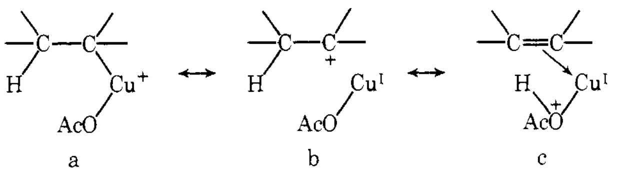
Additions and Corrections

Mechanism of Electron Transfer Oxidation of Alkyl Radicals by Copper(II) Complexes [*J. Am. Chem. Soc.*, **90,** 4616 (1968)]. By J. K. KOCHI, A. BEMIS, and C. L. JENKINS, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Scheme I on page 4622 should be corrected to read:



Stereoselective Chemical Reduction of 5,10-Methenyltetrahydrofolate [*J. Am. Chem. Soc.*, **95,** 5409 (1973)]. By PETER R. FARINA, LINDA J. FARINA, and STEPHEN J. BENKOVIC,* Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802.

The assignment in Figure 1 to the methylene bridge protons of 5,10-methylenetetrahydrofolate is incomplete. The depicted doublet at 4.94 ppm is only one-half of an AX quartet; the remaining half is centered at 3.75 ppm. Instability in the field frequency lock and masking by solvent contributed to the misassignment. The stereochemical preference for one diastereomer in the system illustrated is about 60–70%.

Symmetry Adapted Functions and Normalized Spherical Harmonic (NSH) Hamiltonians for the Point Groups O_h. T_d. D_{4h}. D_{2d}. C_{4v}. D_{2h}. C_{2v} [*J. Am. Chem. Soc.*, **96,** 1693 (1974)]. By J. C. HEMPEL, J. C. DONINI, B. R. HOLLEBONE, and A. B. P. LEVER,* Department of Chemistry, York University, Downsview, Ontario, Canada M3J 1P3.

In both Tables I and II the representation of the basis *xy* in the C_{4v} point group should be B_2.

The bottom function in eq 16 has a sign error. For consistency it should read:

$$|T_{2g}(xy);\ B_{2g};\ A_g;\ A_1\rangle = -i/\sqrt{2}\{|22\rangle - |22\rangle\} \quad (16)$$

One element in Table X also has a sign error. Thus the bottom element in the *DS* column should read +0.11429.

A coefficient is missing from eq 35 which should read:

$$(3/7)DS - (1/21)(5/3)^{1/2}DT - (5/3)(1/21)^{1/2}DQ = \tfrac{1}{2}\,\mathrm{Tr}(^3A_2) + \tfrac{1}{2}\,\mathrm{Tr}(^3B_2) - \mathrm{Tr}(^3B_1) \quad (35)$$

The sentence beginning three lines below eq 35 should read, in part: "When nine spin-allowed triplet–triplet transitions are observed, the energies of the triplet states can be specified with three independent variables . . ." (not four as previously indicated).

On page 1701, 16 lines above the Discussion should read ". . . with $\lambda = -140\ \mathrm{cm}^{-1}$ . . . ."

The Gauche Effect. "Isolation" of Lone Pair–Lone Pair Interactions [*J. Am. Chem. Soc.*, **96,** 5693 (1974)]. By FREDERIC A. VAN-CATLEDGE, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

It has been pointed out to us that the derivation of the function f(*S*), used to approximate the rotational behavior of one-electron interactions between vicinal hybrid orbitals, is faulty owing to inconsistent handling of the quantity S_{pq}^2. We wish to demonstrate that the function f(*S*) remains a good probe for this behavior, though not for the reasons originally stated. Let us consider the one-electron interactions between two hybrids on adjacent, identical nuclei. if we approximate the coupling element H_{pq}' as

$$H_{pq}' \approx KS_{pq}H_{pp} \quad \text{(a-1)}$$

we obtain, for the symmetry-determined MO's

$$(H_{11}' + H_{22}')_{\mathrm{approx}} \propto -(1 - KS_{pq}^2)/(1 - S_{pq}^2) \quad \text{(a-2)}$$

Two points emerge from examination of (a-2): (a) for any value of *K* greater than unity, the qualitative behavior of (a-2) parallels that of f(*S*): (b) for the case in question S_{pq}^2 is small (0–0.05). If *K* is set equal to 2.0, the expression (a-2) may be represented extremely well by f(*S*), i.e.,

$$(1 - 2x)/(1 - x) \approx (1 - x) \quad \text{(a-3)}$$

when *x* is small.

Let us pursue the point further by considering an explicit form for the Hamiltonian governing direct, one-electron interactions between hybrids on adjacent centers

$$\hat{H}' = -\frac{1}{2}\nabla^2 - Z_A'/r_A - Z_B'/r_B \quad \text{(a-4)}$$

where Z_A' is the core charge (assuming "perfect" screening by the inner shell electrons) for atom A. We may now compute the quantity $(H_{11}' + H_{22}')_{\mathrm{exact}}$ and compare its rotational behavior with that of the several functions described above. Table I summarizes such a comparison for N–N interactions with an internuclear separation of 1.46 Å. All functions give minima at 90 ± 5°. Further, the ratio of the important Fourier coefficients is ~4 in each case.

Table I. Fourier Coefficients for Various Functions Representing One-Electron Interactions between Vicinal sp^3 Hybrid Orbitals

Function	10^2V_1	10^2V_2	10^2V_3	$\lvert V_2/V_1\rvert$	ϕ_{min}, deg
f(*S*)	0.460	−1.790	0	3.89	86
Eq (a-2)					
k = 1.5	0.237	−0.912	0.002	3.86	86
k = 2.0	0.473	−1.825	0.004	3.86	86
"Exact"	−0.168	−0.718	0	4.26	93

Extension the these arguments to all the cases previously considered confirms that the function f(*S*) is indeed a reasonable probe to use for rotational effects deriving from one-electron interactions.

Nucleophilic Cleavage of the Sulfur–Sulfur Bond by Phosphorus Nucleophiles. Kinetic Study of the Reduction of Aryl Disulfides with Triphenylphosphine and Water [*J. Am. Chem. Soc.*, **96,** 6081 (1974)]. By LARRY E. OVERMAN,* DAVID MATZINGER, EDWARD M. O'CONNOR, and JOANNE D. OVERMAN, Department of Chemistry, University of California, Irvine, California 92664.

On page 6086, first column, line 15, the sign for β is incorrect; it should read "β for the meta substituents is −1.02."

In Table V the molar extinction coefficients reported for the phenoxides derived from **15** and **16** are incorrect; for **15** $\epsilon_{\mathrm{ArS^-}}$ should be 1,100 and for **16** $\epsilon_{\mathrm{ArS^-}}$ should be 16,300.