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Commentationes

Mixed Basis Functions in Molecular Quantum Mechanics

I. Computational Methods and a Preliminary Study of the Helium Atom

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Mixed sets of functions consisting of 1*s* Slater orbitals and floating spherical Gaussians are proposed as expansion functions for *ab initio* variational type calculations for small molecules. After the discussion of the basic computational methods the results of some trial calculations for the ground state of the helium atom are presented.

Für *ab initio* Rechnungen vom Variationstyp werden im Falle kleiner Moleküle gemischte Funktionssätze, die aus 1*s* Slater-Orbitalen bestehen, vorgeschlagen. Nach einer Diskussion der grundlegenden Rechenmethoden werden die Resultate von einigen Proberechnungen für den Grundzustand des Heliumatoms geschildert.

Introduction

The choice of basis functions is of fundamental importance in all *ab initio* variational type atomic and molecular calculations. From the purely theoretical viewpoint the basis functions should ideally form a complete set; from the computational viewpoint the functions should also possess good convergence properties, since in practice the expansions need to be as compact as possible. Furthermore, one must be able to evaluate all the basic integrals which arise in the course of the calculation with reasonable ease in order to make the computational work worth attempting.

The most widely used functions in atomic calculations have been the Slater type atomic orbitals (STO's), which have the advantage over other sets of functions in that they closely resemble atomic self-consistent orbitals [1–3]. STO's have found wide application in molecular calculations as well, although in the case of the more complex systems the problems associated with the evaluation of multicentre integrals often proves prohibitive, as most of these integrals cannot, in general, be evaluated in closed form. Gaussian type orbitals (GTO's) as expansion functions were first introduced by Boys [4], who showed that all the integrals which arise in a variational energy calculation could be calculated with reasonable ease. However, compared with STO's, Gaussians suffer from the disadvantage that, because they are not so closely related to self-consistent orbitals, their convergence properties are considerably poorer. This results in lengthy expansions. The basic 1*s*-type Gaussian function, defined as

$\psi = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2)$ α being a constant, called the orbital exponent, differs most from a 1*s* Slater orbital at the origin, lacking a cusp there. A 1*s* STO takes the form

$$\psi = (\alpha^3/\pi)^{1/2} \exp(-\alpha r).$$

Consequently, a wavefunction constructed from Gaussians does not obey the nuclear cusp condition [5] and generally exhibits the worst behaviour at and near the nuclei. Hence, just to ensure a reasonably good description of the electron density in the regions near the nuclei, a relatively large number of Gaussians is needed as expansion functions.

The mixed basis sets advocated here arise naturally. Consider a wavefunction which is constructed from a small number of Slater functions, and which gives a reasonably good electron distribution, especially in the regions near the nuclei. To correct the electron density further, and to allow for electron correlation, Gaussians may be just as efficient as Slater functions, since there is no cusp requirement for the additional basis functions. The Gaussian functions could be placed at such points in space so as to be energetically the most effective. Furthermore, it is plausible to think that *p*- and *d*-type Slater functions, which are only used for correction purposes, may be successfully replaced by Gaussian functions of the same symmetry or even by Gaussian lobe functions. The latter are defined as normalized linear combinations of spherical Gaussians centred at different points in space, their transformation properties resembling those of *p*-, *d*- and possibly higher functions.

The use of such mixed basis sets was first proposed by Allen [6]. Calculations were first carried out by Riera and Linnett [7] for the linear, symmetric H_3 molecule. Because their results were encouraging, a more systematic and detailed study of mixed basis sets has been made.

In this paper we report a series of trial calculations on the helium atom, using various mixed basis sets consisting of just 1*s* Slater and floating spherical Gaussian orbitals. The first molecular calculation was carried out on H_2 and this was followed by calculations on the more complex systems of H_3 and H_4. The results are reported in some forthcoming papers. The calculations are *ab initio*, all the integrals having been evaluated to sufficient accuracy to make the resulting energy accurate to 1 part in 10^6. The method of configuration interaction (CI) was employed, i.e. a variational approach, minimizing the energy of a multiconfigurational wavefunction consisting of Slater determinants which were constructed from an orthonormalized set of symmetry orbitals. The final wavefunctions are generally expressed in terms of natural orbitals, obtained by the diagonalization of the spinless first order reduced density matrix.

Computational Methods

A typical CI calculation consisted of three main stages:

(a) Evaluation of the basic integrals;

(b) Construction of an orthonormal set of symmetry orbitals and the transformation of the integrals to this new basis;

(c) Construction of the required configurations and the Hamiltonian matrix followed by its diagonalization yielding the energy and the corresponding wavefunction. Calculation and diagonalization of the spinless first order reduced density matrix to give the natural orbitals and their occupation numbers.

In the larger calculations, e.g. in the case of H_3 and H_4, steps *a*, *b* and *c* were carried out separately, making use of the magnetic tape and disc facilities to store the integrals and other intermediate results. The He and H_2 calculations could easily be performed in a single run.

The computer used for our calculations has been the Cambridge University Computer Laboratory's Titan computer, with a maximum available fast store of 40000 words, requiring approximately 5 µsec for addition or subtraction and 8 and 25 µsec for multiplication and division respectively, in variable mode. All the calculations have been carried out in single precision, which is 11 significant figures in Titan.

The various computational steps will now be discussed in more detail.

a) Evaluation of the Basic Integrals

The integrals to be evaluated are the overlap, kinetic energy, nuclear attraction and electron repulsion integrals in a mixed set of 1*s* Slater and Gaussian type functions.

All the integrals involving only spherical Gaussians were readily calculated according to the expressions given by Boys [4]. The evaluation of the auxiliary functions $F_0(t)$ which occurs in the three-centre nuclear attraction and electron repulsion integrals is discussed in Appendix 1. The overlap, kinetic energy, one and two centre nuclear attraction, Coulomb and hybrid integrals involving only the Slater functions were calculated using the closed formulae of Roothaan *et al.* [8–10]. The remaining integrals, i.e. the three centre nuclear attraction, exchange, three and four centre electron repulsion integrals involving only Slater functions and all the mixed integrals, i.e. involving both types of functions, were evaluated by expanding the Slater functions in terms of Gaussians, followed by term-by-term integration and summation. Huzinaga's expansions were utilized for this purpose [11]. In order to achieve an accuracy of 1 in 10^6 in the total energy, all the one-electron integrals were evaluated using 10 Gaussians to expand the Slater functions. 8 Gaussians were generally used when evaluating two-electron integrals, although in some cases 4 Gaussians proved sufficient; for example, in the He calculations. Most integrals were accurate to within 1 in 10^6, although some multicentre 2-electron integrals were found to be less accurate (~ 1 in 10^4). The effect of this inaccuracy on the energy would, however, be very small. To illustrate the accuracy and convergence properties of the integrals calculated by the Gaussian expansion technique, the values of some exchange integrals are listed in Appendix 2.

The one electron integrals were stored as two-dimensional arrays in the computer, although only the upper (or lower) triangle needs to be evaluated as a result of the symmetric nature of these arrays. The two electron integrals were generated and stored as a one-dimensional array making use of the fact that a real orbital integral given as

$$[ij|kl] = \int \varphi_i(1)\,\varphi_j(1)\,\varphi_k(2)\,\varphi_l(2)\,r_{12}^{-1}\,d\tau_1\,d\tau_2$$

is unaffected by the interchanges of i and j, of k and l and of ij and kl.

In the calculation of the integrals full use was made of spatial symmetry.

In case of a large basis the integrals could be generated in several successive runs on the computer and then stored on magnetic tape or disc for future use.

b) Construction of Orthogonal Symmetry Orbitals

Whenever possible the basic orbitals were transformed so as to give an orthonormal symmetry orbital basis.

In the case of Gaussians which are not centred on the nuclei the symmetry orbitals usually transform according to the irreducible representation of some lower symmetry point group as, for example, in the case of He when 6 Gaussians are used to construct three *p*-type orbitals. The resulting orbitals, usually called Gaussian lobe functions, transform according to the O_h point group. When expanded about the origin the lobe functions are found to include contributions from higher spherical harmonics [12]. Consequently, a He wavefunction which is partly constructed from such lobe functions will have octahedral rather than spherical symmetry. However, this is not expected to introduce serious difficulties, since such functions are induced only to allow for correlation and would not affect the electron distribution, which ought to be symmetrical, to a significant extent.

Two methods of orthonormalization were used, the Schmidt method [13] and Löwdin's symmetric orthogonalization method [14]. Both were found to function satisfactorily, although the Schmidt method was preferred in the later work, when it was convenient to enlarge a given orbital basis by the addition of Schmidt orthogonalized orbitals to the existing orthonormal set.

c) Transformation of Integrals

Since the Slater determinants in the CI expansions are constructed from an orthonormal set of symmetry orbitals, the integrals need to be transformed to the new basis.

The method used is a standard one, explained in detail by Harris [15] for example, it makes use of intermediate arrays as much as possible to reduce comp. time requirements. In the case of two-electron integrals, for example, the number of computational steps is proportional to n^5, n being the number of basis functions used, as opposed to n^8 which would result if the elementary transformation method was used.

This part of the calculation is generally very time consuming, as well as having large store requirements. Hence, for a basis which contains more than 12 orbitals it was generally carried out separately, making use of tape and disc facilities as much as possible to store the integrals and parts of the intermediate working arrays.

d) The CI *Wavefunction and the Hamiltonian Matrix*

A CI wavefunction takes the form

$$\Psi = \sum_i C_i \Phi_i \tag{1}$$

where $\{\Phi_i\}$ is an orthonormal set of configurations, each with the correct spatial and spin symmetry properties; corresponding to the state under study, $\{C_i\}$ is a set of constants chosen so as to minimize the total energy.

For the singlet two-electron case there are two types of configurations,

$$\begin{aligned} \Phi^1 &= |\varphi_i \bar{\varphi}_i| \\ \Phi^2 &= 2^{-1/2}\{|\varphi_i \bar{\varphi}_j| + |\varphi_j \bar{\varphi}_i|\}, \quad i \neq j \end{aligned} \tag{2}$$

where $|\varphi_i \bar{\varphi}_j|$ is a normalized Slater determinant constructed from the spin orbitals φ_i and $\bar{\varphi}_j$ with α and β spins respectively.

The various matrix elements between such configurations are easily calculable, using the set of transformed integrals.

The 3 and 4 electron wavefunctions are discussed in the relevant later papers.

The lowest eigenvalue of the Hamiltonian matrix and the corresponding eigenvector, characterising the ground state of a given system, were calculated using Nesbet's method [16].

e) The Natural Orbitals [17–18]

The set of natural orbitals $\{\chi_i\}$ are defined by the transformation

$$\chi_i = \sum_k U_{ki} \psi_k \tag{3}$$

where $\{\psi_k\}$ is the set of basis functions and $\boldsymbol{U}$ is the unitary matrix which diagonalizes the spinless first order density matrix, given in the ψ_k representation.

The elements of the diagonalized density matrix are known as the occupation numbers of the natural orbitals, indicating the relative importance of each orbital in the CI expansion, their sum being equal to the number of electrons.

Natural expansions have the quickest convergence in any given basis and at any point in the expansion maximum overlap with the exact wavefunction is assured. Hence, the first term in a natural expansion closely resembles the Hartree-Fock wavefunction within the same basis. The total wavefunction to a good approximation is thus conveniently separated into SCF and correlation parts. Consequently, we introduce a quantity called *apparent correlation energy*, defined as the difference between the calculated total and the SCF energies, the latter estimated by the energy associated with the first term in the NO expansion. The magnitude of the apparent correlation energy can then serve as a guide as to the "amount" of correlation allowed for by a given CI wavefunction.

In the case of 2-electron systems the calculation of the natural orbitals is particularly simple. Since the singlet CI wavefunction can be written as

$$\Psi = 2^{-1/2}(\alpha\beta - \beta\alpha) \sum_{i,j} C_{ij} \varphi_i(1)\, \varphi_j(2) \tag{4}$$

the spinless first order reduced density matrix is simply

$$\gamma(1\,|\,1') = \sum_{i,j} (\boldsymbol{C}\boldsymbol{C}^{+})_{ij} \varphi_i(1)\, \varphi_j^*(1')\,. \tag{5}$$

Since $\boldsymbol{C}$ and $\boldsymbol{C}\boldsymbol{C}^{+}$ are both diagonalizable by the same unitary transformation it suffices to diagonalize $\boldsymbol{C}$ to yield the natural orbitals. Expressed in terms of NO's the total wavefunction is also in diagonal form,

$$\Psi = 2^{-1/2}(\alpha\beta - \beta\alpha) \sum_{i} m_i \chi_i(1)\, \chi_i(2)\,. \tag{6}$$

The occupation numbers n_i of the NO's are just $2m_i^2$.

If the number of electrons is greater than two the calculation of the NO's is carried out by the diagonalization of the density matrix. This will be discussed in the forthcoming papers on H_3 and H_4.

Calculations for the Ground State of the He *Atom.*
Two and Three Orbital Calculations

Only radial functions were used in these calculations, orthonormalized by Löwdin's method, the total wavefunction in each case including all the possible configurations. All the orbital exponents were optimized by Powell's [21] method. Details of the various basis sets and the corresponding energies that were obtained are presented in Table 1. For the Gaussian functions the square root of the orbital exponents is also given so as to make the comparison with exponential functions simpler. (The "range" of a Gaussian is proportional to $\alpha^{-1/2}$, α being the exponent, as opposed to an exponential function whose range is proportional to α^{-1} [22]). The wavefunctions are given in Table 2, expressed in natural form, i.e. according to Eq. (6).

The energy results clearly indicate that the main shortcoming of a Gaussian basis lies in the poor description of the electron-nucleus interaction. This is due to the fact that a Gaussian is not a solution of the Schrödinger equation for the hydrogen-like problem, resulting in an electron distribution which is far from correct, consequently severely underestimating the magnitude of the nuclear attraction energy. The electron repulsion energy is much more independent of the basis used, whereas the kinetic energy also shows large fluctuations, paralleling those in the total energy, in accordance with the Virial Theorem [25].

The energy values of the NO expansions truncated to contain only the first, leading term display the same tendencies as the total energies, but the variations shown by the apparent correlation energy are much smaller. It is evident that wavefunctions constructed wholly or in part from Gaussians are poor as a result of unsatisfactory SCF parts and not because they describe correlation badly. Hence the need for a large basis when using Gaussians. It is

Table 1. Basis functions for the 2 and 3 orbital He calculations and the resulting energy terms (in a.u.) together with some accurate results for comparison. The square roots of the orbital exponents of the Gaussians are given in brackets (S = Slater function, G = Gaussian)

Calculation Ref.	Orbital types and exponents	Total energy	Kinetic energy	Nuclear attraction energy	Electron repulsion energy	Energy of truncated NO expansion	Apparent correlation energy
1	1 : G : 0.5231 (0.7233) 2 : G : 4.0063 (2.0016)	−2.75787	2.75787	−6.52205	1.00630	−2.74696	−0.01091
2	1 : S : 1.579 2 : G : 0.4810 (0.6935)	−2.86367	2.86408	−6.75075	1.00230	−2.85358	−0.01009
3	1 : S : 1.325 2 : S : 2.457	−2.87689	2.87686	−6.74418	0.99044	−2.86117	−0.01572
4	1 : G : 0.3730 (0.6107) 2 : G : 1.9629 (1.4010) 3 : G : 13.1908 (3.6319)	−2.85121	2.85118	−6.69625	0.99387	−2.83554	−0.01567
5	1 : S : 1.694 2 : G : 0.972 (0.9859) 3 : G : 4.574 (2.1387)	−2.87331	2.87329	−6.74780	1.00120	−2.86012	−0.01319
6	1 : S : 1.389 2 : S : 2.551 3 : G : 1.388 (1.178)	−2.87852	2.87786	−6.74386	0.98748	−2.86149	−0.01703
7	1 : S : 1.425 2 : S : 2.495 3 : S : 2.805	−2.87850	2.87708	−6.74282	0.98725	−2.86154	−0.01696
Schwartz [23]	Radial limit calculation	−2.879028					−0.01734
Roothaan *et al.* [24]	SCF calculation	−2.86168				−2.86168	

Table 2. The wavefunctions resulting from the 2 and 3 orbital He calculations expressed in natural form; the natural orbitals given in terms of the original basis

Calculation Ref.	Coefficient of configuration $\chi_i(1)\,\chi_i(2)$	Natural orbital χ_i	Coefficient of atomic orbital		
			1	2	3
1	0.999289	1	0.820139	0.290118	
	−0.037710	2	−0.825167	1.126659	
2	0.999146	1	1.187270	−0.19555	
	−0.041308	2	−3.59639	3.78225	
3	0.997749	1	0.692164	0.338112	
	−0.066644	2	−1.896261	1.990120	
4	0.998287	1	0.651603	0.414226	0.083418
	−0.058385	2	−0.058385	−1.064087	1.044166
	−0.003710	3	0.441146	−1.078287	1.218240
5	0.998805	1	1.203741	−0.014630	−0.200268
	−0.048251	2	−2.736116	1.263159	1.945947
	−0.007810	3	−3.293699	−0.565796	3.827433
6	0.997846	1	0.760462	0.284959	−0.020178
	−0.065279	2	−1.948360	1.533277	0.550329
	−0.006558	3	−0.253137	−4.005462	4.306479
7	0.997749	1	0.828095	−0.055060	0.254221
	−0.066644	2	−2.666421	5.914587	−3.205106
	−0.007489	3	3.996217	−25.11450	21.70878

noteworthy that the wavefunction built from two Slater functions and one Gaussian is energetically as good as the one from three Slater functions. Hence it ought to be possible to construct good wavefunctions using just a few Slater type orbitals and possibly a larger number of Gaussians as expansion functions, the latter used as correction functions to improve the SCF part of the wave-function further and to provide the extra flexibility to describe electron correlation.

The best energy, −2.87852 a.u., from calculation 6 compares favourably with the estimated radial or S limit of −2.879028 a.u. [23], despite the small basis. The energy of the truncated NO expansion from the same calculation, −2.86149 a.u., shows similar agreement with the exact SCF energy of −2.86168 a.u. [24]. The best calculated value for the apparent correlation energy is −0.01703 a.u., very close to the accurate radial correlation energy of −0.01734 a.u.[1]

The coefficients of the configurations from the various calculations show the strong convergence usually displayed by the occupation numbers of NO's. The magnitude of the first coefficient, being associated with the SCF part in the wave-function, shows an inverse type relationship with the apparent correlation energy. This behaviour is to be expected since higher configurations represent the correlation part in the wave-function, the coefficients indicating their relative importance, and as they become larger the first coefficient needs to decrease in order for the total wave-function to be normalized.

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[1] The apparent correlation energy is not, in general, an upper bound to the true correlation energy, hence it needs to be used with caution.

Eight Orbital Calculations

In these calculations Gaussian lobe functions were introduced in order to test their effectiveness in the description of angular correlation. The complete orbital basis consists of two 1*s* Slater orbitals centred on the nucleus and six Gaussians positioned octahedrally around the nucleus as shown in Fig. 1.

The various linear combinations of the Gaussians defining the lobe functions are symmetry orbitals which transform according to the irreducible representations of the O_h point group; they are listed in Table 3. The symmetry properties of the orbitals are also tabulated together with the type of orbitals they are to represent.

The first CI wavefunction was constructed from the two 1*s* Slater orbitals and the p_x, p_y, p_z-type lobe functions, resulting in 6 configurations. (The number of configurations could be reduced to 4, since the configurations $p_x p_x$, $p_y p_y$, and $p_z p_z$ could be grouped together.) The exponent and position of the Gaussians, as specified by the distance *d* from the origin, were optimised, the exponents of the Slater orbitals having been kept at their optimum values as found in the relevant 2-orbital calculation. During the optimization procedure it became clear

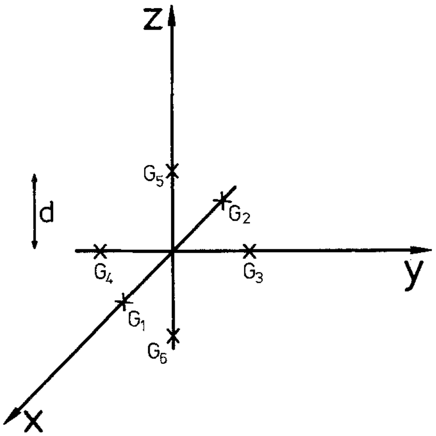

Fig. 1. Distribution of the Gaussians in the eight orbital He calculations

Table 3. The unnormalized symmetry orbitals formed from the octahedrally positioned Gaussians, $G_1 - G_6$

Symmetry orbitals	Symmetry type
$\varphi_1 = G_1 + G_2 + G_3 + G_4 + G_5 + G_6$	a_{1g} (s)
$\varphi_2 = G_1 - G_2$	t_{1u} (p_x)
$\varphi_3 = G_3 - G_4$	t_{1u} (p_y)
$\varphi_4 = G_5 - G_6$	t_{1u} (p_z)
$\varphi_5 = -G_1 - G_2 - G_3 - G_4 + 2G_5 + 2G_6$	e_g (d_{z^2})
$\varphi_6 = G_1 + G_2 - G_3 - G_4$	e_g $(d_{x^2-y^2})$

Table 4. Details of the 8 orbital basis and the calculated energies (a.u.) resulting from the CI calculations together with some literature values

Exponent of Slater functions	$S_1 : 1.325$	$S_2 : 2.457$
Exponent of Gaussians	1.287	
Values of the total energy from the 6 configuration calculation for various values of d (a.u.)	$d = 0.4$	$E = -2.89384$
	$d = 0.2$	$E = -2.89405$
	$d = 0.1613$	$E = -2.89407$
	$d = 0.0914$	$E = -2.89408$
	$d = 0.0143$	$E = -2.89408$
The total energy from the 11 configuration calculation with $d = 0.2$ a.u.	-2.89583	
Energy resulting from a CI calculation using a $1s$, $1s'$, $2p$ Slater basis [26]	-2.89518	
Exact energy [27]	-2.9037244	

Table 5. The 8 orbital 11 configuration wavefunction, yielding an energy of -2.89583 a.u. expressed in natural form (resulting in 8 configurations)

Coefficient of configuration $\chi_i(1)\,\chi_i(2)$	Natural orbital χ_i and its symmetry	Coefficient of atomic orbital							
		S_1	S_2	G_1	G_2	G_3	G_4	G_5	G_6
0.996322	1 (s)	0.340104	0.694452	-0.000755	-0.000755	-0.000755	-0.000755	-0.000755	-0.000755
-0.055088	2 (s)	1.646348	-1.945622	0.068094	0.068094	0.068094	0.068094	0.068094	0.068094
-0.031573	3 (p_x)	0.0	0.0	2.260651	-2.260651	0.0	0.0	0.0	0.0
-0.031573	4 (p_y)	0.0	0.0	0.0	0.0	2.260651	-2.260651	0.0	0.0
-0.031573	5 (p_z)	0.0	0.0	0.0	0.0	0.0	0.0	2.260651	-2.260651
-0.007044	6 (s)	-3.755819	-0.044301	0.724852	0.724852	0.724852	0.724852	0.724852	0.724852
-0.005747	7 (d_{z^2})	0.0	0.0	-5.753096	-5.753096	-5.753096	-5.753096	11.50619	11.50619
-0.005747	8 $(d_{x^2y^2})$	0.0	0.0	9.964656	9.964656	-9.964656	-9.964656	0.0	0.0

that numerical errors may arise as a result of two Gaussians coming too close together, introducing approximate linear dependency into the basis. The total energy is, however, quite insensitive to the separation of the Gaussians, hence to avoid the possibility of round-off errors it was decided to keep the Gaussians well separated in future calculations. A distance of 0.2 a.u. from the origin was settled on as a reasonable and safe value.

The second calculation made use of all the possible configurations, a total of 11, that could be constructed from the given 8 orbital basis. The orbital exponents were left unchanged from the previous calculation.

Details of the basis and the calculated energies from these calculations are given in Table 4.

The energy calculated using the 6 configuration function gives an improvement of 0.01719 a.u. over the function which contains just two Slater orbitals, this representing almost 70% of the total angular correlation energy. With a basis of two 1*s* and three 2*p* STO's Taylor and Parr [26] obtained an energy of -2.89518 a.u., only marginally better than our value.

The inclusion of the remaining three Gaussian lobe functions results in a significant decrease in the energy, bringing it within 4 kcal/mole of the Pekeris value of -2.9037244 a.u. [27]. The wavefunction from the 11 orbital calculation, given in terms of NO's, is presented in Table 5.

Conclusion

The results of the He calculations with mixed basis sets are very encouraging. Clearly, Gaussians are efficient when used to correct a wavefunction constructed from Slater orbitals, which is at least of SCF accuracy. In atomic calculations, of course, there is no need to use Gaussians since they offer no advantage over Slater functions. For molecules, however, mixed sets of the kind used in these calculations may provide a convenient and sufficiently accurate method to obtain energies and possibly other properties of interest as well. The success of Gaussian lobe functions in the description of angular correlation is especially gratifying since it is the *p* and higher Slater orbitals which prove most troublesome in molecular calculations.

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Appendix 1

Evaluation of the Auxiliary Function $F_0(t)$

The auxiliary function $F_m(t)$ defined as

$$F_m(t) = \int_0^1 u^{2m} \exp(-t u^2)\, du \qquad (t > 0;\, m = 0, 1, 2, \ldots)$$

occurs in the nuclear attraction and electron repulsion integrals between Gaussian functions.

In case of 1*s* type Gaussians only $F_0(t)$ needs to be evaluated and the method used rests on the power series expansion [22]

$$F_0(t) = \exp(-t) \sum_{i=0}^{\infty} 2t^i/1 \times 3 \times 5 \ldots (2i+1) .$$

For $t \leqq 16$ the number of terms required in the summation is reasonably small ($\leqq 38$) to achieve the specified accuracy of one part per million, whereas for larger values of t it is possible to make use of the asymptotic expansion

$$\begin{aligned} F_0(t) &= \frac{\Gamma(1/2)}{2t^{1/2}} - \Phi_0(t) \\ &\approx \frac{\Gamma(1/2)}{2t^{1/2}} \quad \text{since} \quad \Phi_0(t) \leqq \frac{1}{2t} \exp(-t) . \end{aligned}$$

Hence $F_0(t) = \pi^{1/2}/2t^{1/2}$ which is accurate to more than six significant figures.

This method was found to be quite satisfactory, requiring, on the average, less than a millisecond comp. time.

Appendix 2

Exchange Integrals $[1S_A\, 1S_B | 1S_A\, 1S_B]$, *Calculated by the Gaussian Expansion Technique, Compared with the Accurate Values* [28], *as a Funtion of the Internuclear Separation R. All Orbital Exponents are* 1.00

R (a.u.)	Number of Gaussians in expansion	Calculated value of integral	Accurate value of integral
1.0	4	0.436694	0.436651
	6	0.436653	
	8	0.436652	
	10	0.436652	
1.5	4	0.296836	0.296835
	6	0.296838	
	8	0.296836	
	10	0.296836	
3.0	4	0.058452	0.058508
	6	0.0585131	
	8	0.0585074	
	10	0.0585080	
5.0	4	0.00370653	0.00371704
	6	0.00371797	
	8	0.00371730	
	10	0.00371667	

The comp. times required to evaluate such integrals were 1.5, 7, 22 and 49 sec for the 4, 6, 8 and 10 Gaussian expansions respectively.

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