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Molecular Integrals in the Approximate Calculation of Electronic Structure

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A self-consistent set of new proposals is made for the calculation of the largest molecular integrals over orthogonal hybrid orbitals used in "neglect of differential overlap" schemes.

Key words: Neglect of differential overlap

1. Introduction

It has been shown elsewhere that, for both conceptual [1] and numerical [2, 3] reasons, the so-called "neglect of differential overlap" (NDO) schemes for the approximate calculation of molecular electronic structure perform most satisfactorily when a basis of *orthogonalized* hybrid atomic orbitals (OHAOs) is used. Using this orthogonalized, localized basis the neglected many-centre repulsion integrals (for example) are indeed very small. We are assuming here that "neglect of differential overlap" actually means "simulation of an orthogonal basis". That this is so can be seen most clearly by consideration of the values of the β's (off-diagonal one electron matrix elements) used in these approximation schemes. The values of the β's are typical of an orthogonal basis, being generally only a fraction of the non-orthogonal basis values (-0.268 and -4.869 a.u. respectively for the C–H bond of CH_2O, for example). Thus the OHAO basis to a large extent *validates* the NDO schemes.

Molecular integrals required for the performance of any orbital basis calculation in the NDO approximation (MO, VB, CI) are

$$\bar{H}_{rr} = \int dv \bar{\phi}_r \hat{h} \bar{\phi}_r \tag{1}$$

$$\bar{H}_{rs} = \int dv \bar{\phi}_r \hat{h} \bar{\phi}_s \tag{2}$$

where

$$\hat{h} = -\tfrac{1}{2}\nabla^2 - \sum_{\alpha} \hat{V}_{\alpha}$$

($\hat{V}_{\alpha}$ is the "core potential" for centre α).

$$\bar{\gamma}_{rs} = \int dv_1 \int dv_2 \bar{\phi}_r^2(1) \frac{1}{r_{12}} \bar{\phi}_s^2(2) \tag{3}$$

(for $r = s$ *and* $r \neq s$)

and possibly

$$(\bar{r}\bar{s}, \bar{t}\bar{u}) = \int dv_1 \int dv_2 \bar{\phi}_r(1)\bar{\phi}_s(1) \frac{1}{r_{12}} \bar{\phi}_t(2)\bar{\phi}_u(2) \tag{4}$$

when $\bar{\phi}_r$, $\bar{\phi}_s$, $\bar{\phi}_t$, $\bar{\phi}_u$ are centred on the same nucleus. In Eqs. (1–4) symbols with an upper "bar" represent quantities defined with respect to an orthogonalized (hybrid) basis, the corresponding quantities with no "bar" refer to a non-orthogonal (hybrid) basis. Thus γ_{rs} and $\bar{\gamma}_{rs}$ denote the repulsion integral between charge densities ϕ_r^2, ϕ_s^2 and between $\bar{\phi}_r^2$, $\bar{\phi}_s^2$ respectively.

This paper is a report of a systematic way of approximating the integrals $\bar{H}_{rr}$, $\bar{H}_{rs}$, $\bar{\gamma}_{rr}$ and $\bar{\gamma}_{rs}$.

The *ab initio* calculation of these integrals is not a trivial matter since the standard methods of integral evaluation are all for the non-orthogonal AOs (or HAOs) and the transformation to an orthogonal basis means, for example, that any *one* $\bar{\gamma}_{rs}$ may involve *all* m^4 (for m AOs) of the integrals

$$(ij, kl) = \int dv_1 \int dv_2 \phi_i(1)\phi_j(1) \frac{1}{r_{12}} \phi_k(2)\phi_l(2) \tag{5}$$

over the non-orthogonal basis since

$$\bar{\gamma}_{rs} = \sum_{i,j,k,l} V_{ir} V_{jr} V_{ks} V_{ls} (ij, kl) \tag{6}$$

where V is the matrix of the transformation AOs → OHAOs.

If the NDO schemes are to have any computational value, it is necessary to have methods of obtaining the integrals (1–3) (at least) directly i.e. not involving transformations like (6).

In the case of electron repulsion integrals the standard approach has been to ignore the effect of orthogonalization on these integrals – to ignore the difference between γ_{rs} and $\bar{\gamma}_{rs}$.[1]

This approximation is based on the fact that as $\phi_r\phi_s \to 0$ then $\bar{\gamma}_{rs} \to \gamma_{rs}$. But the essence of the conventional interpretation of orbital theories of valence is that the

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[1] In fact, much coarser approximations are in current use for $\bar{\gamma}_{rs}$ – the use of γ_{rs} is merely the best approximation in large-scale use.

overlap density $\phi_r\phi_s$ (or $\bar{\phi}_r\bar{\phi}_s$) is *not zero*. The simplifications brought about by the use of an orthogonal basis are due to the fact that, in such a basis, the *overlap density integrates to zero*. Examination of any set of electron repulsion integrals is sufficient to show that, in the all-important region around equilibrium internuclear distances (σ-σ overlap around 0.7) there are differences of up to 20% between the γ_{rs} and $\bar{\gamma}_{rs}$.

The effect of orthogonalization on the $\bar{H}_{rr}$, $\bar{H}_{rs}$ is also not negligible – in particular $\bar{H}_{rs}$ is usually *much* smaller in magnitude than H_{rs} and $\bar{H}_{rr}$ is normally smaller than H_{rr}. That orthogonalization should have a dramatic effect on the H_{rs} values is easily seen from Fig. 1 which is a schematic diagram of the effect of symmetrical orthogonalization on an sp^3 hybrid involved in a C–H bond. The *squares* of the HAOs and OHAOs (which are involved in $\bar{H}_{rr}$ and $\bar{\gamma}_{rr}$) are much more similar than are the orbitals ϕ_r and $\bar{\phi}_r$ themselves. The HAO ϕ_r has a large negative "lobe" added on orthogonalization while the square ϕ_r^2 simply has a steep "valley" imposed on its principal lobe. Thus, we might expect that molecular integrals involving ϕ_r *as such* in the integrand are likely to be much more affected by orthogonalization of the basis than those involving the squares of the HAOs, ϕ_r^2. Presumably these latter types of integral will have similar values in the HAO and OHAO basis.

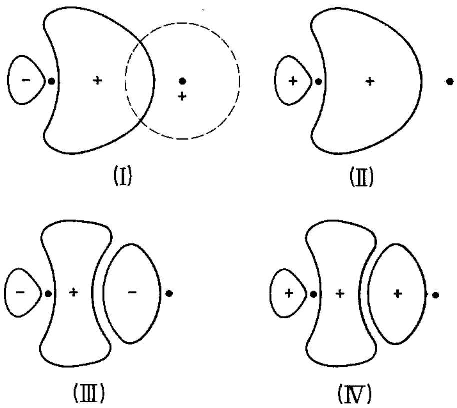

Fig. 1. Effect of symmetrical orthogonalization on an sp^3 HAO (schematic): (I) ϕ_1 (ϕ_2 dotted); (II) ϕ_1^2; (III) $\bar{\phi}^1$; (IV) $\bar{\phi}_1^2$

In previous work [2] we have suggested that for the reasons outlined above, it is better to *compute* the one-electron integrals and seek approximations for the $\bar{\gamma}_{rs}$. However, this may be too pessimistic a view since, as we have just seen, the $\bar{H}_{rr}$ may well be capable of approximation in terms of the H_{rr}. Further, in the investigation of the electronic structure of large and complex polyatomic molecules (e.g. transition metal complexes) even the calculation of the $\bar{H}_{rr}$ and $\bar{H}_{rs}$ is a heavy computational problem because of the necessity of including the effect of large numbers of "core" electrons.

In the past many of these computational difficulties have been avoided by the use of experimental (atomic) quantities in place of the integrals (1–4) (or parts of these integrals) and by the use of "invariance principles" which are now known to be unrealistic [1]. The use of experimental data is certainly an attractive proposition but, unfortunately, it is associated with *unavoidable* difficulties of interpretation. The separations observed between atomic energy levels which are often schematically interpreted at a qualitative level as electron-repulsion (Slater–Condon) parameters are determined quantitatively by the detailed interactions between the electrons. These "atomic integrals" obtained from an analysis of atomic spectral data contain a numerical measure of all kinds of physical effects: mean (Hartree–Fock) repulsions, electron correlations, relativistic effects etc. The numerical values of these parameters, although useful for comparative studies and the extrapolation and interpolation of molecular energies, may well *not be compatible with any explicitly stated orbital basis.* That is, the charge density (for example) obtained from a calculation using these "integrals" may well be uninterpretable.

From the point of view of agreement with experiment, the inclusion of (e.g.) correlation effects may be thought to be an advantage rather than a shortcoming because, of course, electron correlation effects are actually occurring in molecules. But this is only conceivably true if the model used specifically excludes correlation effects: the MO model. What are we to make of (e.g.) a CI calculation using these integrals? If we include electron correlation in the *formulation* of our model (VB, CI, MCSCF) then what is the role of electron repulsion integrals "containing correlation effects"? Have we counted correlation twice? Further, how are we to *interpret* the computed charge density, orbital energies etc.? We may well be in the position of having *computed* a correct molecule energetic property (barrier to rotation, for example) and produced a spurious explanation of the phenomenon! For these reasons we prefer to work with molecular integrals which are (at least in intention) integrals over an explicitly stated "atomic orbital" basis.

2. Pairwise Overlap, Symmetrical Orthogonalization and the Mulliken Approximation

The use of a basis of hybrid atomic orbitals which reflect the likely bonding scheme in a molecule has an important advantage in the study of the orthogonalization procedure. For σ bond systems each HAO has a large overlap with *just one* other orbital – its "bonding partner" in the classical bonding scheme. The overlap integrals with other HAOs are generally much smaller. Thus, it is a good approximation to treat each "bonded pair" of orbitals as only overlapping with each other. Two HAOs ϕ_1, ϕ_2 generate an overlap matrix

$$\boldsymbol{S}=\begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix} \tag{7}$$

where S is much larger (typically 6 or 7 times) than the overlap of ϕ_1 or ϕ_2 with any other HAO in the molecule. The Löwdin orthogonalization matrix is given by:

$$\boldsymbol{S}^{-1/2}=\boldsymbol{V}=\begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} \tag{8}$$

where

$$V_{11}=V_{22}=\frac{1}{2\sqrt{1-S^2}}\left(\sqrt{1-S}+\sqrt{1+S}\right)$$

$$V_{12}=V_{21}=\frac{1}{2\sqrt{1-S^2}}\left(\sqrt{1-S}-\sqrt{1+S}\right) \tag{9}$$

The OHAOs $\bar{\phi}_1$, $\bar{\phi}_2$ are given by

$$(\bar{\phi}_1, \bar{\phi}_2)=(\phi_1, \phi_2)V \tag{10}$$

Expanding the product $\bar{\phi}_1\bar{\phi}_2$ using (9) and (10) we find

$$\bar{\phi}_1\bar{\phi}_2=\frac{1}{(1-S^2)}\left[\phi_1\phi_2-\frac{S}{2}(\phi_1^2+\phi_2^2)\right] \tag{11}$$

If we now make the Mulliken approximation for the HAO overlap density $\phi_1\phi_2$:

$$\phi_1\phi_2=\frac{S}{2}(\phi_1^2+\phi_2^2) \tag{12}$$

we see that

$$\bar{\phi}_1\bar{\phi}_2\equiv 0 \tag{13}$$

That is, the use of the Mulliken approximation followed by symmetrical orthogonalization is completely consistent with "Neglect of differential overlap" (NDO) approximations – the three techniques form a self-consistent set [4]. We now turn to the consequences of this simple fact for the molecular integrals retained in an NDO scheme.

In the past the series expansion of $\boldsymbol{S}^{-1/2}$ (in powers of $\boldsymbol{M}$, the off-diagonal part of $\boldsymbol{S}$) has been used to justify numerical approximations.

$$\boldsymbol{S}^{-1/2}(1+\boldsymbol{M})^{-1/2}=1-\tfrac{1}{2}\boldsymbol{M}+\tfrac{3}{8}\boldsymbol{M}^2-\tfrac{5}{16}\boldsymbol{M}^3+\cdots$$

This expansion technique works well when the elements of $\boldsymbol{M}$ are small: three terms give an accuracy of better than 1% for a typical π-π overlap of 0.25. However, for σ-σ HAO overlaps (0.6–0.8), as many as *twelve to fifteen* terms in the expansion are needed to obtain $\boldsymbol{S}^{-1/2}$ to two places of decimals. Clearly, the series expansion of $\boldsymbol{S}^{-1/2}$ is of little value in obtaining comparative sizes of integrals involving σ orbitals.

3. One-Electron Integrals

If

$$H_{rs}=\int dv\phi_r\hat{h}\phi_s \tag{14}$$

are the HAO one-electron ("core") integrals and the corresponding OHAO integrals are denoted by $\bar{H}_{rs}$:

$$\bar{H}_{rs}=\int dv\bar{\phi}_r\hat{h}\bar{\phi}_s$$

then, using (9) and (10) we have

$$\bar{H}_{11}=\frac{1}{(1-S^2)}\left\{H_{11}(1+\sqrt{1-S^2})+H_{22}(1-\sqrt{1-S^2})-2SH_{12}\right\} \tag{15}$$

$$\bar{H}_{12}=\frac{1}{(1-S^2)}\left\{H_{12}-\frac{S}{2}(H_{11}+H_{22})\right\} \tag{16}$$

$$\bar{H}_{22}=\frac{1}{2(1-S^2)}\left\{H_{22}(1+\sqrt{1-S^2})+H_{11}(1-\sqrt{1-S^2})-2SH_{12}\right\}$$

Now the one-electron Hamiltonian is a combination of an essentially *operator* term ($-\frac{1}{2}\nabla^2$, the kinetic energy operator) and a potential energy term which is a multiplying factor ($\hat{V}$ say):

$$\hat{h}=-\tfrac{1}{2}\nabla^2+\hat{V} \tag{17}$$

Thus

$$H_{rs}=T_{rs}+V_{rs}$$

where

$$T_{rs}=\int dv\phi_r(-\tfrac{1}{2}\nabla^2)\phi_s \tag{18}$$

and

$$V_{rs}=\int dv\phi_r\hat{V}\phi_s$$

and the corresponding definitions hold for $\bar{T}_{rs}$ and $\bar{V}_{rs}$. But, if $\hat{V}$ is simply multiplicative[2] then we can use the Mulliken approximation and we have

$$\int dv\phi_1\hat{V}\phi_2=\int dv\phi_2\hat{V}\phi_1=\frac{S}{2}\left\{\int dv\hat{V}\phi_1^2+\int dv\hat{V}\phi_2^2\right\}$$

i.e.

$$V_{12}=\frac{S}{2}(V_{11}+V_{22}) \tag{19}$$

It is readily seen, that when (18) and (19) are substituted into (16) (or directly from (13)) that the only remaining term is $\bar{T}_{12}$,

$$\bar{H}_{12}=\bar{T}_{12}=\frac{1}{(1-S^2)}\left\{T_{12}-\frac{S}{2}(T_{11}+T_{22})\right\} \tag{20}$$

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[2] An exact $\hat{V}$ would contain non-local core/valence exchange potentials but their effects are small.

The astonishing conclusion is that, using

1) a pairwise overlapping HAO basis
2) the Mulliken approximation

and 3) symmetrical orthogonalization

the all-important bonding integrals $\bar{H}_{rs}$ (the β's) have *no potential energy contribution*

$$\bar{H}_{rs} = \bar{T}_{rs} = \int dv \bar{\phi}_r \left(-\tfrac{1}{2}\nabla^2\right) \bar{\phi}_s \tag{21}$$

This result is astonishing on two counts:

1) If it holds up numerically it is an extremely powerful way of computing the $\bar{H}_{rs}$ integrals – traditionally the most difficult and most frequently parametrized molecular integrals. The one- and two-centre kinetic energy integrals are easy to evaluate; they reduce to a sum of overlap integrals.

and 2) Equation (21) throws some light on the physical nature of the OHAO basis and the important role played by kinetic energy on bond formation ($\bar{T}_{12}$ is negative for positive S, while T_{12} is positive).

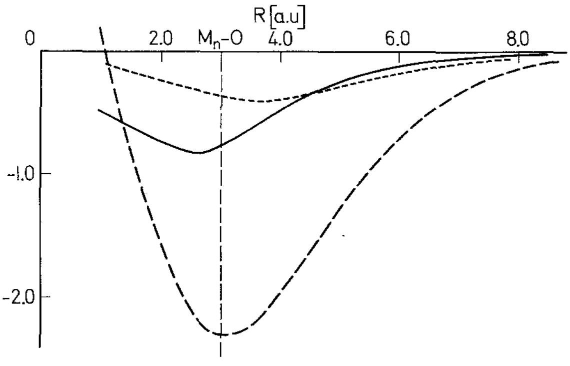

Fig. 2. Approximations for $\bar{H}_{12}$ for Mn–O (sp^3 hybrids): full line, exact calculation; large dashed line Eq. (22) small dashed line $\bar{T}_{12}$. (The vertical line indicates the Mn–O distance in MnO_4^-.)

As regards 1), Fig. 2 shows a plot of $\bar{H}_{12}$ against internuclear distance for an Mn–O fragment. The two HAOs are sp^3 hybrids along the internuclear axis with optimum 4*s* and 2*s* exponents respectively. A point-charge approximation has been made for the atomic "cores". The point in question here is not, of course, how realistic this fragment is, simply how well Eq. (20) works numerically. For comparison purposes the Wolfsberg–Helmholtz-like approximation

$$\bar{H}_{12} = \frac{S}{2}\left(\bar{H}_{11} + \bar{H}_{22}\right) \tag{22}$$

is plotted on the same figure.[3] The surprising conclusion is that (20) performs rather

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[3] Strictly speaking, there are a number of ways of using (22); e.g. using H_{ii} in place of $\bar{H}_{ii}$ or only the one-centre parts of H_{ii} or $\bar{H}_{ii}$. All these results are similar – the curve plotted is representative.

well in practice; rather better than some conventional approximations. The figure also shows one of the disadvantages of formulae of the general form

$$\bar{H}_{12} = \frac{S}{2}(X_1 + X_2)$$

where X_1, X_2 are characteristic of ϕ_1, ϕ_2: the sign of $\bar{H}_{12}$ is determined by the sign of S. This is not true in general, for short internuclear distances we may have $S<0$, $\bar{H}_{12}<0$ using an HAO basis.

The use of the kinetic energy integral as a bonding parameter might be felt to be odd in view of the fact that, in the familiar HAO basis, the kinetic energy integrals are normally *positive*. However, it is easy to verify that, for s-type STOs at least,

$$T_{12} < \frac{S}{2}(T_{11} + T_{22})$$

i.e. (20) is always *negative*. A conjectured "theorem" might be therefore: if $S<0$ then $\bar{T}_{12}<0$. Fig. 3 shows the use of (20) for a C–C fragment compared to the CNDO [5] $\bar{H}_{12}$ formula.

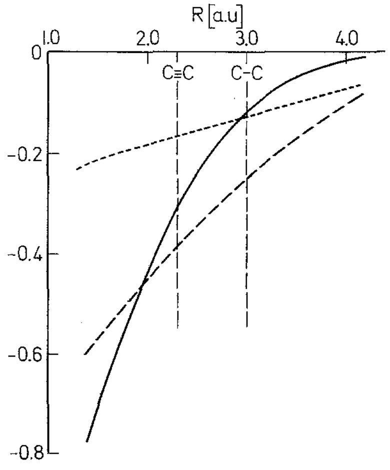

Fig. 3. Comparison of $\bar{T}_{12}$ with the standard CNDO approximation for $\bar{H}_{12}$ for 2s orbitals of carbon: full line exact; large dashed line CNDO; small dashed line $\bar{T}_{12}$. (The two vertical lines show the range of C–C distances in organic molecules.)

The interpretation of (21) has something in common with Linderberg's [6] formula for the β's of π-electron theory:

$$H_{rs} = \int dv \phi_r \nabla \phi_s / |R_r - R_s|$$

This expression has only a "kinetic energy" contribution. However the derivation and justification of Linderberg's formula are quite different from our approach.

Returning to Eq. (15) we can now study the application of the Mulliken approximation to the diagonal one-electron integrals $\bar{H}_{rr}$. Now it is well known that the

Mulliken approximation is at its best when the charge distribution $\phi_1\phi_2$ is non-polar:

$$\phi_1\phi_2 = a\phi_1^2 + b\phi_2^2 \quad \text{with} \quad a = b = \frac{S}{2}$$

Thus, using $H_{11} = H_{22}$ in (15) for the most favourable case, we have

$$\bar{H}_{11} = \frac{1}{(1-S^2)}\{\tfrac{1}{2}(H_{11}+H_{22}) - SH_{12}\} \tag{23}$$

Again, using Eq. (17) to separate kinetic and potential energy and using (19) we have

$$\bar{H}_{11} = \bar{T}_{11} + V_{11} \tag{24}$$

The diagonal elements of the one-electron potential energy operator are *unchanged by symmetrical orthogonalization.* The constraints under which (24) was derived are 1)–3) above *plus* equality of H_{11} and H_{22}. If H_{11} and H_{22} are different we cannot recover (24) formally but we do not expect that V_{11} and $\bar{V}_{11}$ will differ very much numerically, if the magnitude of the difference between H_{11} and H_{22} is not too great. Fig. 4 shows the variation of $\bar{H}_{11}$ and $\bar{T}_{11} + V_{11}$ for the Mn–O fragment used in Fig. 2. The computational advantage of $V_{11} \approx \bar{V}_{11}$ is, of course, that V_{11} only involves one- and two-centre molecular integrals over the HAO basis.

Eq. (24) also has a physical interpretation. The main change occurring on orthogonalization is the change $T_{11} \to \bar{T}_{11}$ and, in general, it is found that $\bar{T}_{rr} > T_{rr}$ i.e. since V_{rr} is negative, $\bar{H}_{rr} > H_{rr}$ ($|\bar{H}_{rr}| < |H_{rr}|$). Thus the principal *atomic* effect of symmetrical orthogonalization is to increase the atomic kinetic energy. These results present a tempting analogy with Ruedenbergs [7] result that bond formation is accompanied by an increase in atomic kinetic energy ($\bar{T}_{11} > T_{11}$) and a decrease in the kinetic energy in the bond regions ($\bar{T}_{12} < T_{12}$). In a sense therefore, symmetrical orthogonalization mimics the atomic electron rearrangements

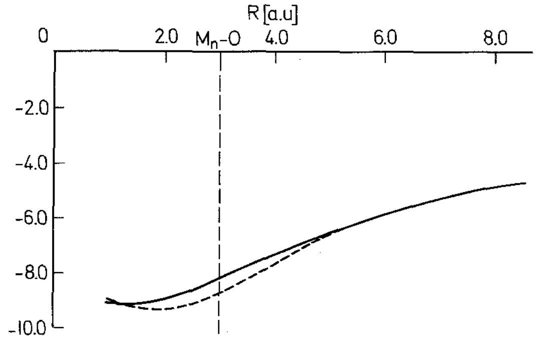

Fig. 4. Effect of symmetrical orthogonalization on $\bar{H}_{11}$ for Mn–O (sp^3 hybrids): full line exact; small dashed line $\bar{T}_{11} + V_{11}$ (vertical line as for Fig. 2)

occurring on molecule formation: the "orbital contraction" effects stressed by Ruedenberg in his analysis of the chemical bond.[4]

If H_{11} and H_{22} do differ significantly enough for the simple Eq. (23) to be suspect (large differences in the electro negativities of ϕ_1 and ϕ_2, for example), then V_{11} and $\bar{V}_{11}$ will differ appreciably. In fact, using (15) we have

$$\begin{aligned} \bar{V}_{11} &= V_{\mathrm{Av}} + \frac{\Delta V}{2\sqrt{1-S^2}} \\ \bar{V}_{22} &= V_{\mathrm{Av}} - \frac{\Delta V}{2\sqrt{1-S^2}} \end{aligned} \tag{25}$$

where $V_{\mathrm{Av}} = \frac{1}{2}(V_{11} + V_{22})$ and $\Delta V = \frac{1}{2}(V_{11} - V_{22})$. The relative accuracy of the approximations can be judged for the two valence AOs of LiH ($\phi_1 = 1s_{\mathrm{H}}$, $\phi_2 = 2s_{\mathrm{Li}}$).

Eq. (24) gives $\bar{H}_{11} = -0.5075$; $\bar{H}_{22} = -0.7514$
Eq. (25) gives $\bar{H}_{11} = -0.4600$; $\bar{H}_{22} = -0.8009$.

The exact integrals are $\bar{H}_{11} = -0.4594$; $\bar{H}_{22} = -0.8023$.
For completeness $\bar{T}_{12} = -0.1211$ while the exact $\bar{H}_{12}$ is -0.1181. Fig. 4 shows the variation in $\bar{T}_{11} + V_{11}$ for the Mn–O fragment of Fig. 2.

Thus the use of the (self-consistent) scheme of pairwise-overlapping HAOs, the Mulliken approximation and symmetrical orthogonalization provides a convenient scheme for the non-empirical evaluation of one-electron integrals over an orthogonalized basis.

4. Electron Repulsion Integrals

The Mulliken approximation $\bar{\phi}_1 \bar{\phi}_2 = 0$ means that the one- and two-centre repulsion integrals are the main two-electron integrals to be evaluated within an NDO framework. Using the Mulliken approximation for $\phi_1 \phi_2$ the relation between the HAO integrals and the OHAO values are:

$$\begin{aligned} \bar{\gamma}_{12} &= A\gamma_{12} - B\gamma_{\mathrm{Av}} \\ \bar{\gamma}_{11} &= A\gamma_{\mathrm{Av}} - B\gamma_{12} + C\Delta\gamma \\ \bar{\gamma}_{22} &= A\gamma_{\mathrm{Av}} - B\gamma_{12} - C\Delta\gamma \end{aligned} \tag{26}$$

where

$$A = \frac{1}{2}\left(1 + \frac{1}{1-S^2}\right); \qquad B = \frac{S^2}{2(1-S^2)}; \qquad C = \frac{2}{\sqrt{1-S^2}}$$

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[4] These comparisons need further study since, as presented here, they are only analogies: orthogonalization is not a phenomenon but a technical device used in orbital basis theories whereas Ruedenberg's results are, of course, physical. However it is worth pointing out that symmetrical orthogonalization always leads to "orbital contraction" in the sense of decreasing $\langle r \rangle$ (the mean value of the distance from the nucleus of an AO).

and

$$\gamma_{\mathrm{Av}}=\tfrac{1}{2}(\gamma_{11}+\gamma_{22}); \qquad \Delta\gamma=(\gamma_{11}-\gamma_{22})/2$$

Now (26) includes the use of the Mulliken approximate twice and the errors in (26) are therefore likely to be those of the Mulliken approximation "squared". In fact the numerical performance of (26) is quite good but falls off quite badly with large S. It is well known from a number of empirical studies [2, 3] that the relation between γ_{rs} and $\bar{\gamma}_{rs}$ is rather closer than (26) would suggest: typically $\bar{\gamma}_{rs}<\gamma_{rs}$ the difference being rarely larger than 20% even for $S\sim 0.8$. Similarly $\bar{\gamma}_{rr}>\gamma_{rr}$ with changes in value of up to 20%. That is, as has been emphasized elsewhere [2, 3] an approximate relationship of the form

$$\bar{\gamma}_{rs}=(1-a)\gamma_{rs}; \qquad \bar{\gamma}_{rr}=(1+a')\gamma_{rr}$$

holds to a good approximation for a given bonded pair $\bar{\phi}_r$, $\bar{\phi}_s$. Now a, a' must be functions of S^2 (at least!) since the *sign* of S has no effect on the transition from γ to $\bar{\gamma}$. It is already evident that the coefficients A, B and C do indeed depend on S^2. In order to a relationship of the form (e.g.)

$$\bar{\gamma}_{rs}=f(S^2)\gamma_{rs}; \qquad \bar{\gamma}_{rr}=g(S^2)\gamma_{rr}$$

it is therefore necessary to make some assumption about an approximate relationship between γ_{12} and γ_{Av} in (26). This relationship need only hold where S is appreciable and, in particular, should go over to unity for $S=1$. The simplest possible assumption which meets the requirements is:

$$\gamma_{12}\approx\left(\frac{1+S^2}{2}\right)\gamma_{\mathrm{Av}}$$

if we use this expression in (26) and set $\Delta\gamma\approx 0$ we obtain

$$\bar{\gamma}_{11}=\frac{1}{1-S^2}\left\{1-\frac{S^2}{4}(3+S^2)\right\}\gamma_{11}$$

$$\bar{\gamma}_{22}=\frac{1}{1-S^2}\left\{1-\frac{S^2}{4}(3+S^2)\right\}\gamma_{22}$$

and

$$\bar{\gamma}_{12}=\frac{1}{1-S^4}\left\{1-\frac{S^2}{2}(1+S^2)\right\}\gamma_{12} \qquad (27)$$

These formulae work extremely well for a whole range of overlaps. The formula for $\bar{\gamma}_{12}$ is particularly accurate: Figs. 5 and 6 show the use of (27) for some representative integrals. It must be stressed that *nowhere* do we use the approximation $\gamma_{12}\approx(1+S^2)\gamma_{\mathrm{Av}}/2$ for the *calculation* of γ_{12}: it is simply a device for obtaining an approximation for the dependence of $\bar{\gamma}_{rr}$, $\bar{\gamma}_{rs}$ on S *in the region of large S*.

In line with our general considerations based on Fig. 1 it is readily seen from Eqs. (27) that the electron repulsion integrals $\bar{\gamma}_{rr}$, $\bar{\gamma}_{rs}$ (which depend on the squares of the OHAOs $\bar{\phi}_r$, $\bar{\phi}_s$) are less acutely dependent on the orthogonalization technique than the $\bar{H}_{rs}$.

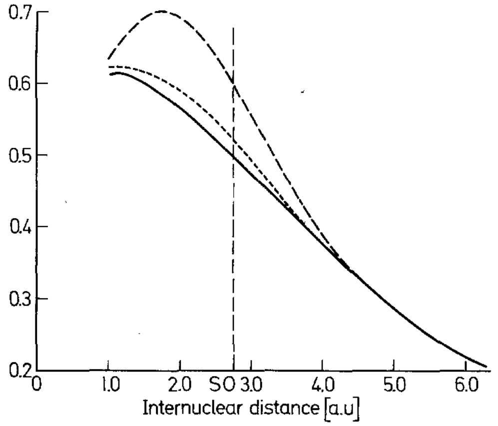

Fig. 5. Effect of symmetrical orthogonalization on $\bar{\gamma}_{12}$ for S–O (sp^3 hybrids): full line exact; large dashed line non-orthogonal γ_{12}; small dashed line Eq. (27) (the vertical line is the equilibrium S–O distance in SO_4^{--})

There is one class of large electron-repulsion integral not touched by this analysis – the one-centre repulsion integrals $\bar{\gamma}_{rs}$ where $\bar{\phi}_r$ and $\bar{\phi}_s$ are centred on the same nucleus. These integrals show a pattern of behaviour very similar to the one-centre integrals $\bar{\gamma}_{rr}$. When one (or both) of ϕ_r, ϕ_s has a large-overlap bonding partner on an adjacent centre the integral $\bar{\gamma}_{rs}$ increases – the amount of increase being in the order

no bonding partners < one bonding partner < two bonding partners.

Thus, to reflect this trend and to recover the special case when $r = s$ we use

$$\bar{\gamma}_{rs} = \sqrt{g(S^2_{rr'})g(S^2_{ss'})}\,\gamma_{rs} \tag{27a}$$

where

$$g(S^2) = \frac{1}{1-S^2}\left[1 - \frac{S^2}{4}(3+S^2)\right]$$

and $\phi_{r'}$ and $\phi_{s'}$ are the bonding partners (if any, otherwise $S_{rr'} = 0$ etc.) of ϕ_r, ϕ_s. The formulae (27) and (27a) give a very good approximation to the effect of orthogonalization on the electron-repulsion integrals retained in the NDO scheme.

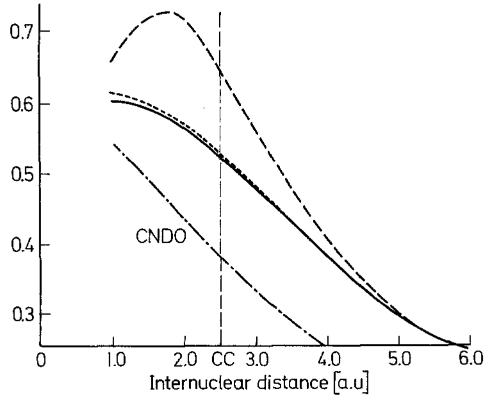

Fig. 6. Effect of symmetrical orthogonalization on $\bar{\gamma}_{12}$ for C=C (sp^2 hybrids): lines as Fig. 5 (the vertical line is the C=C equilibrium distance)

5. Lone Pairs and π Orbitals

A lone pair HAO has no "bonding partner" and therefore the integrals $\bar{H}_{rs}$ are irrelevant here and the other approximations degenerate into the identity between the HAO and OHAO integrals since $S=0$ in this case. There is no unique bonding partner in the case of π AOs involved in a de-localized system of double bonds so that our central assumption breaks down here. However, π-π AO overlaps are always considerably smaller than σ-σ overlaps (typically about 0.2–0.3 compared to 0.6–0.8). Applied to electron-repulsion integrals this means changes of the order of 2% in going from γ_{rs} to $\bar{\gamma}_{rs}$. Similarly the size of the π-π overlaps make the application of the corrections for orthogonalization easier to apply – the success of the early semi-empirical methods for electronic structure of π systems depends on this fact.

6. Applications: Numerical Calculations

With the exception of the one-centre "exchange" integrals (4), we now have all the molecular integrals necessary to perform valence calculations within the NDO approximation scheme.[5] These exchange integrals cannot be computed by methods based on the Mulliken approximation as the one-centre overlap integrals are zero. Also, using an orthogonalized *hybrid* basis these integrals are usually much smaller than the corresponding orthogonalized atomic orbital basis integrals:

$$(\bar{b}_1\bar{b}_2, \bar{b}_1\bar{b}_2)=0.0671, \quad (\bar{2}s\bar{2}p, \bar{2}s\bar{2}p)=0.1596$$

for CH_2O where $\bar{b}_1, \bar{b}_2$ are orthogonalized sp^2 hybrids on carbon. We can therefore usefully test the integral approximations developed above in practice.

The one-electron Hamiltonian for the valence orbitals was the kinetic energy matrix over a "standard" minimal basis of STOs transformed to an OHAO basis (sp^2 hybrids on C and O). The diagonal potential energy terms were calculated from (25) and the electron-repulsion integrals from (27). An SCF MO calculation was carried through which yielded a wavefunction which had a total overlap determinant of 0.93 with the full *ab initio* calculation, compared to an overlap of 0.95 if all the exact values are used for the retained integrals.

The OHAO basis is particularly well adapted to a "bond-pair" description of the electronic structure of molecules. Thus an SCGF [8] calculation was carried out for CH_2O using the same molecular integrals. The resulting total wavefunction had a total overlap of 0.954 with the corresponding *ab initio* calculation. This latter result is not too surprising since, in the SCGF approach, only the "bonding partner" $\bar{H}_{rs}$ are used. That is the SCGF method is particularly suited to use in conjunction with NDO schemes since even the full *ab initio* calculation requires only a fraction of molecular integrals; because of the 2 × 2 "blocked" form of the charge and bond-order matrix. The SCFMO method, on the other hand, in its *ab initio* form requires *all* the molecular integrals so that NDO schemes are potentially

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[5] The most widely used class of NDO schemes ("CNDO"-type) uses only integrals (1–3).

more severe approximations in this model which contains no chemical ideas about the large-scale structure of the charge and bond-order matrix.

7. The Interpretation of Orthogonal-Basis "Bonding" Integrals

Both in the LiH example given above and in the CH_2O case used in the previous section it is noticeable that the use of $\bar{T}_{rs}$ in place of $\bar{H}_{rs}$ *always* gives a number of greater magnitude than the true value for bonded partners $\bar{\phi}_r$, $\bar{\phi}_s$. That is

$$|\bar{T}_{rs}|>|\bar{H}_{rs}| \qquad (\text{both } \bar{T}_{rs}, \bar{H}_{rs}<0)$$

for $\bar{\phi}_r$, $\bar{\phi}_s$ bonded. The actual size of the difference varies from bond to bond, of course. This means that, in the OHAO basis where

$$\bar{H}_{rs}=\bar{T}_{rs}+\bar{V}_{rs} \tag{28}$$

$$\bar{V}_{rs}>0 \quad \text{for} \quad \bar{\phi}_r, \bar{\phi}_s \text{ "bonded".}$$

(Our *approximation* has, of course, been to set the corresponding $\bar{V}_{rs}=0$). In the orthogonalized basis therefore, there can be no question of an interpretation of the bonding parameters as giving a quantitative measure of the binding effect of an electron in the potential field of two nuclei. This interpretation is the usual one and is based on the signs of the contributions to H_{rs} in the non-orthogonal basis: $T_{rs}>0$ and $V_{rs}<0$. In this view, orthogonalization of the basis is simply a *technical device* necessary in order to solve the equations but of no scientific value. In the case of the single-determinant molecular orbital method (*ab initio*, using all integrals) there is no advantage in using an orthogonalized basis since the results are invariant. However almost all other formulations of the problem of molecular electronic structure (CI, VB) are scarcely feasible in a non-orthogonal basis. Also the use of an NDO scheme makes even the MO method basis dependent [1]. Thus it is of considerable interest to pursue the interpretation of the OHAO one-electron integrals. This matter will be taken up elsewhere. The simplest possible justification for $\bar{V}_{rs}\approx 0$ is the charge-density interpretation of the orthogonality condition itself:

$$\int dv\bar{\phi}_r\bar{\phi}_s=0$$

implies that charge distribution $\bar{\phi}_r\bar{\phi}_s$ contains *no net charge*. While this implies that potential energy integrals of the form

$$\int dv\bar{\phi}_r\hat{V}\bar{\phi}_s$$

will be zero if the sources of the potential are all *external* to $\bar{\phi}_r$, $\bar{\phi}_s$, it does not satisfactorily explain the observed fact that $\bar{V}_{rs}>0$.

8. Conclusion

The use of one simple idea (the pairwise overlap of hybrid atomic orbitals) a well-tried approximation (the Mulliken approximation) and a standard technique (symmetrical orthogonalization) leads to a self-consistent scheme for the numerical evaluation of the principal integrals required in the approximate calculation of molecular electronic structure. No use has been made of any specific *model* of molecular electronic structure – the integral formula can be used in *any* orbital-basis expansion technique (MO, CI, VB): in particular none of the approximations is dependent on the MO method. The integrals are approximations to molecular integrals over an explicitly-defined OHAO basis – they are not parameters and contain no empirical factors.

The development of the approximation scheme has thrown into sharp relief the necessity of a careful analysis of the physical interpretation of the OHAO basis and (particularly) the "bonding integrals" over this basis (the $\bar{H}_{rs}$). The usual potential-energy interpretation of these numbers has been shown to be quite wrong since $\bar{V}_{rs} > 0$. There are striking analogies between the changes in molecular integrals and the "orbital contraction" effects used by Ruedenberg in his persuasive analysis of chemical bond formation.

Finally a word about the Mulliken approximation itself. The formal approximation is (12)

$$\phi_r \phi_s = \frac{S_{rs}}{2} (\phi_r^2 + \phi_s^2)$$

but in fact, taken literally as an approximation to the *function* $\phi_r \phi_s$ this approximation is grotesquely bad as the evaluation of both sides of (12) for the two 1s AOs of H_2 will show. But the approximate evaluation of the molecular integrals of H_2 using the Mulliken approximation gives very good answers. Thus the Mulliken approximation (12) is in fact a convenient way of systematizing an *integral* approximation scheme – the molecular integrals being much less sensitive to approximation than the factors in the integrand.

References

1. Cook, D. B.: Theoret. Chim. Acta (Berl.) **40**, 297 (1975)
2. Cook, D. B., Hollis, P. C., McWeeny, R.: Mol. Phys. **13**, 573 (1968)
3. Brown, R. D., Roby, K.: Theoret. Chim. Acta (Berl.) **16**, 194 (1970)
4. McWeeny, R.: Proc. Roy. Soc. (London) **A227**, 288 (1955)
5. Pople, J. A., Segal, G. A.: J. Chem. Phys. **43**, 5136 (1965)
6. Linderberg, J.: Chem. Phys. Letters **1**, 39 (1967)
7. Ruedenberg, K., in: Localisation and delocalisation in quantum chemistry, p. 223. Dordrecht: Reidel 1975
8. Klessinger, M., McWeeny, R.: J. Chem. Phys. **42**, 3343 (1965)

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