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The "Invariance Principle" in Approximate Molecular Orbital Theories

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The widely used invariance "principle" of approximate MO theories is shown to be physically unreasonable and formally unnecessary. The use of ZDO-type schemes in an internally-defined orbital basis is proposed to replace this restrictive principle.

Key words: Differential overlap – Invariance principle – Hybrid atomic orbitals

The results of an LCAOMO calculation are invariant against a wide class of transformations among the AO basis – all those transformations maintaining normalisation and linear independence among the AO basis. In particular, if the basis functions are orthogonal and it is required to remain in an orthogonal basis then the LCAOMO wave function is invariant against *unitary* transformations among the AO basis. More realistically, since it is rare to have infinite rotation axes in molecules and therefore real AOs are used, the calculation is invariant against *orthogonal* transformations among the basis functions. That is, if

$$\int dV\, \boldsymbol{\phi}^{+}\boldsymbol{\phi} = \mathbf{S} = \mathbf{1} \tag{1}$$

and

$$\overline{\boldsymbol{\phi}} = \boldsymbol{\phi}\mathbf{U} \tag{2}$$

such that

$$\int dV\, \overline{\boldsymbol{\phi}}^{+}\, \overline{\boldsymbol{\phi}} = \overline{\mathbf{S}} = \mathbf{1} \tag{3}$$

then

$$\mathbf{U}\mathbf{U}^{+} = \mathbf{U}^{+}\mathbf{U} = \mathbf{1} \tag{4}$$

and, if the elements of **U** are real,

$$\sum_{i} U_{ij}\, U_{ik} = \delta_{jk} \tag{5}$$

Transformation (2) induces a transformation among the energy integrals involved in a LCAOMO calculation

$$\begin{gathered} \overline{\mathbf{h}} = \mathbf{U}^{+}\mathbf{h}\mathbf{U} \\ \text{i.e. } \overline{h}_{ij} = \sum_{r,s} U_{ri}\, h_{rs}\, U_{sj} \end{gathered} \tag{6}$$

and

$$(\overline{ij}, \overline{kl}) = \sum_{r,s,t,u} U_{ri}\, U_{sj}\, U_{tk}\, U_{ul}\, (rs, tu) \tag{7}$$

where

$$h_{ij} = \int dV\, \phi_i\, h\, \phi_j$$

and

$$(ij, kl) = \int dV_1 \int dV_2\, \phi_i(1)\, \phi_j(1) \frac{1}{r_{12}} \phi_k(2)\, \phi(2)$$

and bars denote transformed quantities in an obvious way.

If we now make approximations of the formal Zero Differential Overlap (ZDO) type – that is, using only the scheme of neglecting electron repulsion integrals and making no assumptions about the computation of the remaining integrals – then the invariance of the LCAOMO calculation may well be lost. Certain classes of transformed basis function will be better adapted to the formal ZDO scheme than others: *for some bases, the orbital products*

$$\overline{\phi}_i\, \overline{\phi}_j$$

and the energy integrals involving these products in the integrand will be smaller than for other bases related by orthogonal transformation. The actual optimum type of basis for ZDO approximations is, of course, a matter for empirical investigation.

Pople [1], and many workers following his lead, has attempted to by-pass this problem by imposing an invariance condition on the molecular electron repulsion integrals – *forcing a particular ZDO formal scheme to work equally well* in all bases related by orthogonal transformations. Thus, in the electron repulsion integral case, retaining only integrals of form (ii, jj) in both original and transformed bases we must insist that

$$\delta_{ij}\, \delta_{kl}\, (\overline{ij}, \overline{kl}) = \sum_{r,t} U_{ri}\, U_{rj}\, U_{tk}\, U_{rl}\, (rr, tt) \tag{8}$$

independent of the values of the elements U_{ij} i.e. (8) is forced to be an *identity* for all orthogonal matrices $\mathbf{U}$. This condition can be easily satisfied formally by removing the repulsion integrals from the summation and noting that

$$\delta_{ij} = \sum_{r} U_{ri}\, U_{rj}$$

$$\delta_{kl} = \sum_{t} U_{tk}\, U_{tl}$$

so that (8) becomes

$$(\overline{ii}, \overline{kk}) = (rr, tt) \tag{9}$$

for all i, j, r, t.

That is, insisting on the invariance of the formal ZDO scheme in all bases related by orthogonal transformations leads to the physically absurd conclusion that all the molecular electronic repulsion integrals of the "ZDO type" are equal: all integrals

$$\int dV_1 \int dV_2\ \phi_i(1)\,\phi_i(1)\,\frac{1}{r_{12}}\,\phi_j(2)\,\phi_j(2)$$

have the same value. But we know that these integrals must behave asymptotically like $1/R_{AB}$ (R_{AB} is the distance between the nuclei on which ϕ_i and ϕ_j are centered). *Clearly there can be no principle of invariance of differential overlap schemes against orthogonal transformations.*

In practice the full "principle" of invariance is never used, invariance against restricted classes of orthogonal transformation is frequently enforced: transformations which "mix" basis functions on the same nucleus. It is easy to follow through the argument given above when the matrix **U** has "atomic block form" and the result is that all repulsion integrals of the form

$$(i^A i^A, j^B j^B)$$

are forced to be equal. Here i^A means an orbital ϕ_i centered on nucleus A etc. This result, although not so obviously in error as (10), is a very severe restriction on molecular calculations – the repulsion integrals between all orbitals on atom A and all orbitals on atom B are equal. It means, for example in CH_2O Fig. 1, the integral

$$(\sigma_c\sigma_c,\ \sigma_0\sigma_0)$$

is set equal to the integral $(h_1h_1,\ l_2l_2)$

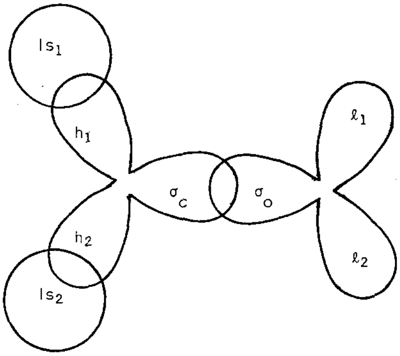

Fig. 1. The valence orbitals of CH_2O (schematic)

In fact, using a minimal STO basis of orthogonalised hybrid AOs the values are

$$(\sigma_c\sigma_c,\ \sigma_0\sigma_0) = 0.5894$$
$$(h_1h_1,\ l_2l_2) = 0.3239$$

a difference of about 50%! (the value used by the CNDO-type method is 0.4108 for both).

Another, equally powerful, objection to the use of an "invariance principle" for differential overlap schemes arises when (say) the ZDO approximation

$$(ij, kl) = \delta_{ij}\, \delta_{kl}\, (ii, kk)$$

is replaced by (say) the "Neglect of diatomic differential overlap" (NDDO) scheme:

$$(i^{A}j^{B}, k^{C}l^{D}) = \delta_{AB}\, \delta_{CD}\, (i^{A}j^{A}, k^{C}l^{C}) \qquad (10)$$

If (10) is inserted into both sides of (7) and the diagonal block form of **U** (which mixes orbitals on the same atom) is used, then the very restrictive Eq. (9) is not recovered. This means that, for a given molecule, the same molecular integral over the same AO basis has different values according to the number of integrals included in the calculation! Thus the two integrals quoted earlier in the context of Fig. 1 in the NDDO scheme would take different values and be computed separately. This "interference" between the number of integrals used in a calculation and their numerical values, while allowing each type of scheme to have its parameters optimised separately, does violence to the physical interpretation of the molecular wave function and the usual scientific method of investigating the effect of approximations one at a time. It is clearly not possible to retain a physically realistic interpretation of the electron repulsion integrals *and* even a restricted "invariance principle".

Since approximate molecular calculations are very widely performed involving the use of the restricted invariance principle and these calculations in general tend to reproduce the results of full calculations moderately well, the effects of the physically unrealistic invariance principle must be offset somewhere else in the approximation scheme. Since many of the energy integrals are parametrised by fitting to a standard set of results [2, 3], these errors must be compensated by the *numerical values* of the fitted parameters. This is an extremely undesirable situation from a methodological point of view: it breaks down the "hierarchy of approximations" whereby one makes a set of *model* approximations *within which* one makes *numerical* approximations. Another by-product of the invariance principle is that it and its parametrisation are derived entirely *within the single determinant scheme* presumably therefore precluding the use of the parametrisation in a many determinant approximation such as PCILO [4] which does not need to obey an "invariance principle".

Now it is entirely desirable that approximate molecular orbital calculations should be independent of the "global molecular co-ordinate system" which is, of course, arbitrary. We must therefore propose some physically and theoretically acceptable method of ensuring this elementary invariance which does not restrict the physical interpretation of the wave function. The use of ZDO approximations has some similarities to the use of approximate force fields in vibrational analysis calculations [5] and it is profitable to compare the two. The force field exerted on the nuclei of a molecule is invariant against orthogonal transformations of the co-ordinates of the nuclei in the same way as the full LCAOMO calculation is invariant against orbital transformations. If, however, an approximate force field is used in such calculations (say the Simple Valence Force Field, SVFF, using simple bond stretches etc.) then the calculation is only invariant against transformations of the nuclear co-ordinates if the SVFF is defined *in an internal system of reference* – not to an arbitrary laboratory – fixed "global" system: it makes sense to discuss a C–H stretching force constant but not a z-axis force constant (if the z axis is arbitrary). The analogy with ZDO approximations in the LCAOMO method is perfect: *the invariance problem only arises if one decides to work with a laboratory-fixed orbital basis not a molecule-fixed orbital basis.*

The definition of an internal set of AO functions is very easy for most molecules of conventional structure: the time-honoured hybrid AOs. For molecules of unconventional, delocalised or "strained" structure the choice of an optimum hybrid set is a well-defined problem on which research is well advanced [6]. The use of an internally-defined AO basis removes the invariance requirement in a mathematically obvious and physically transparent way and therefore enables the investigation of the neglect of small integrals in LCAOMO calculations to be made in a coherent manner. Integrals have the same values at all levels of approximation and these values have an obvious physical interpretation in terms (say) of the distance between centroids of electron distribution. Quite apart from these formal and methodological advantages of the use of an internally-defined AO basis, it has been shown elsewhere [7] that orthogonal hybrid orbitals do provide a very good basis for a numerical attack on approximate LCAOMO methods: many integrals neglected by (say) the NDDO scheme do have very small values in this basis.

The use of an internally defined set of AOs in approximation methods is implicit in the reports of many workers [7, 8] and the use of hybrid AOs within the CNDO scheme has been discussed by Jug [9] who has pointed out that the very restrictive use of a single one-centre repulsion integral is valid in a basis of equivalent hybrids. It has also become usual to (implicitly or explicitly) drop the invariance requirement when working with molecules containing heavy atoms[1] where the use of a single (ii, ii) when ϕ_i may be any one of nd, $(n+1)s$ or $(n+1)p$ is clearly numerically indefensible[2].

In work now in progress [10] we hope to present the results of approximate LCAOMO calculations (as well as more general types of valence calculation) using a set of internally defined hybrid AOs directly and so present a positive numerical defence of the theoretical position adopted in this note. Needless to say, we are well aware of the problems associated with the choice of an internal hybrid basis set in non-equilibrium configurations of molecules and, *a fortiori*, in inorganic and transition metal complexes and are actively pursuing this problem.

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[1] The small integrals which are not of the type (ii, jj) or (ij, ij) are often neglected: see, for example, Clack, D.W.: Mol. Phys. **27** 1513 (1974)

[2] For example, the (double-zeta) 5*d* and 6*s* orbitals of Osmium have radial maxima at 1.35 and 3.80 bohr respectively

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