ are shown. The *solid circles* represent the minima having the lowest energy for each value of N

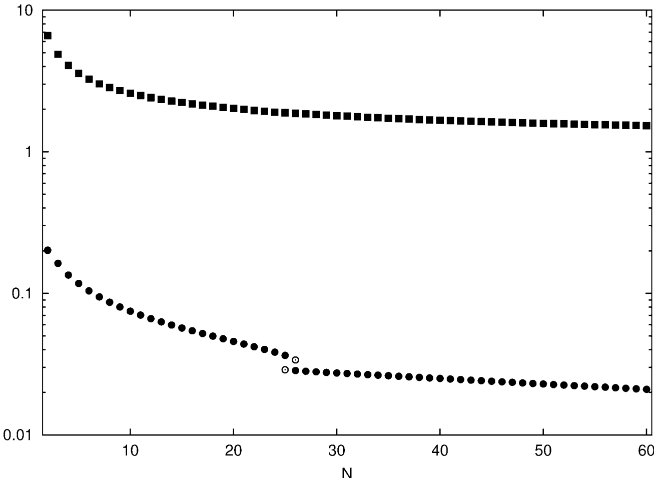

Fig. 1. Logarithmic plot of α (*circles*) and β (*squares*) optimized for the ground state, as a function of N. The solid circles and squares represent the minima having the lowest energy for each value of N

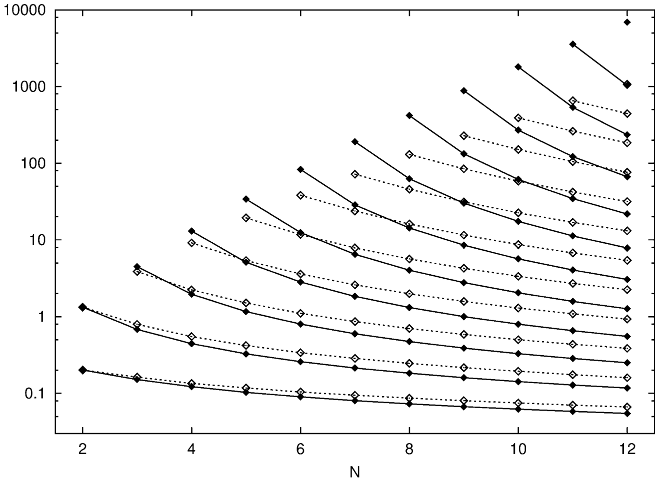

Fig. 3. Comparison of the exponents of the even-tempered basis set (*open diamonds*) and the fully optimized basis set (*solid diamonds*) for the ground state up to $N = 12$. Note the logarithmic scale

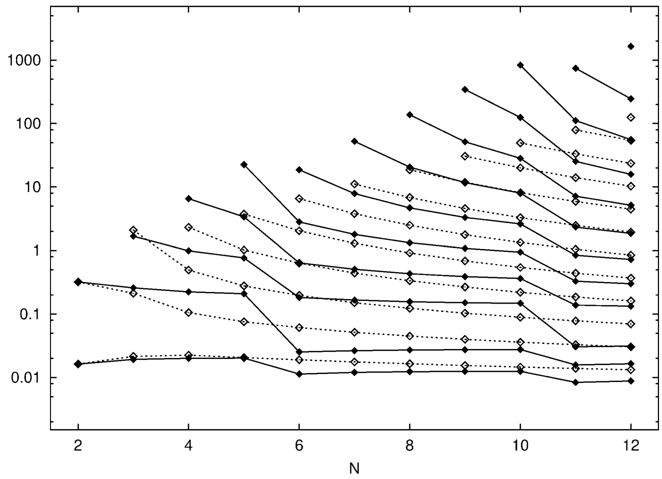

Fig. 4. Comparison of the exponents of the even-tempered basis set (*open diamonds*) and the fully optimized basis set (*solid diamonds*) for the first excited state up to $N = 12$. Note the logarithmic scale

Table 1. Total energy (in units of E_h) along with values of α and β optimized for the ground state

N	Energy	α	β
2	−0.4858127166162751	0.2015	6.6119
3	−0.4958428146670139	0.1630	4.8807
4	−0.4987518973453031	0.1348	4.0742
5	−0.4995626726176849	0.1176	3.5822
6	−0.4998405424527974	0.1042	3.2577
7	−0.4999371721008941	0.0945	3.0214
8	−0.4999742933524680	0.0865	2.8437
9	−0.4999889793017220	0.0802	2.7026
10	−0.4999951119087391	0.0748	2.5888
20	−0.4999999923812162	0.0458	2.0211
30	−0.4999999999458578	0.0274	1.7989
40	−0.4999999999993552	0.0250	1.6703
50	−0.4999999999999871	0.0229	1.5873
60	−0.4999999999999996	0.0210	1.5290

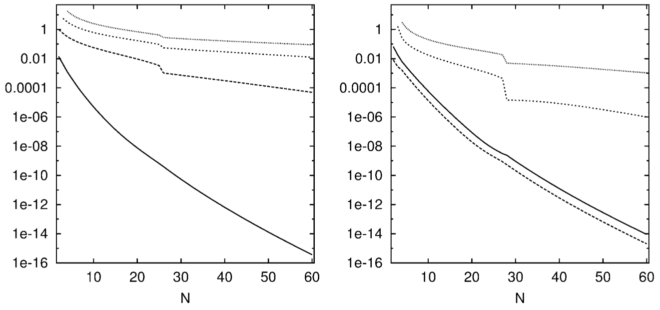

Fig. 5. The logarithm of the absolute error in the total energy (in units of E_h) as a function of N for the ground state (*solid line*) and the first three excited states using basis sets optimized for the ground state (*left plot*) and for the first excited state (*right plot*)

The two-parameter even-tempered basis sets and the N-parameter fully optimized sets constitute two extremes of basis-set parameterization. There are obviously other choices, for example, the four-parameter well-tempered basis sets of Huzinaga and coworkers [11, 12]. Also, Petersson et al. [13] very recently presented a generalized parameterization, containing the even-tempered and fully optimized basis sets as special cases. Nevertheless, in the present study, only even-tempered and fully optimized sets of exponents are considered.

4 Ground-state optimized basis sets

4.1 Even-tempered basis sets

4.1.1 The structure of the basis sets

The total electronic energy and the values of α and β for a selected number of basis functions are listed in Table 1. The results are in complete agreement with the total energies and the even-tempered parameters for the hydrogen atom up to $N = 10$ reported by Schmidt and Ruedenberg [10]. As expected, the values of α and β decrease with increasing N – see also Fig. 1. The decrease is most pronounced for small N; for large N, the plots approach straight lines, indicating that α and β decrease exponentially in N or in some power of N. We note, however, a discontinuity in the plots between $N = 25$ and $N = 26$. For these values of N, there are in fact two independent minima in the energy as a function of α and β; by contrast, for all other N, the energy function has only one minimum, as we have verified by inspection of two-dimensional energy plots. Although, therefore, the optimization of α and β is mostly a straightforward process for the electronic ground state, multiple minima may occur for certain N, making the optimization somewhat more difficult.

4.1.2 The total energy

The total energy of the hydrogen atom is given by $-\frac{1}{2}n^{-2}E_h$, where n is the principal quantum number. The error in the ground-state energy and the energies of the three lowest excited states on a logarithmic scale are plotted in Fig. 5 as functions of N. For the ground state, the energy decreases as discussed by Kutzelnigg and coworkers – namely, exponentially in $\sqrt{N}$. For $N = 10$, which corresponds to the number of uncontracted GTOs in a large molecular basis set such as the correlation-consistent sextuple-zeta basis cc-pV6Z of Dunning [14], the error in the ground state is $2.2 \times 10^{-6}E_h$ – see Table 2. In the largest basis with $N = 60$, the ground-state error is less than $10^{-15}E_h$. By contrast, the errors are much larger for the excited states: 4.9×10^{-5} and $1.3 \times 10^{-2}E_h$. As in the plots of α and β, we note a discontinuity from $N = 25$ to $N = 26$, which is particularly noticeable for the excited states. Clearly, a basis set energetically optimized for the ground state is ill suited to describe excited states.

Let us now see how the description of excited states can be improved by augmenting the optimized ground-state basis sets with diffuse functions. The absolute errors in the energy at $N = 10$ and $N = 60$ for the three lowest states, with up to four additional diffuse or steep functions, are listed in Table 2. Their exponents were

Table 2. The absolute error in the energy (in units of E_h), $\langle r^2 \rangle$ (a_0^2) and Fermi-contact (FC) interaction ($\alpha^2 E_\mathrm{h}$) for the ground state and the first two excited states for $N = 10$ and $N = 60$. The even-tempered basis sets (ET10 and ET60) for the ground state were augmented with up to four additional diffuse functions and up to four additional steep functions

Basis	Ground state			1st excited state			2nd excited state		
	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC
ET10	4.9×10^{-6}	3.9×10^{-4}	4.1×10^{-2}	5.7×10^{-2}	2.5×10^{1}	2.6×10^{-1}	6.2×10^{-1}	2.0×10^{2}	1.3×10^{0}
1 dif.	4.9×10^{-6}	6.0×10^{-4}	4.1×10^{-2}	2.0×10^{-3}	7.2×10^{0}	1.4×10^{-2}	1.1×10^{-1}	1.7×10^{2}	3.5×10^{-1}
2 dif.	4.5×10^{-6}	4.2×10^{-4}	4.1×10^{-2}	1.6×10^{-5}	1.9×10^{-1}	5.0×10^{-3}	7.2×10^{-3}	8.8×10^{1}	4.1×10^{-2}
3 dif.	4.4×10^{-6}	3.9×10^{-4}	4.1×10^{-2}	8.0×10^{-6}	5.2×10^{-2}	5.0×10^{-3}	1.0×10^{-4}	8.2×10^{0}	1.6×10^{-3}
4 dif.	4.4×10^{-6}	3.9×10^{-4}	4.1×10^{-2}	6.2×10^{-6}	3.8×10^{-2}	5.0×10^{-3}	7.3×10^{-5}	3.8×10^{0}	1.4×10^{-3}
1 stp.	2.8×10^{-6}	3.8×10^{-4}	2.5×10^{-2}	5.7×10^{-2}	2.5×10^{1}	2.6×10^{-1}	6.2×10^{-1}	2.0×10^{2}	1.4×10^{0}
2 stp.	2.3×10^{-6}	3.7×10^{-4}	1.6×10^{-2}	5.7×10^{-2}	2.5×10^{1}	2.7×10^{-1}	6.2×10^{-1}	2.0×10^{2}	1.4×10^{0}
3 stp.	2.2×10^{-6}	3.7×10^{-4}	9.7×10^{-3}	5.7×10^{-2}	2.5×10^{1}	2.7×10^{-1}	6.2×10^{-1}	2.0×10^{2}	1.4×10^{0}
4 stp.	2.2×10^{-6}	3.7×10^{-4}	6.0×10^{-3}	5.7×10^{-2}	2.5×10^{1}	2.7×10^{-1}	6.2×10^{-1}	2.0×10^{2}	1.4×10^{0}
ET60	3.6×10^{-16}	2.3×10^{-13}	1.7×10^{-5}	4.9×10^{-5}	5.1×10^{-1}	6.6×10^{-4}	1.3×10^{-2}	9.5×10^{1}	4.9×10^{-2}
1 dif.	3.6×10^{-16}	2.5×10^{-13}	1.7×10^{-5}	1.0×10^{-6}	2.7×10^{-2}	1.8×10^{-5}	2.9×10^{-3}	5.1×10^{1}	1.6×10^{-2}
2 dif.	3.4×10^{-16}	1.4×10^{-13}	1.7×10^{-5}	3.0×10^{-9}	2.3×10^{-4}	2.0×10^{-6}	3.6×10^{-4}	1.6×10^{1}	2.8×10^{-3}
3 dif.	3.3×10^{-16}	9.2×10^{-14}	1.7×10^{-5}	3.1×10^{-13}	7.7×10^{-8}	2.1×10^{-6}	1.5×10^{-5}	1.8×10^{0}	1.8×10^{-4}
4 dif.	3.3×10^{-16}	7.2×10^{-14}	1.7×10^{-5}	4.7×10^{-15}	2.3×10^{-10}	2.1×10^{-6}	8.5×10^{-8}	3.2×10^{-2}	9.8×10^{-7}
1 stp.	2.7×10^{-16}	2.3×10^{-13}	1.3×10^{-5}	4.9×10^{-5}	5.1×10^{-1}	6.6×10^{-4}	1.3×10^{-2}	9.5×10^{1}	4.9×10^{-2}
2 stp.	2.2×10^{-16}	2.3×10^{-13}	1.1×10^{-5}	4.9×10^{-5}	5.1×10^{-1}	6.6×10^{-4}	1.3×10^{-2}	9.5×10^{1}	4.9×10^{-2}
3 stp.	2.0×10^{-16}	2.3×10^{-13}	8.8×10^{-6}	4.9×10^{-5}	5.1×10^{-1}	6.6×10^{-4}	1.3×10^{-2}	9.5×10^{1}	4.9×10^{-2}
4 stp.	1.8×10^{-16}	2.3×10^{-13}	7.1×10^{-6}	4.9×10^{-5}	5.1×10^{-1}	6.6×10^{-4}	1.3×10^{-2}	9.5×10^{1}	4.9×10^{-2}

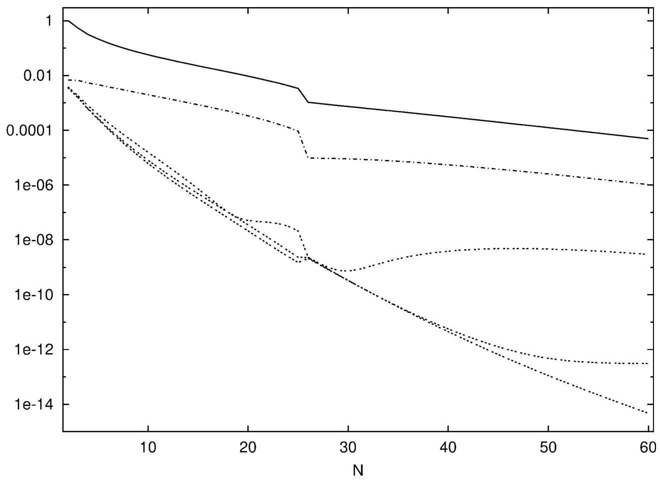

Fig. 6. The logarithm of the error in the total energy (E_h) of the first excited state, using the basis sets optimized for the ground state (*solid line*) and augmented with up to four additional diffuse functions (*dashed lines*)

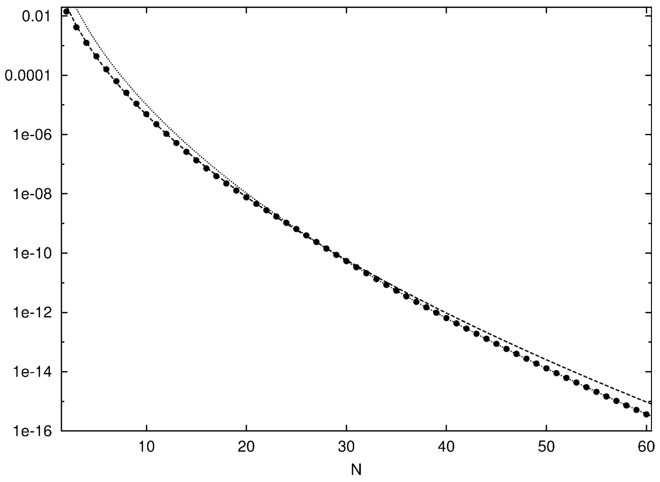

Fig. 7. The logarithm of the error in the total energy (E_h) for the ground state and functions of the form $a \exp\left(-b\sqrt{N}\right)$ fitted to $N \leq 25$ (*dashed line*) and to $N \geq 26$ (*dotted line*)

chosen as an even-tempered extension to those in the original, even-tempered basis sets.

While the augmentation with diffuse functions has very little effect on the ground state, the improvement is significant for the excited states. Still, even with four diffuse functions added, the second excited state is only moderately well described; for higher excited states (not included in the table) the description is still poor. We have also investigated the effect of augmenting the basis sets with steep functions in an even-tempered manner. Unlike for the diffuse augmentation, the addition of steep functions has virtually no effect on the excited-state energies. For the ground state, there is a slight improvement for $N = 10$ and $N = 60$ in Table 2, the error being reduced by a factor of about 2 upon addition of four steep functions.

The error in the energy for the first excited state as a function of N, for basis sets augmented with up to four diffuse functions, is plotted in Fig. 6. This plot clearly illustrates the importance of diffuse functions for the description of excited states. The addition of a single diffuse function reduces the error by more than an order of magnitude – a reduction which otherwise would require a large extension of the basis set. Another observation we make from this plot (in particular, with two diffuse functions added) is that the error in the energy of the first excited state does not always decrease with increasing N. This is of course not surprising in the sense that this basis has not been variationally determined with respect to the first excited state. Still, this behaviour should be kept in mind when excited-state calculations are carried out with ground-state optimized basis sets.

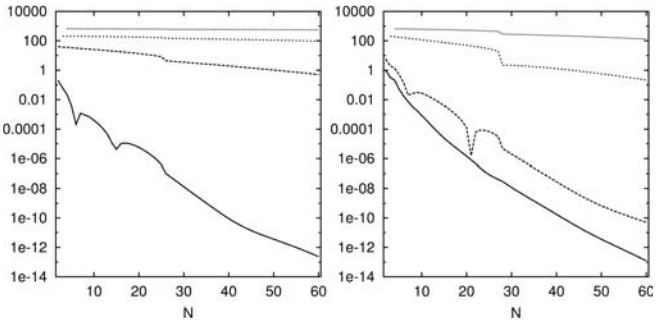

Fig. 8. The logarithm of the absolute error in $\langle r^2 \rangle$ (a_0^2) as a function of N for the ground state (*solid line*) and the first three excited states using basis sets optimized for the ground state (*left plot*) and for the first excited state (*right plot*)

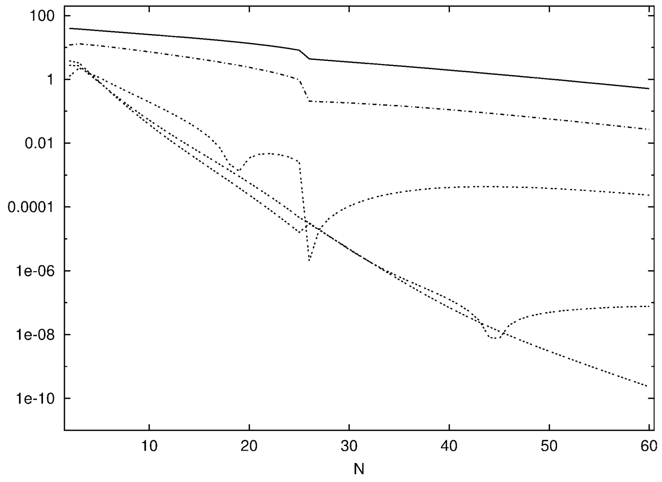

Fig. 9. The logarithm of the absolute error in $\langle r^2 \rangle$ (a_0^2) for the first excited state, using the basis sets optimized for the ground state (*solid line*) and augmented with up to four additional diffuse functions (*dashed lines*)

Kutzelnigg has previously shown that, for an optimized even-tempered basis, the error in the energy of the hydrogen atom is given by $a\exp(-b\sqrt{N})$ [8, 15], where a and b are positive real parameters and N the number of GTOs. If such a functional form is fitted to our data in the full range $3 \le N \le 60$ ($N = 2$ is left out), a reasonably good fit is obtained with $a = 41.4 \pm 3.1 E_\mathrm{h}$ and $b = 5.035 \pm 0.014$. However, the fitted curve systematically overestimates the errors for small and large N and likewise underestimates them for intermediate values. Recalling the kinks in the optimized α and β parameters in Fig. 1 and in the corresponding energies in Fig. 5, a near-perfect agreement is obtained by carrying out two separate fits, one for $3 \le N \le 25$ and one for $26 \le N \le 60$ – see Fig. 7. For $N \le 25$, the fitted parameters are $a = 22.1 \pm 1.3 E_\mathrm{h}$ and $b = 4.866 \pm 0.016$; for $N \ge 26$, we obtain $a = 160.5 \pm 2.0 E_\mathrm{h}$ and $b = 5.242 \pm 0.002$. In short, our calculations are in complete agreement with the asymptotic form derived by Kutzelnigg, although, somewhat unexpectedly, a single set of parameters cannot be used universally, for all N. For $N \le 60$, there are two separate sequences of even-tempered ground-state basis sets; for $N > 60$, more such sequences may exist.

4.1.3 The kinetic energy

For the variationally optimized even-tempered basis sets, the conditions for the virial theorem are satisfied. The error in the kinetic energy is therefore identical to the error in the total energy (but of opposite sign). However, upon augmentation, these conditions no longer hold; consequently, the error in the kinetic energy becomes larger than the error in the total energy, typically by a factor of 3. For the excited states, the difference between the errors in the total and kinetic energies is even larger, by up to 2 orders of magnitude. Nevertheless, the convergence pattern of the kinetic energy is similar to that of the total energy.

4.1.4 The expectation value of r^2

Rapid convergence of the energy does not in any way guarantee the convergence of other properties. In fact, it has been shown that it is possible to construct wave functions arbitrarily close to the exact wave function, whose errors in a given property are arbitrarily large [16].

We first turn our attention to the expectation value of r^2, which represents a measure of the size of the hydrogen atom. For S states (which we consider here), the exact result for the hydrogen atom is $\frac{5}{2}n^4 + \frac{1}{2}n^2$ in units of a_0^2. Clearly, the excited states rapidly become very diffuse.

The absolute value of the error in $\langle r^2 \rangle$ is plotted in Fig. 8. For the ground state, the error in $\langle r^2 \rangle$ displays oscillations, whose nodes can be seen as kinks in the plotted absolute errors. However, the overall convergence is rapid, with an error typically 2 orders of magnitude larger than that in the total energy. By contrast, the description of $\langle r^2 \rangle$ is much poorer for the excited states – see Table 2. Even for $N = 60$, the errors for the first and second excited states are $0.5a_0^2$ and $95a_0^2$, respectively, compared with $2.3 \times 10^{-13} a_0^2$ for the ground state.

For the excited states, it is impossible to converge $\langle r^2 \rangle$ without the addition of diffuse functions. The error in $\langle r^2 \rangle$ for the first excited state, with up to four diffuse functions added, is plotted in Fig. 9. Clearly, the convergence is unsatisfactory for basis sets with less than two diffuse functions added; with four diffuse functions, convergence is smooth, with an error of $2.3 \times 10^{-10} a_0^2$ for $N = 60$. For the second and third excited states, even four diffuse functions are insufficient.

4.1.5 The Fermi-contact interaction

The Fermi-contact interaction, which for exact S states is given by $\frac{4}{3}n^{-3}\alpha^2 E_\mathrm{h}$, where α is the fine-structure constant, is very difficult to describe accurately. For the ground state, the even-tempered basis with $N = 10$ gives an error of $4.1 \times 10^{-2} \alpha^2 E_\mathrm{h}$ – see Table 2. Even our best calculation, with $N = 60$ and four steep functions added, gives an error of $7.1 \times 10^{-6} \alpha^2 E_\mathrm{h}$. Interestingly, this error is larger than the error of $9.8 \times 10^{-7} \alpha^2 E_\mathrm{h}$ in the Fermi-contact interaction in the second excited state, obtained

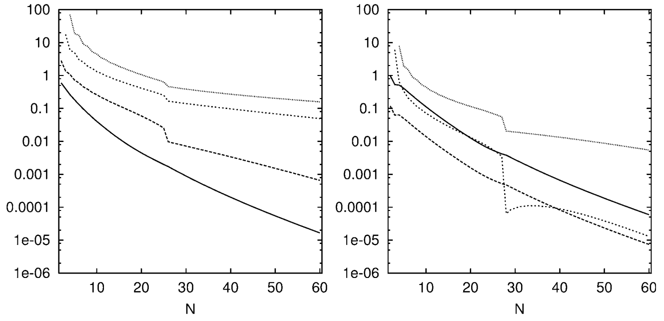

Fig. 10. The logarithm of the absolute error of the FC interaction ($\alpha^2 E_\mathrm{h}$) as a function of N for the ground state (*solid line*) and the first three excited states using basis sets optimized for the ground state (*left plot*) and for the first excited state (*right plot*)

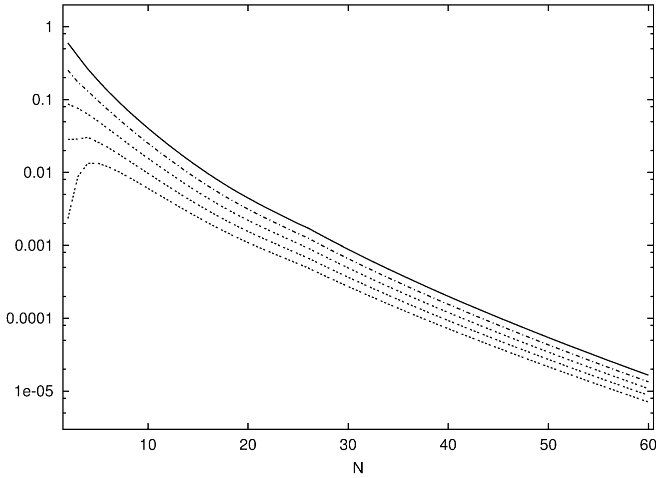

Fig. 11. The logarithm of the absolute error of the FC ($\alpha^2 E_\mathrm{h}$) as a function of N for the ground state using an even-tempered basis set (*solid line*) and even-tempered basis sets with up to four steep functions added

using the basis set with $N = 60$, but augmented with four diffuse rather than steep functions. If only steep functions are added, the Fermi-contact interaction of the excited states is poorly described. Clearly, there is no point in augmenting with steep functions unless the overall description of the electronic state is reasonably good. The logarithm of the absolute error in the calculated Fermi-contact interaction for the (unaugmented) even-tempered basis sets is plotted in Fig. 10. Comparing with Figs. 5 and 8, we note the much slower convergence of the Fermi-contact interaction – in particular, for the ground state.

To illustrate the effect of core functions on the Fermi-contact interaction of the ground state, the absolute error obtained for even-tempered basis sets with up to four additional steep functions is plotted in Fig. 11. For small basis sets, there is a significant but somewhat unsystematic improvement in the calculated Fermi-contact interaction with the addition of steep functions. However, to achieve small errors, the size of the underlying even-tempered basis set is more important than the addition of steep functions.

Table 3. The total energy (E_h) and the lowest and the highest exponents of fully optimized basis sets for the ground state

N	Energy	α_1	α_n
2	−0.4858127166162751	0.2015	1.3325
3	−0.4969792527050514	0.1514	4.5004
4	−0.4992784057143474	0.1219	13.0107
5	−0.4998098322318887	0.1031	34.0613
6	−0.4999455703966486	0.0900	82.9218
7	−0.4999832977891566	0.0803	190.6878
8	−0.4999945613907438	0.0729	418.5580
9	−0.4999981360379370	0.0670	883.5055
10	−0.4999993319768574	0.0621	1803.4949
11	−0.4999997509651780	0.0581	3575.6745
12	−0.4999999038468845	0.0547	6909.3748

4.2 Fully optimized basis

4.2.1 The structure of the basis set and the total energy

The energy and the lowest and highest orbital exponents for the fully optimized ground-state basis sets are listed in Table 3; for plots of the exponents, see Fig. 3. Comparing the fully optimized exponents with the corresponding even-tempered exponents (located on the same vertical line in the figure), we note that the largest exponents of the fully optimized basis are larger than the largest exponents of the ground-state even-tempered basis. Conversely, we also see that the smallest exponents of the fully optimized basis are smaller than the smallest exponents of the even-tempered basis. In short, for a given N, there is a larger spread of exponents in the fully optimized basis than in the even-tempered one. Intuitively, we can understand this by realizing that a full optimization of all exponents enables each exponent to do a better job at representing the electronic state in a given region, allowing the nearby exponents to move into regions further away. We note, however, that the separation between the exponents increases only in the core region (i.e., for large exponents) – in the valence region, it decreases slightly.

To illustrate this behaviour, we consider the exponents of the basis sets with $N = 5$. In the even-tempered case, the exponents are given by 0.118, 0.421, 1.509, 5.406, and 19.365. By comparison, the corresponding fully optimized exponents are 0.103, 0.327, 1.165, 5.124, and 34.061. The largest exponent of the fully optimized basis (34.061) is almost twice as large as the largest exponent of the even-tempered basis – in fact, it is comparable to the largest exponent of the even-tempered $N = 6$ basis (38.232). Likewise, the smallest exponent of the fully optimized $N = 5$ basis (0.103) is smaller than the smallest exponent of the even-tempered $N = 6$ basis (0.104).

By construction, a fully-optimized basis gives a lower total energy than the corresponding even-tempered basis. The improvement in the energy is illustrated in Fig. 12, where, for the two types of basis sets, the errors in the total energy, in $\langle r^2 \rangle$, and in the Fermi-contact interaction are plotted as functions of N. Obviously, for $N = 2$, the error in the energy is identical for the even-tempered and fully optimized basis sets. As N increases, the error decreases more rapidly for the fully optimized

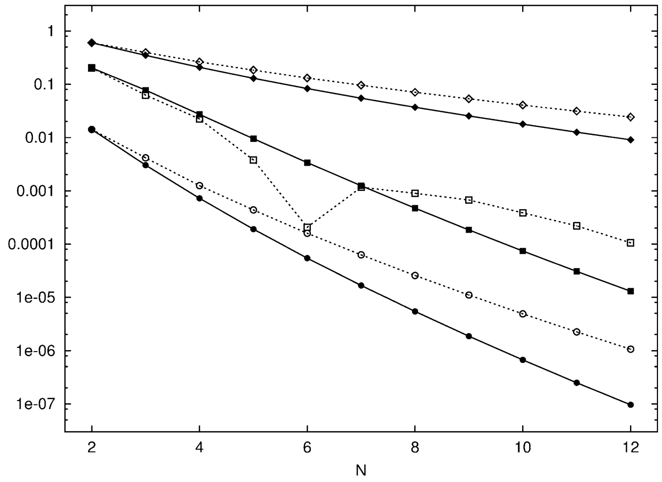

Fig. 12. The logarithm of the absolute errors of the total energy (E_{h}, *circles*), the expectation value of r^2 (a_0^2, *squares*), and the FC interaction ($\alpha^2 E_{\mathrm{h}}$, *diamonds*) for even-tempered (*open symbols*, *dashed line*) and fully optimized (*filled symbols*, *solid line*) as functions of the number of exponents, optimized for the ground state

basis sets than for the even-tempered sets – for example, whereas, for $N = 5$, there is factor of 2 between the errors; for $N = 10$, the difference is about an order of magnitude. We also note that, in the fully optimized case, the error is reduced by a factor of 4.7 from $N = 2$ to $N = 3$; from $N = 11$ to $N = 12$, the factor is 2.6. For the even-tempered basis; the corresponding factors are 3.4 and 2.1, respectively. In short, with increasing N, the performance of the fully optimized basis set improves relative to that of the even-tempered basis set. This behaviour may be understood from the observation that, in the even-tempered basis, the α and β parameters are effectively determined by the optimization of the mid-range exponents, whose contribution to the energy is largest. By contrast, in the fully optimized basis set, each added exponent provides a new degree of freedom, further reducing the energy relative to that of the corresponding even-tempered basis.

The effect of adding diffuse and steep functions to the fully optimized basis sets with $N = 10$ is illustrated in Table 4. While little improvement is observed for the (already well-described) ground-state energy, there is a clear improvement in the energy of the first excited state upon the addition of diffuse functions. As in the even-tempered case, two diffuse functions must be added for an error similar to that of the ground state. Additional diffuse functions give only a marginal improvement in the description.

In our discussion of even-tempered basis sets in Sect. 4.1.2, we found that the errors in the ground-state energies are well represented by two fits of the general form $a\exp(-b\sqrt{N})$, as derived by Kutzelnigg. For basis sets optimized using more than two parameters, Kutzelnigg suggested the slightly more general form $a\exp(-bN^c)$ [8], where, for faster than even-tempered convergence, $\frac{1}{2} < c < 1$. Fitting this functional form to the errors of the fully optimized ground-state basis sets (again leaving out $N = 2$) in Fig. 12, we obtain excellent agreement with $a = 3.5 \pm 0.3E_{\mathrm{h}}$, $b = 3.44 \pm 0.06$, and $c = 0.653 \pm 0.005$. With this form, we predict that 20 and 37 fully optimized GTOs are needed for errors less than 10^{-10} and 10^{-15} E_{h}, respectively, compared with 28 and 58 even-tempered GTOs.

4.2.2 The expectation value of r^2 and the Fermi-contact interaction

Full optimization of the exponents improves not only the energy, but also other properties, such as $\langle r^2 \rangle$ and the Fermi-contact interaction. From Fig. 12, we note that, for the Fermi-contact interaction, the improvement upon full optimization is very systematic but less pronounced than for the energy. For $\langle r^2 \rangle$, the convergence is oscillatory for the even-tempered basis sets, giving accidentally low errors for certain N; the fully optimized basis sets, on the other hand, give a very smooth convergence of the error in $\langle r^2 \rangle$, which, for $N = 12$, is an order of magnitude smaller than the error obtained with the even-tempered basis.

From Table 4, we see that augmentation with diffuse functions improves the description of $\langle r^2 \rangle$ in the same manner as for the energy. Thus, whereas the improvements are modest for the ground state, the augmentation is critical for the first excited state, for which the error is reduced by almost 5 orders of magnitude upon the addition of two diffuse functions. For the second excited state, the error in $\langle r^2 \rangle$ is very large, even with four diffuse functions added.

Table 4. The absolute error in the energy (E_{h}), $\langle r^2 \rangle$ (a_0^2), and FC interaction ($\alpha^2 E_{\mathrm{h}}$) for the ground state and the first two excited states for $N = 10$. The fully optimized basis set (FO10) for the ground state is augmented with up to four additional diffuse functions and up to four additional steep functions

Basis	Ground state			1st excited state			2nd excited state		
	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC
FO10	6.7×10^{-7}	7.4×10^{-5}	1.8×10^{-2}	3.1×10^{-2}	2.1×10^{1}	1.5×10^{-1}	3.8×10^{-1}	1.9×10^{2}	8.4×10^{-1}
1 dif.	6.6×10^{-7}	4.9×10^{-5}	1.8×10^{-2}	1.3×10^{-3}	5.5×10^{0}	1.0×10^{-2}	7.9×10^{-2}	1.6×10^{2}	2.5×10^{-1}
2 dif.	6.3×10^{-7}	2.8×10^{-5}	1.8×10^{-2}	1.5×10^{-6}	4.5×10^{-2}	2.2×10^{-3}	7.0×10^{-3}	8.5×10^{1}	3.8×10^{-2}
3 dif.	6.3×10^{-7}	2.3×10^{-5}	1.8×10^{-2}	1.0×10^{-6}	1.0×10^{-2}	2.2×10^{-3}	1.2×10^{-5}	1.5×10^{0}	5.0×10^{-4}
4 dif.	6.2×10^{-7}	2.2×10^{-5}	1.8×10^{-2}	7.2×10^{-7}	5.9×10^{-3}	2.2×10^{-3}	7.6×10^{-6}	5.4×10^{-1}	6.8×10^{-4}
1 stp.	4.9×10^{-7}	7.6×10^{-5}	7.5×10^{-3}	3.1×10^{-2}	2.1×10^{1}	1.6×10^{-1}	3.8×10^{-1}	1.9×10^{2}	8.6×10^{-1}
2 stp.	4.8×10^{-7}	7.6×10^{-5}	2.8×10^{-3}	3.1×10^{-2}	2.1×10^{1}	1.6×10^{-1}	3.8×10^{-1}	1.9×10^{2}	8.6×10^{-1}
3 stp.	4.8×10^{-7}	7.6×10^{-5}	1.2×10^{-3}	3.1×10^{-2}	2.1×10^{1}	1.6×10^{-1}	3.8×10^{-1}	1.9×10^{2}	8.6×10^{-1}
4 stp.	4.8×10^{-7}	7.6×10^{-5}	5.2×10^{-4}	3.1×10^{-2}	2.1×10^{1}	1.6×10^{-1}	3.8×10^{-1}	1.9×10^{2}	8.6×10^{-1}

Table 5. Total energy (E_h) of the first excited state along with the values of α and β optimized for this state

N	Energy	α	β
2	−0.1168331639545620	0.01630	19.6916
3	−0.1221697382095309	0.02154	9.8583
4	−0.1233742263444045	0.02254	4.6854
5	−0.1243337330016185	0.02061	3.6698
6	−0.1246988390439473	0.01907	3.2163
7	−0.1248697651590596	0.01763	2.9285
8	−0.1249396870277564	0.01650	2.7302
9	−0.1249722590214700	0.01549	2.5821
10	−0.1249866995087120	0.01466	2.4668
20	−0.1249999805704430	0.00991	1.9606
30	−0.1249999997907418	0.00529	1.7578
40	−0.1249999999971520	0.00523	1.6345
50	−0.1249999999999351	0.00497	1.5563
60	−0.1249999999999980	0.00466	1.5014

With regard to the Fermi-contact interaction, we first note that, in the ground state, the addition of steep functions has roughly the same effect on the error as observed for $\langle r^2 \rangle$ upon the addition of diffuse functions. As in the even-tempered case, the addition of steep functions does not improve the description of the Fermi-contact interaction in the first-excited state; in this case, it is more important to add diffuse functions, so as to improve the overall description of the excited state.

5 Excited-state optimized basis sets

5.1 Even-tempered basis

5.1.1 The structure of the basis set and the total energy

The total energies as well as the α and β parameters optimized for the first excited state are given in Table 5. We recall from Fig. 2 that, for the excited-state energy, the number of local minima with respect to variations in α and β increases linearly with N, the number of AOs in the basis. The solutions given in Table 5 correspond to the global minimum for each N.

Comparing the even-tempered basis sets for the ground and excited states in Tables 1 and 5, we first note that α is much smaller in the excited-state basis. In fact, for small N, the difference between the smallest exponents is about an order of magnitude, explaining why it was necessary to add at least two sets of diffuse functions to the ground-state basis to obtain a reasonable description of the lowest excited state. We also note that, initially, the value of α increases with N, achieving a maximum value of 0.023 for $N = 4$. For $N > 4$, α decreases monotonically but there is a dramatic jump in α between $N = 27$ and $N = 28$ – see Fig. 2. For $N \leq 3$, the β parameter is very large compared with the ground-state basis sets; however, for $N \geq 6$, it becomes smaller than in the ground state, although the difference is small.

The absolute errors in the energy, in $\langle r^2 \rangle$, and in the Fermi-contact interaction for the even-tempered basis sets with $N = 10$ and $N = 60$ are listed in Table 6. The first thing to note is that, although these basis sets have been optimized for the first excited state, the errors in the ground-state energy are not much larger than those in the excited-state energy. In fact, with four steep functions added, the error for the ground state is smaller than the corresponding error for the first excited state.

It is instructive to compare the errors in the energies obtained using the excited-state optimized basis sets in Table 6 with the corresponding errors obtained using the ground-state optimized basis sets in Table 2. Whereas the ground-state optimized basis sets only give a good description of the ground state ($N = 60$ gives errors 3.6×10^{-16}, 4.9×10^{-5}, and $1.3 \times 10^{-2} E_h$ for the

Table 6. The absolute error in the energy (E_h), $\langle r^2 \rangle$ (a_0^2) and FC interaction ($\alpha^2 E_h$) for the ground state and the first two excited states for $N = 10$ and $N = 60$. The even-tempered basis sets (ET10 and ET60) for the first excited state are augmented with up to four additional diffuse functions and up to four additional steep functions

Basis	Ground state			1st excited state			2nd excited state		
	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC
ET10	5.9×10^{-5}	8.2×10^{-4}	1.1×10^{-1}	1.3×10^{-5}	2.8×10^{-2}	1.4×10^{-2}	1.8×10^{-2}	1.2×10^{2}	7.1×10^{-2}
1 dif.	5.9×10^{-5}	8.0×10^{-4}	1.1×10^{-1}	1.3×10^{-5}	5.7×10^{-2}	1.4×10^{-2}	7.8×10^{-5}	8.8×10^{0}	3.1×10^{-3}
2 dif.	5.9×10^{-5}	8.0×10^{-4}	1.1×10^{-1}	1.2×10^{-5}	4.3×10^{-2}	1.4×10^{-2}	1.4×10^{-5}	5.3×10^{-1}	4.3×10^{-3}
3 dif.	5.9×10^{-5}	8.1×10^{-4}	1.1×10^{-1}	1.2×10^{-5}	4.0×10^{-2}	1.4×10^{-2}	1.4×10^{-5}	5.5×10^{-1}	4.3×10^{-3}
4 dif.	5.9×10^{-5}	8.1×10^{-4}	1.1×10^{-1}	1.2×10^{-5}	4.0×10^{-2}	1.4×10^{-2}	1.4×10^{-5}	5.4×10^{-1}	4.3×10^{-3}
1 stp.	1.6×10^{-5}	3.8×10^{-4}	7.2×10^{-2}	7.9×10^{-6}	2.3×10^{-2}	8.9×10^{-3}	1.8×10^{-2}	1.2×10^{2}	7.7×10^{-2}
2 stp.	4.8×10^{-6}	2.5×10^{-4}	4.6×10^{-2}	6.5×10^{-6}	2.2×10^{-2}	5.7×10^{-3}	1.8×10^{-2}	1.2×10^{2}	7.8×10^{-2}
3 stp.	1.9×10^{-6}	2.2×10^{-4}	2.9×10^{-2}	6.1×10^{-6}	2.2×10^{-2}	3.6×10^{-3}	1.8×10^{-2}	1.2×10^{2}	8.1×10^{-2}
4 stp.	1.1×10^{-6}	2.1×10^{-4}	1.9×10^{-2}	6.0×10^{-6}	2.2×10^{-2}	2.3×10^{-3}	1.8×10^{-2}	1.2×10^{2}	8.1×10^{-2}
ET60	9.0×10^{-15}	1.2×10^{-13}	5.9×10^{-5}	2.0×10^{-15}	5.0×10^{-11}	7.4×10^{-6}	1.0×10^{-6}	2.2×10^{-1}	1.3×10^{-5}
1 dif.	9.0×10^{-15}	1.2×10^{-13}	5.9×10^{-5}	2.0×10^{-15}	4.9×10^{-11}	7.4×10^{-6}	1.6×10^{-9}	1.2×10^{-3}	2.2×10^{-6}
2 dif.	9.0×10^{-15}	1.1×10^{-13}	5.9×10^{-5}	1.8×10^{-15}	3.1×10^{-11}	7.4×10^{-6}	1.3×10^{-13}	1.3×10^{-7}	2.2×10^{-6}
3 dif.	9.0×10^{-15}	1.1×10^{-13}	5.9×10^{-5}	1.6×10^{-15}	2.0×10^{-11}	7.4×10^{-6}	2.4×10^{-14}	5.6×10^{-9}	2.2×10^{-6}
4 dif.	9.0×10^{-15}	1.1×10^{-13}	5.9×10^{-5}	1.5×10^{-15}	1.4×10^{-11}	7.4×10^{-6}	2.4×10^{-14}	5.1×10^{-9}	2.2×10^{-6}
1 stp.	4.9×10^{-15}	7.6×10^{-14}	4.8×10^{-5}	1.5×10^{-15}	4.9×10^{-11}	6.0×10^{-6}	1.0×10^{-6}	2.2×10^{-1}	1.3×10^{-5}
2 stp.	2.7×10^{-15}	5.1×10^{-14}	3.9×10^{-5}	1.2×10^{-15}	4.9×10^{-11}	4.9×10^{-6}	1.0×10^{-6}	2.2×10^{-1}	1.4×10^{-5}
3 stp.	1.5×10^{-15}	3.8×10^{-14}	3.2×10^{-5}	1.1×10^{-15}	4.9×10^{-11}	4.0×10^{-6}	1.0×10^{-6}	2.2×10^{-1}	1.4×10^{-5}
4 stp.	8.0×10^{-16}	3.1×10^{-14}	2.6×10^{-5}	1.0×10^{-15}	4.9×10^{-11}	3.3×10^{-6}	1.0×10^{-6}	2.2×10^{-1}	1.4×10^{-5}

three lowest states, respectively), the excited-state optimized basis sets describe both the ground state and the first excited state well (errors 9.0×10^{-15}, 2.0×10^{-15}, and $1.0 \times 10^{-6} E_\mathrm{h}$ for $N = 60$). Apparently, an even-tempered basis that has been variationally optimized for a given electronic state also gives a good description of lower states but a poor description of higher states – see Fig. 5, where the errors in the four lowest electronic states as functions of N are plotted, using the basis sets optimized for the ground state (left plot) and for the first excited state (right plot). We emphasize that this holds only for an even-tempered basis – as we shall see, a fully optimized basis is less general, giving a poorer description of all states for which it has not been optimized.

From Table 6, we note that a reasonably accurate description of the second excited state is obtained by adding two diffuse functions to the even-tempered basis optimized for the first-excited state (error 1.3×10^{-13} E_h). Clearly, the resulting basis is a rather flexible one, reproducing the energy of the lowest three states of the hydrogen atom to within $10^{-13} E_\mathrm{h}$.

5.1.2 The expectation value of r^2 and the Fermi-contact interaction

Turning our attention to $\langle r^2 \rangle$, we first note from Table 6 that, with $N = 60$, the error in $\langle r^2 \rangle$ for the ground state ($1.2 \times 10^{-13} a_0^2$) is more than 2 orders of magnitude smaller than the error in $\langle r^2 \rangle$ for the first excited state ($5.0 \times 10^{-11} a_0^2$), even though the basis was variationally optimized for the first excited state. In fact, the ground-state error in $\langle r^2 \rangle$ obtained with the excited-state basis is even smaller than the error obtained using the ground-state optimized basis ($2.3 \times 10^{-13} a_0^2$). From the right plot in Fig. 8, we also see that the excited-state basis sets give a very smooth convergence of $\langle r^2 \rangle$ in the ground state. Clearly, the flexibility in the outer-valence region provided by the excited-state basis sets is well suited to the description of outer-valence properties of the ground state. As observed for the energy, it is necessary to add several diffuse functions to describe $\langle r^2 \rangle$ accurately in the second excited state.

With regard to the Fermi-contact interaction, we first observe that this property is more difficult to describe than are the energy and $\langle r^2 \rangle$ – the errors are both larger and less predictable. At the same time, the quality of the description of the Fermi-contact interaction is fairly uniform for the three lowest states, unlike what we observed for the total energy and for $\langle r^2 \rangle$. Somewhat surprisingly, we find that, when diffuse functions are added to the even-tempered basis with $N = 60$, the error in the Fermi-contact interaction of the second excited state becomes smaller than the error for the lower states. The convergence of the Fermi-contact interaction for the four lowest states, calculated using the excited-state basis sets, is plotted in Fig. 10. While the ground and first excited states display smooth convergence, the errors for the higher states drop dramatically between $N = 27$ and $N = 28$, as the exponents change abruptly – see Fig. 2.

Table 7. Total energy (E_h) and the lowest and the highest exponents of fully optimized basis sets for the first excited state

N	Energy	α_1	α_n
2	−0.1168331639545620	0.01630	0.3211
3	−0.1236675060254134	0.01934	1.6795
4	−0.1246310057307477	0.02007	6.5433
5	−0.1247846962708926	0.02025	22.5608
6	−0.1249503021263345	0.01136	18.6854
7	−0.1249880187190464	0.01205	52.4297
8	−0.1249966322477625	0.01237	137.4150
9	−0.1249987552563279	0.01250	343.7973
10	−0.1249993078240497	0.01256	832.6737
11	−0.1249997270950421	0.00840	743.3744
12	−0.1249999117606748	0.00882	1636.7433

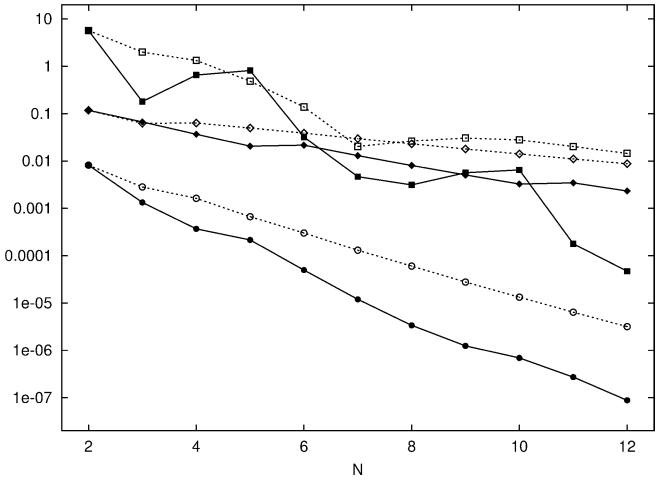

Fig. 13. The logarithm of the absolute errors of the total energy (E_h, *circles*), the expectation value of r^2 (a_0^2, *squares*), and the Fermi-contact interaction ($\alpha^2 E_\mathrm{h}$, *diamonds*) for even-tempered (*open symbols*, *dashed line*) and fully optimized (*filled symbols*, *solid line*) as functions of the number of exponents, optimized for the first excited state

5.2 Fully optimized basis

5.2.1 The structure of the basis set and the total energy

Total energies along with the smallest and largest exponents of the basis sets fully optimized for the first excited state are found in Table 7, where, for each N, we have listed only the solution corresponding to the global minimum. Although the number of local minima increases with N, their number is much smaller than in the even-tempered case – there is one solution for $N = 2$, two solutions for $3 \leq N \leq 7$, and three for $8 \leq N \leq 12$. For $N > 12$, the number of local minima will probably continue to increase in a stepwise manner.

Comparing the excited-state exponents of the fully optimized and even-tempered basis sets in Fig. 4, we note a pattern similar to that observed for the ground state in Fig. 3. In particular, the fully optimized basis sets extend slightly further into the outer (diffuse) region and much further into the inner (core) region of the hydrogen atom. However, there are significant jumps in

Table 8. The absolute error in the energy (E_h), $\langle r^2 \rangle$ (a_0^2), and FC interaction ($\alpha^2 E_h$) for the ground state and the first two excited states for $N = 10$. The fully optimized basis set (FO10) for the first excited state is augmented with up to four additional diffuse functions and up to four additional steep functions

Basis	Ground state			1st excited state			2nd excited state		
	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC	Energy	$\langle r^2 \rangle$	FC
FO10	1.1×10^{-4}	2.8×10^{-3}	2.4×10^{-2}	6.9×10^{-7}	6.5×10^{-3}	3.3×10^{-3}	1.0×10^{-2}	1.0×10^{2}	6.5×10^{-2}
1 dif.	8.4×10^{-5}	1.8×10^{-3}	2.5×10^{-2}	6.6×10^{-7}	5.0×10^{-3}	3.3×10^{-3}	4.5×10^{-5}	6.8×10^{0}	4.1×10^{-4}
2 dif.	7.5×10^{-5}	5.0×10^{-3}	2.5×10^{-2}	5.5×10^{-7}	2.8×10^{-3}	3.3×10^{-3}	2.2×10^{-6}	1.5×10^{-1}	8.9×10^{-4}
3 dif.	7.1×10^{-5}	8.1×10^{-3}	2.5×10^{-2}	5.2×10^{-7}	2.4×10^{-3}	3.3×10^{-3}	2.2×10^{-6}	1.5×10^{-1}	9.0×10^{-4}
4 dif.	6.9×10^{-5}	1.1×10^{-2}	2.5×10^{-2}	5.1×10^{-7}	2.3×10^{-3}	3.3×10^{-3}	2.2×10^{-6}	1.4×10^{-1}	9.0×10^{-4}
1 stp.	1.1×10^{-4}	2.8×10^{-3}	9.0×10^{-3}	6.2×10^{-7}	6.5×10^{-3}	1.4×10^{-3}	1.0×10^{-2}	1.0×10^{2}	6.6×10^{-2}
2 stp.	1.1×10^{-4}	2.8×10^{-3}	2.1×10^{-3}	6.2×10^{-7}	6.5×10^{-3}	5.1×10^{-4}	1.0×10^{-2}	1.0×10^{2}	6.7×10^{-2}
3 stp.	1.1×10^{-4}	2.8×10^{-3}	1.6×10^{-4}	6.2×10^{-7}	6.5×10^{-3}	2.3×10^{-4}	1.0×10^{-2}	1.0×10^{2}	6.7×10^{-2}
4 stp.	1.1×10^{-4}	2.8×10^{-3}	1.2×10^{-3}	6.2×10^{-7}	6.5×10^{-3}	1.0×10^{-4}	1.0×10^{-2}	1.0×10^{2}	6.7×10^{-2}

the exponents going from $N = 5$ to $N = 6$ and from $N = 10$ to $N = 11$, where solutions of a different character become the global minimum, a behaviour similar to what Jensen [6] found for the hydrogen molecule. We recall that, for the excited-state even-tempered basis sets, a similar jump occurs between $N = 27$ and $N = 28$ but does not show up in Fig. 4 since the plot extends only to $N = 12$.

Comparing Tables 6 and 8, we find that, for $N = 10$, the error in the total energy of the first excited state is more than an order of magnitude smaller in the fully optimized basis than in the even-tempered one – see also Fig. 13. The ground state, by contrast, is poorly described by the fully optimized excited-state basis. Surprisingly, the addition of steep functions does not reduce the error in the ground-state energy, whereas diffuse functions give a slightly better description. Moreover, the addition of diffuse functions is essential for an accurate description of the second excited state. Finally, since the underlying basis set was optimized for the first excited state, the augmentation with diffuse or steep functions has little impact on the description of the first excited state, reducing the error in the energy only marginally.

5.2.2 The expectation value of r^2 and the Fermi-contact interaction

From Fig. 13, it is clear that the convergence of $\langle r^2 \rangle$ in the fully optimized basis is somewhat erratic. In fact, for $N = 5$, the error in the fully optimized basis is larger than the error in the even-tempered basis, although the overall convergence is clearly faster in the fully-optimized case. From Table 8, we note that the description of $\langle r^2 \rangle$ is fairly accurate for the two lowest states, even without basis-set augmentation; however, augmentation with diffuse functions is crucial to the description of $\langle r^2 \rangle$ for the second excited state, although convergence is still slow. Strangely enough, for the ground state, the addition of two or more diffuse functions causes the error in $\langle r^2 \rangle$ to increase rather than to decrease. In fact, with four diffuse functions added, the error in $\langle r^2 \rangle$ is about an order of magnitude larger than without augmentation. Finally, we note that the addition of steep functions has no effect on $\langle r^2 \rangle$, for any of the states considered here.

For small N, we see from Fig. 13 that the convergence of the Fermi-contact interaction is similar to that of $\langle r^2 \rangle$. For large N, however, it becomes much slower than for the other properties – see Table 6. From Table 8, we note that the addition of steep functions reduces the error in the Fermi-contact interaction slightly, for the ground state as well as the first excited state. However, as previously found, diffuse functions are needed for an accurate description of the Fermi-contact interaction of the second excited state. Indeed, upon the addition of a single diffuse function, the error for the second excited state becomes 7 order of magnitude smaller than for the first excited state and 2 orders of magnitude smaller than for the ground state; for these two states, three steep functions are needed for the same accuracy.

6 Conclusions

We have carried out a detailed analysis of the errors arising in the description of the hydrogen atom by expanding the wave function in GTOs. For the ground state and the first excited state, basis sets were variationally optimized in an even-tempered and fully unconstrained manner. For the even-tempered basis sets, expansions containing up to 60 s functions have been determined, yielding errors of about $10^{-15} E_h$ for the two lowest S states. Likewise, fully optimized basis sets containing up to 12 GTOs have been determined, with errors of about $10^{-7} E_h$. From these two types of variationally determined basis sets, additional sets were generated by augmentation with diffuse and steep GTOs, whose exponents were chosen in an even-tempered manner.

For the ground state, only one minimum is usually observed, making the basis-set optimization fairly straightforward. By contrast, a large number of local minima exist for the excited-state basis sets, in particular for the even-tempered expansion. The convergence of the exponents is fairly smooth, but in a few cases abrupt changes occur as the global minimum changes its character. The existence of multiple minima complicates the optimization of basis sets and constitutes a potentially difficult problem for systems more complicated than the hydrogen atom.

Using these basis sets, we examined the convergence of the total energy, the kinetic energy, the expectation value of r^2, and the Fermi-contact interaction at the nucleus for the four lowest S states of the hydrogen atom. The convergence of these properties is mostly smooth, although oscillations are observed in a few cases – in particular, for $\langle r^2 \rangle$. In general, $\langle r^2 \rangle$ converges more rapidly than the Fermi-contact interaction, which requires a large number of GTOs for an accurate description. For a similar accuracy in the calculations, the even-tempered basis sets must typically contain two or three GTOs more than the fully optimized basis sets, for properties as well as energies.

A basis set optimized for a given electronic state is ill suited to the description of higher electronic states, both for the total energy and for properties. The lower electronic states, by contrast, are reasonably well described by basis sets optimized for a given electronic state. This is particularly true for the even-tempered basis sets, which, for the hydrogen atom at least, appear to be more universal than the fully optimized basis sets. For an accurate description of higher states, augmentation with diffuse functions is essential – not only for the energy and for $\langle r^2 \rangle$, but in fact also for the Fermi-contact interaction. Apparently, for an accurate description of the density at the nucleus, the overall shape of the wave function must be correct. Unlike the augmentation with diffuse functions, the augmentation with steep functions has usually little impact on the description. In fact, the only property that benefits from steep functions is the Fermi-contact interaction, whose description is somewhat improved by their addition.

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