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Molecular Integrals over Slater-type Orbitals. From pioneers to recent progress

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Abstract

It can readily be demonstrated that atomic and molecular orbitals must decay exponentially at long-range. They should also possess cusps when two particles approach each other. Therefore, Slater orbitals are the natural basis functions in quantum molecular calculations. Their use was hindered over the last four decades by integration problems. Consequently, Slater orbitals were replaced by Gaussian expansions in molecular calculations (in spite of their more rapid decay and absent cusps). From the 90s until today considerable effort has been made by several groups to develop efficient algorithms which have fructified in new computer programs for polyatomic molecules. The key ideas of the different methods of integration: one-center expansion, Gauss transform, Fourier transform, use of Sturmians and elliptical co-ordinate methods are reviewed here, together with their advantages and disadvantages, and the latest developments within the field. A recent approximation separating the variables of the Coulomb operator will be described, as well as its usefulness in molecular calculations. Recently, due to the developments of the computer technology and the accuracy of the experiments, there is a renewed interest in the use of Slater orbitals as basis functions for Configuration Interaction (CI) and Hylleraas-CI atomic and molecular calculations, and in density functional and density matrix theories.

keywords: Slater orbitals, integrals, computer programs, Kato conditions, accurate molecular wave-functions.

1. Introduction

Slater-type orbitals (STO) [1] are the natural basis functions in quantum molecular calculations. Nevertheless, their use has been rather restricted, mostly due to mathematical integration difficulties. Even today there are no simple general algorithms to solve all the integrals appearing in a Hartree-Fock (HF) or Configuration Interaction (CI) molecular calculation, where integrals involving up to four atomic centers may appear. In spite of these difficulties the research on Slater orbitals has always continued. The reason is the requirement for large basis sets of Gaussian orbitals (GTO) and large wave function expansions to perform more accurate calculations of energy and properties of ever larger interesting systems. As a consequence those calculations need enormous computational times. In 1981, in a Congress in Tallahassee about Slater orbitals Milan Randić described the situation: *"Gaussian functions are not the first choice in theoretical chemistry. They are used (...) primarily because molecular integrals can be evaluated, not because they possess desirable properties. Today this may be a valid reason for their use, but tomorrow they may be thought of as bastard surrogates, which served their purpose in the transition period, have no longer viable merits and will fail into oblivion"* [2]. The use of an expansion of GTOs instead of an STO was then a pragmatic solution and originally intended for solving the problems in the calculation of the first molecules on early mainframe computers. The GTO expansion together with the popular distribution of computer programs like GAUSSIAN have contributed that the use of GTOs for accurate calculations of large systems has pushed back the limits with respect size of the systems and dimension of the wave function, *i.e.* HF calculations of clusters of hundreds of atoms, CI calculations including hundred of thousands of Slater determinants. In spite of the rapid development of the computer technology and the availability of supercomputers, the computational times are unreasonably long, so that the computational chemist is restricted *i.e.* to perform numerous test calculations. This motivates the search for basis functions, where fewer would give a good CI, in particular. The possibility of using Slater orbitals, where a minimal basis would consist in one function per atom would suppose an impulse to forwards in theoretical and computational chemistry. Since the difficulties are of pure mathematical nature, *e.g.* definite integrations, it would be worthwhile pursuing investigations of Slater orbitals.

The purpose of this paper is to explain the key ideas about Slater orbitals for readers outside the field. It is beyond our scope to review the whole work of the all authors in this field, what would deserve a longer treatment. The history of Slater orbitals and the first computer programs using them is exposed and the currently used computer programs are listed. The STO and GTO are defined and compared. The methods used in the literature are explained recalling in the key ideas in which these methods are based. The last developments within the field are reported.

2. Early History of the Slater Orbitals

The history of STOs is the history of theoretical chemistry. In 1928 Slater [1] simplified the hydrogen-like orbitals (which are eigenfunctions of the Hamiltonian for a one-electron atom) obtaining the orbitals which bear his name. Curiously Slater called these orbitals at that time *Hartree orbitals*. Slater orbitals are a simplification of the hydrogen-like orbitals, which are eigenfunctions of the atomic one-electron Schrödinger equation.

Brief time-line of events in molecular work over Slater type orbitals to date:

1928 Slater and London.

1929 Hylleraas: He atom.

1933 James and Coodlidge: Hylleraas calculations on H₂.

1949 Roothaan LCAO paper.

1950 Boys: first Gaussian expansion of STO published.

1951 Two-center Coulomb Integrals. Roothaan formulae.

1954 Boys and Shavitt 'Automated calculations'.

1958 Tauber: Work on analytic two-center Exchange integrals: Poisson equation.

1962 Scrocco: first publishes STO work,(in Italian) but with a programme. This follows early molecular work in 1951-53. [3, 4].

1963 Clementi produces tables of optimised single zeta basis sets for atoms. Shavitt B-Functions described.

1970 The Journal of Chemical Physics published work on STO codes by E. Scrocco and R. Stevens. Gaussian 70 prepared for QCPE by J. Pople and R. Ditchfield.

1973 E. J. Baerends: numerical integration over STO used for ADF DFT code.

1978 Filter and Steinborn: Fourier transform work. B-functions and plane-wave expansion of Coulomb operator.

1981 ETO conference in Tallahassee. Weatherford and Jones.

1994 First STOP (Slater Type Orbital Package, QCPE 667 1996) code. Bouferguene and Hoggan.

2001 First SMILES (Slater Molecular Integrals for Large Electronic Systems) code. Fernández Rico, López *et al.*

2008 Gill: Coulomb resolution.

Very soon with Slater at MIT, researchers broached the problem of evaluating the two-electron integrals in this basis. During the 1950s the Chicago group led by Mulliken took on the task of evaluating all the molecular integrals. Roothaan treated the Coulomb and Hybrid two-center integrals [5, 6], Rüdénberg the exchange integrals [7]¹. Among the many authors who were working around the world in the solution of the necessary integrals one may mention Masao Kotani in Japan [8], who wrote the famous tables of integrals which bear his name and that were widely used; Coulson in Oxford (England) proposed a method to evaluate the three- and four-center integrals [9], Löwdin in Uppsala [10], and young American scientist called Harris [11] were involved. Work in the early 50s mostly focused on integrals over STO.

The interest was to make the first theoretical calculations of some molecules starting with the diatomic systems H₂, N₂. For three-center molecules the problem of integration was encountered (orbital translation). Mulliken and Roothaan called this " *The bottleneck of Quantum Chemistry*" [12], Mulliken mentioning it in his Nobel Lecture in 1966, on the molecular orbital method.

Boys in Cambridge published his landmark paper [13] containing the evaluation of three- and four-center integrals using Gaussian functions, for which he derived the so-called *product theorem*: the product of two Gaussian functions located on different centers is a new Gaussian function located on a new center. Thus four-center electron distributions could be reduced to a single-center distributions and evaluation was analytically facilitated. Boys regarded his work as an existence theorem. It was to change the course of molecular computations. Note that the product theorem for Slater orbitals leads to complicated infinite sums, making evaluation awkward compared with the simple closed forms for Gaussians.

In 1954 Boys, Shavitt *et al* [14] expanded Slater orbitals into Gaussians to perform quantum mechanical calculations. In 1963 Clementi presented the so-called basis set using Slater orbitals [15]. Later Pople would base his programs on Boys' pragmatism.

3. History of the STO computer programs

The first (and surely the last) manual calculation of a molecule, the N₂ molecule, was done by Scherr in 1956. It was necessary the work of 2 (sometimes it appears 3) men for 2 years. Afterwards this calculation was reproduced by the first digital computer calculation [16, 17], taking 35 minutes.

In 1962 Shull initiated the Quantum Chemistry Program Exchange (QCPE) at Indiana University.

The first automatic computer program was POLYATOM [18] what used nevertheless GTOs with SCF-LCAO. The program was developed at MIT in 1963 when Slater was there.

¹The two-center two-electron integrals are classified according to the centers a, b . Writing them according the charge distributions $[\Omega(1)|\Omega(2)]$ the Coulomb integrals are $[aa|bb]$, the hybrids $[aa|ab]$ and the exchange integrals $[ab|ab]$. The most difficult are the exchange integrals because the charge distribution of every electron is located over two centers.

In 1963 the program IBMOL [19] was developed by Clementi and others when he visited the Chicago group.

In 1968 a STO code was developed by Scrocco and Tomasi from Pisa. Preliminary work by Scrocco is reported in Italian as early as 1962 [4].

This program was also used by Berthier in France. The program ALCHEMY in 1968 was originally developed using Slater orbitals by Clementi and the staff of the IBM laboratory in San Jose [20], afterwards, the new ALCHEMY 2 by Bader and others used GTOs. The program DERIC [21] by Hagstrom in 1972 perform STO calculations of two-center molecules.

In the 80s, the advent of GAUSSIAN [22] saw development in STO field hibernate somewhat. By the 90s several groups around the world developed new STO computer programs which are now distributed. The program STOP from Bouferguène and Hoggan [23] was published first in 1996. It is based on the single center strategy and was first presented in 1994 at the 8th ICQC in Prague. New versions appeared, the latest for parallel platforms in 2009.

Then in 1998 a program was written using B-functions by Steinborn, Weniger, Homeier *et al*, in Regensburg [24]. The program SMILES by Fernández Rico, López, Ema, and Ramírez in Madrid appeared in 1998 and new versions have appeared, the latest in 2004 for the HF and CI calculations of molecules [25].

The program CADPAC [26] in Cambridge uses techniques like density fitting, involving auxiliary Slater type orbital basis sets to perform Hartree-Fock and Density Functiona Theory (DFT) calculations with a reduced number of indices in requisite integrals. They aimed to obtain better Nuclear Magnetic Resonance (NMR) chemical shifts on the basis involving nuclear cusps.

In the density functional theory field in 2001 the program ADF (Amsterdam Density Functional) [27] begun in 1973 by Baerends *et al* uses Slater orbitals for their calculations. This much-used package offers a very extensive series of atomic basis sets for input, including most elements. It is a numerical grid strategy and this review will not detail it.

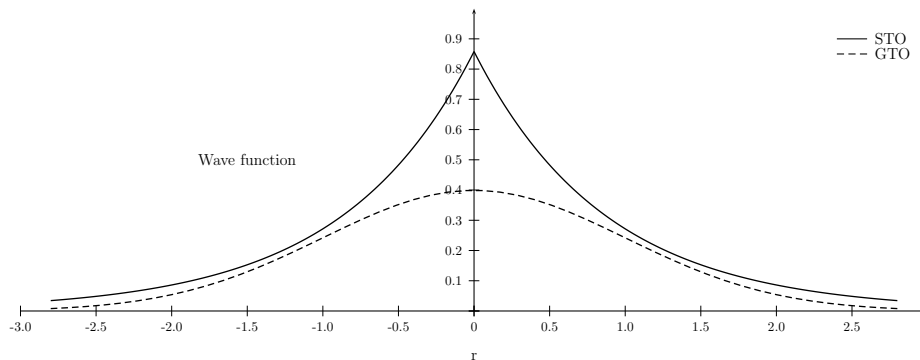
The program ATMOL of Bunge *et al* performs large highly accurate CI calculations on atoms using Slater orbitals [28].

In the first century of the third millennium much interest is concentrated in generating more efficient calculation algorithms, use of non-integer Slater orbitals, numerical solution of integrals when using B-functions and in the electron correlation when using Hylleraas wave functions.

4. Slater Orbitals & Gaussian Orbitals

It is well known that hydrogen-like orbitals are the solution of the Schödinger equation for a one-electron atom. For helium and atoms with more electrons the Schödinger equation has no analytical solution due to the potential term $1/r_{ij}$ which correlates the (otherwise) independent electrons. It is assumed that for systems with $N \geq 2$ this form of the exponential e^{-ar} will be the asymptote of the formal solution. The hydrogen-like orbitals have nodes,

Figure 1: Comparison of the shape of a STO and GTO functions.



i.e. the $2s$ orbital is of the form $(1 - br) e^{-\alpha r}$, and higher quantum number orbitals are similar but STOs are node-less. A related problem appears for gaussians.

In 1928 Slater [1] regarded the hydrogen-like orbitals as polynomials in r which make the calculations messy and proposed the use of single powers of r i.e. linear combinations of hydrogen-like terms.

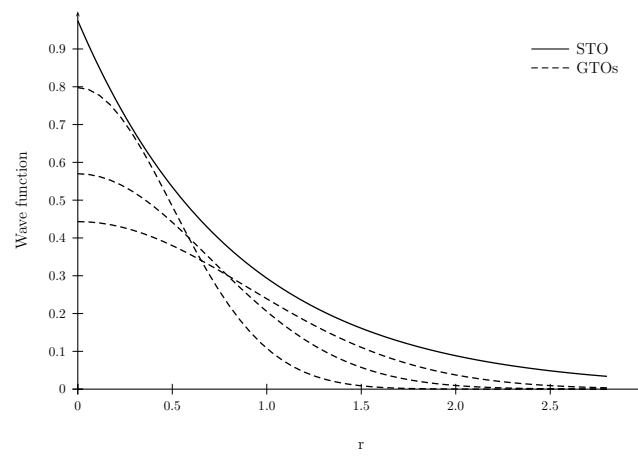
A picture which helps to visualize the differences between Slater and Gaussian orbitals is the representation of the $1s$ orbital function of both types, see Figure 1.

STOs represent well the electron density near the nucleus (cusp) and far from the nucleus (correct asymptotic decay). STOs thus resemble the true orbitals. Conversely, the GTOs have erroneous shape near and far from the nucleus (no cusp). One can observe that far from the nucleus the GTOs tend to zero much faster than STOs.

To reproduce a $1s$ STO using 3 GTOs (the so-called minimal GTO basis) an orbital is obtained with the shape of a Gauss curve, no cusp, see Figure 2. To reproduce a single STO many GTOs are necessary, but the electron cusp at the nucleus is missing. This is one of the reasons of the slow convergence of the wave function solutions to the exact (HF or CI) result. In general, if the basis function is not a formal solution of the Schrödinger equation its convergence is slower. That means that more Slater determinants are required to obtain the same result. Thus Slater orbitals show faster convergence when increasing their number.

Another advantage of Slater orbitals is the size of the basis, one orbital per electron is of reasonable quality and multiple-zeta basis sets converge fast to the Hartree-Fock limit.

Figure 2: Construction of a STO with 3 GTOs.



therefore, the number of integrals to be evaluated is dramatically smaller. CI is spectacularly more efficient. Finally, conceptually the Slater orbitals give a more intuitive description of the atomic orbitals and of the molecular orbitals (MO) formed with them.

The disadvantages of Slater orbitals have been already mentioned: the three- and four-center two-electron integrals are the bottleneck. There is no general analytical solution for them, which would be the most effective and fastest way of calculation. Instead there are a number of approximate methods of calculation, involving infinite series, or truncated approximations to the Coulomb operator itself. They will be treated in the next Sections.

The radial Slater functions do not represent the bonding region adequately, it being then necessary to add higher angular momentum functions.

It is nevertheless possible to use linear combinations restoring radial nodes. This approach is advocated particularly for ADF, where the hydrogen-like basis is obtained by fixing the coefficients for combining Slater functions.

Another disadvantage is that some of the two-center integrals since the times of Roothaan and Ruedenberg have been solved for a co-axial conformation of the atomic coordinate systems (the z-axis point to each other) that is not the molecular frame. Therefore rotations and reflections are necessary. These problems have been solved, but it requires additional calculations [29].

Nowadays, Slater orbitals are used in atomic calculations, especially in highly accurate calculations of atoms using Hylleraas wave functions (with explicit r_{12} dependence, and also in diatomics. They are used in DFT and in Density matrix theories. Traditionally they have been used in semi-empirical calculations where of course the three- and four-center integrals were neglected.

The Gaussian orbitals are generally used in standard quantum mechanical calculations. As explained they are not shaped like analytical orbitals, with no cusp at the nucleus, for that reason they are not good for the calculation of properties where the density at the nucleus has to be well described. Also the radial dependence is not well represented and the number of integrals increases with the dimension of the basis dramatically.

The major advantage of GTOs is the existence of a product theorem. Over many years, workers have improved the calculation of the necessary integrals, having achieved a considerable speed-up. For example the Coulomb operator with a Laplace transform enables to calculate three- and four-center integrals like two center integrals.

Concluding, the main defect of GTO expansions is the absent cusp which slows the convergence and the large number of integrals to be computed.

5. Types of exponentially decaying orbitals, based on eigenfunctions for one-electron atoms

In general one calls Slater-type orbitals those with an exponential radial factor of the form $r^n e^{-\alpha r}$, for n a positive integer (or 0). The atom-centered Slater orbitals are defined as:

$$\varphi_{nlm}(\mathbf{r}) = r^{n-1}e^{-\alpha r}Y_l^m(\theta, \phi), \quad (1)$$

where n, l, m are the quantum numbers. $Y_l^m(\theta, \phi)$ are the spherical harmonics defined using the Condon-Shortley phase:

$$Y_l^m(\theta, \phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}, \quad (2)$$

$P_l^m(\cos \theta)$ are the associated Legendre functions. The spherical harmonics are eigenfunctions of the angular momentum operator \hat{L}^2 and its z -projection \hat{L}_z .

The complex spherical harmonics are used mainly in atoms and in developing theories because it is easier to work out general formulae and derivations with them. The real spherical harmonics are linear combinations of the complex ones. These are used mainly in molecules.

Note that they are written using polar coordinates. They can be also straightforwardly converted into Cartesian Slater orbitals by the exchange:

$$x = r \sin \theta \cos \phi, \quad (3)$$

$$y = r \sin \theta \sin \phi, \quad (4)$$

$$z = r \cos \theta, \quad (5)$$

obtaining in general:

$$\chi_{nlm}(\mathbf{r}) = x^{n_x} y^{n_y} z^{n_z} r^{n-1} e^{-\alpha r}. \quad (6)$$

Cartesian Slater type orbitals are very seldom used compared with Cartesian Gaussians, that are an almost systematic choice.

When the principal quantum number n in Eq. (1) is a non-integer we have the NISTOs (Non Integer Slater Orbitals). The main difficulty when working with these orbitals is during the derivations a binomial has to be used with a non-integer power what leads to an infinite expansion. These orbitals are widely investigated in the present [30]. The additional flexibility of using non-integer quantum numbers brings a lowering in the energy results.

There is the possibility to transform also the polar coordinates to elliptical coordinates. Traditionally the Elliptical Slater orbitals have been used as basis functions for two-center molecules [31]-[33]. These orbitals are known to lead to lower energy results, see Ref. [34]. Using $\xi = \lambda_1 = r_a + r_b$ and $\eta = \mu_1 = r_a - r_b$:

$$\varphi_{nlm}(\mathbf{r}) = \xi^n \eta^l (\xi^2 - 1)^{m/2} (1 - \eta^2)^{m/2} e^{-\alpha \xi} e^{im\phi}, \quad (7)$$

where ξ, η, ϕ are the elliptical coordinates.

Now we go to orbitals which are linear combinations of Slater orbitals: B-functions [35], hydrogen-like, Sturmians [36].

The B-functions are Bessel functions. The orbitals have some helpful properties like a compact Fourier transform. Written in the form

$$B_{nlm}(\mathbf{r}) = \sum_{j=1}^n \frac{(2n-j-1)!}{2^{2n+l-1}(n+l)!(n-j)!(j-1)!} (\zeta r)^{l+j-1} e^{-\zeta r} Y_l^m(\theta, \phi), \quad (8)$$

one can see that they are a linear combination of Slater orbitals. The angular parts are the spherical harmonics.

The hydrogen-like orbitals which are solutions of the Schrödinger equation for the hydrogen atom have a radial part which is a Laguerre polynomial. The polynomial and the exponent coefficient depend on the atomic number Z and the principal quantum number n :

$$\chi_{nlm}(\mathbf{r}) = N_{nl} L_{n-l-1}^{2l+2} \left(\frac{2Zr}{n} \right) r^l e^{-\frac{Zr}{n}} Y_l^m(\theta, \phi). \quad (9)$$

Due to that fact, the hydrogen-like orbitals do not form a complete set (for finite n), they need orbitals of the continuum to be complete. This would be important for the convergence of the solutions.

Shull and Löwdin [37] realized that this was due to the dependence of Z with n that dilates the orbitals and they proposed the following orbitals where these were substituted by adjustable parameters, *i.e.* usual orbital exponents:

$$\chi_{nlm}(\mathbf{r}) = N_{nl} L_{n-l-1}^{2l+2} (2\alpha r) r^l e^{-\alpha r} Y_l^m(\theta, \phi), \quad (10)$$

so these orbitals form a complete set. These orbitals were subsequently called Coulomb Sturmians because they fulfill the so-called Sturm-liouville theorem for eigenfunctions of such differential equations, with central Coulomb attraction.

In the Section 7 methods of the literature we will see how these kinds of orbitals have been used.

6. Types of Integrals over Slater orbitals

Due to the form of the Hamiltonian and of its expectation value we find the following kinds of integrals. First the integrals which appear when using Hartree-Fock and CI wave functions, in general *ab initio* methods. The integrals are classified according the number of electrons and centers which are linked. We present them in order of difficulty.

6.1 One-electron integrals

These are the one- and two-center overlap integrals $\langle a|b \rangle$, kinetic energy integrals $\langle a|b \rangle$ and two-center nuclear attraction ones $\langle a|1/r_b|b \rangle$.

Other case of one-electron integral is the three-center nuclear attraction, originated from the nuclear attraction operators in the Hamiltonian: $\langle a|1/r_c|b \rangle$.

6.2 Two-electron integrals

They can be up to four-centers because of the determinant giving the wave-function and thus the four orbitals which form the integral. According to the number of centers:

The two-center integrals have been traditionally the most investigated, they have the following nomenclature: The Coulomb integrals where the charge distribution of every electron is located at a center: $[aa|bb]$. Hybrid integrals, one charge distribution is located at one center and the other over two centers $[aa|ab]$ and their equivalents $[bb|ab]$. The exchange integral is more difficult it leads in case of different exponents to an infinite sum. Every electron is located in two centers: $[ab|ab]$. To solve these integrals a change to elliptical co-ordinates is useful. The Coulomb operator in elliptical co-ordinates contains associated Legendre functions of the first and second kind, for which integration is very difficult. In the case of slightly different exponents there are some singularities.

In actual calculations, the Coulomb and Hybrid integrals are calculated exactly, numerous methods exist. The exchange integrals are calculated with great accuracy.

The three-center integrals are of several types $[aa|bc]$, $[ab|ac]$. For different exponents there is no general solution.

The four-electron integrals are of the type $[ab|cd]$.

6.3 Three- and four-electron integrals

They appear in the Hylleraas-CI method [38] when using one inter-electronic distance r_{ij} per configuration. For the two-center case they have been solved generally by Budzinski [39]. Three- and higher number of centers have not been solved yet.

These can be many-center integrals, as every electron from right and left in the expectation value operator may be in a different center. These integrals are of the type, *i.e.* the easier $[aa|r_{12}r_{13}|ab|bb]$, to the most difficult $[ab|r_{12}r_{13}|ab|ab]$. Four-electron ones $[aa|r_{12}r_{13}/r_{14}|bb|ab|bb]$, and so on.

For three- and higher number of centers one would find three- and four electron integrals with as many centers as the molecule has up to 8. These integrals are still not solved. Interest nowadays focusses on the solution of two and three center molecules using explicitly correlated methods.

7. Methods in the literature

In this section the main methods of evaluation of the three- and four-center integrals over Slater orbitals from the literature will be explained. The methods are approximate because they consist in transformations, expansions or include numerical integrations. Therefore they are not as effective as analytical integration would be. Nevertheless, using these methods the evaluation of these integrals is possible and the programs are even as competitive as those using Gaussians.

7.1 Single-center expansion

The single-center expansion method requires expanding the Slater orbitals located at different centers at only one of them and then as for atoms to perform the integrations. The translation method consists in selecting an atom as origin then the translation of other orbitals from their atom to the origin. Therefore both methods are essentially the same. To expand one function centered in A at another point B the following expansion:

$$\varphi_{Ai} = \sum_{j=1}^{\infty} \left(\int \varphi_{Ai} \chi_{Bj} d\tau \right) \chi_{Bj}. \quad (11)$$

This formula is due to Smeyers [40]. In brackets, the requisite coefficients. The different methods of single-center expansion differ in the way to calculate these coefficients.

This method was first proposed by Barnett and Coulson [9] in 1956 using radial orbitals (s-orbitals) and was called the zeta function method because of expansions in terms of successive derivatives with respect to exponents.

The method has similarities with the alpha function method of Löwdin [10]. Harris and Michels [41] extended the method to angular general orbitals in 1965. This method has been used by Smeyers, Jones, Guseinov, Fernández Rico *et al*, and others.

The idea is the translation of an orbital from one point to the other. The translation of an spherical harmonic is a limited expansion, the translation of the radial part is nevertheless an infinite expansion. This situation can be best explained with formula of Guseinov [42]:

$$\chi_{n,l,m}(\zeta, r_A) = \sum_{n'=1}^{\infty} \sum_{l'=0}^{n'-1} \sum_{m'=-l'}^{l'} V_{nlm,n'l'm'}(\zeta, R_{AB}) \chi_{n',l',m'}(\zeta, r_B), \quad (12)$$

where V are the coefficients of the expansion. The method is very stable but it requires computation of a lot of terms to obtain sufficient correct decimal digits, therefore this method needs very long computational times.

7.2 Gaussian expansion

This is the Boys-Shavitt method [43], which consist on solving some integrals over Slater orbitals expanding them into a finite series of Gaussians:

$$e^{-\alpha r} = \sum_{i=1}^{N_G} c_i e^{-\alpha_i r^2}, \quad (13)$$

c_i and α_i are obtained by minimizing the least squares. This method and some improvements of this method are used at present in the program SMILES [25]. As N_G is usually larger than the number of the primitives when using only Gaussian basis sets, the number of integrals to calculate is large. The method is very stable and robust. It requires lengthy computational times to get accurate integral values.

7.3 Gaussian transform method

The Gaussian transform method by Shavitt and Karplus 1965 [44] has been probably the most used method. It consists in the Laplace transform of the exponential function, here exemplified by the simplest one i.e. a 1s orbital:

$$e^{-\alpha r} = \frac{\alpha}{2\sqrt{\pi}} \int_0^\infty \left(s^{-3/2} e^{-\alpha^2/(4s)} ds \right) e^{-sr^2}. \quad (14)$$

Every Slater exponential within the integral is transformed into a Gaussian one, for that one has to solve the integrals over s which have a special form. This integral has to be solved numerically. This is the disadvantage of the method.

7.4 Fourier-transform method

The B-functions Eq. (8) proposed by Filter and Steinborn in 1978 [35] have a highly compact Fourier transform. The group of Steinborn has developed this method [24]. The evaluation of integrals using B-functions leads to some integrals including a Bessel function of first kind which is oscillatory:

$$\int_0^\infty r^n e^{-\alpha r} J_{l+1/2}(rx) dr. \quad (15)$$

To evaluate these Safouhi [45, 46] used the SD-transform, due to Sidi [47], which consists in substituting this integral by a sine integral which has the same behavior. It needs numerical integration.

7.5 Use of Sturmians

The Sturmians were proposed by Shull and Löwdin in 1956 [37]. Smeyers used the Sturmians to evaluate three-center nuclear attraction integrals using the one-center expansion [40]. Guseinov 2001 used also them [48]. The Sturmians Eq. (10) fulfil the Sturm-Liouville theorem:

$$\nabla^2 S_{n,l}^m = \left[\alpha^2 - \frac{2\alpha n}{r} \right] S_{n,l}^m. \quad (16)$$

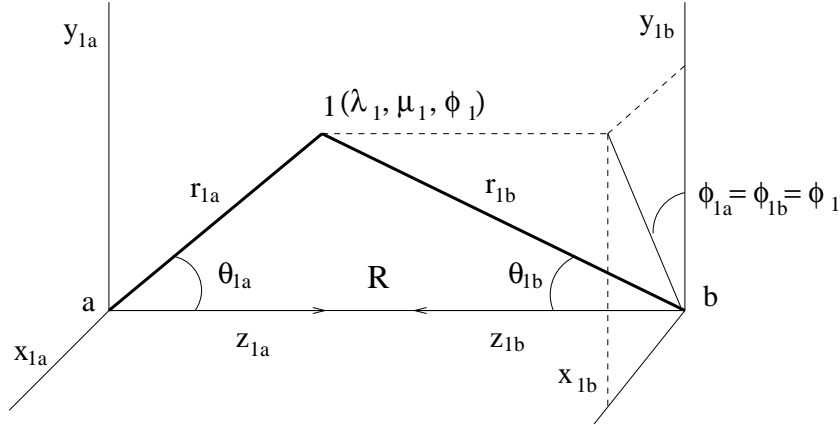
The so-called Coulomb Sturmians orthogonalise the Coulomb potential in their argument. This generally applies to the attraction term, at least for one-electron functions. Geminals useful for explicit correlation have also been used.

A seminal text by Avery gives more details to the interested reader on this subject [36].

7.6 Elliptic coordinate method

The elliptic coordinate method is the transformation of the polar orbital coordinates into elliptical ones λ, μ according to Figure 3. The two coordinate systems pointed to each other so that the elliptical angle ϕ coincides with polar angle ϕ . This transformation is:

Figure 3: Transformation from polar to elliptical coordinates.



$$r_{1a} = \frac{R}{2}(\lambda_1 + \mu_1), \quad r_{1b} = \frac{R}{2}(\lambda_1 - \mu_1), \quad (17)$$

$$\cos \theta_{1a} = \frac{1 + \lambda_1 \mu_1}{\lambda_1 + \mu_1}, \quad \cos \theta_{1b} = \frac{1 - \lambda_1 \mu_1}{\lambda_1 - \mu_1}, \quad (18)$$

$$\sin \theta_{1a} = \frac{[(\lambda_1^2 - 1)(1 - \mu_1^2)]^{1/2}}{\lambda_1 + \mu_1}, \quad \sin \theta_{1b} = \frac{[(\lambda_1^2 - 1)(1 - \mu_1^2)]^{1/2}}{\lambda_1 - \mu_1}, \quad (19)$$

The volume element and the domain change are:

$$\int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \rightarrow \frac{R^3}{8} \int_1^\infty d\lambda_1 \int_{-1}^{+1} d\mu_1 (\lambda_1^2 - \mu_1^2) \int_0^{2\pi} d\phi_1. \quad (20)$$

The method has been used by numerous authors: Mulliken, Rieke, Orloff, Rüdénberg, Roothaan, Eyring, Randic, Saika, Yoshimine, Maslen and Trefry, Guseinov, Bosanac, Randic, Harris, Fernandez Rico, Lopez, Özdogan and many others. Some types of three-electron integrals have been recently solved by Özdogan and Ruiz using this method [49].

8. General Two-electron Exponential type orbital integrals in poly-atomics without orbital translations

8.1 Introduction

Now, the Coulomb resolution will be presented. This is a readily controlled approximation to separating the variables in the $1/r_{12}$ which, in recent work by Gill and by Hoggan is shown to spell the end of exponential orbital translations and ensuing integral bottlenecks.

This section advocates the use of atomic orbitals which have direct physical interpretation, i.e. hydrogen-like orbitals. They are Exponential Type Orbitals (ETOs).

Until 2008, such orbital products on different atoms were difficult to manipulate for the evaluation of two-electron integrals. The difficulty was mostly due to cumbersome orbital translations involving slowly convergent infinite sums. These are completely eliminated using Coulomb resolutions. They provide an excellent approximation that reduces these integrals to a sum of one-electron overlap-like integral products that each involve orbitals on at most two centers. Such two-center integrals are separable in prolate spheroidal coordinates. They are thus readily evaluated. Only these integrals need to be re-evaluated to change basis functions.

The above is still valid for three-center integrals. In four-center integrals, the resolutions require translating one potential term per product. This is outlined here and detailed elsewhere.

Numerical results are reported for the H_2 dimer and CH_3F molecule.

The choice between gaussian and exponential basis sets for molecules is usually made for reasons of convenience at present. In fact, it appears to be constructive to regard them as being complementary, depending on the specific physical property required from molecular electronic structure calculations.

As regards exponential type orbitals (ETOs) such as Slater functions, it seems to be difficult to evaluate two-electron integrals because the general three- and four-center integrals evaluated by the usual methods require orbital translations. Some workers avoid the problem using large Gaussian expansions, as in SMILES [50, 51].

It would be helpful to devise a separation of the variables of integration. This would eliminate orbital translations, although some other translations remain involving a simple analytic potential.

The present work describes a breakthrough in two-electron integral calculations, as a result of Coulomb operator resolutions. This separates the independent variables of the operator and gives rise to simple analytic potentials. The two-center integrals are replaced by sums of overlap-like one-electron integral products. One potential term in these products requires translation in four-center terms, which is significantly simpler to carry out than that of the orbitals. This implies a speed-up for all basis sets, including gaussians. The improvement is most spectacular for exponential type orbitals. A change of basis set is also facilitated as only these one-electron integrals need to be changed. The gaussian and exponential type orbital basis sets are, therefore interchangeable in a given program. The timings of exponential type orbital calculations are no longer significantly greater than for a gaussian basis, when a given accuracy is sought for molecular electronic properties.

Numerical values for all two-electron integrals evaluated using Coulomb resolutions as well as total energies will be tabulated for the H_2 dimer and CH_3F molecule.

8.2 Basis sets

Although the majority of electronic quantum chemistry uses Gaussian expansions of atomic orbitals [13, 43], the present work uses exponential type orbital (ETO) basis sets which satisfy Kato's conditions for atomic orbitals: they possess a cusp at the nucleus and decay

exponentially at long distances from it [52]-[54]. It updates a ‘real chemistry’ interest beginning around 1970 and detailed elsewhere [3, 4, 15, 27, 44, 55, 56]. Slater type orbitals (STOs) [57, 58] are considered here.

STOs allow us to use routines from the STOP package [23, 59] directly. The integrals may be evaluated after gaussian expansion or expressed as overlaps to obtain speed up [60]. Exponents may be optimized solving a secular determinant as in [61].

8.3 Programming strategy

Firstly, the ideal *ab initio* code would rapidly switch from one type of basis function to another.

Secondly, the chemistry of molecular electronic structure must be used to the very fullest extent. This implies using atoms in molecules (AIM) and diatomics in molecules (DIM) from the outset, following Bader (in an implementation due to Rico et al [50] and Tully [62] implemented in our previous work [59, 63], respectively. The natural choice of atomic orbitals, i.e. the Sturmians or hydrogen-like orbitals lend themselves to the AIM approach. To a good approximation, core eigenfunctions for the atomic hamiltonian remain unchanged in the molecule. Otherwise, atom pairs are the natural choice, particularly if the Coulomb resolution recently advocated by Gill is used. This leads us to products of auxiliary overlaps which are either literally one- or two- centered, or have one factor of the product where a simple potential function is translated to one atomic center.

The Slater basis set nightmare of the Gegenbauer addition theorem is completely avoided. Naturally, the series of products required for, say a four-center two-electron integral may require 10 or even 20 terms to converge to chemical accuracy, when at least one atom pair is bound but the auxiliaries are easy to evaluate recursively and re-use. Unbound pairs may be treated using approximate methods.

Now, the proposed switch in basis set may also be accomplished just by re-evaluating the auxiliary overlaps. Furthermore, the exchange integrals are greatly simplified in that the products of overlaps just involve a two-orbital product instead of a homogeneous density. The resulting cpu-time growth of the calculation is n^2 for SCF, rather than n^4 . Further gains may be obtained by extending the procedure to post-Hartree-Fock techniques involving explicit correlation, since the r_{12}^{-1} integrals involving more than two electrons, that previously soon led to bottlenecks, are also just products of overlaps. This Coulomb resolution is diagonal in Fourier space in some cases.

8.4 Avoiding ETO translations for two-electron integrals over three and four centers

Previous work on separation of integration variables is difficult to apply, in contrast to the case for gaussians [64, 65]. Recent work by Gill *et al* [66] proposes a resolution of the Coulomb operator, in terms of potential functions ϕ_i , which are characterized by examining Poisson’s equation. In addition, they must ensure rapid convergence of the implied sum in

the resulting expression for Coulomb integrals J_{12} as products of "auxiliaries" i.e. overlap integrals, as detailed in [66]:

$$J_{12} = \langle \rho(r_1) \phi_i(r_1) \rangle \langle \phi_i(r_2) \rho(r_2) \rangle, \text{ with implied summation over } i. \quad (21)$$

This technique can be readily generalized to exchange and multi-center two-electron integrals. For two-center terms it is helpful to define structure harmonics by Fourier transforms, limiting evaluation to non-zero terms [67].

Note, however, that in four-center integrals, the origin of one of the potential functions only may be chosen to coincide with an atomic (nuclear) position.

Define the potential functions [67]:

$$\phi_i = 2^{3/2} \phi_{nl}(r) Y_l^m(\theta, \phi)$$

Omitting the spherical harmonic term gives radial factors:

$$\phi_{nl}(r) = \int_0^{+\infty} h_n(x) j_l(rx) dx, \quad \text{with } j_l(x) \text{ denoting the spherical Bessel function.} \quad (22)$$

Here, $h_n(x)$ is the n^{th} member of any set of functions that are complete and orthonormal on the interval $[0, +\infty)$, such as the n^{th} order polynomial function (*i.e.* polynomial factor of an exponential). The choice made in [66] is to use parabolic cylinder functions (see also another application [51]), *i.e.* functions with the even order Hermite polynomials as a factor. This is not the only possibility and a more natural and convenient choice is based on the Laguerre polynomials $L_n(x)$: Define:

$$h_n(x) = \sqrt{2} L_n(2x) e^{-x}. \quad (23)$$

These polynomial functions are easy to use and lead to the following analytical expressions for the first two terms in the potential defined in (22):

$$V_{00}(r) = \sqrt{2} \frac{\tan^{-1}(r)}{r}, \quad (24)$$

$$V_{10}(r) = \sqrt{2} \left[\frac{\tan^{-1}(r)}{r} - \frac{2}{(1+r^2)} \right], \quad (25)$$

Furthermore, higher n expressions of $V_{n0}(r)$ all resemble (25) (see [67] eq (23)):

$$V_{n0}(r) = \sqrt{2} \frac{1}{r} \left(\tan^{-1}(r) + \sum_{k=1}^n (-1)^k \frac{\sin(2k \tan^{-1}(r))}{k} \right), \quad (26)$$

and analytical expressions of $V_{nl}(r)$ with non-zero l are also readily obtained by recurrence.

These radial potentials can generally be expressed in terms of hypergeometric functions, whether the choice of polynomial is the present one, *i.e.* Laguerre, or Hermite polynomials, as in [66]. This structure has been used to confirm the results of [67] using a rapid code in C [68].

Spherical harmonics are translated using Talman's approach [69]. The displaced potential in one factor of the product of 'auxiliaries', from four-center integrals is readily expanded in two-center overlaps, after applying Euler's hypergeometric transformation. [70, 71].

The auxiliary overlap integrals $\langle \rho(r_1) \phi_i(r_1) \rangle$ and $\langle \phi_i(r_2) \rho(r_2) \rangle$ will involve densities obtained from atomic orbitals centered on two different atoms in exchange multi-center two-electron integrals. The overlap integrals required in an ETO basis are thus of the type:

$$\langle \psi_a(r_1) \psi_b(r_1) \phi_i(r_1) \rangle = \sum_{\mu=0}^{\mu_{max}} N_{\mu}(n_1, n_2, n_i, l_i, |m_i| \alpha \beta) s(n_1, l_1, m, n_2, l_2, \alpha \beta), \quad (27)$$

with: $\alpha = \zeta_1 R$ and $\beta = \zeta_2 R$. Slater exponents. In three-center overlaps, N_{μ} is a normalised Racah coefficient [71]. In two-center cases the sum reduces to a single normalisation term, N_0 . A Fourier transform approach is also being investigated, extending [67].

The real space core overlaps then take the form:

$$s(n_1, l_1, m, n_2, l_2, \alpha, \beta) = D_{l_1, l_2, m} \sum_{ij}^{\lambda} Y_{ij}^{\lambda} A_i \left\{ \frac{1}{2}(\alpha + \beta) \right\} B_j \left\{ \frac{1}{2}(\alpha - \beta) \right\}, \quad (28)$$

Y_{ij}^{λ} is a matrix with integer elements uniquely determined from n , l and m .

$D_{l_1, l_2, m}$ is a coefficient that is independent of the principal quantum number. It is obtained upon expanding the product of two Legendre functions in this co-ordinate system. Symmetry conditions imply that only $m_1 = m_2 = m$ lead to non-zero coefficients:

$$A_i \left\{ \frac{1}{2}(\alpha + \beta) \right\} = \int_1^{\infty} \exp \left\{ -\frac{1}{2}(\alpha + \beta)\mu \right\} \mu^i d\mu, \quad (29)$$

$$B_j \left\{ \frac{1}{2}(\alpha - \beta) \right\} = \int_{-1}^1 \exp \left\{ -\frac{1}{2}(\alpha - \beta)\nu \right\} \nu^j d\nu. \quad (30)$$

Here, recurrence relations on the auxiliary integrals A and B lead to those for the requisite core integrals [72, 73]. These integrals may be pre-calculated and stored.

Such integrals appear for two-center exchange integrals and three- and four- center integrals (although just in one factor for three-center Coulomb terms). Note that exchange integrals require distinct orbitals ψ_a and ψ_b . In the atomic case, they must have different values for at least one of n, l, m or ζ . In the two-center case, the functions centered at a and b may be the same. The product does not correspond to a single-center density: it is two-centered. Equation (27) then illustrates the relationship to the one-electron two-center overlap integral, although it clearly includes the extra potential term from the Coulomb operator resolution.

This assumes tacitly that the potential obtained from the Coulomb operator resolution be centered on one of the atoms. Whilst this choice can be made for one pair in a four-center product, it cannot for the second. There remains a single translation for this potential in one auxiliary of the two in a product representing a four-center integral and none otherwise.

This method obviates the need to evaluate infinite series that arise from the orbital translations efficiently. They have been eliminated in the Coulomb operator resolution approach,

Table 1: Atomic exchange integrals (6 distinct single center values between pairs of different AOs).

AOs (zeta)	Label	[a(1)b(2)a'(2)b' (1)]	Value
$1s_{a1}$ 1.042 999	1	1 2 1 2	0.720 716
$1s_{a2}$ 1.599 999	2	1 3 1 3	0.585 172
$2s_{a1}$ 1.615 000	3	1 4 1 4	0.610 192
$2s_{a2}$ 1.784 059	4	2 3 2 3	0.557 878
$1s_{b1}$ 1.042 999	5	2 4 2 4	0.607 927
$1s_{b2}$ 1.599 999	6	3 4 3 4	0.602 141
$2s_{b1}$ 1.615 000	7	2 1 2 1	0.720 716
$2s_{b2}$ 1.784 059	8	3 2 3 2	0.557 878

since only orbitals on two centers remain in the one-electron overlap-like auxiliaries. These can be evaluated with no orbital translation, in prolate spheroidal co-ordinates, or by Fourier transformation [67, 71].

8.5 Numerical results of Coulomb resolutions: efficiency

First a test system is studied, built up of four hydrogen atoms. The second example is the full RHF calculation of CH_3F using the Coulomb resolutions.

Consider the H_2 molecule and its dimer/agregates. In an s-orbital basis, all two-center integrals are known analytically, because they can be integrated by separating the variables in prolate spheroidal co-ordinates. A modest s-orbital basis is therefore chosen, simply for accuracy demonstration on a rapid calculation, for which some experimental data could be corroborated.

The purpose of this section is to compare evaluations using the Coulomb resolution to the exact values, obtained analytically. The IBM Fortran compiler used is assumed to be reliable to 14 decimals in double precision. The worst values in the Coulomb resolution approximation have 10 correct decimals for two-center integrals with a 25-term sum.

Timings are then compared for translation of a Slater type orbital basis to a single center (STOP) [59] with the Poisson equation solution using a DIM (Diatomics in molecules or atom pair) strategy and finally to show that the overlap auxiliary method is by far the fastest approach, for a given accuracy (the choice adopted is a sufficient six decimals, for convenient, reliable output).

H_2 molecule with interatomic distance of 1.402 atomic units (a.u.). One and two-center Coulomb integrals may be obtained analytically and Coulomb resolution values compare well with them [66].

The two-center exchange integrals are dominated by an exponential of the interatomic distance and thus all have values close to 0.3. The table is not the full set. All index ‘15’ terms, involving $1s_{a1}(1) 1s_{b1}(2)$ are given, to illustrate symmetry relations.

Note that this is by no means the best possible basis set for H_2 , since it is limited to $l = 0$ functions (simply to ensure that even the two-center exchange integral has an analytic closed form).

Table 2: Two-center exchange integrals. All pair permutations possible. Some are identical by symmetry.

Labels	Value
1515	0.319 902
1516	0.285 009
1517	0.325 644
1518	0.324 917
1527	0.291 743
1528	0.293 736
1538	0.329 543
2525	0.260 034
2516	0.254 814
2517	0.290 533
2518	0.290 149

The total energy obtained for the isolated H_2 molecule is -1.1284436 a.u. as compared to a Hartree-Fock limit estimate of -1.1336296 a.u. Nevertheless, the Van der Waals well, observed at 6.4 au with a depth of 0.057 kcal/mol (from Raman studies) is quite reasonably reproduced [74].

Dimer geometry: rectangular and planar. Distance between two hydrogen atoms of neighboring molecules: 6 a.u. Note that this alone justifies the expression dimer-the geometry corresponds to two almost completely separate molecules, however, the method is applicable in any geometry (for 3 a.u. all three- and four- center integrals evaluated by Coulomb resolution agree with those of STOP to at least 6 decimals).

Timings on an IBM RS6000 Power 6 workstation, for the dimer (all four-center integrals in msec): STOP: 12 POISSON: 10 OVERLAP: 2. Total dimer energy: -2.256998 a.u. This corresponds to a well-depth of 0.069 Kcal/mol, which may be considered reasonable in view of the basis set.

8.6 Selected exchange integrals for the CH_3F molecule (evaluated using the Coulomb resolution)

Geometry and exponents are those of previous work [75]: Tetrahedral angles, with C-H 2.067 and C-F 2.618 a.u.

No symmetry is assumed but geometric relationships are observed, as well as those due to m values, at least to the nano-Hartree accuracy chosen.

For illustrative purposes, three-center exchange integrals are tabulated in a real basis. Timings on IBM RS6000 Power 6 workstation for all two-electron integrals: STOP: 1.21 s, OVERLAP: 0.17 s.

All the two-electron integrals are identical to better than six significant figures with those obtained using the STOP software package [59].

The factor limiting precision in this study is the accuracy of input. The values of Slater exponents and geometric parameters are required to at least the accuracy demanded of the integrals and the fundamental constants are needed to greater precision.

Table 3a: Orbital exponents.

AO No.	n	l	m	zeta
01	1	0	0	5.6727
02	2	0	0	1.6083
3-5	2	1	m	1.5679
06	1	0	0	8.5600
07	2	0	0	2.5600
8-10	2	1	m	2.5200
H	1	0	0	1.2400

Table 3b: Selected examples of three-center exchange integrals.

Integral	Value	Integral	Value
$\langle 2s_C 2s_F 2s_C 1s_{Ha} \rangle$	$0.4970\ 48510 \times 10^{-1}$	$\langle 2s_F 1s_{Ha} 1s_F 2s_C \rangle$	$0.1014\ 05594 \times 10^{-2}$
$\langle 2s_C 2s_F 2s_C 1s_{Ha} \rangle$	$0.8420\ 56635 \times 10^{-2}$	$\langle 2s_F 1s_{Ha} 2s_F 2s_C \rangle$	$0.9341\ 35949 \times 10^{-2}$
$\langle 2s_C 1s_F 1s_C 1s_{Ha} \rangle$	$0.5737\ 90540 \times 10^{-3}$	$\langle 2s_F 1s_{Ha} 2p_{zF} 2s_C \rangle$	$-0.8442\ 95091 \times 10^{-2}$
$\langle 2s_C 1s_F 2s_C 1s_{Ha} \rangle$	$0.3789\ 18525 \times 10^{-2}$	$\langle 2s_F 1s_{Ha} 1s_F 2p_{zC} \rangle$	$0.1813\ 23479 \times 10^{-2}$
$\langle 1s_C 2p_{zF} 2p_{zC} 1s_{Ha} \rangle$	$0.1587\ 58344 \times 10^{-2}$	$\langle 2s_F 1s_{Ha} 2s_F 2p_{zC} \rangle$	$0.1379\ 64387 \times 10^{-1}$
$\langle 2s_C 2p_{zF} 2p_{zC} 1s_{Ha} \rangle$	$0.5258\ 34208 \times 10^{-2}$	$\langle 2s_F 1s_{Ha} 2p_{zF} 2p_{zC} \rangle$	$-0.1135\ 01125 \times 10^{-1}$
$\langle 2p_{zC} 1s_F 1s_C 1s_{Ha} \rangle$	$0.1025\ 32536 \times 10^{-2}$	$\langle 1s_{Ha} 2s_F 1s_{Ha} 2s_C \rangle$	$0.1252\ 319411 \times 10^{-1}$
$\langle 2p_{zC} 1s_F 2s_C 1s_{Ha} \rangle$	$0.6772\ 76818 \times 10^{-2}$	$\langle 1s_{Ha} 2s_F 1s_{Ha} 2p_{zC} \rangle$	$-0.1591\ 49899 \times 10^{-2}$
$\langle 1s_C 1s_F 1s_C 1s_{Ha} \rangle$	$0.1099\ 00118 \times 10^{-6}$	$\langle 1s_{Ha} 2p_{zF} 1s_{Ha} 2p_{zC} \rangle$	$0.1772\ 90873 \times 10^{-2}$
$\langle 1s_C 1s_F 2s_C 1s_{Ha} \rangle$	$0.6794\ 54131 \times 10^{-6}$	$\langle 1s_F 1s_{Hb} 2s_F 1s_C \rangle$	$0.2287\ 77210 \times 10^{-4}$
$\langle 1s_C 2s_F 1s_C 1s_{Ha} \rangle$	$0.1446\ 31297 \times 10^{-2}$	$\langle 1s_{Hb} 2s_F 1s_{Hb} 1s_C \rangle$	$0.1939\ 63837 \times 10^{-2}$
$\langle 1s_C 2s_F 2s_C 1s_{Ha} \rangle$	$0.4235\ 59085 \times 10^{-2}$	$\langle 2s_C 1s_{Ha} 1s_C 1s_{Hb} \rangle$	$0.2034\ 841982 \times 10^{-1}$
$\langle 2p_{zC} 2s_F 1s_C 1s_{Ha} \rangle$	$0.1112\ 10955 \times 10^{-1}$	$\langle 1s_C 1s_{Ha} 1s_C 1s_{Hb} \rangle$	$0.7154\ 932331 \times 10^{-2}$
$\langle 2p_{zC} 2s_F 1s_C 1s_{Ha} \rangle$	$0.6738\ 14908 \times 10^{-1}$	$\langle 2s_C 1s_{Ha} 2s_C 1s_{Hb} \rangle$	$0.1137\ 390852$

8.7 Conclusions

A remarkable gain in simplicity is provided by Coulomb operator resolutions [66], that now enables the exponential type orbital translations to be completely avoided in *ab initio* molecular electronic structure calculations.

This breakthrough that Coulomb resolutions represent (in particular with the convenient choice of Laguerre polynomials) in the ETO algorithm strategy stems from a well-controlled approximation, analogous to the resolution of the identity. The convergence has been shown to be rapid in all cases [67].

The applications to H₂ dimer Van der Waals complexes and CH₃F uses a general code within the STOP package [59]. They show the Coulomb resolution can be used to give fast and accurate results for basis sets of s and p Slater type orbitals. Generalisation is in progress.

Numerical values for the H₂ dimer geometry and interaction energy agree well with complete *ab initio* potential energy surfaces obtained using very large gaussian basis sets and data from vibrational spectroscopy [74].

9. Explicitly Correlated Methods for Molecules

The application and development of such methods to determine accurately the ground and excited states, and properties of diatomic and triatomic molecules is very promising and more interesting for the Computational Chemist than the atomic case. There is nowadays a growing interest in this field. Subroutines and programs which perform these calculations are often requested in the community.

The investigation of these integrals should be approached within the Molecular Orbital method (MO) [76], because the MO wave function is the simplest wave function for a molecular system. As Coulson [77] discussed, the MO method permits the visualization of electrons and nuclei and interpretation of individual electrons and their orbital exponents better than the wave functions written in elliptical coordinates.

The wave functions constructed with elliptical orbitals are of two types, the so-called James-Coodlige [78] wave functions (one-alpha exponent), recently extended to the two-alpha case [33], and Kolos-Wolniewick [79, 80] wave functions (with both orbital exponents alpha, and beta). Both have been applied to the H₂ molecule.

The elliptical wave functions are the natural representation of a two-center problem but for three-center and larger molecules the use of the MO method becomes necessary. Frost [81] used the MO method and the Correlated Molecular Method (CMO) in H₂ calculations. About the extension of the method he wrote: *"The extension of CMO-type wave functions to more complex molecules does not seem feasible at the present time. The new integrals which will be introduced would involve more than two centers if more nuclei were involved and higher atomic orbitals than 1s if more electrons were considered, and their evaluation*

would be extremely difficult”.

Recently, impressive calculations using Hylleraas wave functions have been done for H_2 , see Table 4. Hylleraas [33], the Iterative Complement Iteration method (ICI) [82], and Explicitly correlated Gaussian (ECG) [83] calculations of the hydrogen molecule, Hylleraas calculations on HeH^+ and some species [84] leading to -2.9710784698 a.u. using 9576 configurations and calculations of He_2 using 4800 optimized ECG configurations with energy -5.80748359014 a.u. [83] achieved the the highest known accuracy in molecules (picohartree accuracy is more than that of chemical measurements, *e.g.* a micro cm^{-1} , a nano eV or micro cal/mol. Although one must recall that in the calculation of properties according to Drake [85], only half of the digits of the energy are kept).

Note also that input exponents, distances and some fundamental constants may limit accuracy of calculations compared with measurements and that molecules may not be rigid. Eventually, dynamics and the effect of the Born-Oppenheimer approximation should be included.

Hy-CI was applied in 1976 to LiH molecule by Clary [32] using elliptical STOs. For two-center molecules the three-electron and four-electron integrals occurring in the Hy-CI have been developed by Budzinski [39].

Another type of explicitly correlated wave functions are the ones that use Gaussian orbitals. Clementi *et al* extended the Hy-CI to molecules using Gaussian orbitals [86], and applied it to the calculation of H_3 . The ECG wave function is appropriate also for molecules [83, 87], as the interelectronic distance r_{12} is a Gaussian exponent. This leads to results, which are comparable with Hylleraas calculations [83].

The R_{12} -wave function proposed by Kutzelnigg and Klopper [88, 89] has the merits to fulfill the cusp condition, to use Gaussian functions avoiding the three- and four-center integration problems, and to include precisely r_{12} , involving electrons 1 and 2, close to the nucleus, where the probability that $r_{12} = 0$ is larger, also these electrons are present at any system starting from helium atom. The r_{12} variation influences energy. The R_{12} wave function, developed for molecular calculations is nowadays widely used and combined with all kinds of methods. The occurring three- and four-electron integrals are calculated in terms of two-electron ones. Due to the use of a single r_{12} value, the accuracy achieved for atomic calculations is lower than the accuracy of Hy and Hy-CI calculations. Recent improvements of the method [90]-[92] can achieve microhartree accurate energy results for chemically interesting systems.

Short wave function expansions lead to very good results. When a large number of configurations are used (up to 10000) the energy results are beyond pico-hartree accuracy, while the CI wave function would need in the order of millions of configurations.

10. Highly accurate calculations using STOs

Another problem appearing in these calculations is the digital erosion. For many operations and subtraction numbers of similar value some digits can be lost leading to erroneous results.

Table 4: Highly accurate calculations on the H₂ molecule with different types of wave functions at R=1.4011 a.u.

Authors	type w. f.	Confs.	Energy (a.u.)
1933 James and Coolidge	JC	5	-1.1735
1960 Kolos and Roothaan	KR		-1.17214
1968 Kolos and Wolniewicz	KW		-1.174475
1995 Wolniewicz	KW	833	-1.17447467
2006 Sims and Hagstrom	JC	7034	-1.17447593139984
2007 Nakatsuji	ICI	6776	-1.17447571400027
2008 Cencek and Szalewicz	ECG,opt	4800	-1.17447571400135

Quadruple precision avoids this, about 30 decimal digits are correct on our computer. Other possibility is high precision arithmetic software. Some programs are available like Bailey’s MPFUN [93], the Brent and Miller program packages [94, 95].

One example of the use of Slater orbitals in the present are the highly accurate calculations of small molecules using explicitly correlated wave functions i.e. wave functions where the inter-electronic coordinate r_{ij} is included explicitly in the wave function. These are the Hylleraas and Hylleraas-CI wave functions, ICI method, compared with the explicit correlated Gaussians ECG and the R12 method.

11. Closing remarks

We conclude with the words of G. Berthier: *GTOs are like medicine, you have to use them as long as they are healing, but once they don’t work any more, you much change them, Gaston Berthier, Interview, Paris, 2nd June 1997.*

Recently, a whole book ”Recent Advances in Computational Chemistry: Molecular Integrals over Slater Orbitals” was dedicated to a mathematical review of methods of integration over Slater orbitals and Hylleraas wave functions [96].

12. Acknowledgements

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