

## Pauling's Pair-Defect-Sum Approximation and the Maximum Overlap Method

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A demonstration of Pauling's pair-defect-sum approximation from the maximum overlap method is presented. It is based on the generalized formula of the bond strength that we obtained for the hybridization of atomic orbitals for systems containing more than 2 ligands. This work indicates that the pair-defect-sum approximation is a reasonable result of the generalized formula, but the expansion terms with its higher power are omitted.

### 1. INTRODUCTION

During the last decade, Pauling and his associates published a series of works on the compounds of the transition metals. In their studies the hybrid orbital theory was employed and many empirical formulas were used. One of the fundamental concepts in their treatment is bond strength. According to Pauling<sup>1</sup>, the bond strength  $F$  of an orbital is defined as a value in the bond direction of the angular part of the wave function, normalized to  $4\pi$ . The bond strength is a measure of the energy gained through bond formation. The greater the value of  $F$ , the more energetically favourable is the bond and the directions with maximum bond strengths are favoured by atoms of the ligands. The bond strength of the  $j$ -th bond in our idea is the overlap integral between the orbital of the ligand and the best hybrid atomic orbital (HAO) of the central atom<sup>10</sup>. Many applications of overlap integrals for discussing bonding have been presented by Maksić et al.<sup>2,3</sup>. Because of the difficulty in carrying out the calculations rigorously for a large set of orbitals, Pauling suggested an approximation, which he called the pair-defect-sum approximation to the bond strength<sup>4,5</sup>. This approximation has been subjected to an extensive test by comparing the value of the strength given by it with those given by the exact treatment<sup>6</sup>. These ideas have been applied to elucidate the structure of many compounds, especially of transition-metal compounds<sup>7-9</sup>.

This approximation is based on the equations giving the bond strength  $F_0$  of two equivalent hybrids that have the maximum strength in directions making angle  $\alpha$  with one another. For  $sp^3d^5$  hybrid orbitals, as an example, the value of  $F_0$  is a function of angle  $\alpha$  and is described by the following equation

$$F_0^{sp^3d^5}(\alpha) = (3 - 6x + 7.5x^2)^{1/2} + (1.5 + 6x - 7.5x^2)^{1/2} \quad (1)$$

with  $x = \cos^2(\alpha/2)$ , the maximum strength  $F_{\max}$  equals 3 and occurs at the characteristic angles  $\alpha = 73.15^\circ$  and  $\alpha = 133.62^\circ$ . The  $F_{\max}$  is equal to 2, 4, 5 or 6 for  $sp^3$ ,  $sp^3d^5f^7$ ,  $sp^3d^5f^7g^9$  or  $sp^3d^5f^7g^9h^{11}$  hybrids, respectively<sup>10</sup>. If the approximate bond strength of orbital  $i$  is to be calculated and is denoted by  $F_i$ , and the strengths of other orbitals  $j$  at angle  $\alpha_{ij}$  with orbital  $i$ , where  $j$  equals 1, 2, ...,  $k$  and  $j \neq i$ , the »defect« in the strength of orbital  $j$  is defined as the difference between the maximum value  $F_{\max}$  and the  $F_o(\alpha_{ij})$ , and then the approximate bond strength of orbital  $i$  is given by

$$F_i = F_{\max} - \sum_j [F_{\max} - F_o(\alpha_{ij})] \quad (2)$$

where the summation is over all the angles a reference orbital makes with all the other orbitals. Now we shall give a demonstration that the above equation can be derived from the maximum overlap method under the approximation of omitting higher terms in the expansion of our generalized formula of bond strength<sup>11</sup>. All notation used here is the same as in the preceding papers<sup>11-12</sup>.

## 2. DEMONSTRATION

It should be noted that Eq. (1) and (2), derived originally by Pauling, were based on the equations of two equivalent and orthonormal hybrids, but they may be useful to estimate the bond strength of an orbital in a multiple-bond molecule.

In fact, Pauling and his associates derived the exact bond strength for 7 systems with 3—8 ligands and the corresponding bond angles equivalent by geometrical symmetry operations and with only one independent bond angle, and these exact bond strengths were compared with the corresponding bond strengths found from the pair-defect-sum approximation. The resulting values were found to be in excellent agreement.

It is easily seen that if there are two ligands surrounding the central atom  $M$  and forming a molecule  $ML_k$  with  $k = 2$ , then the approximate bond strength, from Eq. (2), of any hybrid  $i$  is equal to the value calculated from Eq. (1). The problem is to estimate  $F_i$  of hybrid  $i$  in molecule  $ML_k$  with  $k > 2$ .

We have derived a general formula of bond strength for molecule  $ML_k$  with  $k > 2$  under the approximations that the projection method is utilized and that the angle between any two bonds  $M-L_i$  and  $M-L_j$  should be identical:

$$F = \frac{1}{k} [\sqrt{a + (k-1)c} + (k-1)\sqrt{a-c}] \quad (3)$$

where constant  $a$  is the total number of atomic orbitals which take part in forming the hybrid orbitals, and  $c$  is a function of bond angle  $\alpha$ <sup>11</sup>.

From the expansion formula

$$(1+y)^{1/2} = 1 + \frac{1}{2}y - \frac{1}{8}y^2 + \frac{1}{16}y^3 - \frac{5}{128}y^4 + \dots, \quad (|y| \leq 1) \quad (4)$$

and parameters  $a$  and  $c$  have been found in the preceding paper as

$$\begin{cases} a = \sum_l (2l+1) \\ c = \sum_l (2l+1) P_l(\cos \alpha) \end{cases} \quad (5)$$

where  $l$  is the angular momentum quantum number of a set of atomic orbitals, and  $P_l(\cos \alpha)$  is the Legendre polynomial, the absolute value of which in the range  $[0, \pi]$  is less than or equal to one. Thus, we have

$$\left| \frac{c}{a} \right| \leq 1 \quad \text{and} \quad \left| \frac{(k-1)c}{a} \right| \leq 1$$

Therefore we can expand Eq. (3) as follows:

$$F = \frac{\sqrt{a}}{k} \left[ \sqrt{1 + \frac{(k-1)c}{a}} + (k-1) \sqrt{1 - \frac{c}{a}} \right] \\ = \sqrt{a} \left[ 1 - \frac{(k-1)}{8} \left( \frac{c}{a} \right)^2 + \frac{(k-1)(k-2)}{16} \left( \frac{c}{a} \right)^3 - \frac{5(k-1)(k^2-3k+3)}{128} \left( \frac{c}{a} \right)^4 + \dots \right]$$

This equation may be rewritten as the following form:

$$F = \sqrt{a} \left[ 1 - \frac{(k-1)}{8} \left( \frac{c}{a} \right)^2 - \frac{5(k-1)}{128} \left( \frac{c}{a} \right)^4 - \dots \right] \\ + \frac{(k-1)(k-2)}{16} \left( \frac{c}{a} \right)^3 - \frac{5(k-1)(k^2-3k+2)}{128} \left( \frac{c}{a} \right)^4 + \dots$$

$$= \sqrt{a} \left\{ 1 - (k-1) + (k-1) \left[ 1 - \frac{1}{8} \left( \frac{c}{a} \right)^2 - \frac{5}{128} \left( \frac{c}{a} \right)^4 - \dots \right] \right\} + g \sqrt{a}$$

where

$$g = (k-1) \left[ \frac{(k-2)}{16} \left( \frac{c}{a} \right)^3 - \frac{5(k-1)(k-2)}{128} \left( \frac{c}{a} \right)^4 + \frac{7(k-2)(k^2-2k+2)}{256} \left( \frac{c}{a} \right)^5 \right. \\ \left. - \frac{21(k-1)(k-2)(k^2-2k+2)}{1024} \left( \frac{c}{a} \right)^6 + \dots \right] \tag{6}$$

and then

$$F = \sqrt{a} \left\{ 1 - (k-1) + \frac{(k-1)}{2} \left[ 1 + \frac{1}{2} \left( \frac{c}{a} \right) - \frac{1}{8} \left( \frac{c}{a} \right)^2 + \frac{1}{16} \left( \frac{c}{a} \right)^3 - \frac{5}{128} \left( \frac{c}{a} \right)^4 + \dots \right. \right. \\ \left. \left. + 1 - \frac{1}{2} \left( \frac{c}{a} \right) - \frac{1}{8} \left( \frac{c}{a} \right)^2 - \frac{1}{16} \left( \frac{c}{a} \right)^3 - \frac{5}{128} \left( \frac{c}{a} \right)^4 - \dots \right] \right\} + g \sqrt{a}$$

and using Eq. (4) again, the above equation becomes

$$F = \sqrt{a} \left\{ 1 - (k-1) \left[ 1 - \frac{1}{2} \left( \sqrt{1 + \frac{c}{a}} + \sqrt{1 - \frac{c}{a}} \right) \right] \right\} + g \sqrt{a} \\ = \sqrt{a} - (k-1) \sqrt{a} - \frac{1}{2} (\sqrt{a+c} + \sqrt{a-c}) + g \sqrt{a} \tag{7}$$

Substituting the formula of  $F$ , from Eq. (3), for  $k = 2$  and the maximum bond strength  $F_{\max} = \sqrt{a}^{10-12}$  into Eq. (7), we obtain

$$F = F_{\max} - (k-1) [F_{\max} - F_{k=2}] + g \sqrt{a} \tag{8}$$

Because the bond angles are identical in this situation, it means that the hybridization is equivalent under the projection method, the term of  $(k-1)F_{k=2}$  in the above equation may be replaced by a summation of the bond strengths of  $(k-1)$  hybrid orbitals calculated from Eq. (3), which is equivalent to Pauling's formula  $F_o(\alpha)$  at  $k = 2$  and  $c = 0$ <sup>10</sup>. Therefore, we

finally obtain the same equation as that introduced by the pair-defect-sum approximation, after the last term of  $g \sqrt{a}$  in Eq. (8) is omitted:

$$F_i = F_{\max} - \sum_{j=1 (j \neq i)} [F_{\max} - F_o(a)] \quad (9)$$

The foregoing statement indicates that the pair-defect-sum approximation suggested by Pauling is an excellent one for the calculation of bond strength in accordance with the basic principle of the maximum overlap method. The deviation of the approximation may be evaluated by the term  $g \sqrt{a}$  of Eq. (6).

### 3. SOME RESULTS

Some calculated results are listed in the following table. Since it is required that bond angles be equal for the above treatment to hold, our calculations were carried out only for the trigonal pyramid ( $k = 3$ ) with equal angles  $\alpha$  and for the tetrahedron ( $k = 4$ ).

TABLE I  
Exact and approximate values of bond strength and the calculated error comparison

System	Basis	Bond angle	$F_{\text{exact}}$	$F_{\text{approx.}}$	$\Delta F$	$g \sqrt{a}$	
Trigonal pyramid ( $k = 3$ )	sp <sup>3</sup> ( $a = 4$ )	90°	1.97120	1.96812	0.00308	0.00302	
		95°	1.98407	1.98277	0.00130	0.00130	
		100°	1.99317	1.99280	0.00038	0.00038	
		105°	1.99848	1.99844	0.00004	0.00004	
		*109.47°	2.00000	2.00000	0.00000	0.00000	
		115°	1.99767	1.99776	-0.00008	-0.00008	
	120°	1.99156	1.99215	-0.00059	-0.00058		
	sp <sup>3</sup> d <sup>5</sup> ( $a = 9$ )	50°	2.89520	2.87878	0.01642	0.01464	
		60°	2.96975	2.96700	0.00276	0.00273	
		70°	2.99852	2.99849	0.00003	0.00002	
		*73.15°	3.00000	3.00000	0.00000	0.00000	
		75°	2.99954	2.99955	-0.00001	-0.00001	
		80°	2.99449	2.99474	-0.00025	-0.00025	
		90°	2.97674	2.97898	-0.00224	-0.00223	
		100°	2.96571	2.96980	-0.00409	-0.00405	
		110°	2.97149	2.97456	-0.00307	-0.00305	
		120°	2.98735	2.98822	-0.00088	-0.00088	
		sp <sup>3</sup> d <sup>5</sup> f <sup>7</sup> ( $a = 16$ )	40°	3.90996	3.89825	0.01170	0.01116
			53°	3.99897	3.99896	0.00001	0.00001
	*54.88°		4.00000	4.00000	0.00000	0.00000	
	57°		3.99887	3.99889	-0.00002	-0.00002	
	65°		3.98297	3.98415	-0.00119	-0.00119	
	80°		3.97334	3.97570	-0.00237	-0.00236	
	95°		3.99742	3.99749	-0.00007	-0.00007	
*100.43°	4.00000		4.00000	0.00000	0.00000		
105°	3.99843		3.99840	0.00003	0.00003		
110°	3.99417		3.99396	0.00021	0.00021		
120°	3.98605		3.98527	0.00078	0.00078		
Tetrahedron ( $k = 4$ )	sp <sup>3</sup>		*109.47°	2.00000	2.00000	0.00000	0.00000
	sd <sup>5</sup>	109.47°	2.43649	2.43810	-0.00161	-0.00161	
	sp <sup>3</sup> d <sup>5</sup>	109.47°	2.94949	2.96100	-0.01151	-0.01114	
	sp <sup>3</sup> d <sup>5</sup> f <sup>7</sup>	*109.47°	3.99229	3.99176	0.00054	0.00054	

The exact values of the bond strength ( $F_{\text{exact}}$ ) are calculated from Eq. (3) and the approximate ones ( $F_{\text{appro}}$ ) from Eq. (7) without  $g \sqrt{a}$ ,  $\Delta F = F_{\text{exact}} - F_{\text{appro}}$ , and the estimated error  $g \sqrt{a}$  is calculated from Eq. (6) retaining only the first four terms. The exact values of some systems presented in reference 6 are marked an asterisk (\*). There are characteristic angles observed in particular systems. Generally, the closer  $\alpha$  comes to the characteristic angle, the smaller the error of  $F$ , though this is not an absolute rule as shown in Figures 1—7 in reference 6. It should be noted that there are seven sets of bonding situations with only one independent bond angle, which have been considered in reference 6. We shall present a more complete discussion in a subsequent paper.

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## SAŽETAK

**Paulingovo približenje zbroja defekata parova i metoda maksimalnog prekrivanja**

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Pokazano je da se Paulingovo približenje zbroja defekata parova može dobiti iz metode maksimalnog prekrivanja ako se zanemare neki manji članovi.