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## The Principle of Maximum Overlap

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**Abstract:** It is shown that the principle of maximum overlap can be extended to include the effects of overlap phase patterns as well as magnitudes. For the highest orbitals of a system, this extension takes the form of a "principle of most negative overlap", which is able to provide a simple explanation of the enhanced interactions of orbitals when oriented in a mutually trans relationship.

### I. Introduction

It is a principle familiar to every student of valence theory that the *overlap* of orbitals gives a useful measure of the strength of their interactions. Pauling<sup>2</sup> originally introduced a "principle of maximum overlap" in constructing directed hybrid orbitals, and the notion that "better" overlap implies stronger orbital interactions and tighter chemical bonding has subsequently come to be appreciated as one of the most useful conceptual devices for analyzing the electronic structure of complex molecules in terms of their nuclear geometry.<sup>3</sup>

Implicit in more refined applications of the maximum-overlap concept is the observation that the Hamiltonian matrix element between orbitals  $\varphi_i$  and  $\varphi_j$ ,

$$h_{ij} = \langle \varphi_i | \mathcal{H} | \varphi_j \rangle \quad (1)$$

is in some measure proportional to (the negative of) their overlap integral  $s_{ij} = \langle \varphi_i | \varphi_j \rangle$ ,

$$h_{ij} \propto -s_{ij} \quad (2a)$$

Such an assumption implicitly or explicitly underlies elementary Hückel theory and other approximate molecular orbital methods in forms such as

$$h_{ij} = -\text{constant} \cdot \left| \frac{h_{ii} + h_{jj}}{2} \right| \cdot s_{ij} \quad (2b)$$

$$h_{ij} = -\text{constant} \cdot (h_{ii}h_{jj})^{1/2} \cdot s_{ij} \quad (2c)$$

whose basis has been extensively discussed.<sup>4</sup> For the present purpose we shall regard (2a) as a bridge between full quantum-chemical calculations (as expressed in terms of  $h_{ij}$ 's) and a convenient set of concepts (based on overlaps  $s_{ij}$ ). We shall show that a more detailed consideration of the quantum-mechanical equations permits one to recognize a more refined form of the principle of maximum overlap than is commonly employed.

The objective is to analyze the interactions of a set of  $N$  orbitals  $\varphi_1, \varphi_2, \dots, \varphi_N$  in a system with an effective one-electron operator  $\mathcal{H}$  and (real) matrix elements  $h_{ij} =$

$\langle \varphi_i | \mathcal{H} | \varphi_j \rangle$ ,  $\epsilon_i = h_{ii} = \langle \varphi_i | \mathcal{H} | \varphi_i \rangle$ . The true eigenorbitals  $\psi_i$  of the system are certain linear combinations of the  $\varphi_j$ 's,

$$\psi_i = \sum_{j=1}^N c_j^{(i)} \varphi_j \quad (3)$$

corresponding to eigenvalues  $\lambda_i = \langle \psi_i | \mathcal{H} | \psi_i \rangle$  which are the successive roots of the characteristic polynomial (secular determinant)  $P(\lambda) = 0$ ,<sup>5</sup>

$$P(\lambda) = \det | h_{ij} - \lambda \delta_{ij} |_{N \times N} = 0 \quad (4)$$

We may suppose that the off-diagonal elements  $h_{ij}$  are sufficiently small in comparison with the diagonal energy differences  $\epsilon_i - \epsilon_j$  that it is useful to regard  $\psi_i$  as a "perturbed" form of the original  $\varphi_i$ , but the analysis will proceed in terms of *exact* properties of the secular determinants (4) rather than by formal low-order perturbation theory.

We wish to consider a situation in which a particular orbital of interest, say  $\varphi_n$ , is well-separated from the remaining orbitals, and  $\psi_n$  is therefore approximated as a large contribution from  $\varphi_n$  plus smaller corrections from the remaining orbitals  $\varphi_i, \varphi_j, \varphi_k, \dots$ ,

$$\psi_n = c_n \varphi_n + \{c_i \varphi_i + c_j \varphi_j + c_k \varphi_k + \dots\} \quad (5a)$$

with

$$c_n^2 \gg c_i^2, c_j^2, c_k^2, \dots \quad (5b)$$

(Since the choice of  $\psi_n$  is implicitly understood, we have simplified the notation for the coefficients  $c_i^{(n)} = c_i$ .) These remaining orbitals are assumed to be of similar energies,

$$\epsilon_i \approx \epsilon_j \approx \epsilon_k \approx \dots \quad (6a)$$

and their interaction matrix elements with  $\varphi_n$  are of similar magnitudes,

$$|h_{ni}| \approx |h_{nj}| \approx |h_{nk}| \approx \dots \quad (6b)$$

Under these assumptions, elementary considerations give no (correct) clue as to the relative magnitudes of  $c_i^2, c_j^2, c_k^2, \dots$

in the expansion (5a); that is, while elementary considerations properly suggest (5b), they do not single out which, if any, of the remaining orbitals will interact *most* strongly with the "parent" orbital  $\varphi_n$  in the final eigenstate (5a).

While the interactions among orbitals can appear very complex, important simplifying features may often be recognized by considering only pairs, triples, or other small subsets of orbitals in interaction. The effects arising from such smaller subsets are then "added together" to gain a useful conceptual picture of the overall interactions, and this is the general approach which will be taken in this paper. The simplest such model would be that of *pairwise* additivity, whose utility has been particularly emphasized by Hoffmann.<sup>6</sup> However, the pair picture cannot serve in the present case to distinguish the relative strengths of the interactions of  $\varphi_i, \varphi_j, \varphi_k, \dots$  with  $\varphi_n$ . Rather, the first elements of a more refined picture can only emerge from a proper treatment of at least *four* orbitals interacting simultaneously, so that we shall presently turn to the case  $N = 4$  for a proper extension of the principle of maximum overlap.

We shall find that when  $\varphi_n$  lies *below* the manifold  $\varphi_i, \varphi_j, \varphi_k, \dots$  (as ordered by the corresponding orbital energies), it interacts preferentially with those orbitals which can be simultaneously *in-phase* both with  $\varphi_n$  and other orbitals in the manifold which themselves have positive overlap with  $\varphi_n$ ; in other words,  $\varphi_i$  will be favored to interact with  $\varphi_n$  if many of the triples ( $\varphi_n, \varphi_i, \varphi_\alpha$ ) are entirely in-phase with one another, but will be suppressed if such triples tend to have one orbital out-of-phase with respect to the other two. In this case, one speaks quite naturally of a "principle of maximum overlap" in an extended sense of simultaneous overlap among three (or more) orbitals. However, when  $\varphi_n$  lies *above* the manifold, we shall show by the same line of reasoning that it must interact preferentially with orbitals which tend to form *out-of-phase* triples with  $\varphi_n$  and other members of the manifold, so that one speaks naturally of a "principle of *most negative* overlap" for the orbitals of highest energy. These ideas appear quite reasonable in retrospect, yet the proper basis for such extended maximum-overlap principles lies intrinsically in the domain of simultaneous interactions among *more* than two orbitals, such as are usually ignored in elementary treatments. These extended maximum-overlap principles are nevertheless found to have significant implications for a general picture of the electronic structure of complex molecules.

In this context, we may recall that elementary first-order perturbation theory provides a simple prediction of the coefficients in the expansion (5a), namely,

$$c_i \propto h_{ni}/(\epsilon_n - \epsilon_i) \quad (7)$$

This is often taken as a basis for the principle of maximum overlap, since the contribution  $c_i$  of  $\varphi_i$  to the final eigenfunction increases linearly with  $h_{ni}$ , and thus with the overlap. Under the assumptions in (6), however, formula 7 would lead one to expect

$$|c_i| \approx |c_j| \approx |c_k| \approx \dots (?) \quad (8)$$

In general, this gives a quite incorrect picture of the orbital coefficients of (5a), reflecting that (7) (like the "pairwise-additivity" picture to which it closely corresponds) is unable to draw out the full scope of the principle of maximum overlap.

## II. Extended Principles of Maximum Overlap

Our starting point is a simple *exact* formula for the ratio of coefficients arising from any chosen solution of a finite set of secular equations. If  $\psi = \psi_n$  is the eigenfunction

$$\psi = \sum_{i=1}^N c_i \varphi_i \quad (9)$$

corresponding to the root  $\lambda = \lambda_n$  of eq 4, it is proved in the Appendix that

$$\frac{c_i^2}{c_j^2} = \frac{P_i(\lambda = \lambda_n)}{P_j(\lambda = \lambda_n)} \quad (10)$$

where  $P_i(\lambda)$  is the *reduced* characteristic polynomial (of order  $N - 1$ ) which results when orbital  $\varphi_i$  is *excluded* from the original basis set, and  $P_j(\lambda)$  is similarly the result of excluding  $\varphi_j$  (e.g., excluding the  $j$ th row and column of the secular determinant). Equation 10 specifies that these polynomials are to be evaluated at the appropriate root,  $\lambda = \lambda_n$ , of the *full* characteristic polynomial of order  $N$  in order to get the proper ratio of coefficients.

As mentioned above, we wish to examine the case  $N = 4$ , so that  $P_i(\lambda)$  and  $P_j(\lambda)$  are both cubic polynomials. If the four orbitals of interest are denoted  $\varphi_n, \varphi_1, \varphi_2$ , and  $\varphi_3$ , the polynomial  $P_i(\lambda)$ , for example, can be written as

$$P_i(\lambda) = \begin{vmatrix} \epsilon_j - \lambda & h_{jk} & h_{jn} \\ h_{jk} & \epsilon_k - \lambda & h_{kn} \\ h_{jn} & h_{kn} & \epsilon_n - \lambda \end{vmatrix} \quad (11)$$

where  $(i, j, k)$  is some choice of  $(1, 2, 3)$ .

It is a general consequence of the Hylleraas-Undheim-MacDonald<sup>7</sup> "interleaving theorem" that both the numerator and denominator of the right-hand side of (10) are positive if  $\varphi_n$  lies below the manifold  $\varphi_1, \varphi_2, \varphi_3$ ,

$$P_i(\lambda_n) > 0, P_j(\lambda_n) > 0 \text{ (if } \epsilon_n < \epsilon_1, \epsilon_2, \epsilon_3) \quad (12a)$$

whereas they are both negative if  $\varphi_n$  lies above these orbitals,

$$P_i(\lambda_n) < 0, P_j(\lambda_n) < 0 \text{ (if } \epsilon_n > \epsilon_1, \epsilon_2, \epsilon_3) \quad (12b)$$

To see this, one may simply examine the form which the cubic polynomial  $P_i(\lambda)$  must have when plotted against  $\lambda$ , as in Figure 1. The intersections of the curve  $P_i(\lambda)$  with the horizontal axis are simply the Rayleigh-Ritz variational estimates ( $\bar{\lambda}_i$ ) for a secular determinant of order three, and according to the general Hylleraas-Underheim-MacDonald theorem, these must "interleave" the solutions ( $\lambda_i$ , marked with  $\times$ 's on the axis) of the secular determinant of order four,

$$\lambda_1 < \bar{\lambda}_1 < \lambda_2 < \bar{\lambda}_2 < \lambda_3 < \bar{\lambda}_3 < \lambda_4 \quad (13)$$

Thus,  $\lambda_n$  necessarily lies *outside* the outermost crossing point in Figure 1, either to the left of  $\bar{\lambda}_1$  (if  $n$  denoted the lowest energy level, as in (12a)) or to the right of  $\bar{\lambda}_3$  (if  $n$  denoted the highest energy level, as in (12b)). In the former case (12a), the polynomial  $P_i(\lambda)$  is positive (as it approaches its first crossing from the left), while in the latter case (12b), it is negative, having passed its final crossing into the negative region on the right.

In view of (12a) and (12b), we may now examine (10) for the dependence of  $c_i^2/c_j^2$  on the possible signs of the off-diagonal elements  $h_{ij}$  (or the corresponding overlap integrals  $s_{ij}$ ). Let us first write the reduced characteristic polynomial (11) in the form

$$P_i(\lambda) = f_i(\lambda) - \tau_{jkn} \quad (14)$$

where

$$f_i(\lambda) \equiv (\epsilon_j - \lambda)(\epsilon_k - \lambda)(\epsilon_n - \lambda) - h_{jk}^2(\epsilon_n - \lambda) - h_{jn}^2(\epsilon_k - \lambda) - h_{kn}^2(\epsilon_j - \lambda) \quad (15)$$

$$\tau_{jkn} \equiv -2h_{jk}h_{jn}h_{kn} \quad (16)$$

This decomposition is advantageous in that  $f_i(\lambda)$  contains all the dependence on  $\lambda$ , but none on the phases of the  $h_{ij}$ 's, whereas  $\tau_{jkn}$  is a simple constant which exhibits the dependence on phase. If we arbitrarily change the phase of (say)

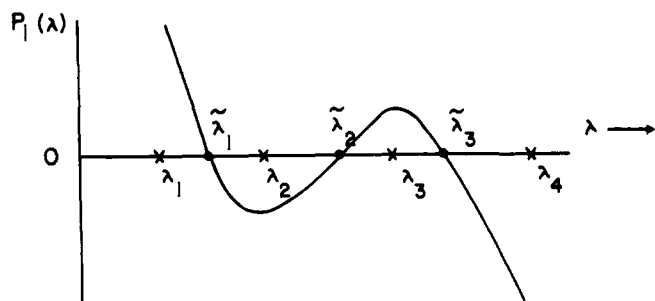


Figure 1. Characteristic polynomial of order three, illustrating the "interleaving theorem".

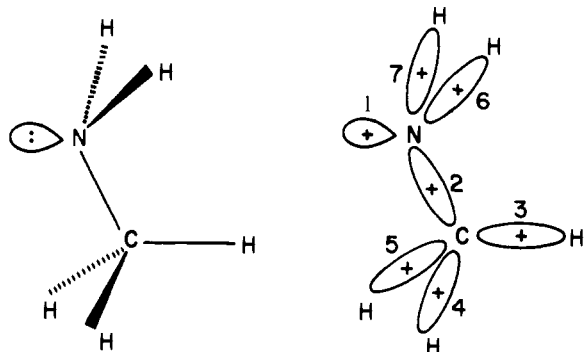


Figure 2. Geometry and numbering of localized bond orbitals in methylamine.

orbital  $\varphi_j$ , the signs of the matrix elements  $h_{jn}$ ,  $h_{jk}$ , ... will likewise be altered, but the product  $h_{jk}h_{jn}h_{kn}$  is left invariant. That is, the signs of individual matrix elements  $h_{jk}$  (or  $s_{jk}$ ) may be meaninglessly altered by mere changes of orbital phase, but the sign of each  $\tau_{jkn}$  has unambiguous physical significance, and the cases  $\tau_{jkn} > 0$  (e.g.,  $s_{jk}s_{jn}s_{kn} > 0$ , "orbitals in-phase") and  $\tau_{jkn} < 0$  (e.g.,  $s_{jk}s_{jn}s_{kn} < 0$ , "orbitals out-of-phase") can be clearly distinguished. Equation 10 is now

$$\frac{c_i^2}{c_j^2} = \frac{f_i(\lambda) - \tau_{jkn}}{f_i(\lambda) - \tau_{ikn}} \quad (17)$$

and by assumptions (6),

$$\begin{aligned} f_i(\lambda) &\approx f_j(\lambda) \approx f_k(\lambda) \approx \dots \\ |\tau_{jkn}| &\approx |\tau_{ikn}| \approx |\tau_{ijn}| \approx \dots \end{aligned} \quad (18)$$

In these approximations, the ratios  $c_i^2/c_j^2$  ( $i, j = 1, 2, 3$ ) are left to depend only on the pattern of overlap phases as reflected in the signs of  $\tau_{jkn}$ ,  $\tau_{ikn}$ .

Consider first the case in which  $\psi_n$  is the lowest lying level, so that, by (12a), the numerator and denominator of (17) are both positive. It is then clear that  $c_i^2$  will exceed  $c_j^2$  if simultaneously  $\tau_{jkn} < 0$  while  $\tau_{ikn} > 0$ ; that is, the interaction will tend to magnify the coefficients of orbitals which can be simultaneously in-phase with  $\varphi_n$  and other orbitals  $k$ , and to diminish the coefficients of orbitals which are intrinsically out-of-phase. This is in agreement with the extended principle of maximum overlap stated previously, and with intuition. Of course, if  $\varphi_i$  and  $\varphi_j$  have identical phase patterns with respect to  $\varphi_n$  and other orbitals  $k$ , then their interactions with  $\varphi_n$  will again be comparable.

The second case is that in which  $\psi_n$  is the highest lying level, so that the numerator and denominator of (17) are both negative by (12b). In this case, the largest coefficient will evidently be associated with that orbital  $\varphi_i$  for which  $\tau_{ikn} < 0$  but  $\tau_{jkn} > 0$ , e.g., with the orbital (if any) which is most out-of-phase with  $\varphi_n$  and other orbitals  $\varphi_k$ . As mentioned previously, this might be paraphrased as a "principle of most negative overlap"

Table I. Hamiltonian Matrix Elements  $h_{ij}$  (Hartree atomic units)

	1	2	3	4	6
1	-0.5834	-0.1478	+0.0790	-0.0577	-0.1382
2		-1.0011	-0.1490	-0.1497	-0.2134
3			-0.8638	-0.1431	-0.0693
4				-0.8639	-0.0695
6					-0.9284

Table II. Overlap Matrix Elements  $s_{ij}$

	1	2	3	4	6
1	1.0000	0.0779	-0.0893	0.0719	0.0812
2		1.5999	0.1585	0.1585	0.2067
3			1.6807	0.2076	0.1146
4				1.6808	0.1146
6					1.6192

for the highest orbital of a system:<sup>8</sup> if  $\varphi_n$  has overlap of (approximately) equal magnitude with orbitals  $\varphi_1$ ,  $\varphi_2$ , and  $\varphi_3$ , this overlap being positive for  $\varphi_1$  and  $\varphi_2$  but negative for  $\varphi_3$  (with  $\varphi_1$ ,  $\varphi_2$ , and  $\varphi_3$  all having mutually positive overlaps), then  $\varphi_n$  will interact most strongly with the orbital of most negative overlap, and the final (highest-energy) eigenfunction will be predominantly a mixture of  $\varphi_n$  and  $\varphi_3$ .

The effects we have described might appear to hold only under such restrictive conditions as not to be of general interest. However, it has recently been recognized<sup>9</sup> that the special geometrical relationships prevailing around, e.g., the tetrahedral centers of saturated hydrocarbons, cause these extended maximum-overlap principles to be manifested in quite surprising and widespread fashion in organic chemistry, particularly in various forms of "trans effects". It is therefore interesting that such effects can be accounted for in terms of a rather natural extension of the maximum-overlap principle, which takes account of the pattern of overlap phases.

### III. Numerical Illustration

Methylamine ( $\text{CH}_3\text{NH}_2$ ; see Figure 2) provides a concrete example to illustrate the foregoing theory. Its molecular orbitals (MO's) can be regarded approximately as linear combinations of the seven "bond orbitals" (BO's)  $\varphi_1, \varphi_2, \dots, \varphi_7$  depicted schematically in Figure 2. Of these,  $\varphi_1$  represents the localized lone-pair orbital on nitrogen, while  $\varphi_2, \dots, \varphi_7$  represent localized bonds constructed from directed atomic hybrids in the manner suggested by simple valence theory.<sup>10</sup> The detailed form of these BO's and the evaluation of their matrix elements need not concern us here. Suffice it to say that the Hamiltonian and overlap matrix elements  $h_{ij}$ ,  $s_{ij}$  tabulated in Tables I and II correspond to a fairly realistic (e.g., INDO-SCF level)<sup>11</sup> representation of the true MO's of methylamine.

The orbital  $\varphi_n$  of the previous discussion is now identified with  $\varphi_1$  (the lone-pair orbital), which will dominate the highest occupied MO. From Table I one can see that the assumptions (6) are only crudely, but adequately, satisfied. Perusal of the overlap matrix elements (Table II) will immediately reveal that the trans C-H bond, orbital  $\varphi_3$ , is singled out by the "principle of most negative overlap" to interact preferentially with  $\varphi_1$  (though the magnitude of its overlap with  $\varphi_1$  would not attract special attention), since  $\tau_{13k}$  is negative for every other orbital  $k$ , whereas  $\tau_{12k}, \tau_{14k}, \dots, \tau_{17k}$  are invariably positive. The final coefficients in the highest occupied MO strongly reflect this preference, the ratios  $c_3^2/c_k^2$  actually taking the values 12.280, 5.702, and 4.215 for  $k = 2, 4$ , and  $6$ , respectively.

Despite the fact that assumptions (6) are not accurately satisfied (e.g., the  $h_{ij}$  elements vary by factors of two to three), the manner in which the overlap-phase effects first appear at

$N = 4$  can be crudely illustrated in this model. We have solved the smaller eigenvalue problems for  $N = 3, 4,$  and  $5$  (chosen variously from the seven orbitals of the full problem, but with  $\varphi_1$  and  $\varphi_3$  always included), and computed values of  $c_3^2/c_k^2$  for  $k = 2, 4,$  and  $6$  in each of these truncated problems. Table III presents the values of these ratios in comparison with the full calculations ( $N = 7$ ) and with the predictions (eq 7) of perturbation theory.

Most conspicuous in Table III is the total failure of low-order perturbation theory to anticipate the dominance of the trans orbital  $\varphi_3$ .<sup>12</sup> This dominance is also missed in the  $N = 3$  calculations, for while the energies depend on whether the three orbitals are in-phase or out-of-phase, there is, of course, no basis for attributing this energy change to one orbital of the triple rather than another. However, at the level  $N = 4$  the variational principle can begin to "choose" between one triple and another on the basis of their overlap phase patterns, and the trans coefficient  $c_3$  is then seen to emerge rather prominently in each  $4 \times 4$  problem in which it occurs. At the  $N = 5$  level, one can see how these effects tend to "add together" to further emphasize the preference for  $\varphi_3$ , as is clear also in the full calculations with  $N = 7$  orbitals.

The decisive role of overlap phase can be confirmed by still another simple calculation. If the matrix element  $h_{13}$  of Table I is arbitrarily reversed in sign, the contribution of  $\varphi_3$  to the highest MO drops abruptly (the new values of  $c_3^2/c_k^2$  being 0.6791, 0.4734, and 0.0777 for  $k = 2, 4,$  and  $6$ , respectively), as would be anticipated from the arguments of section II.

#### IV. Summary

A simple formula for the ratios of eigenvector coefficients allows one to analyze the effects of the *overlap phase patterns* on the structure of molecular orbitals. The results of such an analysis can be conveniently summarized in terms of a natural extension of the principle of maximum overlap, which takes account of the in-phase or out-of-phase character of interactions among three and more orbitals. Such extensions are of direct consequence to the electronic properties of complex molecules, inasmuch as a trans orientation of orbitals characteristically leads to the pattern of overlap phases which is particularly favored by the "principle of most negative overlap" for the highest occupied molecular orbital. This provides a simple theoretical basis for the expectation that interactions among localized bond orbitals oriented in mutually trans relationships will often be the dominating feature of the valence molecular orbitals.

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#### Appendix

Suppose  $c_i$  and  $c_j$  are nonvanishing elements in the null eigenvector of some singular Hermitian  $N \times N$  matrix  $\mathbf{D}$  with elements  $d_{ij}$  (for example,  $d_{ij} = h_{ij} - \lambda s_{ij}$  or  $d_{ij} = h_{ij} - \lambda \delta_{ij}$ ). We wish to prove that

$$\frac{c_i^2}{c_j^2} = \frac{|\mathbf{D}_i|}{|\mathbf{D}_j|} = |\mathbf{D}_i \mathbf{D}_j^{-1}| \quad (\text{A1})$$

where

$$\mathbf{D}_i = \left\{ \begin{array}{l} \text{matrix formed from } \mathbf{D} \text{ by striking} \\ \text{row } i \text{ and column } i \end{array} \right. \quad (\text{A2})$$

If  $\mathbf{D}$  is the secular matrix for the eigenvalue problem of order  $N$ , each  $|\mathbf{D}_i|$  will be a secular determinant of order  $N - 1$ , as noted in the text.

To prove eq A1, we first derive some alternative expressions

**Table III.** Ratios of Coefficients  $c_3^2/c_k^2$  (for  $k = 2, 4,$  and  $6$ ) in the Highest Occupied Molecular Orbital of Methylamine, As Calculated in Various Levels  $N$  of Truncation, and by Low-Order Perturbation Theory

$N$	Orbitals	$c_3^2/c_2^2$	$c_3^2/c_4^2$	$c_3^2/c_6^2$
3	1, 2, 3	0.8732		
3	1, 3, 4		1.2800	
3	1, 3, 6			1.6318
4	1, 2, 3, 4	1.3422	6.0970	
4	1, 2, 3, 6	1.4926		2.6102
4	1, 3, 4, 6		2.4609	1.1755
5	1, 2, 3, 4, 6	2.3345	6.5848	3.3066
7	All	12.2797	5.7022	4.2148
Perturbation theory, eq 7		0.6340	1.8754	0.4945

for  $c_i$  and  $c_i/c_j$  by partitioning the matrix equation  $\mathbf{Dc} = 0$  in the form

$$0 = \begin{pmatrix} \mathbf{D}_N & \mathbf{d}_N \\ \mathbf{d}_N^t & d_{NN} \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ c_N \end{pmatrix} = \begin{pmatrix} \mathbf{D}_N \mathbf{c} + c_N \mathbf{d}_N \\ \mathbf{d}_N^t \mathbf{c} + c_N d_{NN} \end{pmatrix} \quad (\text{A3})$$

where  $\mathbf{d}_N$  denotes the  $N$ th column of  $\mathbf{D}$  except for the diagonal element  $d_{nn}$ . Equation A3 gives successively the equations

$$\mathbf{c} = -c_N \mathbf{D}_N^{-1} \mathbf{d}_N \quad (\text{A4a})$$

$$d_{NN} = \mathbf{d}_N^t \mathbf{D}_N^{-1} \mathbf{d}_N \quad (\text{A4b})$$

provided  $\mathbf{D}_N$  is nonsingular. In particular, the  $i$ th component of the vector equation (A4a) reads

$$c_i = -c_N (\mathbf{D}_N^{-1} \mathbf{d}_N)_i \quad (\text{A5})$$

For compactness, let  $\mathbf{A}$  be the matrix defined by

$$(\mathbf{A})_{ij} = A_{ij} = -(\mathbf{D}_j^{-1} \mathbf{d}_j)_i \quad (\text{A6})$$

so that (A5) can be written as

$$A_{ij} = c_i/c_j \quad (\text{A7})$$

It is easy to recognize such equations as

$$A_{ij} = A_{ji}^{-1} = A_{ik} A_{kj} \quad (\text{A8})$$

The next step is to find a suitable expression for elements of the inverse matrix  $\mathbf{D}_j^{-1}$ . By the usual rule for forming the inverse, we can write

$$(\mathbf{D}_j^{-1})_{mn} = \frac{\text{cofactor of } d_{nm} \text{ in } \mathbf{D}_j}{|\mathbf{D}_j|} \quad (\text{A9})$$

Let us denote

$$\mathbf{D}_{kl,mn} \equiv \left\{ \begin{array}{l} \text{matrix formed from } \mathbf{D} \text{ by striking} \\ \text{rows } k \text{ and } l \text{ and columns } m \text{ and } n \end{array} \right. \quad (\text{A10})$$

and

$$\sigma_{kl} = k - \Theta(k - l) = \begin{cases} k & \text{if } k < l \\ k - 1 & \text{if } k \geq l \end{cases} \quad (\text{A11})$$

where  $\Theta$  is the Heaviside symbol. The symbol  $\sigma_{kl}$  is merely the proper row number of the original  $k$ th row in a matrix where the original  $l$ th row has been struck. With these definitions the numerator of (A9) is

$$\text{cofactor} = (-1)^{\sigma_{nj} + \sigma_{mj}} |\mathbf{D}_{nj,mj}| \quad (\text{A12})$$

so that by eq A7, A9, and A12,

$$A_{ij} |\mathbf{D}_j| = - \sum_{\substack{k=1 \\ (k \neq j)}}^N (-1)^{\sigma_{kj} + \sigma_{ij}} d_{kj} |\mathbf{D}_{kj,ij}| \quad (\text{A13a})$$

$$A_{ji} |\mathbf{D}_i| = - \sum_{\substack{k=1 \\ (k \neq i)}}^N (-1)^{\sigma_{ki} + \sigma_{ji}} d_{ki} |\mathbf{D}_{ki,ji}| \quad (\text{A13b})$$

Let us now consider  $|\mathbf{D}_{i,j}|$ , the determinant of the matrix defined as

$$\mathbf{D}_{i,j} = \begin{cases} \text{matrix formed from } \mathbf{D} \text{ by striking} \\ \text{row } i \text{ and column } j \end{cases} \quad (\text{A14})$$

We shall evaluate this determinant in two ways, once by expansion along the "jth row", then again down the "ith column"; by "jth row" we mean the row whose elements are  $d_{j1}, d_{j2}, \dots$ , though this will actually occur in row  $j+1$  of  $\mathbf{D}_{i,j}$  if  $j > i$ , and similar comments apply to the "ith column". In the first case we get

$$|\mathbf{D}_{i,j}| = \sum_{\substack{k=1 \\ (k \neq j)}}^N (-1)^{\sigma_{kj} + \sigma_{ji}} d_{jk} |\mathbf{D}_{ij,jk}| \quad (\text{along "jth row"}) \quad (\text{A15a})$$

and in the second

$$|\mathbf{D}_{i,j}| = \sum_{\substack{k=1 \\ (k \neq i)}}^N (-1)^{\sigma_{ki} + \sigma_{ij}} d_{ki} |\mathbf{D}_{ik,ji}| \quad (\text{down "ith column"}) \quad (\text{A15b})$$

Now from the symmetry ( $d_{ij} = d_{ji}$ ) of  $\mathbf{D}$  and the obvious symmetries

$$|\mathbf{D}_{ij,jk}| = |\mathbf{D}_{jk,ij}| = |\mathbf{D}_{kj,ij}|, |\mathbf{D}_{ik,ji}| = |\mathbf{D}_{ki,ji}| \quad (\text{A16})$$

of the definition (A10), one can recognize from (A13a) and (A15a) that

$$A_{ij} |\mathbf{D}_j| = (-1)^{\sigma_{ij} + \sigma_{ji} + 1} |\mathbf{D}_{i,j}| \quad (\text{A17a})$$

and from (A13b) and (A15b) that

$$A_{ji} |\mathbf{D}_i| = (-1)^{\sigma_{ji} + \sigma_{ij} + 1} |\mathbf{D}_{i,j}| \quad (\text{A17b})$$

from which it follows that

$$A_{ij} |\mathbf{D}_j| = A_{ji} |\mathbf{D}_i| \quad (\text{A18})$$

which, in view of (A7), is the desired result.

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- (8) Of course, such a statement implies a certain phase convention, but no set of orbital sign changes can disguise the uniqueness of the orbital of "odd" overlap.
- (9) T. K. Brunck and F. Weinhold, *J. Am. Chem. Soc.*, submitted for publication.
- (10) The detailed computational procedure for obtaining MO's in the LCBO framework (e.g., the construction of unitary matrices relating AO's to BO's, and subsequent transformation of the SCF equations into the BO basis) will be described elsewhere. In the present application, idealized geometries and orbital hybridizations were employed throughout, and contributions from antibonding BO's were ignored (as suggested by ref 9), but the qualitative conclusions should be insensitive to these specific choices.
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## <sup>19</sup>F Nuclear Magnetic Resonance Studies of Lipid Bilayer Systems. 1

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**Abstract:** A fluorinated lipid, 1-palmitoyl-2-8,8-difluoropalmitoyl-*sn*-glycero-3-phosphorylcholine, has been synthesized and the dynamic properties of lipid bilayer systems containing this molecule have been studied using fluorine-19 NMR. Spin-lattice relaxation rates and nuclear Overhauser effects have been measured over a range of temperatures and the results have been interpreted in terms of correlation times for specific motions involving the *gem*-difluoromethylene group. The correlation times are shown to be consistent with <sup>1</sup>H and <sup>13</sup>C relaxation data of similar lipid bilayer systems. The data, however, prove to be particularly valuable in characterizing a motion on the time scale of translational diffusion.

### Introduction

In recent years much effort has been devoted to the characterization of the hydrocarbon chain mobility of phospholipids in bilayer membranes. The subject is of interest because the bilayer is an indigenous component of virtually all biological membranes.<sup>2</sup> The phospholipid motions are intimately linked to the activity of proteins and the transport of metabolites within and through the membrane.<sup>2</sup> Characterization of the

anisotropic motion in the liquid crystalline lipid bilayer has also proven to be a challenging problem in physical chemistry.

EPR nitroxide spin-label studies<sup>3-6</sup> and nuclear magnetic resonance relaxation studies<sup>7-10</sup> have yielded valuable results concerning the segmental rotational motions and translational diffusion of the phospholipids, but both methods have been subjected to some criticism. Spin labels can perturb the structure of the bilayer. This is shown by the fact that in identical lipid bilayer systems, even after correction for time