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Atomic Spherical Orbitals

I. On the Angular Implications of the Differential Overlap Approximations

Gilles Klopman
Chemistry Department, Case Western Reserve University, Cleveland, Ohio, USA

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It was found that the use of conventional Slater type overlap, resonance and kinetic integrals are not compatible with the use of Differential Overlap approximations (DOA). We propose a new set of basis functions, Spherical Orbitals, (SO's) that relieve some of the shortcomings generated by the use of DOA's.

The general topology of the SO's is presented along with formulae to be used to solve the inherent integrals.

Key word: Atomic spherical orbitals

The use of Differential Overlap Approximations (DOA) such as the Mulliken [1], Wolfsberg-Helmholz [2], Pople [3] and other Neglect of Differential Overlap [4] have become increasingly common in the literature. These approximations are used for the purpose of decreasing the number of integrals to be evaluated in MO calculations of molecules, and are essentially of the type:

$$\text{DOA} \dashrightarrow \phi_a\phi_b = 1/2S_{ab}\{\phi_a\phi_a + \phi_b\phi_b\}\,. \tag{1}$$

That is they provide an approximation to the differential charge distribution $\phi_a\phi_b$ as a function of the overlap S_{ab} between ϕ_a and ϕ_b.

I wish to report here the results of our analysis of the geometrical implications of DOA and to propose a new set of basis functions that appear to be more appropriate to use in a general DOA context.

Let us consider first the expressions of the nuclear attraction integrals, as given by Roothaan [5] for Slater type orbitals:

$$\begin{aligned} &[a|2s_b2s_b] = N[a|3S_b] \\ &[a|2p_{\sigma b}2p_{\sigma b}] = N\{[a|3S_b] + 3[a|3D\Sigma_b]\} \\ &[a|2p_{\pi b}2p_{\pi b}] = N\{[a|3S_b] - 3/2[a|3D\Sigma_b]\}\,. \end{aligned} \tag{2}$$

We may equally express the $p_{\sigma b}$ and $p_{\pi b}$ as functions of two orthogonal p orbitals u and $v(S_{uv}=0)$ in a system of 45 degrees rotated axis.

$$\text{i.e. } p_{\sigma b}=\frac{1}{\sqrt{2}}(u+v)$$
$$p_{\pi b}=\frac{1}{\sqrt{2}}(u-v)\,. \tag{3}$$

If we now recalculate the nuclear attraction integrals and introduce the DOA, we obtain:

$$\begin{aligned}[][a|2p_{\sigma b}2p_{\sigma b}]&=\tfrac{N}{2}\{[a|uu]+2[a|uv]+[a|vv]\}\xrightarrow{\text{DOA}}\tfrac{N}{2}\{[a|uu]+[a|vv]\}\\ [a|2p_{\pi b}2p_{\pi b}]&=\tfrac{N}{2}\{[a|uu]-2[a|uv]+[a|vv]\}\xrightarrow{\text{DOA}}\tfrac{N}{2}\{[a|uu]+[a|vv]\}\end{aligned} \tag{4}$$

and consequently:

$$[a|2p_{\sigma b}2p_{\sigma b}]=[a|2p_{\pi b}2p_{\pi b}]=N[a|3S_b]=[a|2s_b2s_b]\,. \tag{5}$$

In this expression, the $[a|3D\Sigma_b]$ term of Eq. (2) has dissappeared and as a result, we see that the use of DOA, forced us to modify integrals even though differential overlap does not appear explicitly in their expression. This was recognized by Pople and coworkers [3] as the "invariance in space requirement" and usually accepted in most "all valence electrons" treatments [6]. A similar demonstration can be made for the Coulomb repulsion integrals where it can be shown that the introduction of DOA requires that only the spherical component be retained in the expression of the integrals representing them. That is, amongst all integral components NU such as NS, $NP\Sigma$, $NP\Pi$, $ND\Sigma$, etc. [5] in integrals $[NU|N'U']$, only the NS component is to be retained.

One important aspect of the problem that seems to have been neglected in the literature is that concerning the possible implications of DOA on other integrals such as on the overlap integral itself. Thus it was found above that some 2 center integrals had to be modified even though apparently DOA was not involved specifically. It is merely the fact that they had an angular component that determined that they had to be truncated. A similar situation actually does occur in the calculation of the overlap or resonance integrals where, for example, the difference between the $\langle 2s_a|2p_{\sigma b}\rangle$ and $\langle 2s_a|2p_{\pi b}\rangle$ integrals is essentially linked to the angular difference between the p_σ and p_π orbitals. It may therefore be anticipated that, as when $[a|2p_\sigma 2p_\sigma]$ and $[a|2p_\pi 2p_\pi]$ is not corrected to include the implications of DOA, the failure of correcting the overlap integrals themselves will also result in an error. This does not imply that the DOA, as applied to overlap integrals is not correct, but merely that it is not consistent with the use of DOA for the other integrals.

As a matter of fact, a truncated integral expression such as Eq. (5) must result either from a truncated operator or a "modified" p function. Since the truncation applies only to the angular component, it must be assigned to the latter. As a result, self consistency can be reached only if "all" integrals were calculated accordingly, that is with the same basis of "modified" p functions. Actually, we found that the inclusion of a virtual p_σ orbital in a Slater base MO calculation of Li_2, where DOA is strictly applied, yields a deep energy minimum and practically complete depopulation of the 2*s* orbital in favor of the 2*p* orbital.

Table 1. MO and energy of Li_2 calculated under various approximations

Method		Coef. of the highest occupied MO			Total energy (eV)		Bonding energy (eV)
		1*s*	2*s*	2*p*σ	Li_2	$2Li_{calc.}$	
1. Alch.		−0.1491	0.5260	0.1194	−14.8409		—
2. 1*s*2*s*	DOA	−0.1474	0.5716	—	−14.8306	−14.8381	+0.0075
3. STO		−0.1335	0.3021	0.4399	−14.9141		−0.07597
4. SO		−0.1399	0.4726	0.2420	−14.8524		−0.0143
							exp. (−0.0441)

This is seen in Table 1 when comparing lines 1, 2, and 3. Line one reproduces the results obtained from a straightforward *ab initio* calculation[1] of Li_2 at a distance of 5.05 a.u. with a basis set consisting of 1*s*, 2*s*, and 2*p*σ Slater type orbitals of exponents 2.6875, 0.65, and 0.65 respectively. Lines 2 and 3 show the results of similar calculations in which DOA [Eq. (1)] was strictly applied. It can be seen that when the basis set consisted only of 1*s* and 2*s* orbitals (line 2) the results compare very favorably to the *ab initio* ones, but the inclusion of the virtual *p*σ orbital (line 3) very drastically perturbs the results.

It is therefore necessary to find a solution to the problem and, after considering various possibilities, we found and wish to suggest "spherical orbitals" (SO) to be used as a base in lieu of the Slater orbitals for the calculation of two center integrals. These can be pictorially illustrated as below (Fig. 1).

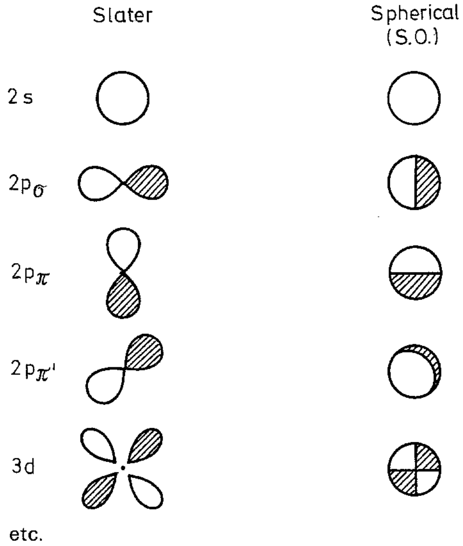

Fig. 1. Correspondence between Slater and spherical orbitals

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[1] The calculations were performed with the Alchemy program at the Centre de Calcul d'Orsay by Mrs. Lefebvre-Brion.

These SO's are essentially the normalized radial components of the Slater orbitals corrected to include the proper symmetry that would have been generated by the sign of the truncated angular component.

$$\text{i.e. } 2p_\sigma\,(\text{Slater}) = \sqrt{\frac{a^5}{\pi}}\, e^{-ar} r_a \cos\theta$$

$$2p_\sigma\,(\text{SO}) = \sqrt{\frac{a^5}{3\pi}}\, e^{-ar} r_a \left\{\frac{\cos\theta}{|\cos\theta|}\right\}.$$

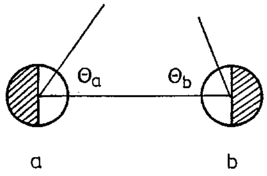
This ensures that after proper normalization, the orthogonality between the various SO's is maintained.

The normalized SO's necessary for the calculation of Resonance integrals then are:

$$\left.\begin{aligned} 0p\sigma &= \sqrt{\frac{a}{2\pi}}\, e^{-ar} r^{-1} \\ 1p\sigma &= \sqrt{\frac{a^3}{\pi}}\, e^{-ar} \\ 2p\sigma &= \sqrt{\frac{a^5}{2\pi}}\, e^{-ar} r \end{aligned}\right\} \frac{\cos\theta}{|\cos\theta|}\,.$$

Let us first recognize that, for the 2 center nuclear-attraction and Coulomb integrals, all the requirements made necessary by the use of DOA to maintain space invariance are automatically introduced. Indeed, the fact that all integrals involving a distribution of the u^2 kind such as in $[a|uu]$ are unaffected by the sign of u and therefore the condition represented by Eq. (5) is automatically fulfilled. Furthermore, since all the p functions of the base are orthogonal with each other, all integrals involving a distribution of the kind uv, which is set equal to $\frac{1}{2}S_{uv}[u^2+v^2]$, remain cancelled by the fact that $S_{uv}=0$. Before examining the implications of these "space invariant" orbitals on the overlap integrals, let us first establish a practical way of solving integrals involving SO's.

Due to the appearance of the module of the angular part in the denominator of their expression, we have not found a straightforward way of integrating those integrals involving two SO's on different centers. However, by changing the integration limits, solving by parts the radial component of the integral, and applying the proper sign to the resulting terms, it is possible to solve the problem. Let us consider the $[2p_{\sigma a}|2p_{\sigma b}]$ overlap integral:



we may decompose the integral in three parts, Fig. 2, that can be evaluated (integrated) independently (see appendix).

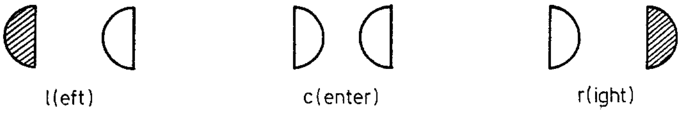


Fig. 2. Components in the $[2p_\sigma|2p_\sigma]$ overlap of SO's

so that the total overlap is equal to:

$$[2p_{\sigma a}|2p_{\sigma b}] = -l + c - r\,.$$

In a similar fashion, one may show, in general, that

$$\begin{aligned}
[np_{\sigma b}|n'p_{\sigma b}] &= -l + c - r\\
[ns_a|n'p_{\sigma b}] &= l + c - r\\
[np_{\sigma a}|n's_b] &= -l + c + r\\
[ns_a|n'p_{\pi b}] &= 0
\end{aligned}$$

and $[ns_a|n's_b] = [np_{\pi a}|n'p_{\pi b}] = l + c + r = [ns_a|n's_b]_{\mathrm{Slater}}$ where n and n' are the principal quantum numbers of the various orbitals. As a result, not only are the overlaps, but also the resonance and kinetic integrals (both functions of overlap) affected by this introduction of "angular invariant orbitals". In the appendix, we give the detailed mathematics that is necessary for the evaluation of the integrals. Preliminary molecular calculations, based on spherical orbitals, have been considered and it was found that the DOA approximation based on overlaps obtained from Spherical Orbitals restores a reasonable estimate of the molecular properties of Li_2. This is seen by comparing the results of line 4 of Table 1 obtained with SO's to those of the previous lines. It is seen that the use of spherical orbitals allowed the population of the p orbital to be considerably reduced, and that the total energy comes now much closer to that of the *ab initio* calculations of line 1. The p orbitals are apparently still slightly overpopulated due to some other implications[2] of DOA but the remaining problem is certainly of lesser importance.

Finally, it should be pointed out that the set of spherical orbitals is not suitable for use in *ab initio* techniques because, due to the absence of a node in the plane of asymmetry, the kinetic energy associated with a spherical p orbital is infinite.

Their main use should thus be restricted to semi-empirical methods in which the kinetic integrals are not explicitely defined such as in the CNDO, INDO and MINDO methods [6]. In these cases, overlaps calculated from spherical orbitals are consistent with the NDO approximation and may provide a more appropriate framework for the estimation of the two center integrals by DOA. This might help define methods that are more appropriate to obtain good estimates of distance dependence between atoms and help arrange in the right order the various molecular orbitals with respect to the type of bond involved in the specific MO's.

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[2] This is probably due to the neglect of the $\langle ns^a 2p_\sigma^a|Z_b\rangle$ integrals.

Appendix

In prolate spheroidal coordinates, defined by

$$\lambda=\frac{r_a+r_b}{R} \quad \mu=\frac{r_a-r_b}{R} \quad \cos\theta_a=\frac{1+\lambda\mu}{\lambda+\mu} \quad \cos\theta_b=\frac{1-\lambda\mu}{\lambda-\mu}$$

where the integration limits for μ are normally $(d\mu)_{-1}^{+1}$, they become (see Fig. 2)

$$\text{for } l \quad (d\mu)_{-1}^{-1/\lambda} \quad \begin{pmatrix}\text{such that } \cos\theta_a \leqq 0\\ \cos\theta_b \geqq 0\end{pmatrix},$$

$$\text{for } c \quad (d\mu)_{-1/\lambda}^{1/\lambda} \quad \begin{pmatrix}\text{such that } \cos\theta_a \geqq 0\\ \cos\theta_b \geqq 0\end{pmatrix},$$

$$\text{for } r \quad (d\mu)_{1/\lambda}^{1} \quad \begin{pmatrix}\text{such that } \cos\theta_a \geqq 0\\ \cos\theta_b \leqq 0\end{pmatrix}.$$

The general form of the integrals to be solved is then:

$$S^x(n_a, n_b, p, t)=N \int_1^\infty d\lambda \int_{x_0}^{x_1} (\lambda+\mu)^{n_a-1}(\lambda-\mu)^{n_b-1}(\lambda^2-\mu^2)e^{-p(\lambda+\mu t)}d\mu$$

where S^x is the l, c, or r overlap component, $p=1/2(a+b)R$ and $t=\frac{a-b}{a+b}$.

x_0, x_1, are the integration limits appropriate to the x component of the overlap. N includes the product of the normalisation constants $N_1 \cdot N_2$ and the other constants generated by the transformation in spheroidal coordinates.

These integrals have been found very difficult to solve analytically in view of the fact that upon integration over μ, a negative power of λ, (the next integration variable) appears in the exponential. In order to solve the problem we replaced $e^{-p\mu t}$ by its series development and thus obtained successive approximations. The results are fast converging since t is usually very small. The general expression for the resulting integral type

$$I_{\text{type}}(n, m)=\int_1^\infty \lambda^n e^{-p\lambda}d\lambda \sum_{l,c,r} \int_{x_0}^{x_1} \mu^m \sum_{i=1}^\infty \frac{(pt)^{i-1}}{(i-1)!}\mu^{i-1}d\mu \text{ is:}$$

for type 1, $[s|p\sigma]$ integrals:

$$I_1(n, m)=\sum_{i=1}^\infty \frac{[2J(n-m-i)-(1+(-1)^{m+i})J(n)]}{(m+i)} \cdot \frac{(pt)^{i-1}}{(i-1)!}$$

for type 2, $[p\sigma|s]$ integrals:

$$I_2(n, m)=\sum_{i=1}^\infty \frac{[-2(-1)^{m+i}J(n-m-i)+(1+(-1)^{m+i})J(n)]}{(m+i)} \cdot \frac{(pt)^{i-1}}{(i-1)!}$$

and for type 3, $[p\sigma|p\sigma]$ integrals:

$$I_3(n, m)=\sum_{i=1}^\infty \frac{[(1-(-1)^{m+i}) \cdot (2J(n-m-i)-J(n))]}{(m+i)} \cdot \frac{(pt)^{i-1}}{(i-1)!}$$

where

$$J(x)=\int_1^\infty \lambda^x e^{-p\lambda}d\lambda$$

$$=-\frac{(-p)^{-x-1}Ei(-p)}{(-x-1)!}+e^{-p}\sum_{k=0}^{k=-(x+2)} \frac{(-p)^k}{(-x-1)(-x-2)\ldots(-x-1-k)}$$

and $Ei(-p)=0.577215665+\sum_{k=1}^\infty \frac{(-p)^k}{kk!}+ln(p)$, (when $x<0$)

and $J(x)=\frac{x!e^{-p}}{p^{x+1}}\left[1+p+\frac{1}{2}p^2+\ldots\frac{1}{x!}p^x\right]$ (when $x \geqq 0$).

The various overlap integrals then become:

$$[0s|2p\sigma]=\tfrac{1}{4}\sqrt{\frac{ab^5}{6}}\cdot[I_1(2,0)-2I_1(1,1)+I_1(0,2)]$$

$$[1s|2p\sigma]=\tfrac{1}{8}\sqrt{\frac{a^3b^5}{3}}\cdot[I_1(3,0)-I_1(2,1)-I_1(1,2)+I_1(0,3)]$$

$$[1p\sigma|1s]=\tfrac{1}{4}\sqrt{a^3b^3}\cdot[I_2(2,0)-I_2(0,2)]$$

$$[1p\sigma|2s]=\tfrac{1}{8}\sqrt{\frac{a^3b^5}{3}}\cdot[I_2(3,0)-I_2(2,1)-I_2(1,2)+I_2(0,3)]$$

$$[1p\sigma|2p\sigma]=\tfrac{1}{8}\sqrt{\frac{a^3b^5}{3}}\cdot[I_3(3,0)-I_3(2,1)-I_3(1,2)+I_3(0,3)]$$

$$[2s|2p\sigma]=\tfrac{1}{48}\sqrt{a^5b^5}\cdot[I_1(4,0)-2I_1(2,2)+I_1(0,4)]$$

$$[2p\sigma|2p\sigma]=\tfrac{1}{48}\sqrt{a^5b^5}\cdot[I_3(4,0)-2I_3(2,2)+I_3(0,4)]$$

$$[0p\sigma|2p\sigma]=\tfrac{1}{4}\sqrt{\frac{ab^5}{6}}\cdot[I_3(2,0)-2I_3(1,1)+I_3(0,2)]\,.$$

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Prof. Dr. G. Klopman
Chemistry Department
Case Western Reserve University
Cleveland, Ohio 44106
USA