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Generalized Hybrid Orbitals

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A new set of generalized hybrid atomic orbitals is proposed for use in the theory of molecular electronic structure. The hybrids have conceptual and (when expanded in terms of Gaussian functions) computational advantages over conventional hybrids which are essentially adapted to spherically-symmetric environments. Formaldehyde is used to illustrate the use of these orbitals.

Key words: Hybrid orbitals

1. Introduction

In quantitative theories of molecular electronic structure it has become traditional to use a set of "atom-centred functions" of the form

$$\chi_i^{\mathrm{A}} = f(r_{\mathrm{A}})Y_l^m(\theta_{\mathrm{A}}, \phi_{\mathrm{A}}) \tag{1}$$

as basic units in the expansion of the molecular wave function. In (1) the Y_l^m are the usual harmonics and f_i is a function of the scalar distance from nucleus A; $(r_{\mathrm{A}}, \theta_{\mathrm{A}}, \phi_{\mathrm{A}})$ is a set of spherical polar co-ordinates local to nucleus A. The reasons for this choice are both historical and scientific, principally:

a) A wave function constructed from functions (1) can be given a convenient valence interpretation through the density matrix: the electron density is easily analysed into "atomic" and "overlap" contributions.
b) Most molecular wave functions are optimized by using the variation principle which minimizes the average energy associated with a given form of approximate wave function. The largest contribution to the energy of a molecule is the sum of the energies of the separate atoms and functions like (1) give this energy very well.
c) The hydrogen atom orbitals are of the form (1) as are the Hartree–Fock orbitals of polyelectronic atoms.
d) The various molecular integrals arising from the use of (1) in conjunction with the usual non-relativistic Hamiltonian are, in the main, computationally tractable and methods for their evaluation are well known.

In practice a molecular wave function is, explicitly or implicitly, expanded as a sum of determinants of some spin-oribtals ϕ_i:

$$\Phi = \sum_k D_k\Phi_k \tag{2}$$

where

$$\Phi_k = \det\{\phi_i\phi_j \ldots\} \tag{3}$$

and the spatial part of the spin-orbitals ϕ_i are either atomic orbitals (linear combinations of functions (1)) or linear combinations of atomic orbitals. With very few exceptions these atomic orbitals are *fixed by the nature of the atoms in the molecule* – they are not optimized for a particular molecule. Thus the full burden of the optimization of the wave function falls on the *linear* coefficients D_k and the *linear* coefficients determining the ϕ's in terms of the χ's. If the set of AOs occupied in the ground state of the molecule proves qualitatively or quantitatively inadequate to expand a molecular wave function then other atom-based functions are added to the basis – typically "polarization functions" of higher l and m values. This concentration of effort on the *linear* optimization has two aspects. In the first place it is technically easier to extend the *number* of functions like (1) rather than to optimize the form of (1). Secondly, problems of interpretation quickly become acute – how are the contributions to a molecular charge density from "AOs" unoccupied in the separate atoms to be interpreted?

It is a matter of common knowledge that the use of (1), (2) and (3) can be made to expand any molecular wave function to an arbitrary degree of accuracy by using long enough expansions of the ϕ_i and the Φ_k. This fact provides the theoretical underpinning for the standard methods. However, the use of (1), (2) and (3) in an unrestricted way has the rather unfortunate effect of replacing a scientific problem (the interpretation of valence) by a mathematical one (the best series expansion of the solution of a differential equation). The natural question to ask is:

> Does the use of (1), (2) and (3) constitute a mathematical approach to the problem of molecular electronic structure *which is adapted to the description of the physical processes occurring on bond formation?*

The electronic re-distribution occurring on bond formation might be qualitatively grouped into (at least) the following three effects:

a) Atomic (or orbital) contraction or expansion on the approach of another atom.
b) Destruction of atomic spherical symmetry.
c) Inter-atomic electron redistribution.

These processes are characteristic of each *bond* terminating at a given atom. Now, since expansion (2) is capable of being made arbitrarily accurate these effects must be contained in a comparison of a computed accurate molecular wave function and the wave functions for the separate atoms. But the nature of the expansion (2) and the *form* of the functions (1) makes the extraction of this information and the assessment of effects a), b) and c) rather difficult.

Taking a specific example, if a "minimal basis" of AOs is used for the calculation of the formaldehyde (CH_2O) molecule then, because of the nature of the AO's, processes a) and b) receive almost no consideration. The fixed form of $f(r_c)$ for each AO means, for example, that the contraction (or expansion) of the $2s$, $2p$ AOs of carbon cannot take place. Further, the use of the Y_l^m means that the removal of spherical symmetry around the carbon atom is only partially allowed for. The different carbon contribution to the C–H and C–O σ bonds is severely restricted. Only process c) is capable of being treated adequately by this method and it may well be that by constraining the AOs not to change the numerical magnitude of effect c) is over- or under-estimated. The problems can be overcome to some extent by the use of additional *s, p, d* AOs; atom-based functions. The use of additional *s*-type functions will enable a study of the contraction of the carbon 2*s* AO to be made by comparison of the relative values of coefficients in the molecule and in the separate atom. The loss of spherical symmetry can similarly be studied by the addition of several sets of AOs with different radial functions – e.g. to allow the C–H and C–O σ bonds to have different carbon AO contributions. But all this is rather pedestrian: the use of a set of functions which are determined by a spherically symmetrical potential (factorizable into the form (1)) is clearly not at all well adapted to the study of the processes occurring on bond formation. There are no parameters in (1), for example, which measure orbital contraction effects – everything hinges on *comparisons* of *linear coefficients* which contain information about all the effects a), b) and c). What is more the use of extended AO bases is often very time-consuming and numerically unstable.

A more useful and chemically interpretable approach would be one which uses atom-based functions which, for example, depend *explicitly* on direction in space and contain *in their functional forms* the possibility of introducing effects a), b) and c) in a physically transparent way. Conventional hybridization goes some way towards meeting these criteria and suitable atomic functions suggest themselves when the mathematical reasons for the use of (1) are reviewed.

2. Generalized Hybrid Orbitals

The conventional treatment of the Schrödinger equation for the hydrogen atom is to use a system of spherical polar co-ordinates (r, θ, ϕ) and hence separate the three-dimensional partial differential equation into equations for functions of r, θ and ϕ separately. The solutions are well known and take the form (1), in particular

$$\phi_{n,l,m} = R_{nl}(r) Y_l^m(\theta, \phi) \tag{4}$$

where

$$R_{nl}(r) = L_{n+l}^{2l+1}(2r/n) \exp(-r/n) r^l \tag{5}$$

and the Laguerre polynomials (L_{n+l}^{2l+1}) ensure orthogonality for AOs with the same values of l and m. Naturally, the spherical polar system is the most appropriate co-ordinate system to use *for an isolated atom* where there are no preferred directions in space. However, an atom in a molecule does have at least one preferred direction – the axis whose direction coincides with the bond direction. Thus it is of interest to see if there are solutions of the hydrogen atom Schrödinger equation in systems of co-ordinates which reflect the existence of a preferred direction in space. There are two obvious candidates for such a co-ordinate system; cylindrical co-ordinates (r, z, θ) and parabolic co-ordinates (ζ, η, ϕ). The hydrogen atom equation does not separate in cylindrical co-ordinates but it *does* separate in parabolic co-ordinates. The solutions of the hydrogen atom Schrödinger equation in parabolic co-ordinates are used in the theory of the Stark effect where an electric field is the source of the preferred direction. The solutions are [1], apart from normalization,

$$\phi_{n_1 n_2 m}(\zeta,\eta,\phi)=\exp(\pm \mathrm{i}m\phi)\exp\left[-\frac{\epsilon}{2}(\zeta+\eta)\right](\zeta\eta)^{m/2}L^{m}_{n_1+m}(\epsilon\zeta)\,L^{m}_{n_2+m}(\epsilon\eta) \tag{6}$$

where $n_1, n_2 = 1, 2, \ldots; m = 0, \pm 1, \pm 2, \ldots; n = n_1 + n_2$; and $\epsilon = Z/n$.

When plotted [1] these functions have a characteristic "directional hybrid" appearance. The asymptotic form of (6), for large values of the argument, is

$$\phi_{n_1 n_2 m} \simeq h_{n_1 n_2 m}(r, z)\exp(-Zr/n)\exp(im\phi),$$

a function of the familiar "mixed" polar/Cartesian co-ordinates.

Now in the theory of polyelectronic atoms (and the conventional theory of molecular electronic structure) functions of the same *general* form are used for AOs but the rigid form of the Laguerre polynomials is abandoned in favour of a more flexible variational form and the orbital exponent $1/n$ is replaced by a variational parameter δ. This yields the usual expression for AOs - a linear combination of STOs:

$$\phi_{nlm} = Y^{m}_{l}(\theta,\phi)\sum c_i r^{n_i}\exp(-\delta_i r). \tag{7}$$

Thus the *general form* of the hydrogen atom AOs suggests a *variational form* for the AOs of isolated atoms.

A similar transition from the form (6) suggests an "AO-in-molecule" form of

$$\chi = \sum_i h_i(r, z)\exp(-\delta_i r) \tag{8}$$

where h_i is a function defining the general form of an individual hybrid orbital and δ_i is an orbital exponent *for that hybrid.* Taking the simplest example, the usual hybrids formed from a simple *linear* combination of the $2s$, $2p$ AOs are

$$\chi = a2s + b2p_\sigma$$

which can be written in the form (8) as:

$$\chi_i = N\left(\frac{a_i r}{\sqrt{3}} + b_i z\right)\exp(-\delta_i r) \tag{9}$$

for $2s$, $2p$ with the same exponent (the $\sqrt{3}$ factor is included to ensure that N is dependent only on δ). Thus, in the CH_2O example the "sp^2" hybrids involved in the C-H and C-O σ bonds could each be of the general form (9) with different values of a_i, b_i and δ_i. The form of (8) can, of course, be chosen so that the generalized hybrid orbitals go over smoothly into the ordinary AOs as an atom is removed from a molecular environment. In particular, as the carbon atom is removed from CH_2O the values of a_i, b_i and δ_i vary continuously until, at infinite separation, they describe the usual $2s$, $2p$ set. For CH_2O the π MO is normally described by a linear combination of the $2p_\pi$ AOs; however, there is nothing in principle against using a more general form of π AO which, although having conventional symmetry, concentrates density into the internuclear region. That is, using (6) as a guide, π AOs do not need to be symmetrical in a plane perpendicular to the molecular plane passing through each atom.

The use of a set of functions of this type enables the physical processes outlined earlier to be correlated in a straightforward way to the values of the parameters a_i, b_i and δ_i. Thus the change in δ_i (from the separate atom value to the molecular value) measures the individual orbital contractions (or expansions) on bond formation. The differences *among* a set of δ_i of orbitals on a given nucleus also measure the effects of the bonded atoms and so incorporate deviations from spherical symmetry. The a_i, b_i coefficients measure the relative s and p contributions *to each bond.* There is, of course, no reason why the a_i, b_i should be chosen to be constrained by the usual rule that hybrids on the same centre should be orthogonal since the use of a separate δ_i for each hybrid will destroy the conventional orthogonality requirement.

A set of generalized hybrids of the form (9) cannot be generated by an orthogonal transformation from a single set of separate-atom AOs ($2s$, $2p$). Thus the choice of optimum hybrids (by choice of the a_i, b_i and δ_i) becomes a degree of freedom to be optimized *even in the single-determinant MO model.* This latter effect is in line with chemical intuition *and* with the results of models of electronic structure more general than MO. In VB methods and separate electron-pair theories the choice of an optimum hybrid basis is a very important consideration and (in the conventional hybrid theory) an optimum linear transformation among the AO set is used to define these hybrids (unless *all possible* VB structures are included). We can therefore define and use, within the MO model, optimum hybrids which are of qualitative *and quantitative* value - they are not simply the result of a formal, but numerically worthless, transformation.

3. Computational Considerations : Expansion Methods

The definition and use of any set of basis orbitals for the elucidation of molecular electronic structure can only be of quantitative value if methods are developed for the computation of the molecular integrals

$$\int dv\chi_i\left(-\frac{1}{2}\nabla^2\right)\chi_j \quad \int dv\chi_i\left(-\frac{1}{r_\alpha}\right)\chi_j$$

and

$$\int dv_1\int dv_2\chi_i(1)\chi_j(1)\frac{1}{r_{12}}\chi_k(2)\chi_l(2) \tag{10}$$

which arise in the solution of the matrix equations of any orbital-basis theory - MO, VB/CI. The form of the χ_i which we have suggested has an STO-like exponential factor and all the difficulties associated with the calculation of many-centre STO integrals occur again if (8) is used as it stands. In fact the computational difficulties are made more acute by the unusual nature of the "angular functions". However, the general qualitative forms of the hybrid orbitals suggests an alternative approach.

Hybrid orbitals of the form (8) consist of a number of "lobes" of different sign; in particular the simplest hybrids with $n = 2$ in (9) consist of two lobes with centres along an axis containing the parent nucleus. By finding the line of nodes separating these positive and negative lobes it is easy to find the centroids of the lobes as a function of a_i, b_i and δ_i of (9) (or a more general hybrid (8)). In fact, for $n = 2$, the centroid of the major (positive) lobe is

$$\frac{5\sqrt{3}}{24b\delta_i}\left\{\frac{-a^4 + 18a^2b^2 + 24\sqrt{3}ab^3 + 27b^4}{a^3 + 3\sqrt{3}a^2b + 9ab^2 + 3\sqrt{3}b^3}\right\} \tag{11}$$

atomic units along the hybrid-nucleus axis and the minor (negative) lobe is

$$\frac{5\sqrt{3}}{24b\delta_i}\left\{\frac{a^4 - 18a^2b^2 + 24\sqrt{3}ab^3 - 27b^4}{-a^3 + 3\sqrt{3}a^2b - 9ab^2 + 3\sqrt{3}b^3}\right\} \tag{12}$$

atomic units in the opposite direction. We can now use a function to represent each lobe of the hybrid: spherical Gaussian functions are the obvious candidates. Placing a spherical Gaussian function on each lobe centroid, we can seek the optimum α in

$$\left(\frac{2\alpha}{\pi}\right)^{3/4}\exp(-\alpha r^2)$$

for each lobe as a function of a_i, b_i and δ_i for each hybrid. Now the "radial" factors of the hybrid *and* the centroid of each lobe are determined by δ_i. It is therefore natural to ask if there is a "scaling relation" for the Gaussian lobe fits to the hybrids analogous to the familiar scaling relation for Gaussian fits to STO functions. It turns out that there is - it is only necessary to fit the hybrid lobes for one value of δ_i ($\delta_i =$ 1.0, usually for convenience) and the fits to all other hybrids of the same form (same a_i, b_i) are determined. (It must be said that if no scaling relation could be found this would have been a severe limitation on the use of (9) - large amounts of numerical data would be needed in order to optimize a particular δ_i). We can therefore perform (e.g.) 2-term (one spherical Gaussian per lobe) fits *once and for all* for the principal types of hybrid:

$a_i = \frac{\sqrt{3}}{2}$;	$b_i = \frac{\sqrt{3}}{2}$;	"sp^3"
$a_i = 1$;	$b_i = \sqrt{\frac{2}{3}}$;	"sp^2"
$a_i = \sqrt{\frac{3}{2}}$;	$b_i = \frac{1}{\sqrt{2}}$;	"sp"
$a_i = \sqrt{3}$;	$b_i = 0$;	"s"
$a_i = 0$;	$b_i = 1$;	"p"

If greater numerical accuracy is required the length of the Gaussian fit to each lobe can be increased - the same scaling theorem is applicable to the optimum exponents α. Table 1 lists the 2-term fits for these main ($n = 2$) hybrid types. The optimum expo-

Table 1. Two-term Gaussian lobe fits to (n = 2) s,p hybrid orbitals

Hybrid Type	Centroids[a]	Exponents	Coefficients	Overlap[b]
p	±1.875	0.200999	±0.812898	0.953322
		0.200999		
sp	1.514156	0.150465	1.024623	0.954640
	−2.235844	0.311268	−0.217884	
sp^2	1.619845	0.154404	1.037945	0.961192
	−2.130155	0.201888	−0.409704	
sp^3	1.666667	0.161292	1.022153	0.958790
	−0.208333	0.203659	−0.476756	

[a] Distances in Bohrs throughout.

[b] Overlap with actual STO hybrid of the given type.

nents are listed for $\delta_i = 1.0$ in (9); for exponent δ_i the optimum Gaussian exponents are obtained by multiplying the listed values by δ_i^2. The centroids of the hybrid lobes on which the Gaussian functions are centred are given by (11) and (12). Using these expansions of the hybrid orbitals, the molecular integrals (10) are trivially easy to compute; they reduce to linear combinations of the standard forms for s-type Gaussian functions [2].

4. Applications: The Formaldehyde Molecule

The formaldehyde molecule has a rather varied electronic structure for a simple organic molecule: C–H bonds, a polar C–X σ bond, a π bond and lone pairs. This molecule shows, therefore, something of the directionally-dependent radial density (particularly at the carbon atom) which is only poorly described by the use of conventional spherically-based atomic orbitals. A calculation has therefore been performed using a basis of generalized hybrids fitted by the expansions of Table 1 (a 2-term conventional Gaussian expansion was used for the carbon and oxygen 1s "cores"). Single-term 1s functions were used for the single-lobe hydrogen 1s functions. Thus the generalized hybrid basis for CH_2O is:

ϕ_1 : 1s on carbon (exponent δ_1)

ϕ_2 : sp^2-type on carbon - CO σ bond - (exponent δ_2)

$$\left.\begin{array}{l}\phi_3 : \\ \phi_4 :\end{array}\right\} \left.\begin{array}{l} sp^2\text{-type on carbon} \\ \text{- CH } \sigma \text{ bonds -}\end{array}\right\} \text{(exponent } \delta_3)$$

ϕ_5 : π AO on carbon (exponent δ_4)

ϕ_6 : 1s on oxygen (exponent δ_5)

ϕ_7 : sp^2-type on oxygen - OC σ bond - (exponent δ_6)

$$\left.\begin{array}{l}\phi_8 : \\ \phi_9 :\end{array}\right\} \left.\begin{array}{l} sp^2\text{-type on oxygen} \\ \text{- lone pairs -}\end{array}\right\} \text{(exponent } \delta_7)$$

ϕ_{10} : π AO on oxygen (exponent δ_8)

$$\left.\begin{array}{l}\phi_{11} : \\ \phi_{12} :\end{array}\right\} \text{hydrogen 1}s\text{ AOs (exponent } \delta_9)$$

All nine exponents were optimized by minimizing the total electronic energy of a standard SCFMO calculation. The minimization procedure used was a quasi-Newton method [3] which constructs approximations to the gradient and Hessian matrices. Table 2 shows the results of the exponent optimization. In order to have a strict comparison of hybrids of the form (9) the "separate atom" δ's are, in fact, the best atomic $2s$ and $2p$ functions constrained to have the same exponent[1]. Table 3 gives the effect of the optimization on the total energy and the individual orbital energies.

It is evident from Table 2 that the hybrids involved in σ bonds contract quite markedly on bond formation and that this contraction is dependent on the type of bond in which a "given hybrid" occurs (C–H or C–O in our case). The oxygen lone-pair hybrid exponents are essentially unchanged since these orbitals are not involved to any great extent in the changes occurring on molecule formation and so their form is determined by the local "atomic" potential. In contrast, however, the exponents of both π AOs *decrease* on molecule formation showing that these *expand* on bond formation. It is worth noting at this point that the π AOs change in such a way as to *increase* bonding overlap; 0.152 for the separate-atom AOs, 0.198 for the optimized orbitals. But the σ orbitals contract, leading to *reduced* σ–σ overlap integrals; 0.792 for the CO σ overlap

Table 2. Separate atom and molecular exponents for CH_2O

Label[a]	δ_{Atom}	δ_{Molecule}
1	5.6727	5.7583
2	1.5693	1.7301
3	1.5693	1.8860
4	1.5693	1.4295
5	7.6579	7.7893
6	2.2318	3.7617
7	2.2318	2.2372
8	2.2318	2.0632
9	1.0000	1.0713

[a] See text for orbital numbering

Table 3. Orbital energies for CH_2O

Separate Atom δ's	Molecule-Optimized δ's
−20.5075	−20.3898
−11.0792	−10.9925
−1.5648	−1.4307
−0.8534	−0.8105
−0.5655	−0.5800
−0.4498	−0.5740
−0.3293	−0.3076
−0.2022	−0.1980
Total energy	
−106.9777	−107.1535

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[1] Computed for us by Mr. D. Firsht.

for separate atom exponents, 0.457 for the optimized molecular exponents. It is clear from even these preliminary results (if clarification were required) that chemical bond formation is *not* to be correlated with maximum overlap of hybrid orbitals. The various physical effects contributing to the re-arrangement of electron density on bond formation cannot be reduced to a simple "overlap effect".

It might be objected that the σ orbital contraction effects are an artifact of the calculation in the sense that we have used a rather limited expansion of the core orbitals and perhaps the σ orbitals contract to compensate for this. That this is not so is most easily seen by a study of the σ orbitals based on the oxygen atom of CH_2O. The $1s$ core AO on oxygen contracts a small amount; the OC sp^2 hybrid contracts but the lone-pair sp^2 hybrids *are left unchanged* by the optimization process. If the orbital contraction were an artifact connected with the short $1s$ expansion it would surely show a uniform tendency to contraction among the σ orbitals of that atom. It is, of course, easy to verify this conclusion by performing calculations with longer core expansions.

The calculated σ bond hybrid orbital contraction effects are very much in line with the work of Ruedenberg [4] who has stressed the importance of intra-atomic electronic re-arrangements in bond formation. In his work on the σ bond in H_2^+ particularly, Ruedenberg has shown the contributions of both orbital contractions and overlap effects. We shall present a study of the energetics of bond formation using generalized hybrid orbitals in a later publication. A study of the π orbital expansion effects in the light of Ruedenberg's work is also urgent.

The total energy of CH_2O is only very slightly improved by the hybrid orbital optimization process (0.16%) but this small absolute improvement is associated with large changes in electron populations. Table 4 gives the (orthogonalized hybrid basis) density matrix before and after exponent optimization. It is evident from Table 4 that the total energy of a model wave function is a poor measure of the capabilities of that wave function to describe the rather loosely bound valence electrons. In point of fact the optimization method used was one which depended on the stability of the parameters being varied *and* on the gradients of the total energy with respect to these parameters - the process was terminated when the parameters ceased to change *and* the gradients were close to zero. This method thus has the incidental advantage that the virial theorem is satisfied to quite high accuracy by the optimized wave function (−0.499 compared to −0.493 for the separate-atom exponents). The virial theorem is, of course, crucial to Ruedenberg's analysis of chemical bonding.

5. Conclusions

A new approach to the definition and use of hybrid atomic orbitals is presented here which enables a detailed study of the energetics and electron density changes on bond formation to be made. Physical effects such as local charge redistributions and local orbital contraction effects can be studied in a natural and chemically transparent way. Many of these effects are very difficult to identify and study using the conventional AOs which are adapted to the description of systems with spherical symmetry. The

Table 4. Separate-atom orbitals. Orthogonal density matrix

	1	2	3	4	5	6	7	8	9	10	11	12
1	1.9867											
2	0.0657	0.8545										
3	0.0579	0.0619	1.1667									
4	0.0579	0.0619	0.0339	1.1667								
5	0.0000	0.0000	0.0000	0.0000	1.1023							
6	0.0035	−0.0792	0.0113	0.0113	0.0000	1.9944						
7	−0.0604	0.9694	−0.0214	0.0214	0.0000	0.0665	1.7721					
8	0.0047	0.0977	0.1609	−0.3050	0.0000	0.0079	−0.0774	1.8553				
9	0.0047	0.0977	−0.3050	0.1609	0.0000	−0.0779	0.0774	0.1055	1.8553			
10	0.0000	0.0000	0.0000	0.0000	0.9948	0.0000	0.0000	0.0000	0.0000	0.8977		
11	−0.0764	0.0296	0.9179	0.0431	0.0000	−0.0064	−0.0628	−0.1563	0.3136	0.0000	0.9716	
12	−0.0764	0.0296	0.0431	0.9179	0.0000	−0.0064	−0.0628	0.3136	−0.1563	0.0000	−0.1459	0.9716

Molecule-optimized orbitals. Orthogonal density matrix

	1	2	3	4	5	6	7	8	9	10	11	12
1	1.9645											
2	0.0705	1.4472										
3	0.1131	0.0197	0.9887									
4	0.1131	0.0197	0.0028	0.9887								
5	0.0000	0.0000	0.0000	0.0000	1.0948							
6	0.0188	−0.1664	0.0164	0.0164	0.0000	1.9497						
7	−0.1056	0.8573	−0.0464	−0.0464	0.0000	0.2584	0.6701					
8	−0.0051	0.1199	0.1514	−0.2484	0.0000	0.0370	−0.1873	1.8913				
9	−0.0051	0.1199	−0.2484	0.1514	0.0000	0.0370	−0.1873	0.0489	1.8913			
10	0.0000	0.0000	0.0000	0.0000	0.9955	0.0000	0.0000	0.0000	0.0000	0.9052		
11	−0.1176	0.0383	0.9480	0.0315	0.0000	0.0013	−0.0439	−0.1458	0.2155	0.0000	1.1043	
12	−0.1176	0.0383	0.0315	0.9480	0.0000	0.0013	−0.0439	0.2155	−0.1458	0.0000	−0.0675	1.1043

use of a basis of generalized hybrid AOs means that the all-important question of optimum hybrid basis can be asked even in the MO model - the best set of generalized hybrid orbitals for a molecule of low symmetry cannot be generated by a *linear* transformation from a conventional AO set. Further, the optimum hybrids for (e.g.) a bent-bond description of the double bond in C_2H_4 will not be related linearly to the optimum σ/π hybrids and so *even in the MO model* the question of "natural" or optimum hybrids has a meaningful answer. These matters will be the subject of later publications.

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