match no. 11 pp. 69-73 1981

A NOTE ON HYBRIDIZATION

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(Received September 1980)

INTRODUCTION

Hybridization is understood mainly as a mathematical trick for describing localized atomic orbitals. The practical use of this notion is at a qualitative level. Through it one can explain various geometrical characteristics of the chemical bonds of the carbon atoms, for example. The well known hybridized orbitals are of so called equivalent type. We are interested in nonequivalent localized orbitals by simple reason: changing any hydrogen atom with arbitrary heteroatom evidently will disturbe the equivalence of hybridized orbitals.

An attempt to account this nonequivalence may be seen in β-variation technique. Have to be noted that the connection of the hybridization with the group theory is not yet exploited.

The aim of this letter is to discuss this connection and to stress on some examples for possible applications.

RESULTS:

For our purposes we shall consider $\phi = (s, p_x, p_y, p_z)$ as orthonormal bases in four dimensional euclidian space R^4. Going to other orthonormal bases ψ in R^4 is just what we call hybridization. The 4x4 matrix of the linear operator doing this will be noted L. That is :

$$\psi = L\phi \tag{1}$$

By our requirement we have :

$$I = \langle\psi|\psi\rangle = \langle L\phi|L\phi\rangle = \langle L^t L\phi|\phi\rangle = \langle\phi|\phi\rangle$$

from where follows :

$$L^t L = I \qquad \det L = \pm 1 \tag{2}$$

or in details :

$$L_{ki}L_{kj} = \delta_{ij} \qquad (i,j = 1,\dots,4) \tag{3}$$

We recognize the group O(4) in (2). So we have isomorphism between hybridization and O(4) group. The next question which arises is the number of independent parameters specifying the group element of O(4). There are four normalizing and six orthogonal conditions for sixteen entities of L, i.e. we can choose six of them arbitrary.

The last question is how to do this.

Fortunately O(4) group is locally isomorphic to the Lorentz group which is well studied. Their representations are not well suitable for analysis which we want to do. The most popular of them, for example SO(3)xSO(3) representation in four dimensions, must be replaced by SU(2)xSU(2) representation, that includes complex parameters.

Many years ago, Fedorov /1-3/ offered a remarkable vector parametrization of O(3), O(4) and the Lorentz groups. We shall shortly present some of his results.

The main idea is to use a caconical way to juxtapose a skew-symmetrical 3x3 matrix to every vector in R^3, a well known fact from mechanics of solid body /4/.

$$a = (a_1,\ a_2,\ a_3) \Longleftrightarrow A = \begin{bmatrix} o & -a_3 & a_2 \\ a_3 & o & -a_1 \\ -a_2 & a_1 & o \end{bmatrix} \tag{4}$$

An analogical idea works in four dimensions. There are more possibilities (two) to juxtapose a skew-symmetrical 4x4 matrix to every vector $a \varepsilon R^3$, namely :

$$a \longmapsto a_\pm = \begin{bmatrix} A & \pm a^t \\ \mp a & o \end{bmatrix} \tag{5}$$

Now we are ready to write down the representation of O(4) group as :

$$O(a,c) = \frac{(I+a_+)\ (I+c_-)}{\sqrt{(1+a^2)\ (1+c^2)}} \tag{6}$$

The six parameter dependence is obvious and what is more important they do not obey to any limitations. So we have a mapping $R^3 x R^3 = R^6 \rightarrow O(4)$.

If we are interested in inverse mapping it is easy to see that :

$$\begin{bmatrix} A + C & (a - c)^t \\ -(a - c) & o \end{bmatrix} = 2\frac{O - O^t}{trO} \tag{7}$$

The last equations determine the vector parameters a and c uniquely. It is interesting to find out the values of parameters for :

tetragonal hybridization

$$\begin{aligned} te_1 &= \tfrac{1}{2}(s - p_x - p_y + p_z) \ ; \\ te_2 &= \tfrac{1}{2}(s + p_x - p_y - p_z) \ ; \\ te_3 &= \tfrac{1}{2}(s - p_x + p_y - p_z) \ ; \\ te_4 &= \tfrac{1}{2}(s + p_x + p_y + p_z) \ , \end{aligned} \tag{8}$$

trigonal hybridization

$$\begin{aligned} tr_1 &= \frac{1}{\sqrt{3}} \ (s + \sqrt{2}p_x) \ ; \\ tr_2 &= \frac{1}{\sqrt{3}} \ (s - \frac{\sqrt{2}}{2}p_x + \frac{\sqrt{6}}{2}p_y) \ ; \\ tr_3 &= \frac{1}{\sqrt{3}} \ (s - \frac{\sqrt{2}}{2}p_y - \frac{\sqrt{6}}{2}p_y) \ ; \\ tr_4 &= p_z, \end{aligned} \tag{9}$$

and

diagonal hybridization

$$\begin{aligned} di &= \frac{1}{\sqrt{2}} s - \frac{1}{\sqrt{2}} p_x \; ; \\ di_2 &= \frac{1}{\sqrt{2}} s + \frac{1}{\sqrt{2}} p_x \; ; \\ di_3 &= p_y \; ; \\ di_4 &= p_z \; . \end{aligned} \tag{10}$$

By (7) we find that these hybridizations realize the following cases :

$$\begin{aligned} a(te) &= (0,-1,0) \qquad c(te) = (0,0,1) \\ a(tr) &= -(\sqrt{2}+1,\ \frac{\sqrt{2}+1}{\sqrt{3}+1}\sqrt{2},\ \frac{\sqrt{2}}{\sqrt{3}+1}) = c(tr) \\ a(di) &= (0,\ 0,\ \sqrt{2}-1) = c(di) \end{aligned} \tag{11}$$

REMARKS:

Here we shall point out two possibilities:

First: Continously parametrizied hybrid orbitals may be used in the variational formalism. This should be explored in two directions - by the simple Ritz variational principle or by the principle of the minimal interaction.

Second: Allowing time dependence of the vector parameters we may consider dynamical problems. For instance - it is not so hard to find a smooth curve even a line (there are no topological obstructions) $a_t = a(di)(1-t) + a(tr)t$ for $0 \leq t \leq 1$ in R^3 joining the diagonal and the trigonal hybridization. Under appropriate conditions this will describe the hydrogenation of acetylene to ethylene.

As a conclusion we may say that for the purposes of the theory of the localized orbitals the using of the standard hybridizations is not enough.

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