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Hybridization in Planar XY_4 Molecules

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Maximum overlap hybrid orbitals for planar XY_4 molecules are described assuming various orbitals for ligand and central atoms. Distribution of s and d character in square $s^n p^2 d^{2-n}$ hybridization as a function of interatomic distances, and for different relative effective charges of bonded atoms is given. Maximum overlap hybrids, when compared with those based on Pauling's criterion of hybrid strength, show a generally smaller contribution of d_{z^2} orbital in the hybridization, especially evident for $\mu_{\text{ligand}} < \mu_{\text{metal}}$, when in some cases they reduce to simple dsp^2 hybrids. Calculations are based on tabulated overlap integrals data for Slater functions.

INTRODUCTION

Simple *s-p-d* hybrids introduced by Pauling, provide a qualitative description of directional properties of most molecules. However, as a result of high symmetry of atomic orbitals, several different hybrid orbitals are possible for many molecular geometries. Thus, for planar XY_4 molecules the hybridization at the central atoms is dsp^2 or d^2p^2. More general orbitals are constructed by a superposition of all atomic orbitals from the set *s,p* and *d* of appropriate symmetry. These more general hybrids are of the form $s^n p^2 d^{2-n}$ in the above case, where n may take any value between 0 and 1. In the first part of this work[1] we have discussed hybridization applying the principle of maximum overlap. The discussion was restricted to cases with equal charge of bonded atoms ($\mu_a = \mu_b$), and the orbitals used were belonging to the third shell. To obtain a more complete picture of hybridization in planar XY_4 structures the discussion is extended in this paper to cases with charge asymmetry ($\mu_a \neq \mu_b$), and in addition we wish to investigate bonding when different, not only $n=3$, orbitals are used.

MAXIMUM OVERLAP ORBITALS

The equivalency of s and d_{z^2} orbitals in molecules of tetragonal symmetries leads to more general orbitals

$$\psi = c_1 (dsp^2) + c_2 (d^2p^2)$$

for description of planar XY_4 bonds. Explicitly

$$\psi_x = \frac{1}{2} \cos\alpha\,(s) + \frac{1}{\sqrt{2}}\, p_x + \frac{1}{2}\, d_{x^2-y^2} + \frac{1}{2} \sin\alpha\,(d_{z^2})$$

ψ_x being a hybrid orbital directed along the x axis. The remaining orbitals are obtained by symmetry considerations. The parametar α measures a relative s-d content of hybrids and may vary from 0 and $\pi/2$. Thus, a family of orbitals is available, individual hybrids differing slightly in the shape only, being more or less concentrated along the bond axes. In order to fix the value of the parameter α we will apply the principle of maximum overlap, which requires orbitals with the largest overlapping. This principle has long been advocated as a good criterion for discussing bonding in different molecules*, but has only recently been applied. The delay was caused by nonavailability of several required overlap integrals, some of which were only recently tabulated[2].

General procedure for construction of maximum overlap hybrids was developed by Murrell[3]. The application is considerably simplified for systems with several equivalent bonds when the procedure is reduced to finding a total s-p-d content of hybrids only. The individual orbitals are obtained by an equal distribution of this content. To obtain contributions of s,p,d orbitals we have to know overlap matrix elements R_{ij} between the ligand orbital Φ_i and central orbital χ_i. Thus, the coefficients of s and d orbitals in hybrids of planar XY_4 molecules are

$$\frac{R_s}{2\,(R_s^2 + R_d^2)^{1/2}} \quad \text{and} \quad \frac{R_d}{2\,(R_s^2 + R_d^2)^{1/2}}$$

Where R_s and R_d are overlap integrals between an unspecified ligand orbital Φ and central atom s and d orbital respectively. (Denominator is due to the normalization).

The main result of an application of the principle of maximum overlap in constructing hybrid orbitals (as compared with the approximation of maximum orbital amplitude) is a variation of the hybrid composition depending on the nature of the ligand orbital. In this discussion we will assume atomic orbitals represented by Slater functions, for which tables of overlap integrals are available. No application to a special case is considered, and the aim of this investigation is rather to observe general trends in planar XY_4 hydridization. For that purpose the choice of the assumed ligand and central atom orbitals is not essential. Tables of overlap integrals of Leifer, Cotton and Leto[4] cover a fair range of parameters sufficient for present investigation.

RESULTS AND DISCUSSION

To estimate the effect of the presence of various effective nuclear charges we assume central atom orbitals for n=4, the variable part of which is of the form

$$\chi' = \frac{1}{2}\,[\cos\alpha\,(4s) + \sin\alpha\,(4d_{z^2})]$$

Ligand orbitals are assumed to be $\Phi = 2s$ and $\Phi = 3s$. Figures 1. and 2. illustrate the dependance of the s *content* (measured by $n = \cos^2\alpha$ *in* $s^n p^2 d^{2-n}$) against the scale parameter $\mu\varrho$ (μ is the effective atomic charge given by Slater rules,

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* For references see part I.

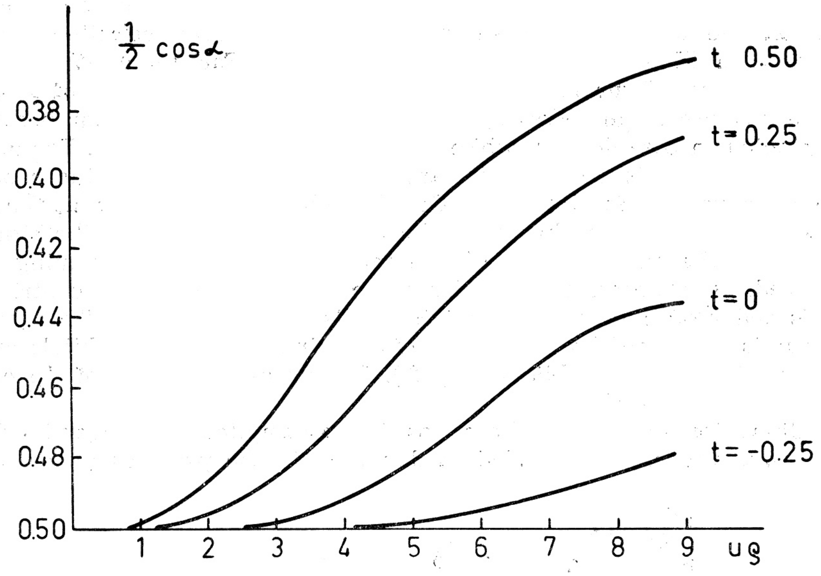

Fig. 1. *s* character of the maximum overlap orbitals for assumed ligand orbitals $\Phi = 2s$, while central atom orbitals belong to the shell $n = 4$. Various curves present cases of different atomic charges of bonded atoms, $t = (\mu_y - \mu_x) / (\mu_y + \mu_x)$.

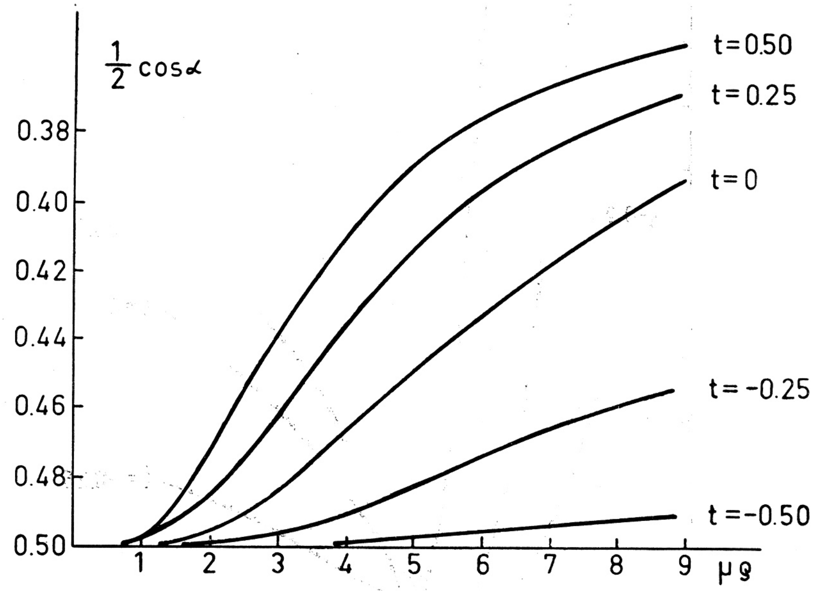

Fig. 2. *s* character of the maximum overlap orbitals for assumed ligand orbitals $\Phi = 3s$ and central orbitals of the shell $n = 4$.

ϱ is the interatomic distance measured in atomic units $\varrho = r/a_H$, a_H is Bohr's radius of H-atom). Various curves represent the variation of the role of *s* orbital on the assumed relative difference in nuclear effective charges between atom X and Y, $t = (\mu_y - \mu_x) / (\mu_y + \mu_x)$. For $t = 0$, (the case of charge symmetry of the bond), a significant decrease of the role of *s* orbital with the increase of $\mu\varrho$ follows. This is in agreement with similar behaviour already noted in case $\Phi = 3s$, while χ belongs to the third shell[1]. For $\mu_y > \mu_x$ the amplitude of this variation is larger, *i.e.* the influence of the *s* orbital in the hybridization is decreased. On the other side in cases $\mu_y < \mu_x$, *i.e.* cases when the effective charge on the central atom is larger, the situation is reversed. The participation of the metal *s* orbital is becoming more pronounced, as demonstrated *e.g.* by curve $t = -0.50$ when the contribution of d_{z^2} is reduced to much bellow 1% for its optimum region. This general behaviour is confirmed by similar results obtained for ligand orbitals $\Phi = 3s$ and same central atom orbitals (Fig. 2.). In this case the role of d_{z^2} orbital is even more depressed.

A discussion of bonding based on the assumption that ligand orbitals are *s* orbitals is easily extended as discussed in the previous paper. Fig. 3

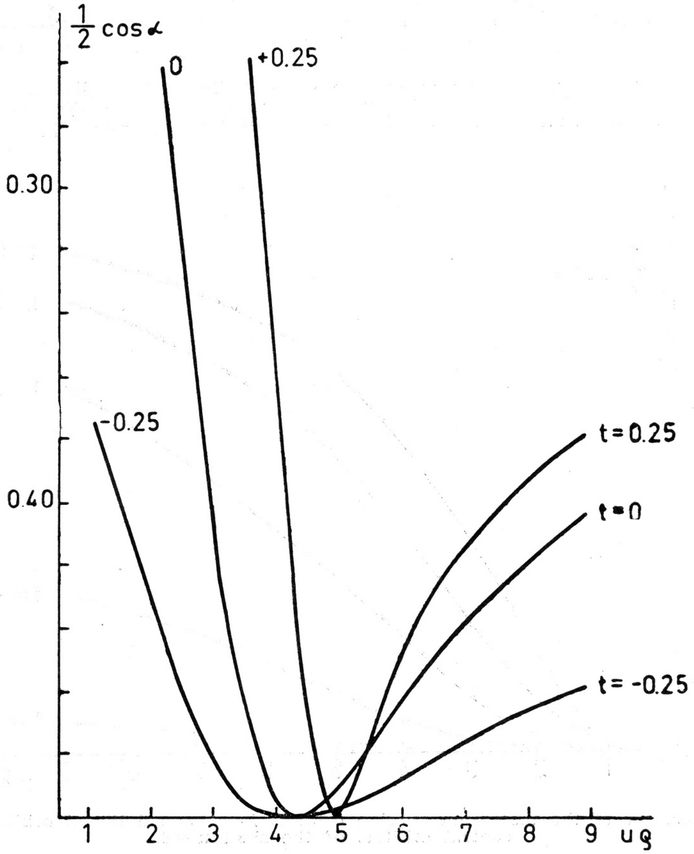

Fig. 3. *s* character of the maximum overlap orbitals for assumed ligand orbital $\Phi = 2p$ and central atom orbitals of the shell $n = 4$.

illustrates the variation of *s* content against the scale factor $\mu\varrho$ for different relative charge asymmetry t when ligand orbitals are $2p$, and the central atom belongs again to $n = 4$. The curves are of a typical form (resembling Morse curves) and are shifted to the right for $t > 0$, while for $t < 0$ they become shallow and move slightly to the left. This behaviour can again be summarized by a general rule that the contribution of the central atom *s* orbital is more dominant as $t < 0$ (for larger values of $\mu\varrho$). From the data when ligands are assumed to be $2s$ and $2p$ one can construct the corresponding curves for any linear combination of the above orbitals. The behaviour of the curves at Fig. 3. for smaller $\mu\varrho$ values results from decrease in the overlap due to contributions of negative sign when atoms are too close.

So far valence shell $n = 4$ of the central atom has been assumed. The general results hold if $n = 3$ and the ligand orbitals are $2s$ and $3s$. There are no new elements to spoil the distribution of *s*—*d* content which reflects the regularities in magnitudes of the corresponding elements R_{ij} of the overlap matrix. This holds even when the central atom is described by orbitals belonging to different shells, *e.g.* mixing of $3d$ and $4s$ orbitals. In this case we note an even smaller importace of the orbital d_{z^2} in hybridization as compared with cases presented in Fig. 1. and 2.

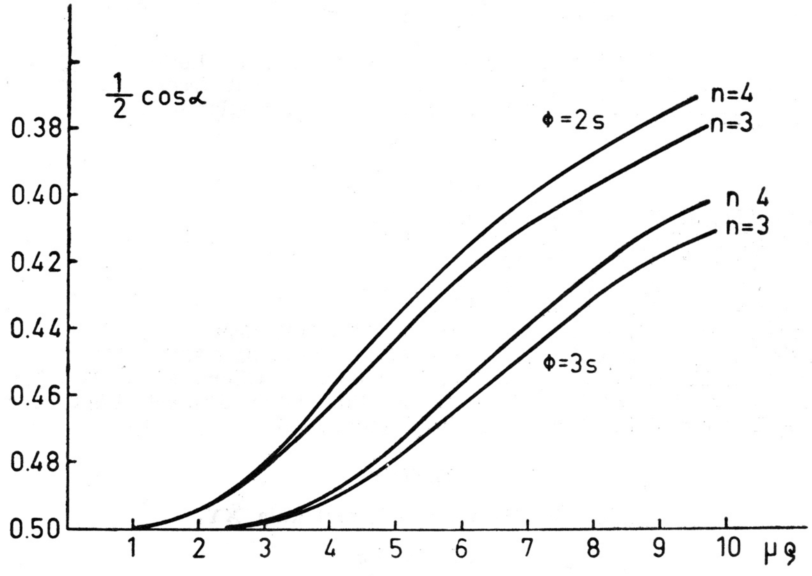

Fig. 4. Relative variation of *s*-content in the hybridization for various ligand and central atom orbitals.

These results are obtained using Slater orbitals, which are not an orthogonal set of functions. This may sometimes bring serious difficulties and in order to estimate the effect of orthogonalization, at least in some cases, Fig. 4. illustrates a relative change in the hybridization content resulting after a change of ligand or central atom orbitals. First, we note that (in case $t = 0$) the variation of *s* content is almost independent of the choice of the central atom valence shell. On the other side a variation of the ligand orbitals ($\Phi = 2s$, $3s$) has a somewhat larger effect on the value of s content. Similarity of the curves for assumed $\Phi = 2s$ and $\Phi = 3s$ indicate that an introduction of orthogonal Slater orbitals at ligands will not affect the results qualitatively. This is even more true for orthogonalization of central atom orbitals, as the corresponding curves (for $n = 3$ and $n = 4$; $\Phi = 2s$ or $3s$) hardly differ at all.

CONCLUSIONS

1. Application of Maximum Ovcerlap Principle in construction of more general hybrid orbitals leads to results which depend on the choice of ligand orbitals.

2. s-content in planar $s^n p^2 d^{n-2}$ hybrids varies with the scale parameter $\mu\rho$ so that for larger values of this factor the contribution of s orbital decreases, while d_{z^2} becomes more important.

3. The s-content of hybrids is sensitive on the difference of the effective (Slater) charges of bonded atoms. Cases $t > 0$ favour a contribution from d_{z^2} in bonding, while cases $t < 0$ indicate predominant s contribution.

4. This general behaviour is neither essentially dependent on the assumption about ligand orbitals, nor is considerably influenced by variation of central atom orbitals, and, therefore, will not change significantly when orthogonal orbitals are introduced.

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IZVOD

Hibridizacija planarnih molekula XY_4

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Primjenjen je princip maksimalnog prekrivanja da se nađe udio s i d orbitala u hibridizaciji $s^n p^2 d^{2-n}$. Rezultati prikazani u slikama 1—4 dobiveni su korišćenjem tabelarnih vrijednosti integrala prekrivanja za Slaterove funkcije. Pretpostavljamo da elektroni centralnog atoma pripadaju ljuski $n = 4$, dok su ligandi opisani orbitalama $2s$, $2p$ i $3s$. Promatrani su slučajevi različite asimetrije naboja atoma koji formiraju vezu. Općenito za $(\mu_Y - \mu_X) / (\mu_Y + \mu_X) < 0$ (gdje je μ efektivni naboj atoma) je uloga d_{z^2} orbitale znatno smanjena.

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