# How specific exponential type orbitals recently became a viable basis set choice in NMR shielding tensor calculation.

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## Abstract

This paper advocates use of the atomic orbitals which have direct physical interpretation, i.e. Coulomb Sturmians and hydrogen-like orbitals. They are exponential type orbitals (ETOs). Their radial nodes are shown to be essential in obtaining accurate nuclear shielding tensors for NMR work. The present work builds on a 2003 French PhD and many numerical results were published by 2007. The improvements in this paper are noteworthy, the key being the actual basis function choice.

Until 2008, their products on different atoms were difficult to manipulate for the evaluation of two-electron integrals. Coulomb resolutions 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 co-ordinates. They are thus readily evaluated. Only these integrals need to be re-evaluated to change basis functions.

In this paper, a review of the translation procedures for Slater type orbitals (STO) and for Coulomb Sturmians follows that of the more recent application to ETOs of a particularly convenient Coulomb resolution.


Keywords: Coulomb Sturmian basis, nodal structure, Coulomb resolutions, *ab initio* quantum chemistry.

# 1 Introduction

The criteria for choice between gaussian and exponential basis sets for molecules do not seem obvious 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.

The present work describes a breakthrough in two-electron integral calculations, as a result of Coulomb operator resolutions. This is particularly significant in that it eliminates the arduous orbital translations which were necessary until now for exponential type orbitals. The bottleneck has been eliminated from evaluation of three- and four- center integrals over Slater type orbitals and related basis functions.

The two-center integrals are replaced by sums of overlap-like one-electron integrals. 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.

Atomic orbitals are physically meaningful one-electron atom eigenfunctions for the Schrödinger equation. This gives well-known analytical expressions: hydrogen-like orbitals.

Boundary conditions allow the principal quantum number n to be identified as the order of the polynomial factor in the radial variable. It must therefore be positive and finite. It is also defined such that $n - l - l$ is greater than or equal to 0. This gives the number of zeros of the polynomial (radial nodes). Here, $l = 0$ or a positive integer, which defines the angular factor of the orbital. (i.e. a spherical harmonic, or, more rarely, its Cartesian equivalent) The number $n$ gives the energy of the one-electron atomic bound states. Frequently, basis set studies focus on the radial factor. That is, for our present purposes, the angular factor can be assumed sufficiently defined as a spherical harmonic.

The key issue is whether to choose basis sets with exponential or gaussian asymptotic factors.

Certain physical properties, such as NMR shielding tensor calculations directly involve the nuclear cusp and correct treatment of radial nodes, which indicates that basis sets such as Coulomb Sturmians are better suited to their evaluation than gaussians [85, 37, 38].

There is also evidence to suggest that CI expansions converge in smaller exponential basis sets compared to gaussians [45, 44]. Benchmark overlap similarity work is available [46, 47]

# 2 Wave-function quality

The following quantity:

$$-1/2\frac{\nabla\rho(r)}{\rho(r)}$$

is used to test wave-function quality. It is smooth, to varying degrees, in different basis sets. Atomic positions must give cusps. The importance for stable and accurate kinetic energy terms, particularly in DFT.

Much molecular quantum chemistry is carried out using gaussian basis sets and they are indeed convenient and lead to rapid calculations. The essential advantage they had over exponential basis sets was the simple product theorem for gaussians on two different atomic centers. This allows all the two-electron integrals, including three- and four- center terms to be expressed as single-center two-electron integrals.

The corresponding relationship for exponential type orbitals generally led to infinite sums and the time required, particularly for four-center integrals could often become prohibitive.

Recent work by Gill has, nevertheless been used to speed up all three and four center integral evaluation, regardless of basis using the resolution of the Coulomb operator [15, 16, 36]. This work by Gill is used here to reduce the three- and four- center two-electron integrals to a sum of products of overlap-like (one-electron) integrals, basically two-centered. This algorithm was coded in a Slater type orbital (STO) basis within the framework of the STOP package [4] (in fortran) during summer 2008. Note, however, that other exponential or gaussian basis sets can readily be used. The set of one-electron overlap-like auxiliary integrals is the only calculation that needs to be re-done. They may be re-evaluated for the basis set that the user selects for a given application. This procedure makes the approach highly versatile, since a change of basis set requires relatively few simple new evaluations. A modular or object oriented program is being designed to do this efficiently [36, 48, 94].

The present article gives illustrative test results on molecular systems e.g. the $H_2$ dimer.

The layout is as follows: the review begins with a brief recap of basis sets and programming strategy in the next two sections. Atom pairs are the physical entity used for integral evaluation, both in the Poisson equation technique and the Coulomb resolution. Two sections are devoted to these progressively more powerful techniques which both reduce two-electron to one-electron integrals. The overlaps required for the Coulomb resolution differ by a potential factor from orbital overlaps. Their evaluation is nevertheless analytic, using well-known techniques summarized in the subsequent section. Finally, to illustrate what can be gained by eliminating orbital translations, the translation of Slater type orbitals is reviewed briefly, from recent work on BCLFs. A few numerical results are given on the dimer of molecular hydrogen which show progressive speed-up particularly for the Coulomb resolution given a pre-selected accuracy, which proves sufficient to provide satisfactory confirmation of experimental work on this dimer.

# 3   Basis sets

Although the majority of electronic quantum chemistry uses gaussian expansions of atomic orbitals [19, 20], 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 [58, 59, 60]. It updates a tradition beginning around 1970 and detailed elsewhere [28, 29, 30, 22, 21, 23, 24, 25, 26, 27, 31, 32, 51]

Two types of ETO are considered here: Slater type orbitals (STOs) [56, 57] and Coulomb Sturmians and their generalisation, which may be written as a finite combination thereof [102]. Otherwise, STOs may be treated as multiple zeta basis functions in a similar way to the approach used with gaussian functions.

Many exponential type functions exist [102]. Preferential use of Sturmian and related functions with similar radial nodes is discussed [36].

Coulomb Sturmians have the advantage of constituting a complete set without continuum states because they are eigenfunctions of a Sturm-Liouville equation involving the nuclear attraction potential i.e. the differential equation below.

$$\nabla_{\vec{r}}^2 \mathcal{S}_{nl}^m(\beta, \vec{r}) = \left[\beta^2 - \frac{2\beta n}{r}\right]\mathcal{S}_{nl}^m(\beta, \vec{r}).$$

The exponential factor of Coulomb Sturmians; $e^{-\beta r}$ has an arbitrary screening parameter $\beta$. In the special case when $\beta = \zeta/$n with n the principal quantum number and $\zeta$ the Slater exponent,

we obtain hydrogen-like functions, which do not span the same space and require inclusion of continuum states to form a complete set [102]. Hydrogen-like functions are, however well known as atomic orbitals: the radial factor contains the associated Laguerre polynomial of order $2l + 1$ with suffix $n - l - 1$ and the exponential $e^{-\zeta r/n}$ as indicated above. The angular factor is just a spherical harmonic of order $l$. These functions are ortho-normal. The optimal values of the $\beta$ parameters may be determined analytically by setting up secular equations which make use of the fact that the Sturmian eigenfunctions also orthogonalise the nuclear attraction potential, as developed by Avery [74].

$$\int \mathcal{S}_{nl}^m(r, \theta, \phi) \, \mathcal{S}_{n'l'}^{m'}(r, \theta, \phi) \, \frac{dr}{r} \; = \; \delta_{nn'll'mm'}.$$

These ortho-normal functions are further generalised by varying $\alpha$ from the Coulomb Sturmian value of 1. In such a case, the basis remains ortho-normal and othogonalises $a/r^\alpha$. This eliminates the $r^2$ term, arising for quadrupole moments when $\alpha = -2$, thus confirming the very recent numerical observations in the Guseinov group [107]. Similarly, it would be expected that $\alpha = -1$ ETOs would constitute the optimal basis for magnetic dipole integrals of NMR shielding. Furthermore, a negative value of $\alpha$ will not modify the number of radial nodes: the functions will simply breath. Definitions: the generalised exponential functions constitute finite complete orthonormal sets. Their expression is as follows:

$$\chi_{nlm}(\mathbf{r}) = \left[ \frac{(-1)}{\sqrt{2n}} \right]^\alpha N_{nl} L_{n-l-1-\alpha}^{2l+2-\alpha} \left( 2\,\zeta r \right) r^l e^{-\zeta r} Y_l^m(\theta, \phi) \tag{3.1}$$

Here, N is the normalisation constant previously obtained for Coulomb Sturmians, L is the associated Laguerre polynomial of order $2l + 2 - \alpha$ with suffix $n - l - 1 - \alpha$ (recall that $\alpha = 1$ defines the Coulomb Sturmians.

Define a variable including the screening constant:

$$x = 2\,\zeta r$$

Subsequently, rewriting the norm as $N(\alpha)_{nl}$ and introducing $p = 2l + 2 - \alpha$ and $q = n + l + 1 - \alpha$ gives the simplified expression for the generalised orthonormal basis sets of ETO, used by Guseinov.

$$\chi_{nlm}(\mathbf{x}) = N(\alpha)_{nl} L_q^p(x) \, r^l e^{-x/2} Y_l^m(\theta, \phi) \tag{3.2}$$

In past applications, no obvious advantage has been evidenced for the functions with negative $\alpha$ indices over the well-known Slater type orbitals, Coulomb Sturmians ($\alpha = 1$) or Shull-Loewdin functions ($\alpha = 0$). In fact, the infinite series arising when Hartree-Fock two-electron integrals that do not possess closed forms (three and four center terms) are evaluated converge much more slowly when the negative $\alpha$ functions are used. This has recently also proven to be the case of a set of electric field integrals [108].

This paper records the precedent of electric quadrupole integrals, already published by Guseinov's colleagues, where the negative $\alpha$ basis converges as well as (if not better than) the STO [107] and presents a new application to the dipole integrals in the NMR experimental setup.

The investigations are extended to comparisons with previous work on the nuclear dipole integrals that are so important to the evaluation of nuclear shielding tensors and NMR chemical shifts.

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Furthermore, these nuclear magnetic dipole integrals are closely related to the one-electron nuclear attraction integral, required in all Hartree-Fock and DFT work.

Alternative ETOs would be Slater type orbitals and B-functions with their simple Fourier transforms. Strictly, they should be combined as linear combinations to form hydrogen-like or, better, Sturmian basis sets prior to use.

STOs allow us to use routines from the STOP package [55] directly, whereas Coulomb Sturmians still require some coding. The relationship to STOs is used to carry out calculations over a Coulomb Sturmian basis with STOP until the complete Sturmian code is available. The present state-of-the-art algorithms require at most twice as long long per integral than GTO codes but the CI converges with fewer functions and the integrals may be evaluated after gaussian expansion or expressed as overlaps to obtain speed up [63].

After a suitably accurate electron density has been obtained for the optimized geometry over a Coulomb Sturmian basis set, the second order perturbation defining the nuclear shielding tensor should be evaluated in a Coupled perturbed Hartree Fock scheme.

The integrals involved may conveniently be evaluated using B-functions with linear combinations giving the Coulomb Sturmians.

$$\mathcal{S}_{nl}^m(r) \;=\; (2\alpha)^{3/2} \frac{2^{2l+1}}{2l+1)!!} \sum_{l=0}^{n-l-1} \frac{(-n+l+1)_t\,(n+l+1)_t}{t!\,(l+3/2)_t} B_{t+1,l}^m(r)$$

The techniques exploit properties of Fourier transforms of the integrand.

Note that either HF or DFT can serve as zero order for the present nuclear shielding tensor calculation over ETOs.

A full *ab initio* B-function code including nuclear shielding tensor work is expected to be complete shortly.

Some tests show that Slater type orbitals (STO) or B-functions (BTO) are less adequate basis functions that Coulomb Sturmians, because only the Sturmians possess the correct nuclear cusp and radial behavior.

# 4    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) at the outset, following Bader (in an implementation due to Rico et al [50] and Tully [41] implemented in our previous work [55], 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 needs to be 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 a smaller number of terms since the integals can be predicted to be small, using a Schwarz inequality.

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.

## 5    Atom pairs: solving Poisson's equation

All the molecular integrals over CS required for standard SCF may be evaluated using analytical two-center terms based on the solution of Poisson's equation for the Coulomb potential in an ETO basis. This uses the Spectral forms (involving incomplete gamma functions and regular and irregular solid harmonics) defined initially in [52, 63, 53] and subsequently generalized to ensure numerical stability as shown in a brief summary below.

Recalling the definition of a Slater Type Orbital:

$$\chi_{n,\ l,\ m,\ \varsigma}(r,\theta,\phi) = N_1\ r^{n-1}e^{-\varsigma r}\ Y_l^m(\theta,\phi)\ .$$

Define the radial factor $g(r)$ :

$$g(r) = r^{n-1}e^{-\varsigma r}\ .$$

Then, (from the Spectral forms in [63]), the potential due to this distribution is immediately written:

$$\Pi_l(g) = r^2 F(r)\ ,$$

Where g is short for g(r) and F(r) is given below, with a suitable variable of integration; u:

$$F(r) = \int_0^1 du\ g(ru)\ u^{l+2} + \int_1^\infty du\ g(ru)\ u^{1-l}.$$

This expression is used to write all radially dependent one and two-center integrals in analytical closed form.

The next section describes a more profound advance, that reduces the atom-pair evaluation to one-electron overlap-like integrals. It is related to the Poisson equation technique, as detailed in [63] and [33].

## 6    Avoiding ETO translations for two-electron integrals over 3 and 4 centers

Previous work on separation of integration variables is difficult to apply, in contrast to the case for gaussians [43] cf [40]. Recent work by Gill *et al* [15] proposes a resolution of the Coulomb operator, in terms of potential functions $\phi_i$, 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 [15].

This is based on separating the variables of $\frac{1}{r_{12}}$, by determining suitable functions of $r_1$ and $r_2$ that treat these variables equivalently and constitute a complete set which orthogonalises the Coulomb operator. The associated potentials $\phi_i$ provide an expansion, or resolution of $\frac{1}{r_{12}}$ similar to that of the identity (using the summation convention):

$$| g_i > < g_i | = I \tag{6.3}$$

This is the completeness property of a set of orthonormal functions, within a particular Hilbert space. Similarly, for the Coulomb operator, suitable potentials give:

$$\frac{1}{r_{12}} = | \phi_i > < \phi_i | \tag{6.4}$$

This Coulomb resolution is based on a complete set of functions which may be determined such that they impose the identity as matrix representation of the Coulomb operator, $\frac{1}{r_{12}}$ in this basis:

$$< f_i | \frac{1}{r_{12}} | f_j > = \delta_{ij} \tag{6.5}$$

The completeness relation for the associated potentials can also be written in the form (8.19) The functional expression of the above gives:

$$\frac{1}{r_{12}} = \phi_i(r_1)\,\phi_i(r_2) \tag{6.6}$$

The potential functions $\phi_i$, are solutions of Poisson's equation. The functions chosen may also be based on Coulomb Sturmians (see the work by Avery).
Completeness of the functions $f_i$ allows us to expand a density in terms of them:

$$< \rho(r) | = < \rho(r) | \frac{1}{r_{12}} | f_i(r) > < f_i(r) | \tag{6.7}$$

J is re-written:

$$J_{12} = < \rho(r_1) | \frac{1}{r_{12}} | \rho(r_2) > = < \rho(r_1) | \frac{1}{r_{12}} | f_i(r_1) > < f_i(r_1) | \frac{1}{r_{12}} | f_j(r_2) > < f_j(r_2) | \frac{1}{r_{12}} | \rho(r_2) > \tag{6.8}$$

summing over i and j. Introducing the orthogonalised operator from 8.20 to resolve the two- electron integral into a sum of products of 1-electron overlap-like integrals:

$$J_{12} = < \rho(r_1) | \frac{1}{r_{12}} | f_i(r_1) > < f_i(r_2) | \frac{1}{r_{12}} | \rho(r_2) > \quad \text{with implied summation over } i \tag{6.9}$$

And recalling the defining relation for potentials (i.e. one electron functions of a single radial variable):

$$| \frac{1}{r_{12}} | f_i(r) > = | \phi_i(r) > \tag{6.10}$$

$$J_{12} = < \rho(r_1)\,\phi_i(r_1) > < \phi_i(r_2)\,\rho(r_2) > \quad \text{with implied sumation over i} \tag{6.11}$$

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This technique can be readily generalized to exchange and multi-center two-electron integrals. Note, however, that the origin of one of the potential functions only may be chosen to coincide with an atomic (nuclear) position.

Define potential functions $\phi_i$ in the scope of a Coulomb operator resolution, as follows:

$$\phi_{nl}(r) = \int_0^{+\infty} h_n(x) j_l(rx) dx \quad \text{with} \quad j_l(x) \text{ denoting the spherical Bessel function} \tag{6.12}$$

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 [15] is to use parabolic cylinder functions (see also another application [105]), 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:

$$h_n(x) = \sqrt{2} \, L_n(2\,x) e^{-x} \tag{6.13}$$

These polynomial functions are easy to use and lead to the following analytical expressions for the first two terms in the potential defined in (6.2):

$$V_{00}(r) = \sqrt{2} \, \frac{\tan^{-1}(r)}{r} \tag{6.14}$$

$$V_{10}(r) = \sqrt{2} \, \Big[ \frac{\tan^{-1}(r)}{r} - \frac{2}{(1 + r^2)} \Big] \tag{6.15}$$

Furthermore, higher $n$ expressions of $V_{n0}(r)$ all resemble (6.5) (see [16] eq (23)):

$$V_{n0}(r) = \sqrt{2} \, \frac{1}{r} (1 + \sum_1^n (-1)^k \frac{\sin(2\,k\,\tan^{-1}(r))}{k}) \tag{6.16}$$

and analytical expressions of $V_{nl}(r)$ with non-zero $l$ are also readily obtained by recurrence. The auxiliary overlap integrals $< \rho(r_1)\,\phi_i(r_1) >$ and $< \phi_i(r_2)\,\rho(r_2) >$ will involve densities obtained from atomic orbitals centered on two different atoms in most multi-center two-electron integrals. The integrals required in an ETO basis are thus of the type:

$$< \psi_a(r_1)\,\psi_b(r_1)\,\phi_i(r_1) > \tag{6.17}$$

Such integrals appear for two-center exchange integrals and all three- and four center integrals. Note that exchange integrals require distinct orbitals $\psi_a$ and $\psi_b$. In the atomic case, they must have different values for at least one of $n, l, m$ or $\zeta$. 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. The above equation 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.

The overlap integrals may be evaluated by separating the variables in prolate spheroidal coordinates, following Mulliken and Roothaan [42] and using recurrence relations in [18]:

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$$S(n_1, l_1, m, n_2, l_2, \alpha, \beta) = \alpha^{n_1+1/2} \beta^{n_2+1/2} \left[ (2n_1)! \, (2n_2)! \right]^{-1/2} s(n_1 l_1 m n_2 l_2 \alpha \beta)$$

$$= N(n_1, n_2, \alpha\beta) s(n_1, l_1, m, n_2, l_2, \alpha\beta)$$

where: $\alpha = k_1 R$ and $\beta = k_2 R$. The $k_1, k_2$ are Slater exponents.

The core overlaps are given by:

$$s(n_1, l_1, m, n_2, l_2, \alpha, \beta) = \int_1^\infty \int_{-1}^1 exp \left\{ -\frac{1}{2}(\alpha + \beta)\mu - \frac{1}{2}(\alpha - \beta)\nu \right\} (\mu + \nu)^{n_1} (\mu - \nu)^{n_2} T(\mu, \nu) d\mu d\nu$$

$$\mu = \frac{r_a + r_b}{R}$$

$$\nu = \frac{r_a - r_b}{R}$$

$r_a$ and $r_b$ are the instantaneous position vectors of the electron from the two centers labeled a and b, respectively and separated by a distance R. We also define, suing the normalised spherical tensors S:

$$T(\mu, \nu) = S_{l_1}^m(\mu, \nu)_a S_{l_2}^m(\mu, \nu)_b$$

.

The core overlaps then take the form:

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

$Y_{ij}^\lambda$ is a matrix with integer elements uniquely determined from $n$, $l$ and $m$. It is obtained as a generalised binomial coefficient, in the expansion of $(r_a - r_b)^n (r_a + r_b)^n$

$D_{l_1, l_2, m}$ 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.

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

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

Here, recurrence relations on the auxiliary integrals A and B lead to those for the requisite core integrals [18, 17].

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. The structure of these potential functions in (6.5) and (6.6) shows that the translation may be accomplished readily in the prolate spheroidal co-ordinates. This point is addressed in detail in a submitted manuscript [36].

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, 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 [36, 16].

# 7 Numerical results compared for efficiency

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 the demonstration on a rapid calculation, for which some experimental data could be corroborated.

The purpose of this section is to compare evaluations using the translation of a Slater type orbital basis to a single center (STOP) [55] 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 just six decimals, for reasons explained below).

$H_2$ molecule with interatomic distance of 1.402d0 atomic units (a.u.) The first table (Table 1) assembles the full set of all Coulomb integrals; with one and two-centers evaluated using STOP, Poisson and overlap methods. Exponents may be found from the atomic integrals which do not include the constant factor (5/8 here).

Table 1.

| AOs (zeta) | $1s_{a1}$ | $1s_{a2}$ | $2s_{a1}$ | $2s_{a2}$ |
|---|---|---|---|---|
| $1s_{a1}$ 1.042999 | 1.042999 | 0 | 0 | 0 |
| $1s_{a2}$ 1.599999 | 0.934309 | 1.599999 | 0 | 0 |
| $2s_{a1}$ 1.615000 | 0.980141 | 0.870304 | 1.615000 | 0 |
| $2s_{a2}$ 1.784059 | 0.901113 | 0.923064 | 1.189241 | 1.784059 |
| $1s_{b1}$ 1.042999 | 3.455363 | 0.364117 | 0.659791 | 1.621644 |
| $1s_{b2}$ 1.599999 | 0.433097 | 0.332887 | 0.635867 | 1.541858 |
| $2s_{b1}$ 1.615000 | 0.323691 | 0.248050 | 0.529300 | 1.276630 |
| $2s_{b2}$ 1.784059 | 0.402387 | 0.324872 | 0.636877 | 2.014196 |

Table 2.
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 | comment |
|---|---|---|---|---|
| $1s_{a1}$ 1.042999 | 1 | 1212 | 0.720716 | - |
| $1s_{a2}$ 1.599999 | 2 | 1313 | 0.585172 | - |
| $2s_{a1}$ 1.615000 | 3 | 1414 | 0.610192 | - |
| $2s_{a2}$ 1.784059 | 4 | 2323 | 0.557878 | - |
| $1s_{b1}$ 1.042999 | 5 | 2424 | 0.607927 | - |
| $1s_{b2}$ 1.599999 | 6 | 3434 | 0.602141 | - |
| $2s_{b1}$ 1.615000 | 7 | 2121 | 0.720716 | = 1212 |
| $2s_{b2}$ 1.784059 | 8 | 3232 | 0.585172 | = 2323 |

Table 3.
Two-center exchange integrals. All pair permutations possible. Some are identical by symmetry.

| Labels | value | comment |
|---|---|---|
| 1515 | 0.319902 | - |
| 1516 | 0.285009 | = 1525 |
| 1517 | 0.325644 | = 1535 |
| 1518 | 0.324917 | = 1545 |
| 1527 | 0.291743 | = 1536 |
| 1528 | 0.293736 | = 1547 |
| 1538 | 0.329543 | = 1548 |
| 2525 | 0.260034 | - |
| 2516 | 0.254814 | - |
| 2517 | 0.290533 | - |
| 2518 | 0.290149 | - |

The two-center integrals are dominated by an exponential of the interatomic distance and thus all ave values close to 0.3. The table is not the full set. All '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).

The total energy obtained for the isolated $H_2$ molecule is -1.1284436 Ha as compared to a Hartree-Fock limit estimate of -1.1336296 Ha. Nevertheless, the Van der Waals well, observed at 6.4 au with a depth of 0.057 kcal/mol is quite reasonably reproduced [82].

Dimer geometry: rectangular and planar. Distance between two hydrogen atoms of neighboring molecules: 6 au. Largest two-center integral between molecules: $4.162864 \ 10^{-5}$. (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).
Timings on a Power 6 workstation, for the dimer (all 4-center integrals in msec):
STOP: 12 POISON: 10 OVERLAP: 2.

Total dimer energy: -2.256998 Ha. This corresponds to a well-depth of 0.069kcal/mol, which may be considered reasonable in view of the basis set. 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.

## 7.1   The NMR nuclear shielding tensor.

More complete work is referred to here and the present description is a brief summary [87, 88, 91]. In NMR, the nuclear shielding tensor is a second order perturbation energy correction, for derivatives with respect to the nuclear dipole moment and the external field.
The perturbed Fock matrix element when including the effect of the external field contains both one and two electron terms. In this example, we focus on the one electron terms.
The purpose of the present section is to give a case study of one of the contributing energy integrals involving the dipole $1/r_N^3$ operator.
In the applied magnetic field, the question of gauge invariance must be resolved. A method of circumventing the problem was devised by Ditchfield using the London GIAO [92]. These Gauge Including Atomic Orbitals reduce to STO for zero field and contain the required phase factor otherwise [87, 88, 101].
The integrals were evaluated for GTO at zero field and nuclear shielding tensor or chemical shifts have been available since Gaussian 72 based on this pioneering work [27] and distributed to academics by QCPE. It is nevertheless important that users input the appropriate structure in order to obtain accurate chemical shifts corresponding to the species studied and note that for work in solution (or in solids) some structural changes may occur.
Define the nuclear shielding tensor as a second order energy perturbation:

$$\sigma_{\alpha\beta}^N = \left[ \frac{\partial^2 \left\langle 0 \left| \mathcal{H}(\vec{\mu}_N, \vec{B}_0) \right| 0 \right\rangle}{\partial \mu_{N,\alpha} \, \partial B_{0,\,\beta}} \right]_{\vec{\mu}_N = \vec{0}, \ \vec{B}_0 = \vec{0}} \tag{7.18}$$

with $\vec{\mu}_N$ the nuclear dipole moment of nucleus $N$ and $\vec{B}_0$ the external field. $|0\rangle$ is a closed shell ground state Slater determinant. $\alpha$ and $\beta$ stand for cartesian coordinates.
A coupled Hartree-Fock treatment of the above equation leads to [87, 88, 100]:

$$\sigma_{\alpha\beta}^N = Tr \left[ P_\beta^{(0,1)} h_\alpha^{(1,0)} + P^{(0)} h_{\alpha\beta}^{(1,1)} \right] \tag{7.19}$$

where $P^{(0)}$ and $P_\beta^{(0,1)}$ are the density matrix of zero order and first order with respect to the external magnetic field, $h_\alpha^{(1,0)}$ is the core Hamiltonian of the first order with respect to nuclear dipole moment and $h_{\alpha\beta}^{(1,1)}$ is the second order one-electron Hamiltonian with respect to the nuclear moment $\mu_\alpha$ and the external field $B_\beta$.

The non-zero orders in (7.19) involve integrals which are absent from *ab initio* Hartree-Fock calculations. In this work, we focus our attention on integrals involving $1/r_N^3$ in their operator. These integrals appearing in the second order expression for the approximate perturbed Hamiltonian:

$$h_{\mu\nu,\,\alpha\beta}^{(1,1)} = \frac{\mu_0}{4\pi}\frac{e^2}{2m_e}\left\langle \chi_\mu \left| \frac{\vec{r}_\nu \cdot \vec{r}_N \delta_{\alpha\beta} - r_{\nu,\alpha} r_{N,\beta}}{r_N^3} + \frac{(\vec{R}_{\mu\nu} \wedge \vec{r})_\beta (\vec{r}_N \wedge \vec{\nabla})_\alpha}{r_N^3} \right| \chi_\nu \right\rangle \tag{7.20}$$

The integral which we have chosen to investigate in detail within the Fourier transform approach, is the three-center one electron integral:

$$I = \left\langle \chi_\mu \left| \frac{\vec{r}_\nu \cdot \vec{r}_N \delta_{\alpha\beta} - r_{\nu,\alpha} r_{N,\beta}}{r_N^3} \right| \chi_\nu \right\rangle \tag{7.21}$$

here $\vec{r}_N$ is the instantaneous position of the electron with respect to the nuclei $N$.

### Analytical treatment.

This is to be found in the Appendix.

The above algorithm is available in Fortran, within the STOP (Slater Type Orbital Package) set of programs, at the coupled perturbed Hartree-Fock level with the ETOs axpanded in Slater type orbitals.

DFT coding proves more accurate for NMR chemical shifts because it accounts for the majority of the electron correlation energy. In this case, the ETOs are fitted to large Gaussian expansions, following the algorithm in [105] and Gaussian03 is subsequently used.

### Application.

The $^{15}N$ chemical shifts measured for a set of benzothiazoles are evaluated with the above expressions. These molecules possess a ring nitrogen and have been studied previously in our group [101]. The measurements were made in natural abundance. The intensity of signals due to the nitrogen must be amplified by a 2-D NMR technique involving cross-polarization to benefit from the intensity of proton resonances coupled to that of the $^{15}N$ in the molecule.

The *in vivo* NMR benefited from measurements by Bruno Combourieu: these molecules are metabolized by bacteria and researchers in the group try to follow the pathway by NMR. Since such studies are very difficult to do, we tried calculating some chemical shifts accurately from structures to assign them (see acknowledgements).

The Y substituent, generally a hydroxide was found to be in the position indicated (for mechanistic reasons, it is the only accessible and stabilised position for ring hydroxylation which has been found to take place *in vivo* after experiments in our group).

In solution, these molecules undergo a tautomeric equilibrium reaction transferring a proton towards this nitrogen as shown in the figure below (also used for nomenclature; P= protonated on resonating nitrogen).

Summary of NDDO-PM3 fitted STO molecular-site calculations on unprotonated tautomers (b). It is possible to conclude when the Gaussian03/PBE 6-311++G(2d,p) calculation (c) differs substantially from the measured value (a) (ppm/$CH_3NO_2$) that the resonating nitrogen is mostly protonated. This serves as a guideline for *ab initio* structures studied for these equilibria.

XBT $\rightleftharpoons$ PXBT
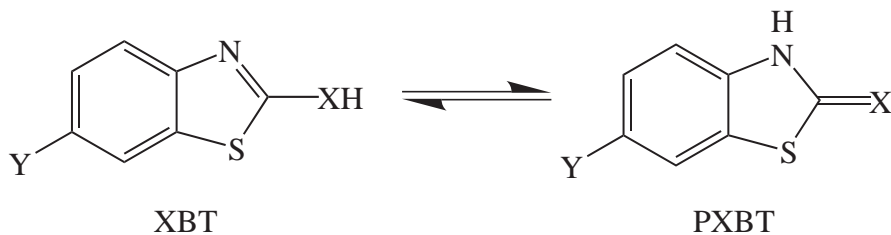
| molecule | substituent | a | b | c |
|---|---|---|---|---|
| BT:benzothiazole: | No X | -72.5 | -71.8 | -61.4 |
| OBT: | X=O | -238.8 | -238.9 | -133.3 |
| OHOBT: | X=O; Y=OH | -240.4 | -239.9 | -135.3 |
| ABT: | X=NH | -153.1 | -152.1 | -131.6 |
| OHABT: | X=NH; Y=OH | -153.1 | -153.6 | -132.3 |
| MBT: | X=S | -199.6 | -199.9 | -79.9 |
| OHMBT: | X=S; Y=OH | -205.5 | -205.5 | -83.2 |
| MTB: | X=N(CH$_3$)CONHCH$_3$ | -124.0 | -125.4 | -141.0 |

The above results prompted use of a structure, protonated on the resonating N, (denoted P) to obtain the zero-order wave-function, in all cases apart from benzothiazole (BT) and ABT. Below, the same cases are treated in the DFT work.

Note that the basis sets including hydrogen-like orbitals perform better than the STO basis sets that in turn improve upon dense-core Gaussian basis sets [6-311++G(2d,p)].

Next, examining the generalised basis sets, compare b,c, d, and f with the measured chemical shifts and evaluate the difference in ppm. Note that

TABLE: DFT Calculations. Differences between calculated and observed $^{15}N$ chemical shifts for commercial benzothiazoles and some metabolites (in ppm).
a-Measured values with respect to nitromethane standard in deuterated methanol solvent
(B. Combourieu in [101]) error bars of 2 ppm.
b-Coupled perturbed STO.
c-Gaussian [89] augmented with hydrogen-like AOs (c.f. Coulomb Sturmians $\alpha = 1$.
d-Gaussian [89].
e-Generalised ETO $\alpha = -1$
f-Generalised ETO $\alpha = -2$
Note. b through f involve solvation models, detailed below.

| molecule | substituent | a-c | a-b | a-d | a-e | a-f |
|----------|-------------|-----|-----|-----|-----|-----|
| BT:benzothiazole: | No X | 1.3 | 8.3 | 11.1 | 1.2 | 2.8 |
| POBT: | X=O | 4.6 | 11.7 | 20.0 | 3.8 | 5.3 |
| POHOBT: | X=O; Y=OH | 4.5 | 7.4 | 14.9 | 2.9 | 5.2 |
| ABT: | X=NH | 1.1 | 3.8 | 21.5 | 0.9 | 3.1 |
| OHABT: | X=NH; Y=OH | 4.5 | 10.1 | 20.8 | 2.8 | 6.1 |
| PMBT: | X=S | 3.0 | 11.2 | 21.2 | 2.1 | 4.5 |
| POHMBT: | X=S; Y=OH | 2.5 | 10.1 | 18.8 | 1.7 | 4.8 |

Basis sets augmented with hydrogen-like orbitals are within 5 ppm of the experimental values (measured within 2 ppm) for the discrete solvated model. This model explicitly includes several deuterated methanol molecules to cater for the specific hydrogen bonding interactions.

a Measured chemical shift for ring nitrogen.
b STO: DFT PBE 6-311++G(2d,p) calculations with two discrete $CD_3OD$ molecules on OH, NH, and SH (one on N, O, S) for minimal total energy.
c Gaussian 2003 as (b) with hydrogen-like orbital DFT PBE aug-6.311G**(2d, p) calculations.
d Gaussian 2003 DFT PBE 6-311++G(2d,p) calculations.
The content of this table is original and based on the previous work of the author [36] i.e. geometries are re-optimized from the co-ordinates of [36].


## Conclusion.

Another step on the way to *ab initio* ETO basis nuclear screening tensor calculations has been accomplished.
It is essential to use a basis set which comprises orbitals with the correct nuclear cusp behavior. This implies a non-zero value of the function at the origin for spherically symmetric cases and satisfying Kato's conditions. Hydrogen-like atomic orbital basis sets therefore perform better than Slater type orbitals which are an improvement upon even large Gaussian basis sets.
The NDDO-PM3 molecular site approach has the advantage of rapidity. Calculations take about a minute instead of 50-75 hours on the IBM-44P-270. They cannot be systematically improved, however once the site Slater exponents have been fitted. Note that the 2s Slater exponent fluctuates wildly in fits, providing further evidence that shielding must be of the form (2-r) for the 2s ETO. Fundamental work on orbital translation is also in progress to speed up these calculations within the test-bed of the STOP programmes [95, 83, 84].

The interplay of these discrete molecule solvent models and accurate *in vivo* NMR measurements is satisfactory, in that the structures postulated give calculated chemical shifts to similar accuracy as obtained for experimental values (on the order 2ppm). It should be stressed that energy minimization in this case does evidence directional hydrogen bonds but can lead to several possible solvent geometries. Further study, using molecular dynamics techniques would be useful in the modeling of solvent shells and is planned in the future. In view of the complex systems studied, this is highly satisfactory.

## 8    Conclusions

It is a remarkable gain in simplicity that the Coulomb operator resolution [15] now enables the exponential type orbital translations to be completely avoided, although some mathematical structure has been emerging in the BCLFs used to translate Slater type orbitals and even more in the Shibuya-Wulfman matrix used to translate Coulomb Sturmians.

This breakthrough in the ETO algorithm strategy represents a well-controlled approximation, analogous to resolutions of the identity. The convergence has been shown to be rapid in all cases [16].

## 9    Acknowledgements

## 10    Appendix: analysis of nuclear dipole integrals for NMR in a Slater basis

The operator, $(\vec{r}_\nu \cdot \vec{r}_N \delta_{\alpha\beta} - r_{\nu,\alpha} r_{N,\beta}) / (r_N^3)$, can be expressed as a combination of terms involving cartesian co-ordinates. These terms take the following general form:

$$\frac{X^{\nu,i} X^{N,j}}{r_N^3} \tag{10.22}$$

where $X^{N,j}$ stands for cartesian coordinates of the electron with respect to the nuclei $N$.
Now, it is more convenient to express the cartesian co-ordinates as sums of spherical polar coordinates with their complex conjugates. These co-ordinates are of the general form:

$$x = r\sqrt{\frac{2\pi}{3}} \left[ Y_1^{-1}(\theta_{\vec{r}}, \varphi_{\vec{r}}) - Y_1^1(\theta_{\vec{r}}, \varphi_{\vec{r}}) \right]$$
$$y = ir\sqrt{\frac{2\pi}{3}} \left[ Y_1^{-1}(\theta_{\vec{r}}, \varphi_{\vec{r}}) + Y_1^1(\theta_{\vec{r}}, \varphi_{\vec{r}}) \right] \tag{10.23}$$
$$z = r\frac{4\pi}{3} Y_1^0(\theta_{\vec{r}}, \varphi_{\vec{r}})$$

The product of a STO by a cartesian coordinate can be expressed as a combination of STO, since:

$$rY_L^M(\theta_{\vec{r}}, \varphi_{\vec{r}})\chi_{n,l}^m(\zeta, \vec{r}) = rY_L^M(\theta_{\vec{r}}, \varphi_{\vec{r}}) \times r^{n-1} e^{-\zeta r} Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}}) \quad = (-1)^M \sum_{\lambda=\lambda_{min},2}^{\lambda_{max}} \langle lm | L - M | \lambda m + M \rangle r^n e^{-\zeta r} Y_\lambda^{m+M}$$

here we have used the Gaunt coefficients [90, 103] and the Condon and Shortley phase convention for spherical harmonics $Y_l^m(\theta_{\vec{r}}, \varphi_{\vec{r}})$ [86].

Consequently, the integral (7.21) is reduced to a sum of terms of the form:

$$\left\langle \chi_\mu \left| \frac{Y_1^j(\theta_{r\vec{N}}, \varphi_{r\vec{N}})}{r_N^2} \right| \chi_\nu \right\rangle \tag{10.25}$$

with just a $1/r^2$ dependence and where $j = -1, 0, 1$.

Using the Fourier transform formalism requires the integral representation of the operator involved in (10.25). We obtain:

$$\overline{\left( \frac{Y_1^j(\theta_{r\vec{N}}, \varphi_{r\vec{N}})}{r_N^2} \right)}(\vec{p}) = \frac{2i}{\sqrt{2\pi}} \frac{Y_1^j(\theta_{\vec{p}}, \varphi_{\vec{p}})}{p} \tag{10.26}$$

This immediately allows us to write the inverse Fourier transform:

$$\frac{Y_1^j(\theta_{r\vec{N}}, \varphi_{r\vec{N}})}{r_N^2} = -\frac{i}{2\pi^2} \int \frac{e^{-i\vec{p}\cdot\vec{r}_N} Y_1^j(\theta_{\vec{p}}, \varphi_{\vec{p}})}{|\vec{p}|} \, d\vec{p} \tag{10.27}$$

Now, this places us in a position to write the Fourier integral for the present term in the NMR nuclear shielding tensor calculation. After expanding the Slater type orbitals in terms of B-functions and substituting (10.27) in (10.25), the present integral becomes:

$$\begin{aligned} \mathcal{I} = -\frac{i}{2\pi^2} \int & \frac{e^{i\vec{p}\cdot\vec{R}_N} Y_1^j(\theta_{\vec{p}}, \varphi_{\vec{p}})}{|\vec{p}|} \\ & \times \langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}) | e^{-i\vec{p}\cdot\vec{r}} | B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \vec{R}_2) \rangle_{(\vec{r})} \, d\vec{p} \end{aligned} \tag{10.28}$$

whereas the three-center nuclear attraction integral is :

$$\mathcal{I} = \frac{1}{2\pi^2} \int \frac{e^{i\vec{p}\cdot\vec{R}_N}}{|\vec{p}|^2} \times \langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}) | e^{-i\vec{p}\cdot\vec{r}} | B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \vec{R}_2) \rangle_{(\vec{r})} \, d\vec{p} \tag{10.29}$$

The three-center dipolar integral (13) appears in a form closely related to that of the three-center nuclear attraction integrals required at the HF-SCF level of electronic structure calculation (and also used in electronic DFT work).

In both above integrals note the presence of the common factor in B-function Fourier transform work first studied by the Steinborn group: eq (5.4 and 5.5). See also [106] i.e.:

$$\langle B_{n_1,l_1}^{m_1}(\zeta_1, \vec{r}) | e^{-i\vec{p}\cdot\vec{r}} | B_{n_2,l_2}^{m_2}(\zeta_2, \vec{r} - \vec{R}_2) \rangle_{(\vec{r})} \tag{10.30}$$

The analytical treatment developed here has not required any hypothesis on the relative position of nucleus (aligned or not) and any restriction on quantum numbers. Consequently, the equation (10.28) is completely general and may be directly evaluated from routines available in a quantum calculation software.

Note that such an integral satisfies all applicability conditions of non-linear transformations for extrapolation described by A. Sidi [97]. Previous work on three-center nuclear integral evaluation [96] has been used to develop an efficient program to compute this dipolar $1/r_N^3$ three-center integral.

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