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S Wilson

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DISTRIBUTED GAUSSIAN BASIS SETS: SOME RECENT RESULTS AND PROSPECTS*

S. WILSON†

*Rutherford Appleton Laboratory,
Chilton, Oxfordshire OX11 0QX, England*

Abstract

Recent years have witnessed a growing interest in the systematic implementation of finite basis set expansions using Gaussian basis sets in both non-relativistic and relativistic molecular electronic structure studies. A promising development is the distributed basis set in which the exponents and the distribution of the Gaussian functions are generated according to empirical prescriptions. A particularly simple distributed basis set is the Gaussian Cell model in which the functions are arranged on a regular lattice, with one function centred on each lattice point and all functions having the same exponent. Not surprisingly, this simple model does not achieve high accuracy. However, recent work on one-electron diatomic and triatomic systems has demonstrated that, with simple refinements, it can be very significantly enhanced and accuracies approaching $1 \mu\text{Hartree}$ can be achieved for the total energy. Alternatively, a Laplace transform can be used to obtain an integral representation of the elliptical function in terms of Gaussian functions. This Laplace transform provides a prescription for the generation of a systematic sequence of distributed basis sets of Gaussian functions from a sequence of atomic even-tempered sets. The prospects for distributed basis sets in Hartree-Fock studies and beyond, for both non-relativistic and relativistic molecular electronic structure calculations, are surveyed briefly.

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†e-mail: s.wilson@rl.ac.uk

I. Introduction

The controlled reduction of basis set truncation errors is an essential prerequisite of a quantitative quantum chemistry and recent years have witnessed a growing interest in the systematic implementation of the algebraic approximation^{1, 2}, i.e. finite basis set expansions, in both non-relativistic and relativistic studies.

Basis set truncation effects are widely recognized as the main source of error in contemporary molecular electronic structure calculations. Over thirty years ago in 1963, Schwartz³ emphasized that

... an orderly plan of attack is... essential for any mathematical analysis of the convergence rate. The old habit of picking the "best" (chosen by art) choice of a fixed number of terms is to be discarded if one wants to see how the problem converges.

He continued

One must choose a set of basis functions and then gradually add more ... in some systematic manner.

Ruedenberg and his co-workers⁴ pointed out that even-tempered basis sets¹ afforded a systematic method for generating atomic orbital basis sets⁵⁻⁹. Feller and Ruedenberg¹⁰ and Schmidt and Ruedenberg¹¹ showed that sequences of such basis sets can be constructed that systematically approach a complete set and thus approach the Hartree-Fock limit. Wilson¹ pointed out that, in spite of this progress,

The vast majority of contemporary molecular calculations adopt a pragmatic approach ... The art of selecting a basis set is based on previous experience in treating similar systems using basis sets of comparable quality.

Huzinaga¹² has suggested that calculations in which the basis set truncation error is not controlled should be termed

quasi-empirical.

The same point has been made by Davidson and Feller¹³ who state that

the smaller the basis set the more ab initio calculations assume an empirical flavor.

Clementi¹⁴ has complained that

In the seventies a "McDonald's Fast Food" mentality had spread among the users of quantum chemistry programs, and the idea of optimizing a basis set ... was abandoned because of the heavy labour involved

and as a result the

chemical literature ... was flooded with computations which essentially compared experiments with basis set superposition error data.

Recently, Taylor¹⁵ has again emphasized the importance of the error associated with basis set truncation

The ultimate accuracy of any calculation is determined by the one-particle basis set. This is one of the most obvious, yet one of the most ignored, observations about quantum chemical calculations. For example, it is in general just not possible to get the right answer for the right reasons using a DZP [double-zeta plus polarization] basis. This is not an argument against using such sets, but their limitations must be kept constantly in mind.

¹Even-tempered Gaussian basis sets were first suggested by R. McWeeny in his *D. Phil.* thesis (Oxford, 1948).

For about fifty years the algebraic approximation in the form of the Linear Combination of Atomic Orbitals (L.C.A.O.) method was regarded as the poor relation of the finite difference methods which have been employed in atomic structure calculations since the pioneering work of Hartree¹⁶ in the 1930s. In the 1970s, it was recognized that the algebraic approximation facilitated the integration over the continuum that arises in the description of electron correlation by means of many-body theories¹⁷. In the 1980s, it was shown that in studies of the relativistic atomic and molecular electronic structure problem, the algebraic approximation affords a representation of not only the positive energy branch but also the negative energy branch of the relativistic spectrum¹⁸. This facilitates the study of not only a relativistic many-body perturbation theory but also the covering theory, quantum electrodynamics¹⁹. Systematic implementation of the algebraic approximation has allowed, for example, the Dirac-Hartree-Fock energies of atoms to be determined to an accuracy which matches that achieved in finite difference calculations; typically $10^{-8} - 10^{-9}$ Hartree²⁰. For molecules the situation is far less satisfactory²¹ and, even in non-relativistic molecular structure calculations, the basis set truncation error is often seen as the largest source of error¹.

Over the past decade, fully numerical Hartree-Fock calculations for diatomic molecules have been reported using first finite difference methods²²⁻²⁵ and then finite element techniques²⁶⁻²⁷. Most of these calculations have been formulated within the framework of non-relativistic quantum mechanics. They provide invaluable benchmarks against which finite basis set calculations can be compared and facilitate the appraisal of methods suggested for the systematic development of molecular basis sets²⁸⁻³⁵.

Atom-centred basis sets have been most widely used in molecular calculations but, in calculations designed to match the accuracy achieved in numerical Hartree-Fock studies of diatomic molecules, it has recently been shown that they can be usefully supplemented by off-centre sets³⁰⁻³³. Indeed, by including bond centred functions in a systematically constructed basis set for the ground state of the nitrogen molecule it has been possible to obtain an energy that is within a few μ Hartree of the numerical result. The success of these calculations suggests investigation of the construction of basis sets including off-atom basis functions in more general terms.

A promising development is the distributed basis set³⁶⁻³⁷ in which the exponents and the distribution of the Gaussian functions are generated according to empirical prescriptions. It should be noted that Gaussian functions are particularly well suited for such a procedure since, unlike exponential basis functions, they do not introduce a cusp. This approach is distinct from the use Gaussian lobe functions³⁸ and the Floating Spherical Gaussian Orbital (F.S.G.O.) model³⁹⁻⁴¹ in that there is no attempt to mimic higher harmonics directly and non-linear optimization is avoided. This allows the use of large basis sets resulting in high precision. In this article, we describe two distributed Gaussian basis sets which have been discussed recently.

A particularly simple distributed basis set is the Gaussian Cell model, introduced by Murrell and his coworkers in 1974⁴²⁻⁴³, in which the functions are arranged on a regular lattice, with one function centred on each lattice point and all functions having the same exponent. Not surprisingly, this simple model does not achieve high accuracy. However, recent work on one-electron diatomic and triatomic systems have demonstrated how, with simple refinements⁴⁴⁻⁴⁶ it can be very significantly enhanced and accuracies approaching 1 μ Hartree can be achieved.

An alternative method for generating a distributed basis set is based on a Laplace transform. The 'natural' basis functions for diatomic molecules are elliptical functions. A Laplace transform can be used to obtain an integral representation of an elliptical function in terms of Gaussian functions. This Laplace transform provides a prescription for the generation of a systematic sequence of distributed basis sets of Gaussian functions from a sequence of atomic even-tempered sets⁴⁷.

In section II, a brief overview of methods for constructing basis sets for atomic and molecular electronic structure calculations is provided giving particular attention to systematic approaches. The theoretical aspects of the distributed basis set approach are discussed in section III concentrating on the Gaussian Cell model and its extensions and on distributions determined by a Laplace transform of elliptical functions. Some recently obtained results are described in section IV whilst in the final section, section V, the prospects for the distributed Gaussian basis set method are assessed.

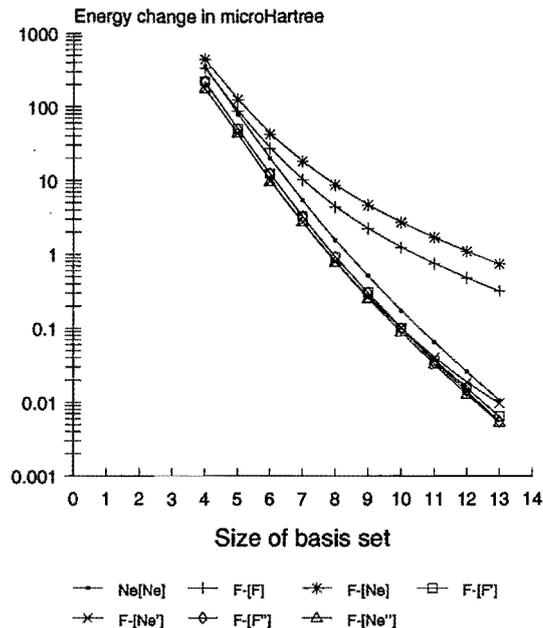


Figure 1: Convergence of the matrix Hartree-Fock energy for the F^- ion with increasing size of basis set. See text for details.

II. Basis Set Construction

A. Atomic basis sets

Atomic basis sets have traditionally been designed by invoking the variation principle so as to obtain the most accurate energy values with the smallest number of basis functions. More recently, there has been a growing interest in the development of sequences of basis sets which formally approach completeness as the number of functions is increased and which, with the power of contemporary computing machines, can be used to obtain atomic Hartree-Fock energies to a very high precision. This approach is illustrated in Figure 1 where a systematic sequence of even-tempered basis sets of Gaussian-type functions is used to calculate the Hartree-Fock energy for the ground state of the F^- ion⁴⁸. In this Figure, the notation $A[B]$ indicates that system A is studied using a sequence of basis sets originally designed for B . $[B']$ indicates that a diffuse function is added to basis sets $[B]$. $[B'']$ indicates that two diffuse function of each symmetry type are added to the basis set $[B]$. It can be seen that provided one diffuse function of each symmetry type is added to the basis set designed for the neutral species, the anion can be accurately described within the Hartree-Fock model within the algebraic approximation.

In relativistic atomic structure calculations systematically constructed sequences of basis sets can yield Dirac-Hartree-Fock energies of an accuracy comparable with that obtained in finite difference studies. This is illustrated in Table 1 for the ground state of the argon atom¹⁹. Relativistic effects are at their most important for the heavy elements. For such systems it is important to take account of the finite size of nuclei. It is only in recent years that it has become widely recognized that once the point nucleus model is abandoned in favour of the more physical finite nucleus model the Gaussian function becomes a more appropriate choice

of basis function²¹.

Table 1
Matrix Dirac-Hartree-Fock calculations for the Ar ground state using a systematic sequence of exponential-type basis sets[†]

| N | α | β | $-E$ |
|--------------------------|----------|---------|--------------|
| 9 | 0.500 | 1.550 | 528.64394819 |
| 10 | 0.484 | 1.516 | 528.68336415 |
| 11 | 0.470 | 1.486 | 528.68431173 |
| 12 | 0.458 | 1.462 | 528.68428973 |
| 13 | 0.447 | 1.440 | 528.68443068 |
| 14 | 0.437 | 1.421 | 528.68443246 |
| 15 | 0.429 | 1.404 | 528.68444856 |
| 16 | 0.421 | 1.389 | 528.68444990 |
| 17 | 0.413 | 1.376 | 528.68445050 |
| $E_{finite\ difference}$ | | | 528.68445077 |

[†] All energies are given in Hartree units.

Taken (with correction) from the work of Quiney, Grant and Wilson¹⁹

B. Molecular basis sets

Molecular basis sets are almost invariably constructed from atomic basis sets. In 1960, Nesbet⁴⁹ pointed out that molecular basis sets containing only basis functions types necessary to reach the atomic Hartree-Fock limit, the so-called isotropic basis set, cannot possibly account for polarization in molecular binding. Two approaches to the problem of designing molecular basis sets can be identified:-

- a) the addition of atom-centred polarization functions to the atomic basis sets
- b) the addition of off-centre functions of the same symmetry as the atomic Hartree-Fock basis set.

In the early sixties, Reeves, Harrison and Fletcher⁵⁰⁻⁵² established important elements of the current 'mainstream' usage of Gaussian basis sets. They concluded that⁵³

no significant advantage was gained by letting the basis functions float away from the nuclear centres, that orbital exponents should be distributed approximately in geometric progression, and that it is not advantageous to optimize separate sets of Gaussians for the description of individual shells.

These conclusions support approach a) and form the foundation of the majority of current mainstream practice (see the review by Shavitt⁵³ for a masterly overview). However, these conclusions were drawn from calculations using basis sets consisting of a small number of functions ($\sim 10 - 10^2$). Today, the so-called 'direct' algorithms⁵⁴, which avoid the storage of the two-electron integrals over the basis functions, have enabled calculations using in excess of 10^3 to be carried out on a workstation and calculations using basis sets of a size approaching 10^4 to be seriously contemplated. It is, therefore, timely to reconsider approaches a) and b) in the light of these developments. We note that these approaches are not mutually exclusive in that hybrid prescriptions for basis set design can be adopted.

The idea of using of bond functions in molecular structure calculations is an old one⁵⁵. Indeed, a number of authors have advocated the use of basis functions located at the bond centre in both self-consistent field and in calculations taking account of correlation effects⁵⁶⁻⁶⁵. Such functions were introduced to provide the same effects as the addition of a set of polarization functions but at a considerably lower cost. Davidson and Feller¹³ point out that

For first-row diatomics the introduction of a single (s,p) set at the centre of the bond provides 90% of the energy lowering obtained with a single set of d functions at the nuclear centres.

In 1980, Čársky and Urban noted that general rules for selecting exponents and positions of the bond functions are still lacking⁶⁶.

In previous work on the ground state of the nitrogen molecule^{30 31} a basis set designated [30s15p15d15f : 27s12p10d bc] (the notation [A : B bc] is used where A denotes the atom-centred basis sets and B the bond-centred basis sets) was found to lead to a total energy that is within 2.3 μ Hartree of the finite difference result. This basis set contains a total of 510 atom centred basis functions, 255 functions on each atomic centre, and 113 functions in the bond centred subset, making the total number of basis function 623. Of these 250 atom-centred functions contribute to the description of the ground state of the nitrogen molecule in the Hartree-Fock ansatz as do 93 of the bond centred functions.

Given the success of calculations using off-atom basis functions, we were led to investigate approach b) in more detail. Very recently, Moncrieff and Wilson⁶⁷ have demonstrated that the Hartree-Fock ground state of the N_2 molecule can be described to an accuracy of $\sim 50 \mu$ Hartree using a basis set of *s* and *p* functions only. The functions were distributed along the line passing through the nuclei. They also considered electron correlation effects using these basis sets. In other recent work, distributed basis sets for molecular electronic structure calculations have been considered in rather more general terms⁴⁴⁻⁴⁶ and this work will be discussed in section III.

C. Systematic generation of atomic basis sets

In the algebraic approximation, the atomic self-consistent field orbitals

$$\phi_i(n, l, m) = f_{nl}(r) r^\ell Y_\ell^m(\theta, \varphi) \quad (1)$$

are approximated as a linear combination of N primitive basis functions, $\chi_{k\ell m}^N$,

$$\phi_i^N(n, l, m) = \sum_{k=1}^N c_{k,nl}^N \chi_{k\ell m}^N \quad (2)$$

These basis functions can be written

$$\chi_{k\ell m}^N = R_{k\ell}(r) r^\ell Y_\ell^m(\theta, \varphi) \quad (3)$$

where the $Y_\ell^m(\theta, \varphi)$ are normalized spherical harmonics. If the basis functions are chosen to be Gaussian-type functions then the radial factor has the form

$$R_{k\ell}(r) = N_\ell(\zeta_{k\ell}^N) \exp(-\zeta_{k\ell}^N r^2) \quad (4)$$

with normalization constant

$$N_\ell(\zeta_{k\ell}^N) = \{(\zeta_{k\ell}^N)^{2\ell+3} 2^{4\ell+7} / \pi(2\ell+1)!!^2\}^{\frac{1}{2}} \quad (5)$$

Klahn⁶⁸ has presented a generalized Müntz-Szász theorem⁶⁹⁻⁷⁴ which essentially states that a set of Gaussian-type functions is asymptotically complete in $L(R^+)$, if and only if and

$$\lim_{N \rightarrow \infty} \Gamma_\ell(N) = \infty, \quad \forall \ell \quad (6)$$

where

$$\Gamma_\ell(N) = \sum_{k=1}^N \frac{\zeta_{k\ell}^N}{1 + (\zeta_{k\ell}^N)^2}, \quad \forall \ell \quad (7)$$

Now it has been observed that exponents which have been carefully optimized for atoms often form a good approximation to a geometric progression^{4 50 51}

$$\zeta_{k\ell}^N = \alpha_\ell^N (\beta_\ell^N)^k, \quad \beta_\ell^N > 1, \quad k = 1, 2, \dots, N \quad (8)$$

Conversely, if it is assumed that the exponents do form a geometric progression and the parameters α_ℓ^N and β_ℓ^N are optimized for atoms then there is found to be little lost in accuracy^{4 5}. Basis sets developed in this way are termed even-tempered basis sets and open up the possibility of constructing the large and flexible basis sets that are inevitably required for calculations of high precision.

As the number of basis functions, N , is increased we require that our basis set approach a complete set. The generalized Müntz-Szász theorem⁶⁸ can be used to show that this is not

the case if α_ℓ and β_ℓ are held fixed as N is increased. One possible choice which does lead to a complete set as $N \rightarrow \infty$ is

$$\alpha_\ell^N \rightarrow 0 \quad (9)$$

$$\beta_\ell^N \rightarrow 1 \quad (10)$$

$$(\beta_\ell^N)^N \rightarrow \infty \quad (11)$$

These limits ensure that the lowest exponent for each ℓ value tends to 0

$$\zeta_{\min,\ell} = \alpha_\ell \beta_\ell \rightarrow 0 \quad (12)$$

the largest exponent for each ℓ tends to ∞

$$\zeta_{\max,\ell} = \alpha_\ell (\beta_\ell)^N \rightarrow \infty \quad (13)$$

and the spacing between the exponents is successively reduced

$$\beta_\ell \rightarrow 1 \quad (14)$$

The limits can be guaranteed by generating successive basis sets according to the following empirical recursions⁷⁵

$$\alpha_\ell^N = \left[\frac{\beta_\ell^N - 1}{\beta_\ell^{N-1} - 1} \right]^{a_\ell} \alpha_\ell^{N-1}, \quad a_\ell > 0 \quad (15)$$

and

$$\ln \beta_\ell^N = \left[\frac{N}{N-1} \right]^{b_\ell} \ln \beta_\ell^{N-1}, \quad -1 < b_\ell < 0 \quad (16)$$

which are essentially the expressions first given by Schmidt and Ruedenberg¹¹.

The prescription given above for generating atomic basis sets in a systematic fashion is, of course, not unique. Amongst the alternative, but closely related approaches, are the universal basis sets⁷⁶ and universal systematic sequences of basis sets⁷⁵, geometric basis sets⁷⁷, and well-tempered basis sets⁷⁸. The approach of Haywood and Morgan⁷⁹ should also be mentioned.

D. Systematic generation of molecular basis sets

Most work on the design of molecular basis sets has concentrated on the development of polarization sets which can be added to atomic basis sets to describe the molecular environment. Our recent work comparing finite difference with finite basis set calculations has demonstrated that a sub- μ hartree level of accuracy for the total Hartree-Fock energy can be achieved when a systematic design of a molecular basis set is undertaken²⁸⁻³⁵. It should be emphasised that there is no unique solution to the problem of designing molecular basis sets. Formally, a one-centre expansion can be made but this will be poorly convergent for heavy atoms located off the expansion centre².

III. Distributed Gaussian Basis Sets

Off-atom functions effectively introduce linear combinations of higher harmonics centred on the atom. Partial wave expansions of an off-centre $1s$ -type Gaussian function have been discussed, for example, by Christoffersen *et al*⁸⁰ and by Kaufmann and Baumeister⁸¹.

A modified form of the Rayleigh expansion⁸² may be written

$$\exp(\mathbf{r}_1 \cdot \mathbf{r}_2) = \sum_{\ell=0}^{\infty} (2\ell + 1) i_\ell(r_1, r_2) P_\ell(\cos \gamma) \quad (17)$$

in which $i_\ell(x)$ is a modified Bessel function and $P_\ell(\cos \gamma)$ is a Legendre polynomial of order ℓ . γ is the angle between the directions \mathbf{r}_1 and \mathbf{r}_2 . Using the expansion (17) in an s -type Gaussian function, $\exp(-\zeta|\mathbf{r} - \mathbf{r}_\lambda|^2)$, with \mathbf{r}_1 assigned to \mathbf{r} and \mathbf{r}_2 assigned to \mathbf{r}_λ , gives

$$\exp(-\zeta|\mathbf{r} - \mathbf{r}_\lambda|^2) = \exp[-\zeta(r^2 + r_\lambda^2)] \sum_{\ell=0}^{\infty} (2\ell + 1) i_\ell(2\zeta r r_\lambda) P_\ell(\cos \gamma) \quad (18)$$

The addition theorem for surface spherical harmonics allows equation (18) to be written

$$\exp\left(-\zeta|\mathbf{r}-\mathbf{r}_\lambda|^2\right)=4\pi\exp\left[-\zeta(r^2+r_\lambda^2)\right]\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{+\ell}i_\ell(2\zeta r r_\lambda)Y_{\ell m}(\Omega_r)Y_{\ell m}^*(\Omega_{r_\lambda})\quad(19)$$

which is the expansion of an off-centre Gaussian function.

Gaussian functions are appropriate functions for electronic structure calculations not only because of the widely recognized fact that they lead to molecular integrals which can be evaluated efficiently and accurately but also because they do not introduce a cusp into the approximation for the wave function at a physically inappropriate point. It should also be noted that Gaussian functions are suitable for the description of wave functions in the vicinity of nuclei once the point nucleus model is abandoned in favour of a more realistic finite nucleus model.

A. The Gaussian Cell model

The original Gaussian cell model^{42 43} is a distributed Gaussian basis set in which the basis functions have a single common exponent and are arranged on a regular lattice. The normalized basis functions may be written

$$\chi_m(\mathbf{r})=\left(\frac{2\zeta}{\pi}\right)^{\frac{3}{4}}\exp\left(-\zeta|\mathbf{r}-\mathbf{r}_\lambda|^2\right)\quad(20)$$

where ζ is the orbital exponent. $\mathbf{r}_{\{\lambda\}}$ is a point on a regular lattice defined by

$$\mathbf{r}_{\{\lambda\}}=\{\pm m_x\lambda_x,\pm m_y\lambda_y,\pm m_z\lambda_z\},$$

$$m_x=1,2,\dots,n_x;m_y=1,2,\dots,n_y;m_z=1,2,\dots,n_z\quad(21)$$

n_x, n_y, n_z are taken to be odd and the lattice point $\{0,0,0\}$ is taken to coincide with the mid-point of the bond. It will be assumed that

$$\lambda_x=\lambda_y=\lambda_z=\lambda\quad(22)$$

Furthermore, the nuclei will be taken to lie on the z -axis and positioned on one of the lattice points, so that

$$\lambda=\frac{\frac{1}{2}R}{i},\left\{1\leq i\leq\frac{1}{2}(n_z-1)\right\}\quad(23)$$

where i is an integer. Murrell *et al*^{42 43} emphasized the importance of ensuring the coincidence of a lattice points with each of the nuclear positions.

B. Laplace transform of an elliptical function

The 'natural' basis functions for calculations on diatomic molecules are elliptical functions. They have been employed in diatomic molecular electronic structure studies by a number of authors⁸³⁻⁹² and may be defined as follows

$$\frac{1}{\sqrt{2\pi R^3}}\exp(-\alpha\lambda)\exp(-\beta\mu)\lambda^s\mu^t[(\lambda^2-1)(1-\mu^2)]^{\frac{|s-t|}{2}}\exp(\nu\varphi)\quad(24)$$

where α and β are screening parameters and s and t taken integer values $0, 1, 2, \dots$. (λ, μ, φ) are the usual prolate spheroidal coordinates $\lambda = \frac{1}{2R}(r_a + r_b)$, $1 \leq \lambda \leq \infty$; $\mu = \frac{1}{2R}(r_a - r_b)$, $-1 \leq \mu \leq 1$; φ , $0 \leq \varphi \leq 2\pi$. R is the nuclear separation and r_a (r_b) is the distance from nucleus a (b). $\nu = 0, \pm 1, \pm 2, \dots$ determines the angular symmetry of the function: $\sigma, \pi, \delta, \dots$. Elliptical basis functions have been employed in electronic structure calculations for diatomic molecules and have been shown to afford high accuracy^{28 88 90-92}.

The approximation of elliptical functions by a finite expansion of Gaussian-type functions has been investigated recently⁴⁷. Attention was restricted to the use of $1s$ Gaussian-type functions to approximation the simplest elliptical basis functions with $s = t = 0$ and $\nu = 0$, that is

$$\chi(\lambda, \mu; \alpha, \beta, R) = \frac{1}{\sqrt{2\pi R^3}}\exp(-\alpha\lambda)\exp(-\beta\mu)\quad(25)$$

The 1s Gaussian-type functions centred on the point p are now written as

$$(2\eta/\pi)^{\frac{3}{4}} \exp(-\eta r_p^2) \quad (26)$$

where η is a screening parameter. Expressing χ in terms of the coordinates $r_a (= R(\lambda + \mu))$ and $r_b (= R(\lambda - \mu))$ gives a product of two exponential functions

$$\chi(r_a, r_b; \zeta_a, \zeta_b, R) = \frac{1}{\sqrt{2\pi R^3}} \exp(-\zeta_a r_a) \exp(-\zeta_b r_b) \quad (27)$$

where the screening constants for the exponential functions, ζ_a and ζ_b , are related to those for the elliptical function, α and β , by

$$\zeta_a = \frac{1}{2R}(\alpha + \beta) \quad (28)$$

and

$$\zeta_b = \frac{1}{2R}(\alpha - \beta) \quad (29)$$

An exponential function can be related to an integral over Gaussian functions by means of the Laplace transform⁸²

$$\exp(-\zeta r) = \frac{\zeta}{2\sqrt{\pi}} \int_0^\infty d\eta \eta^{-\frac{3}{2}} \exp\left(-\frac{\zeta^2}{4\eta}\right) \exp(-\eta r^2) \quad (30)$$

The discrete representation of this integral may be written

$$\exp(-\zeta r) \approx \sum_{p=1}^N c_p \exp(-\eta_p r^2) \quad (31)$$

and this relation has been used by Silver⁹³ and, more recently, by Kutzelnigg⁹⁴ to develop approximations for exponential functions in terms of Gaussian functions. In the work of Silver⁹³, the exponents η_p were chosen to be the points of a Gaussian quadrature scheme and the coefficients, c_p , are related to the corresponding weights. On the other hand, Kutzelnigg⁹⁴ took the exponents, η_p , to be an even-tempered set.

Use of the Laplace transform for the elliptical function provides an exact representation of χ by means of a continuous distribution of Gaussian functions over the variables η_a and η_b :

$$\chi(r_a, r_b; \zeta_a, \zeta_b, R) = \frac{1}{\sqrt{2\pi R^3}} \frac{\zeta_a \zeta_b}{4\pi} \int_0^\infty d\eta_a \int_0^\infty d\eta_b \eta_a^{-\frac{3}{2}} \eta_b^{-\frac{3}{2}} \left(-\frac{1}{4} \left[\frac{\zeta_a^2}{\eta_a} + \frac{\zeta_b^2}{\eta_b} \right] \right) \exp(-\{\eta_a r_a^2 + \eta_b r_b^2\}) \quad (32)$$

Equation (32) can be converted into a finite expansion in terms of Gaussian-type functions by performing the double integration with any one of a number of numerical quadrature schemes. In the expansion

$$\chi(r_a, r_b; \zeta_a, \zeta_b, R) \approx \sum_{p=1}^N \sum_{q=1}^N c_{ap} c_{bp} \exp(-\eta_p r_a^2) \exp(-\eta_q r_b^2) \quad (33)$$

the parameters η_p and c_p are specified by the chosen quadrature. Using the Gaussian product theorem⁹⁵, (33) may be written

$$\chi(r_a, r_b; \zeta_a, \zeta_b, R) \approx \sum_{p=1}^N \sum_{q=1}^N c_{ap} c_{bp} \gamma_{pq} \exp(-\eta_{pq} r_{pq}^2) \quad (34)$$

where the coefficients γ_{pq} are given by

$$\gamma_{pq} = \exp\left(-\frac{\eta_p \eta_q}{\eta_p + \eta_q} R^2\right) \quad (35)$$

and the screening parameters are

$$\eta_{pq} = \eta_p + \eta_q \quad (36)$$

The coordinate r_{pq} is defined with respect to the point (x_{pq}, y_{pq}, z_{pq}) where

$$x_{pq} = \frac{\eta_p x_a + \eta_q x_b}{\eta_p + \eta_q} \quad (37)$$

with similar relations for y_{pq} and z_{pq} .

IV. Some Recent Results

A. The Gaussian Cell model revisited

The original Gaussian Cell model basis set, with one function centred on each lattice point and all functions having the same exponent, may be written

$$S_{\text{Gaussian Cell Model}} = S_1^{(\lambda_1)} \oplus S_1^{(\lambda_2)} \oplus \dots \oplus S_1^{(\lambda_N)} \quad (38)$$

or

$$S_{\text{Gaussian Cell Model}} = \sum_{p \in \{L\}} \oplus S_1^{(\lambda_p)} \quad (39)$$

where

$$S_1^{(\lambda_p)} = \left\{ (2\zeta/\pi)^{\frac{3}{2}} \exp(-\zeta r_p^2) \right\} \quad (40)$$

The convergence behaviour of this method is illustrated in Table 2 where some results recently obtained by Ralston and Wilson⁴⁴ are reproduced. Not surprisingly, this simple model does not achieve high accuracy; indeed, the lowest energy reported in Table 1 is in error by $\sim 7705 \mu\text{hartree}$. However, more recent work on one-electron diatomic^{44 45} and triatomic⁴⁶ systems has demonstrated that, with simple refinements, it can be very significantly enhanced and accuracies approaching $\sim 1 \mu\text{Hartree}$ can be achieved for the total energy.

Table 2
Calculations for the H_2^+ ground state using a regular cubic lattice distributed basis set[†]

| <i>Lattice</i> | <i>N</i> | <i>i</i> | <i>E</i> | ζ | λ |
|----------------|----------|----------|------------|---------|---------------|
| 5 × 5 × 5 | 125 | 1 | -0.582 046 | 1.407 4 | 1 |
| 5 × 5 × 5 | 125 | 2 | -0.577 133 | 0.618 4 | $\frac{1}{2}$ |
| 7 × 7 × 7 | 343 | 1 | -0.591 606 | 1.545 2 | 1 |
| 7 × 7 × 7 | 343 | 2 | -0.587 718 | 0.675 2 | $\frac{1}{2}$ |
| 7 × 7 × 7 | 343 | 3 | -0.586 792 | 0.616 3 | $\frac{1}{3}$ |
| 9 × 9 × 9 | 729 | 1 | -0.592 429 | 1.556 8 | 1 |
| 9 × 9 × 9 | 729 | 2 | -0.593 043 | 0.907 2 | $\frac{1}{2}$ |
| 9 × 9 × 9 | 729 | 3 | -0.592 283 | 1.556 8 | $\frac{1}{3}$ |
| 9 × 9 × 9 | 729 | 4 | -0.590 744 | 0.747 4 | $\frac{1}{4}$ |
| 11 × 11 × 11 | 1331 | 2 | -0.594 929 | 1.174 9 | $\frac{1}{2}$ |
| Exact | | | -0.602 634 | | |

[†] All energies are given in Hartree units.

The internuclear distance is set at its equilibrium value of 2.0 bohr

B. Molecular lattice basis sets

It is clear that the major failing of the Gaussian Cell model is its lack of flexibility particularly in the regions close to the nuclei. However, methods for constructing basis sets for accurate atomic Hartree-Fock calculations are well established. Ralston and Wilson⁴⁴, therefore, introduced the molecular lattice basis sets which may be written

$$S_{\text{Molecular Lattice Basis Set}} = S_1^{(\lambda_1)} \oplus S_1^{(\lambda_2)} \oplus \dots \oplus S_1^{(\lambda_{q-1})} \oplus S_{N_{\text{atom}}}^{(\lambda_q)} \oplus S_1^{(\lambda_{q+1})} \dots \oplus S_1^{(\lambda_N)} \quad (41)$$

or

$$S_{\text{Molecular Lattice Basis Set}} = \left(\sum_{p \in \{L'\}} \oplus S_1^{(\lambda_p)} \right) \oplus \left(\sum_{q \in \{A\}} \oplus S_{N_{\text{atom}}}^{(\lambda_q)} \right) \quad (42)$$

where atomic basis sets are centred on lattice points which coincide with nuclei and a single function is centred on each of the lattice points which do not coincide with nuclei with all of these functions having the same exponent. If $\{A\}$ denotes the atomic nuclei and $\{L\}$ the full set of lattice points then

$$\{L'\} = \{L\} - \{A\} \quad (43)$$

The atomic basis set may be chosen to be even-tempered sets.

$$S_{N_{atom}}^{(\lambda_p)} = \left\{ (2\zeta_k/\pi)^{\frac{3}{2}} \exp(-\zeta_k r_p^2); \zeta_k = \alpha_{(N_{atom})} \beta_{(N_{atom})}^k; k = 1, 2, \dots, N_{atom} \right\} \quad (44)$$

The convergence behaviour of these molecular lattice basis sets is illustrated in Table 3 where results, taken from the work of Ralston and Wilson⁴⁴, show that this approach can yield an accuracy of $\sim 27 \mu\text{Hartree}$ for the H_2^+ ground state at its equilibrium geometry. In these calculations, N_{atom} was set to 10 and the atomic even-tempered parameters were taken from the tables of Schmidt and Ruedenberg¹¹.

Table 3
Calculations for the H_2^+ ground state using a molecular regular cubic lattice distributed basis set[†]

| <i>Lattice</i> | <i>N</i> | <i>i</i> | <i>E</i> | ζ | λ |
|----------------|----------|----------|------------|---------|---------------|
| 5 × 5 × 5 | 143 | 1 | -0.602 462 | 0.691 9 | 1 |
| 5 × 5 × 5 | 143 | 2 | -0.602 462 | 0.518 2 | $\frac{1}{2}$ |
| 7 × 7 × 7 | 361 | 1 | -0.602 508 | 0.738 1 | 1 |
| 7 × 7 × 7 | 361 | 2 | -0.602 536 | 0.688 1 | $\frac{1}{2}$ |
| 7 × 7 × 7 | 361 | 3 | -0.602 532 | 0.622 8 | $\frac{1}{3}$ |
| 9 × 9 × 9 | 747 | 1 | -0.602 515 | 0.718 4 | 1 |
| 9 × 9 × 9 | 747 | 2 | -0.602 593 | 0.831 7 | $\frac{1}{2}$ |
| 9 × 9 × 9 | 747 | 3 | -0.602 586 | 0.732 5 | $\frac{1}{3}$ |
| 9 × 9 × 9 | 747 | 4 | -0.602 570 | 0.673 8 | $\frac{1}{4}$ |
| 11 × 11 × 11 | 1349 | 1 | -0.602 517 | 0.706 6 | 1 |
| 11 × 11 × 11 | 1349 | 2 | -0.602 607 | 0.880 1 | $\frac{1}{2}$ |
| 11 × 11 × 11 | 1349 | 3 | -0.602 597 | 0.748 8 | $\frac{1}{3}$ |
| Exact | | | -0.602 634 | | |

[†] All energies are given in Hartree units.

The internuclear distance is set to its equilibrium value of 2.0 bohr

C. Systematically extended molecular lattice basis sets

The molecular lattice basis set, although a considerable improvement on the original Gaussian Cell model, does not afford an accuracy approaching the $1 \mu\text{Hartree}$ level even for the simplest of molecules, the hydrogen molecular ion. The molecular lattice even-tempered basis set was, therefore, introduced⁴⁵. This is defined as

$$S_{\text{Molecular Lattice Even-tempered Basis Set}} = S_{N_{\text{lattice}}} \oplus S_{N_{\text{lattice}}} \oplus \dots \oplus S_{N_{\text{lattice}}} \oplus S_{N_{\text{atom}}} \oplus S_{N_{\text{lattice}}} \dots \oplus S_{N_{\text{lattice}}} \quad (45)$$

or

$$S_{\text{Molecular Lattice Even-tempered Basis Set}} = \left(\sum_{p \in \{L'\}} \oplus S_{N_{\text{lattice}}}^{(\lambda_p)} \right) \oplus \left(\sum_{q \in \{A\}} \oplus S_{N_{\text{atom}}}^{(\lambda_q)} \right) \quad (46)$$

where atomic basis sets are located on each of the nuclei and "lattice" basis sets are centred on each lattice point. The "lattice" basis sets are identical and may be taken to be even-tempered.

$$S_{N_{\text{lattice}}}^{(\lambda_p)} = \left\{ (2\zeta_k/\pi)^{\frac{3}{2}} \exp(-\zeta_k r_p^2); \zeta_k = \alpha_{(N_{\text{lattice}})} \beta_{(N_{\text{lattice}})}^k; k = 1, 2, \dots, N_{\text{lattice}} \right\} \quad (47)$$

The convergence behaviour of these systematically extended molecular lattice basis sets are displayed in Table 4 for a $5 \times 5 \times 5$ lattice where it can be seen that the lowest energy is in error by just $4 \mu\text{hartree}$. The convergence pattern for three difference lattices are shown in Figure 2.

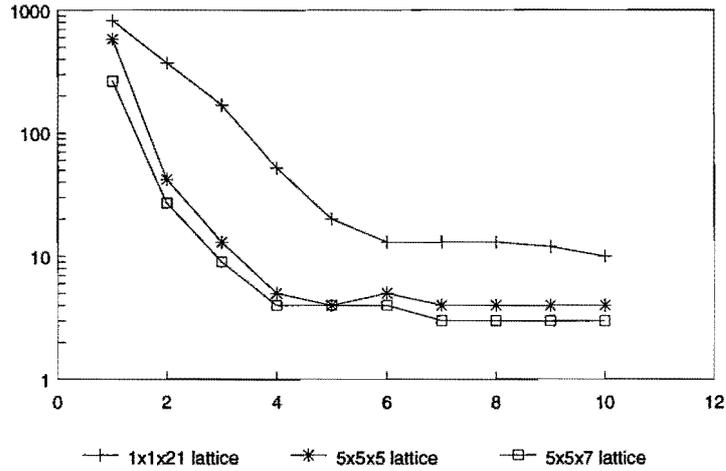


Figure 2: Convergence of the ground state energy of the hydrogen molecular ion for a distributed Gaussian basis set of s-type functions using a regular linear lattice and a regular cubic lattice together with systematic sequence of even-tempered functions on each lattice point.

Table 4

Calculations for the H_2^+ ground state using a $5 \times 5 \times 5$ molecular regular cubic lattice of systematically constructed distributed basis sets with $i = 2^\dagger$

| $N_{lattice}$ | N | M | E_0 | δ |
|---------------|------|------|-----------|----------|
| 1 | 143 | 143 | -0.602052 | 582 |
| 2 | 266 | 255 | -0.602592 | 42 |
| 3 | 389 | 368 | -0.602621 | 13 |
| 4 | 512 | 476 | -0.602629 | 5 |
| 5 | 635 | 591 | -0.602630 | 4 |
| 6 | 758 | 705 | -0.602629 | 5 |
| 7 | 881 | 820 | -0.602630 | 4 |
| 8 | 1004 | 933 | -0.602630 | 4 |
| 9 | 1127 | 1047 | -0.602630 | 4 |
| 10 | 1250 | 1165 | -0.602630 | 4 |
| Exact | | | -0.602634 | |

[†] All energies are given in Hartree units and energy differences in μ Hartree. The internuclear distance is set to its equilibrium value of 2.0 bohr

Calculations using a molecular lattice distributed basis set have also been carried out⁴⁶ the linear H_3^{2+} , a simple polyatomic system for which the results of finite element studies have recently been published⁹⁶.

D. Laplace-transform based distributed basis sets

The prescription for distribution of the basis set obtained by considering the analytical relation between elliptical functions and Gaussian functions using a Laplace transform provides an alternative technique for the construction molecular distributed basis sets. It provides a method for generating systematic sequences of molecular basis sets from systematic sequences of atomic basis sets. Here, we shall consider a systematic sequence of even-tempered atomic basis sets.

The exponents for an atom-centred even-tempered basis set of Gaussian-type functions are defined by the geometric series

$$\eta_p = \alpha\beta^p, \quad p = 1, 2, \dots, N \quad (48)$$

For this choice of generating formula, the exponents in the expansion (34) are given by

$$\eta_{pq} = \alpha(\beta^p + \beta^q), \quad p, q = 1, 2, \dots, N \quad (49)$$

and, for a diatomic system with nuclei placed on the z -axis, the coordinate r_{pq} is defined with respect to the point $(0, 0, z_{pq})$ where

$$\begin{aligned} z_{pq} &= \frac{\beta^{p-q} z_a + z_b}{\beta^{p-q} + 1}, \quad p \geq q \\ z &= \frac{z_a + \beta^{q-p} z_b}{1 + \beta^{q-p}}, \quad q \geq p \\ p, q &= 1, 2, \dots, N \end{aligned} \quad (50)$$

In this way, a systematic sequence of atomic even-tempered basis sets can be used to generate a sequence of molecular basis sets. Convergence of the calculated energy of the hydrogen atom and the hydrogen molecular ion observed with a systematic sequence of even-tempered basis sets of $1s$ Gaussian functions is displayed in Figure 3. For the H_2^+ ion the energy obtained with the basis set distributed along the line passing through the nuclei according to the Laplace transform of an elliptical functions is compared with that obtained with atom-centred $1s$ Gaussian functions. The atom-centred basis set exhibits smooth behaviour with increasing number of functions but is not capable of describing the H_2^+ ground state⁴⁹. The Laplace transform based distribution, on the other hand, displays a smooth convergence pattern with increasing basis set size and monotonically decreasing energy values.

V. Prospects

Basis sets capable of supporting high precision calculations (*i.e.* total energies approaching the 1μ hartree level of accuracy) for molecules within the Hartree-Fock model are now a reality. Such basis sets can be efficiently constructed if the usual approach in which basis functions are taken to be atom centred is abandoned and functions centred on, for example, the bond centre are introduced. The distributed basis set concept provides a general approach to the construction of basis sets which include off-atom functions. Just as the introduction of even-tempered basis sets showed that it was not necessary to exhaustively optimize exponents if schemes are devised for their systematic extension (indeed, for atoms such an approach can yield an accuracy comparable with that achieved in finite difference calculations), so the introduction of distributed basis sets provides systematic schemes for the placing of the functions in space. The two distributions described in this article, the Gaussian Cell model and its extensions and the Laplace transform of an elliptical function, have been shown to be capable of an accuracy approaching 1μ hartree.

Basis sets capable of supporting high precision electron correlation calculations are under development⁹⁷. The accurate approximation of the solutions of the Hartree-Fock problem for a molecule is a necessary precursor for any treatment of correlation effects. Not only is the correlation energy defined with respect to the total Hartree-Fock energy but the solutions of the Hartree-Fock equations define the quasi-particles in terms of which a description of the many-body system is developed⁹⁸⁻¹⁰⁴.

Basis sets capable of supporting high precision in non-relativistic studies can be easily modified to serve as a basis for relativistic molecular structure calculations. Essentially, additional contracted basis functions are required in the relativistic case to describe the contraction

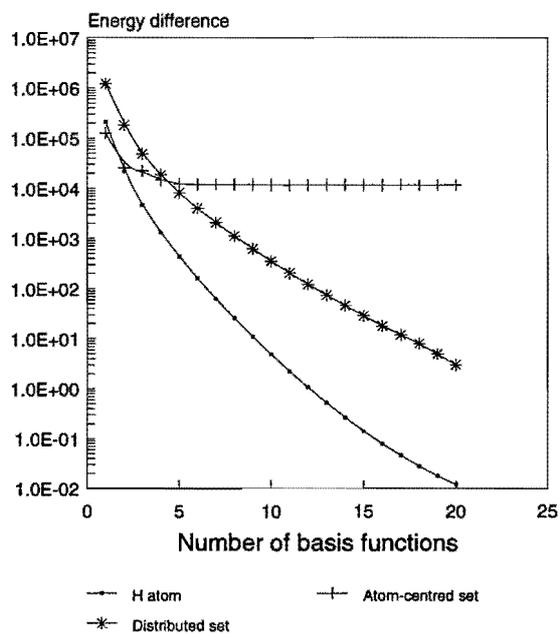


Figure 3: Convergence of the calculated energy of the hydrogen atom and the hydrogen molecular ion observed with a systematic sequence of even-tempered basis sets of $1s$ Gaussian functions. For the molecular systems the basis sets are either atom-centred or distributed along the line passing through the nuclei according to the Laplace transform of an elliptical functions.

of the single particle state functions in the core region whilst additional diffuse functions are needed to account for the expansion of the valence single particle state functions. In relativistic electronic structure calculations within the algebraic approximation matched basis sets must be employed for the large and small components of the wave function. The large and small components of the relativistic wave function must be approximated in terms of basis functions which satisfy the condition¹⁹

$$\chi_{i\kappa}^S \propto \left(\frac{d}{dr} + \frac{\kappa}{r} \right) \chi_{i\kappa}^L \quad (51)$$

There is a one-to-one correspondence between the large and small component basis functions. If the large component basis set contains s functions then the small component basis sets must contain p functions with the same exponents; if the large component basis set contains p functions then the small component basis set must contain functions which are a linear combination of s and d functions; in general, if the large component basis functions have the form

$$\chi_{im\kappa}^L = N_{i\kappa} r^\ell \exp(-\zeta_i r^2) \Omega_{jm}^{\text{sgn}(\kappa)}(\theta, \varphi) \quad (52)$$

then the small component basis functions have the form

$$\chi_{im\kappa}^S = i N_{i\kappa} ((\ell + \kappa + 1) - 2\zeta_i r^2) r^{\ell-1} \exp(-\zeta_i r^2) \Omega_{jm}^{-\text{sgn}(\kappa)}(\theta, \varphi) \quad (53)$$

where κ is the usual angular quantum number, $2j = 2|\kappa| - 1$, $-j \leq m \leq j$. The restriction of the large components basis set to functions of low symmetry when using distributed basis sets imposes corresponding restrictions on the small component basis set¹⁰⁵.

By restricting basis sets to functions of low symmetry distributed basis sets lead to efficient integral evaluation algorithms; an essential ingredient of the 'direct' self-consistent field procedures⁵⁴ which are required for both non-relativistic and relativistic calculations using large basis sets. Furthermore, when basis sets are systematically constructed and extended there is considerable scope for integral approximation.

Finally, it should be mentioned that distributed Gaussian basis sets provide a natural vehicle for the determination of point charge models of molecular systems which are required for hybrid quantum mechanical/classical calculations. Many of the techniques suggested by Hall and his coworkers¹⁰⁶⁻¹⁰⁸ for obtaining point charge models from floating spherical Gaussian orbital electronic structure calculations can be applied to the results of distributed Gaussian basis set studies¹⁰⁹. Hybrid methods offer considerable scope for the study of molecules in different environments, *e.g.* on surfaces, in solution and in cages.

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