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Valence-Bond Bond-Order Formulation for Contact Nuclear Spin–Spin Coupling[1a]

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Abstract: The valence-bond theory of contact nuclear spin–spin coupling is formulated in terms of Penney–Dirac bond orders. For molecular systems in which there are only small deviations from a localized bond description, the coupling constants are related to the nonlocal bond orders of four-electron fragments. Terms in the coupling constant expression which are of first order in these bond orders are called "direct" contributions, whereas terms which are of second or higher order are called "indirect" contributions. It is suggested that this classification provides a clearer and more useful description of the coupling mechanism than others (*e.g.*, through-bond *vs.* through-space) which have been used in the past. The bond-order formulation is shown to be useful for semiempirical estimates of coupling constants. Illustrations of the utility of esr hyperfine splittings and nmr coupling constants for the determination of fragment bond orders are given and the results are applied to a number of systems.

The widespread interest in the spin–spin coupling constants determined by nuclear magnetic resonance spectroscopy has given rise to a variety of attempts to describe the mechanisms by which the electrons "transmit" the orientation of one nuclear spin to its coupled partner. For directly bonded protons, the interaction is simple and the description given in the original Ramsey–Purcell paper is adequate.[2a] For coupling between nonbonded atoms, however, the situation is more complicated and some confusion appears to exist. In certain treatments, emphasis has been placed on identifying qualitatively different mechanisms which are not clearly defined in terms of any theoretical model; the dichotomy between "through-space" and "through-bond" contributions is a case in point.[2b] Moreover, in some cases where theoretical formulations have been given, the mechanism discussed is not dominant for the coupling under consideration.[3,4] Thus a clarification of existing theory and terminology is needed.

In this paper, perturbation theory and Penney–Dirac bond orders[5,6] are used to obtain a simple form for the average energy valence-bond model[7] of the contact contribution to proton coupling constants. For the most common molecular systems, in which the deviations from perfect pairing are small, vicinal and long-range coupling constants are expressed in terms of the bond orders for four-electron fragments. The resulting formulas provide a natural separation into *direct* and *indirect* contributions to the coupling.

The bond-order formulation also serves as a convenient starting point for the semiempirical estimation and correlation of coupling constants. With fragment bond orders obtained from nmr and esr data, coupling

(1) (a) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for partial support of this research; (b) University of Arizona; (c) Harvard University.

(2) (a) N. F. Ramsey and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952); (b) D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 246 (1961); L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961); N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy to Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 5.

(3) S. Alexander, *J. Chem. Phys.*, **34**, 106 (1961).

(4) S. Koide and E. Duval, *ibid.*, **41**, 315 (1964).

(5) W. G. Penney, *Proc. Roy. Soc.* (London), **A158**, 306 (1937).

(6) D. Clarkson, C. A. Coulson, and T. H. Goodwin, *Tetrahedron*, **19**, 2153 (1963).

(7) For a review, see M. Barfield and D. M. Grant, *Advan. Magn. Resonance*, **1**, 149 (1965).

constants in many systems can be evaluated by a very simple procedure.

Section I presents the Penney–Dirac bond-order theory for the contact nuclear spin coupling. Some applications utilizing nmr and esr data are given in section II. In section III, certain mechanisms for spin coupling are discussed and an attempt is made to provide a correct and consistent terminology. The Appendix is concerned with the relation between the results given in this paper, which uses the average energy approximation, and a treatment in terms of a summation over a finite set of excited valence-bond triplets.[8]

I. Bond-Order Formulation of Spin Coupling

For a molecular system of $2n$ electrons the singlet ground-state valence-bond (VB) wave function, $^1\Psi_0$, is given by

$$^1\Psi_0 = \sum_j c_j {}^1\psi_j \quad (1)$$

where the c_j's are the coefficients corresponding to the lowest eigenvalue of the secular determinant and the $^1\psi_j$'s are the linearly independent, nonpolar VB functions.[9]

$$^1\psi_j = 2^{-n/2}\sum_R (-1)^R R[\{(2n)!\}^{-1/2} \times$$

$$\sum_P (-1)^P P\phi_a(1)\beta(1)\phi_b(2)\alpha(2)\ldots$$

$$\phi_{2n}(2n)\alpha(2n)] \quad (2)$$

In eq 2 P represents the $(2n)!$ permutations of the electrons among the orbitals and their associated spins, and R denotes the 2^n interchanges of the α and β spin functions for the pairs of orbitals that are bonded together.

Second-order perturbation theory in the "mean energy approximation" leads to eq 3[10] for the contact coupling constant, $J_{NN'}$, between N and N'

$$J_{NN'} = -(2/3h\Delta E)(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times$$

$$\langle {}^1\Psi_0 | \sum_{t,u} \delta(r_{tN})\delta(r_{uN'})S_t \cdot S_u | {}^1\Psi_0 \rangle \quad (3)$$

where ΔE is the "mean excitation energy" and the standard notation is employed. Substitution of eq 1 into eq 3 and use of the Dirac identity[11]

$$P_{tu}{}^s = (1/2)(1 + 4S_t \cdot S_u) \quad (4)$$

where $P_{tu}{}^s$ represents the interchange of the spin of electrons t and u, yields[12]

$$J_{NN'} = -(6\Delta E)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times$$

$$\sum_{j,l} c_j c_l \langle {}^1\psi_j | \sum_{t,u}\delta(r_{tN})\delta(r_{uN'})(2P_{tu}{}^s - 1) | {}^1\psi_l \rangle \quad (5)$$

There are two types of integrals to be evaluated in eq 5

$$I_1 = \langle {}^1\psi_j | \sum_{t,u} \delta(r_{tN})\delta(r_{uN'}) | {}^1\psi_l \rangle \quad (6)$$

and

$$I_2 = \langle {}^1\psi_j | \sum_{t,u} \delta(r_{tN})\delta(r_{uN'})P_{tu}{}^s | {}^1\psi_l \rangle \quad (7)$$

With the assumption of orthogonality of the atomic orbitals $\phi_a, \phi_b, \ldots, \phi_{2n}$ in eq 2, each of the integrals I_1 and I_2 contains a sum over terms corresponding to unpermuted and singly permuted electrons. Since the spin exchange operator, $P_{tu}{}^s$ in eq 7, has exactly the same effect as an electron permutation P in eq 2, there will be terms in both I_1 and I_2 which have the form of valence-bond Coulomb and exchange integrals.[12] Evaluation of I_1 and I_2 over the $^1\psi_j$ of eq 2 gives

$$I_1 = (1/2)^{n-i_{jl}} \sum_{t,u} \{\phi_t{}^2(N)\phi_u{}^2(N') +$$

$$f_{jl}{}^{tu}\phi_t(N)\phi_u(N')\phi_t(N')\phi_u(N)\} \quad (8)$$

and

$$I_2 = -(1/2)^{n-i_{jl}}\sum_{t,u}\{f_{jl}{}^{tu}\phi_t{}^2(N)\phi_u{}^2(N') +$$

$$\phi_t(N)\phi_u(N')\phi_t(N')\phi_u(N)\} \quad (9)$$

where $\phi_t(N)$ and $\phi_u(N')$ denote the values of the atomic orbital wave functions at N and N', respectively. In the superposition diagram of $^1\psi_j$ and $^1\psi_l$, i_{jl} is the number of islands and $f_{jl}{}^{tu}$ is the exchange factor for orbitals t and u.[9] Substitution of eq 8 and 9 into eq 5 results in the general expression for $J_{NN'}$

$$J_{NN'} = (2h\Delta E)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times$$

$$\sum_{t,u}\{p(t,u)\phi_t{}^2(N)\phi_u{}^2(N') +$$

$$(1/2)[1 + p(t,u)]\phi_t(N)\phi_u(N')\phi_t(N')\phi_u(N)\} \quad (10)$$

Here $p(t,u)$ is the Penney–Dirac bond order, which is defined by the equation[5,6]

$$p(t,u) = -(4/3)\langle {}^1\Psi_0 | S_t \cdot S_u | {}^1\Psi_0 \rangle =$$

$$(1/3)\sum_{j,l} c_j c_l (1/2)^{n-i_{jl}}[1 + 2f_{jl}{}^{tu}] \quad (11)$$

An alternative derivation of eq 10 makes use of the formulation of McWeeny and Mizuno,[13] who expressed the average energy approximation to $J_{NN'}$ in the form

$$J_{NN'} = -(3h\Delta E)^{-1}(16\pi\beta\hbar/3)^2 \times$$

$$\gamma_N\gamma_{N'}Q_c(1_N,2_{N'};1_N,2_{N'}) \quad (12)$$

where $Q_c(1_N,2_{N'};1_N,2_{N'})$ is the "density of spin coupling" evaluated with electron 1 at nucleus N and electron 2 at nucleus N'. Further, the function $Q_c(1,2; 1,2)$ can be related to the elements of the spinless two-electron density matrix ("spinless pair function")[13]

$$Q_c(1,2;1,2) = -(1/2)P_2(1,2;1,2) - P_2(2,1;1,2) \quad (13)$$

where in valence-bond theory $P_2(1,2;1,2)$ is given by

$$P_2(1,2;1,2) = \sum_{t,u}\{\phi_t{}^2(1)\phi_u{}^2(2) +$$

$$(1/2)[3p(t,u) - 1]\phi_t(2)\phi_u(1)\phi_t(1)\phi_u(2)\} \quad (14)$$

Substitution from eq 13 and 14 into eq 12 leads directly to eq 10.

Equation 10 shows that all electrons having nonvanishing densities at the nuclei can be involved in the spin coupling. However, it is reasonable to assume that electrons other than those centered on N and N' make a negligible contribution. If, further, the atoms which contain the coupled nuclei are well separated in space,

(8) M. Barfield, *J. Chem. Phys.*, **46**, 811 (1967); see also footnote 15 of M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959).

(9) L. Pauling, *ibid.*, **1**, 280 (1933).

(10) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(11) P. A. M. Dirac, "The Principles of Quantum Mechanics," Oxford University Press, Oxford, 1947, p 222.

(12) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).

(13) R. McWeeny and Y. Mizuno, *Proc. Roy. Soc.* (London), **A259**, 554 (1961); see also, M. Barfield, *J. Chem. Phys.*, **44**, 1836 (1966).

the second term in eq 10 can be neglected in comparison with the first.[12] With these approximations, which are probably less drastic than those implicit in the semi-empirical valence-bond method,[14] the coupling constant expression can be written

$$J_{NN'} = -2(3h\Delta E)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times$$

$$\sum_{t,u} \phi_t^2(N)\phi_u^2(N')\langle{}^1\Psi_0|\mathbf{S}_t\cdot\mathbf{S}_u|{}^1\Psi_0\rangle =$$

$$(2h\Delta E)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'} \times$$

$$\sum_{t,u}\phi_t^2(N)\phi_u^2(N')p(t,u) \quad (15)$$

where the summations are restricted to the orbitals which are centered on atoms N and N', respectively.

For coupling between protons, for which $\phi_h^2(H)$ and $\phi_{h'}^2(H')$ denote the densities at nucleus H and H' arising from the 1s atomic orbitals ϕ_h and $\phi_{h'}$, respectively, evaluation of the constants in eq 12 yields simply[15]

$$J_{HH'} = 4185(\Delta E)^{-1}p(h,h') \quad (16)$$

where ΔE has units of electron volts. Because of the definition of the Penney–Dirac bond orders (eq 11), eq 15 and 16 are equivalent to those derived in the original valence-bond formulation.[12]

Within the limitations of the assumptions, the measured coupling constant $J_{HH'}$ and an estimate of ΔE provide an experimental "determination" of the Penney–Dirac bond order. Furthermore, the bond order is related to the exchange contribution to binding energy. The total valence-bond energy can be written[16]

$$E = E_0 + E_{ex} \quad (17)$$

$$E_0 = Q - (1/2)\sum_{t,u}K(t,u)$$

$$E_{ex} = (3/2)\sum_{t,u}p(t,u)K(t,u)$$

where E_0 is the binding energy corresponding to random orientation of the electron spins and E_{ex} is the additional energy contributed by correlation between the spins of pairs of electrons. Here Q is the valence-bond Coulomb integral and $K(t,u)$ is the valence-bond exchange integral for orbitals t and u.[9] For completely localized bonds, $p(t,u)$ would equal unity for bonded atoms and zero otherwise. In delocalized systems $p(t,u)$ can be nonzero and either positive or negative depending on the sign and magnitudes of certain interbond exchange integrals. Because of the relationship between Penney–Dirac bond orders and coupling constants, the latter can give useful information about delocalization.[17] However, great care must be used in going from the coupling constants to the exchange energy, since approximate bond orders and energy integrals are involved.[18]

In the single-determinant molecular-orbital formulation by McConnell,[19] there is also a relationship between coupling constants and bond orders. However, the fact that only positive couplings can result makes the

simple molecular orbital treatment of less general validity. Extensions to multideterminant functions or to sums over excited states[19] avoid the difficulty but lead to more complicated expressions.

A. Interbond Bond Orders in the Four-Electron Fragment. A molecular fragment with four electrons in two bonds provides the simplest example of nuclear spin coupling between nondirectly bonded orbitals. For this case, there are two singlet valence-bond structures

with ${}^1\psi_1$ the "perfect-pairing structure." If the wave function (eq 1) is written

$$^1\Psi_0 = c_1{}^1\psi_1 + c_2{}^1\psi_2 \quad (18)$$

the fragment bond orders $p^0(t,u)$ as defined in eq 11 have the simple form

$$p^0(r,r') = p^0(s,s') = c_1^2 + c_1c_2 \quad (19a)$$

$$p^0(r,s) = p^0(r',s') = c_2^2 + c_1c_2 \quad (19b)$$

$$p^0(r,s') = p^0(r',s) = -\frac{p(r,r')p(r',s')}{p(r,r') + p(r',s')} = -c_1c_2 \quad (19c)$$

in agreement with the requirement that for a singlet state $\Sigma_{t>u}p(t,u) = n$ where $2n$ is the number of electrons. If deviations from perfect pairing are small, $(c_2^2 << c_1c_2)$, the interbond bond orders reduce to

$$p^0(r,s) = p^0(r',s') =$$

$$-p^0(r',s) = -p^0(r,s') = c_1c_2 \quad (20)$$

To first order, the coefficients are

$$c_1 = 1$$

$$c_2 = (1/2)\left\{\frac{K(r,s) + K(r',s') - K(r,s') - K(r',s)}{K(r,r') + K(s,s') - K(r,s) - K(r',s')}\right\}$$

$$(21)$$

and $p^0(r,s)$ becomes

$$p^0(r,s) = (1/2)\left\{\frac{K(r,s) + K(r',s') - K(r,s') - K(r',s)}{K(r,r') + K(s,s')}\right\}$$

$$(22)$$

where $K(a,b)$ denotes the formal two-electron valence-bond exchange integral associated with orbitals a and b. In writing eq 22, the nonbonded exchange integrals $K(r,s)$ and $K(r',s')$ appearing in the denominator have been neglected with respect to the much larger integrals $K(r,r')$ and $K(s,s')$.

Since the interbond orders in eq 20 all have the same magnitude and differ only in sign, the assumption that deviations from perfect pairing are small implies that a single bond order describes the spin-coupling features for any pair of bonds. Consequently, the coupling constant contributions from the different nonbonding interactions in such a pair of bonds have a relationship which could be exploited in testing theoretical calculations.

B. Coupling Constant in Terms of Interbond Bond Orders. The above results can be utilized for the cal-

(14) J. C. Slater, *Rev. Mod. Phys.*, **25**, 199 (1953).
(15) H. G. Hecht, *Theor. Chim. Acta*, **1**, 222 (1963).
(16) W. Moffitt, *Proc. Roy. Soc.* (London), **A199**, 487 (1949).
(17) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960); *J. Chem. Phys.*, **33**, 316 (1960).
(18) H. G. Hecht, D. M. Grant, and H. Eyring, *Mol. Phys.*, **3**, 577 (1960).
(19) H. M. McConnell, *J. Chem. Phys.*, **24**, 460 (1956); J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964); **9**, 301 (1965).

culation of coupling constants in molecules with more than four electrons by consideration of a system with N bonds, $\sigma_j-\sigma'_j$, in addition to the bonds r–r' and s'–s.[7] Only valence-bond structures with no more than two bonds broken relative to the perfect pairing structure are included in the wave function.[7,20,21] Thus for the bond order $p(r,s)$ the contributing structures are of the form

$^1\psi_1$

$^1\psi_2$

$^1\psi_3$

$^1\psi_4$
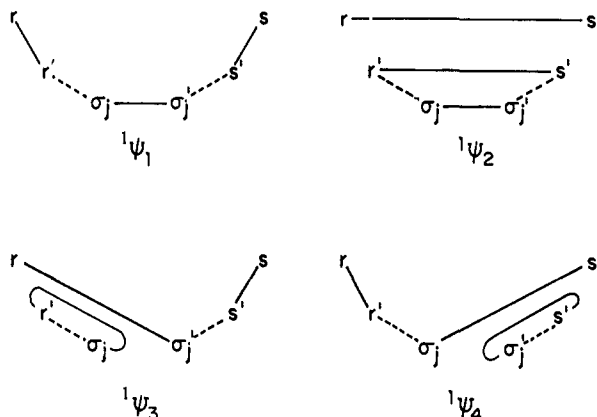
with $^1\psi_1$ the perfect pairing structure, $^1\psi_2$ the direct interaction structure corresponding to $^1\psi_2$ of the four-electron system (see section IA), and $^1\psi_3$, $^1\psi_4$ indirect interaction structures involving the bond σ_j–σ'_j. These structures are a direct generalization of the ethane fragment structures,[20] the single intervening carbon–carbon bond in the ethane fragment being replaced here by any one of the σ_j–σ'_j bonds in the molecule. If perturbation theory is used to calculate the coefficient of these structures in the wave function and the interbond bond orders $p^0(r,s)$ given in eq 22 are transferable, the expression for $p(r,s)$ (eq 11) becomes[7,21]

$$p(r,s) = p^0(r,s) + \sum_j^N p^0(r,\sigma_j)p^0(\sigma'_j,s) \times$$

$$\left\{1 + \frac{K(\sigma_j,\sigma'_j)}{K(r,r') + K(s',s)}\right\} \quad (23)$$

where terms of third and higher order have been neglected. Here $p(r,s)$ is the total Penney–Dirac bond order between r and s, while $p^0(r,s)$, $p^0(r,\sigma_j)$, and $p^0(\sigma'_j,s)$ are the interbond bond orders; e.g., $p^0(r,\sigma_j)$ is obtained from the structures of the two-bond four-electron fragment r–r', σ_j–σ'_j.

If the intrabond exchange integrals are equal to the same accuracy as that of the approximations made in deriving eq 23, there results the concise formula

$$p(r,s) = p^0(r,s) + (3/2)\sum_j^N p^0(r,\sigma_j)p^0(\sigma'_j,s) \quad (24)$$

The first term on the right-hand side of eq 24 describes a direct interaction between the bonds which contain r and s and the summation is over indirect contributions, each of which is associated with one of the N bonds σ_j–σ'_j.[22]

In the case of spin coupling between protons, r and s are replaced by h and h', and $J_{HH'}$ is obtained from eq 16 and 24 as

$$J_{HH'} = 4185(\Delta E)^{-1} \times$$

$$\left\{p^0(h,h') + (3/2)\sum_j^N p^0(h,\sigma_j)p^0(\sigma'_j,h')\right\} \quad (25)$$

Equation 25 is the formula which is used in the subsequent sections for an analysis of proton–proton coupling constants. If the bonds h–r' and s'–h' are located on the same atom (geminal) or on adjacent atoms (vicinal), the direct bond order term $p^0(h, h')$ usually dominates $J_{HH'}$. For h and h' further removed from each other (four or five bonds), the indirect terms included in eq 25 are generally expected to be most important. For coupling between protons separated by more than five bonds in a saturated system, a variety of higher order terms in addition to the eq 25 contributions may be involved; however, the total coupling will generally be small.

A simple refinement of eq 25 would be provided by the introduction of separate ΔE values corresponding to the particular singlet–triplet excitations involved in each of the bond-order contributions. If this were done for the indirect term and σ_j,σ'_j represented π orbitals, the expression in eq 25 would be of the same general form as the π-electron contribution equations derived previously with somewhat different assumptions and approximations.[23,24]

II. Bond-Order Estimates of Proton Spin Coupling

The primary application of the present formulation is to the estimation and correlation of coupling constants. The basis for this is provided by eq 25 and the assumption of the approximate transferability of the interbond orders $p^0(r,s)$ and ΔE values among related compounds. To obtain the required bond orders for any particular coupling, semiempirical valence-bond calculations or measurements on appropriate systems can be employed. Of particular utility are experimental coupling constant and hyperfine splitting data. From the discussion in section I and eq 16, it is clear that a known coupling constant can be used to determine the corresponding bond order if a reasonable ΔE value is available. When the direct term is dominant (e.g., as in most vicinal couplings) and eq 25 is applicable, an estimate of $p^0(h,h')$ is obtained. The connection with hyperfine splittings can be made by noting that if u in eq 11 denotes the phantom orbital in the valence-bond description of the radical, $p(t,u)$ is the atomic orbital spin polarization for orbital t.[25] Since the latter is simply related to the hyperfine constant,[25] a splitting measurement provides information about the bond order in the radical. For protons, in particular, we can write the hyperfine constant a^H as

$$a^H(\text{Mcps}) = -1420p(h,u)$$

$$a^H(\text{Oe}) = -508p(h,u) \quad (26)$$

if the interaction is dominated by the direct term, $p(h,u) \cong p^0(h,u)$. However, some care is required in

(20) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(21) M. Barfield, *ibid.*, **41**, 3825 (1964); in this reference the expression corresponding to eq 23 of the present paper is in error due to the neglect of certain second-order terms; the necessary correction was given by E. Duval [*J. Chem. Phys.*, **45**, 2855 (1966)] and is included in ref 7.
(22) A similar separation was made in ref 3.

(23) H. M. McConnell, *J. Mol. Spectrosc.*, **1**, 11 (1957).
(24) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).
(25) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); see eq 2.4 and 2.5 and the discussion below them.

transferring the esr hyperfine bond orders to the nmr coupling problem. First, structural and bonding changes occur in going from the radical fragments to the molecule of interest. Second, the removal of one of the atoms can have a nonnegligible effect on the bond order. Thus for the three-electron radical analog (r,s–s') of the four-electron two-bond fragment, the bond order $p^0(r,s)$ is

$$p^0(r,s) = -p^0(r,s') =$$
$$\frac{1}{2}\left\{\frac{K(r,s) - K(r,s')}{K(s,s')}\right\} \cong \frac{K(r,s)}{2K(s,s')} \quad (27)$$

Comparing eq 27 with eq 22, we see that the radical fragment bond order for the same structure and exchange integrals is expected to be somewhat larger than that for the molecule; for $K(r,r') \le K(s,s')$, we have

$$p_{\text{mol}}(r,s) \lesssim p_{\text{rad}}(r,s) \lesssim 2p_{\text{mol}}(r,s) \quad (28)$$

These considerations, plus some others given in a previous discussion,[24] suggest that the most reliable applications are to be found in π-electron radicals where the differences between the esr and nmr bond orders are minimized. However, more approximate treatments of radicals in which the unpaired electron is in a σ orbital are possible as well. Also, the esr bond orders can be effectively employed to obtain ratios of coupling constants in a given system or related systems where the transferability correction may manifest itself as a constant factor. For hyperfine splittings of nuclei other than protons (or deuterons) account has to be taken of the hybridization (i.e., s character) of the atomic orbital involved. This is exactly analogous to the situation for nmr coupling constants of nonproton nuclei.

A. Bond Orders from Esr Hyperfine Splitting Parameters. Since the estimation of π-electron contributions to coupling constants from hyperfine splitting data has been described previously,[23,24] we discuss here certain results that indicate the more general applicability of the approach. One type of system is the radical in which the unpaired electron is localized primarily in a σ orbital (s') that forms a bond to the hydrogen whose coupling constant is being considered in the singlet molecule. Thus, the measured value of a^H yields an approximate value for the *total* bond order $p_{\text{rad}}(s',h)$ between s' and the hydrogen 1s orbital ϕ_h in the radical; for the molecule with $\phi_{h'}$ bonded to s', $p(h,h') \cong -(1/2)p_{\text{rad}}(s',h')$. From eq 16 and 26, we have

$$J_{\text{HH}'} = \frac{4185a^H(\text{Oe})}{2(508)\Delta E} = 4.1\frac{a^H(\text{Oe})}{\Delta E} = 1.5\frac{a^H(\text{Mcps})}{\Delta E}$$
$$(29)$$

Some examples are the ethynyl radical (I), the vinyl radical (II), and the phenyl radical (III). In I, the split-

I II III
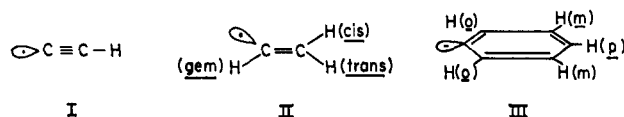
ting constant[26] is $a^H = 16$ Oe of unknown sign (assumed positive); in II, the splitting constants[26] are $a^H(gem) = \pm 16$ Oe, $a^H(cis) = 34$ Oe, and $a^H(trans) = 68$ Oe with cis and trans of the same sign (assumed posi-

tive) and the assignments in part based on theoretical considerations;[27] in III, the splitting constants[28] are $a^H(o) = 18.1$ Oe, $a^H(m) = 6.4$ Oe of unknown sign (assumed positive), and $a^H(p)$ not resolved. With eq 29 applied to I and $\Delta E = 10$ eV, we obtain for acetylene, $J_{\text{HH}'} = 6.5$ cps (exptl, 9.6 cps);[29] for ethylene, radical II yields $J_{\text{HH}'}(cis) = 14$ cps (exptl, 11.7 cps)[29] and $J_{\text{HH}'}(trans) = 28$ cps (exptl, 19.1 cps);[29] for benzene from III there results $J_{\text{HH}'}(o) = 7.4$ cps (exptl, 6–9 cps),[30] $J_{\text{HH}'}(m) = 2.6$ cps (exptl, 2–3 cps),[30] and $J_{\text{HH}'}(p)$ small (exptl, 0.3–0.5 cps).[30] Thus a general correspondence exists between the estimated and experimental values, particularly for the ratios in a given compound. However, there are quantitative differences which could be due to structural changes in going from the radical to the molecule and/or inaccuracies in the bond-order estimation formula. One case where the latter would be expected to be important is in the geminal coupling. Here eq 29 and the vinyl data yield $J_{\text{HH}'}(gem) = \pm 6.6$ cps as compared with the experimental value of 2.5 cps.[29] A problem in the geminal comparison, as in that for the other coupling constants, is that the signs of most of the hyperfine splitting constants for σ radicals are as yet unknown. If the nmr coupling constant is taken to be of known sign, then considerations corresponding to those outlined above will of course serve to determine the sign of the hyperfine interactions.

The agreement between the experimental coupling constant and the estimates from hyperfine data does not determine the nature of the spin coupling mechanism. It suggests only that the mechanism involved is similar in the radical and the corresponding singlet molecule. From theoretical considerations, it appears that $J_{\text{HH}'}(cis)$ and $J_{\text{HH}'}(trans)$ in ethylene and $J_{\text{HH}'}(o)$ in benzene are all dominated by the direct bond-order term $p^0(h,h')$, while $J_{\text{HH}'}(m)$ in benzene involves a number of indirect (second-order) contributions corresponding to the sum in eq 25. The coupling in acetylene is probably a mixture of direct σ bond and indirect π bond terms. The importance of the latter would explain the fact that the estimated value is lower than experiment, since the σ–π fragment bond order $p^0(\sigma,\pi)$ in the singlet molecule is approximately equal to that in the radical, rather than to half its value.[24]

The angular dependence of the vicinal H–H coupling has been investigated[20] by use of a six-electron fragment VB treatment with theoretical estimates for the exchange integrals. Since accurate theoretical values for VB integrals are difficult to obtain, a semiempirical approach based on esr results is also of interest. Whiffen[31] has recently summarized proton hyperfine splitting data for π-electron radicals and radical ions of the form $\cdot$C–CHR$_2$, $\cdot$C–NHR, and $\cdot$C–OH. In correspondence with the theoretical results of McLachlan[32]

(26) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(27) F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964).

(28) J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965), and their references to earlier work.

(29) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).

(30) See, for example, J. Martin and B. P. Dailey, *J. Chem. Phys.*, **37**, 2594 (1962).

(31) D. H. Whiffen in "La Structure Hyperfine Magnetique des Atoms et des Molecules," Centre National de la Recherche Scientifique, Paris, 1967, p 169; W. Gordy and C. G. McCormick, *J. Amer. Chem. Soc.*, **78**, 3244 (1956); W. Derbyshire, *Mol. Phys.*, **5**, 225 (1962); M. A. Collins and D. H. Whiffen, *ibid.*, **10**, 317 (1966).

(32) A. D. McLachlan, *ibid.*, **1**, 233 (1958); D. B. Chesnut, *J. Chem. Phys.*, **28**, 43 (1958).

and of Chesnut,[32] Whiffen finds that a^H can be written

$$a^H = B_0 + B_2 \cos^2 \phi \qquad (30)$$

where B_0 and B_2 are constants depending on the type of radical and ϕ is the dihedral angle between the π orbital containing the unpaired electron and the C–XH plane; the results are $B_0 = 10$ Mcps and $B_2 = 144$ Mcps for ·C–CHR$_2$, $B_0 = 2$ Mcps and $B_2 = 106$ Mcps for ·C–NHR, and $B_0 = -9$ Mcps and $B_2 = 87$ Mcps for ·C–OH. Use of these data for the vicinal H–C–X–H coupling requires a larger correction than was necessary in the σ radicals due to the formation of a C–H bond involving the π orbital that contained the unpaired electron in the radical; that is, the $2p$ π orbital of the radical goes over into a sp^3 hybrid orbital in the singlet molecule. Since it is the direct interaction which is dominant in the vicinal coupling and the direct interaction in turn is primarily determined by the π-electron exchange integral (see section III), one might expect that the bond order in the singlet molecule would be reduced by an additional factor of $^3/_4$ over the factor of $^1/_2$ already included in the σ radicals. Introduction of this correction into eq 23 and use of a $\Delta E = 10$ eV yields

HC–C–H′: $J_{HH'}$ (cps) $= 1.1 + 17 \cos^2 \phi$ (31a)

HC–N–H′: $J_{HH'}$ (cps) $= 0.2 + 12 \cos^2 \phi$ (31b)

HC–O–H′: $J_{HH'}$ (cps) $= -1.0 + 10 \cos^2 \phi$ (31c)

One failing of eq 31 is that, because they were obtained from the hyperfine interaction which is symmetric about $\phi = 90°$, no account is taken of the asymmetry in the coupling constant. Nevertheless, the comparison is informative. For ethane, eq 31a yields $\langle J_{HH'} \rangle_{av} = 9.6$ cps, $J_{HH'}(cis) = J_{HH'}(trans) = 18$ cps, and $J_{HH'}(gauche) = 5.3$ cps, which are to be compared with the experimental values[29] $\langle J_{HH'} \rangle_{av} = 8.1$ cps, $J_{HH'}(trans) = 18$ cps, and $J_{HH'}(gauche) = 3.2$ cps. For HCNH′ and HCOH′, the available measurements are not as complete as those for HCCH. However, the calculated values of $\langle J_{HH'} \rangle_{av}$ are 6.2 cps in HCNH′ and 4 cps in HCOH′ as compared with experimental results of ~5.0[33] and 4.5 cps,[34] respectively.

B. Bond Orders from Nmr Coupling Constants. Indirect contributions are expected to be of major importance for most H–H′ couplings between nuclei separated by more than three bonds. If vicinal interbond orders occur in the coupling constant expression (e.g., $p^0(h,\sigma)$ in eq 25), strong dihedral angle dependencies are expected. Cases of this type which have been considered previously by the valence-bond method include long-range couplings[33] with indirect contributions from σ bonds[21] and π bonds[24]; also geminal couplings in which indirect terms arise from π bonds have been analyzed.[36] As an additional illustration, the coupling over five saturated bonds is discussed here because it has a particularly simple form. The indirect mechanism is

expected to be of major importance and only a single term contributes in the nearest neighbor approximation. With the labeling of the orbitals in the butanic fragment (IV) the bond σ–σ' is the only one having orbitals cen-

IV

tered on atoms (C$_2$ and C$_3$) which are neighbors to C$_1$ and C$_4$, respectively. From eq 25, the indirect contribution, $^1J_{HH'}$, to the five-bond H–H coupling constant is given by

$$^1J_{HH'} = 4185(\Delta E)^{-1}(3/2)p^0(c,\sigma)p^0(\sigma',c') \qquad (32)$$

since $p^0(h,\sigma) = -p^0(c,\sigma)$ and $p^0(\sigma',h') = -p^0(\sigma',c')$ by eq 20. The bond orders in eq 32 are of the vicinal type so that the dependence on dihedral angle has the approximate form given in eq 31a or, more exactly, from the theory of the vicinal coupling[37] (see section III)

$$p^0(c,\sigma) = A \cos^2 \phi + B \cos \phi + C \qquad (33)$$

With the experimental values of *trans* and *gauche* coupling constants in ethane of 18 and 3.2 cps,[29] respectively, and neglect of the constant C in eq 33, the empirical bond orders obtained from eq 16, 20, and 33 with $\Delta E = 10$ eV are

$$p^0(c,\sigma) = 0.056 \cos^2 \phi - 0.012 \cos \phi$$

$$p^0(\sigma',c') = 0.056 \cos^2 \phi' - 0.012 \cos \phi' \qquad (34)$$

where ϕ and ϕ' are the dihedral angles about the C$_1$–C$_2$ and C$_3$–C$_4$ bonds, respectively. Substitution of these bond orders into eq 32 leads to calculated values of $^1J_{HH'}$ which are between 0 and $+0.96$ cps.[38] The latter value occurs for ($\phi = \phi' = 180°$) and thus would be expected in the all-*trans* arrangement depicted in the illustration (IV). However, the calculated coupling does *not* depend on the dihedral angle between the vicinal C$_1$–C$_2$ and C$_3$–C$_4$ bonds so that other geometries could give the same result.

Although no five-bond H–H′ couplings in saturated hydrocarbons seem to have been measured, there are values[39] of 1.25 and 1.7 cps for HCOCCH′ interactions in which there were two and three coupling paths, respectively. Moreover, the compounds studied suggested that the five-bond couplings are indeed independent of the dihedral angle about the C$_2$–C$_3$ bond. For unsaturated systems, many five-bond couplings have been reported[35] and some of these appear to be due to a mechanism corresponding to eq 32.

Also of interest in relation to the five-bond couplings are recent observations of long-range proton hyperfine interactions in iminoxy radicals.[40] It has been found that for the σ-orbital fragment with $\phi = \phi' = 180°$ (V) the hyperfine splitting is 2.4 Oe. When this value is
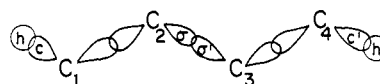
(33) E. W. Randall and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **8**, 365 (1962); E. Grunwald, *J. Phys. Chem.*, **67**, 2208 (1963).

(34) J. J. Vebel and H. W. Goodwin, *J. Org. Chem.*, **31**, 2040 (1966); in a private communication, they estimate $J_{HH'}(trans) = 9.5$ cps and $J_{HH'}(gauche) = 3.2$ cps, in comparison with $J_{HH'}(cis) = J_{HH'}(trans) = 9.0$ cps and $J_{HH'}(gauche) = 1.5$ cps.

(35) For a review of the data, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(36) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963).

(37) M. Karplus, *ibid.*, **85**, 2870 (1963).

(38) A maximum coupling of about 0.5 cps is obtained if the bond orders in eq 34 are based on the smaller values of the vicinal coupling constants which are most often observed in cyclic systems. These results are larger than the coupling of 0.15 cps estimated by H. Frischleder and G. Bär, *Mol. Phys.*, **11**, 359 (1966).

(39) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966).

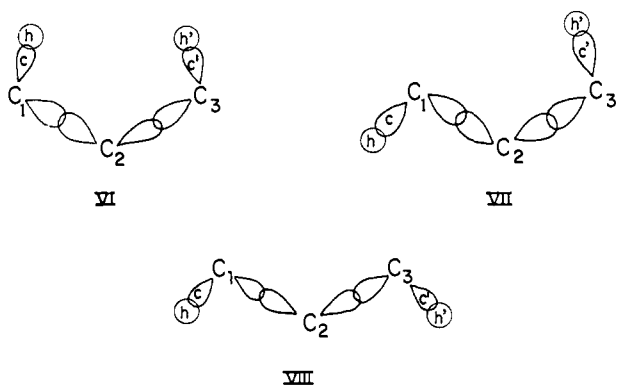(40) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., B*, 722 (1966).

X
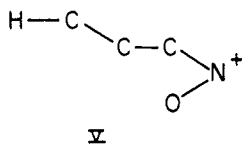
substituted into eq 29, which is appropriate for σ radicals, there results a five-bond H–C–C–C–N–H' coupling of 0.98 cps for $\Delta E = 10$ eV, in reasonable correspondence with the estimates given above. However, this comparison must be regarded as a qualitative one since only a fraction ($\sim$0.5) of the unpaired electron is in a nitrogen σ orbital[41] which is not sp^3 hybridized. There is an indication in the observations of long-range hyperfine splittings in iminoxy radicals[40] that the magnitude does depend on the dihedral angles ϕ and ϕ', but further work on appropriate rigid systems is required to obtain more quantitative information.

III. Mechanism of Contact Nuclear Spin Coupling

In this section, we discuss some of the mechanisms that have been introduced for the interpretation of coupling constants.

A. Direct *vs.* **Indirect Bond-Order Coupling.** The formulation given in eq 23–25 in terms of interbond bond orders provides a separation into "direct" and "indirect" contributions. Here "direct" refers to the $p^0(r,s)$ term, while "indirect" refers to the $p^0(r,\sigma_j)$ $p(\sigma'_j,s)$ terms. As already pointed out, the direct contribution is expected to be dominant when the atoms containing the coupled nuclei are bonded to the same atom or to adjacent atoms, that is, for geminal and vicinal H–H couplings. The direct term can be important for longer range couplings if the conformations are such that the bonds containing the coupled nuclei are sufficiently close to result in nonnegligible values for any or all of the exchange integrals in the numerator of eq 22. An example might be planar conformation (VI–VIII) of a propanic fragment. In the conformation depicted in VI, the C–H bonds are in close proximity and all of the exchange integrals may contribute. In conformation VII, $K(h,h')$ and $K(h,c')$ are probably smaller in magnitude than $K(c,c')$ and $K(h',c)$, whereas in VIII, $K(c,c')$ would be expected to provide the dominant contribution to the direct coupling. In this connection, Meinwald and Lewis[42] have suggested that "rear-lobe" interactions between the hybrid orbitals (corresponding to $K(c,c')$) are an important factor in

VI

VII


VIII

(41) M. C. R. Symons, *J. Chem. Soc.*, 1189 (1963).
(42) J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, 83, 2769 (1961).

conformation VIII of the propanic fragment, although no valence-bond theoretical estimates have been made.

The indirect bond-order terms, which are associated with the second-order sum in eq 25, contribute when the bonds containing the coupled nuclei both have nonnegligible interactions with some other bond in the molecule. For saturated hydrocarbons or unsaturated systems with localized π bonds, only the bonds on nearest neighbor atoms usually are significant, so that the indirect terms must be in either a geminal or vicinal relationship to both of the bonds containing the coupled nuclei. This criterion greatly limits the number of terms which have to be included, as illustrated in section IIB.

B. "Through-Bond" *vs.* **"Through-Space" Coupling.** The dichotomy between "through-bond" and "through-space" coupling has been widely quoted in discussions of coupling constant data.[2,43] However, there appears to be some confusion in the use of this terminology, in part because unambiguous definitions of the assumed mechanisms have not been given. A "through-bond" coupling is here defined as one that is transmitted entirely through the bonds; *i.e.*, by a path which includes the bonds containing the coupled nuclei and one bond between every intervening pair of atoms in the chain linking the coupled nuclei. For directly bonded atoms, this is, of course, the dominant term. Correspondingly, a "through-space" coupling is defined as one that is transmitted entirely through space, *i.e.*, for a pair of atoms which are not bonded, the only important contribution arises from their exchange integral ($K(h,h')$ for protons). The bonds referred to here are the ones implied in the usual chemical formula and the perfect pairing structure.

If the above definitions are employed, it turns out that most proton coupling constants that have been analyzed in detail fall neither into the pure "through-space" or pure "through-bond" class, but are some combination of these two limiting mechanisms. To see this most clearly, we look at the VB description[20] of vicinal coupling in the ethanic fragment, which has been used[2b] as the example for a "through-bond" mechanism and the absence of a "through-space" mechanism. With the labeling of the orbitals in the six-electron fragment (IX) the vicinal H–H coupling, $J_{HH'}$, is given by eq

IX
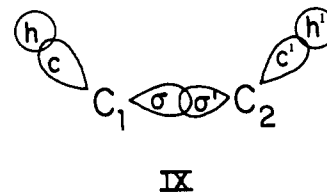
25 as

$$J_{HH'}(vic) = 4185(\Delta E)^{-1}\{p^0(h,h') + $$

$$(3/2)p^0(h,\sigma)p^0(\sigma',h')\} \quad (35)$$

where $p^0(h,h')$ is related to exchange integrals by eq 22

(43) For some recent discussions, see S. Ng and C. H. Sederholm, *J. Chem. Phys.*, 40, 2090 (1964); A. D. Cross, *J. Amer. Chem. Soc.*, 86, 4011 (1964); K. L. Servis and J. D. Roberts, *ibid.*, 87, 1339 (1965); J. Jonas and H. S. Gutowsky, *J. Chem. Phys*, 42, 140 (1965); J. Burdon, *Tetrahedron*, 21, 1101 (1965); P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, 88, 2459 (1966).

$$p^0(h,h') =$$

$$(1/2)\left\{\frac{K(h,h') + K(c,c') - K(c,h') - K(c',h)}{K(c,h) + K(c',h')}\right\} \quad (36)$$

If only nearest neighbor exchanges are included[20] and $K(c,h) = K(c',h')$, $p^0(h,h')$ reduces to

$$p^0(h,h') = \{K(c,c')/4K(c,h)\} \quad (37)$$

Since $K(c,c')$ varies with dihedral angle ϕ between the vicinal hybrids[7,37,44] according to

$$K(c,c') = A\cos^2\phi + B\cos\phi + C \quad (38)$$

where A, B, and C are constants for the particular system, the $p^0(h,h')$ contribution to $J_{HH'}$ has a corresponding angular dependence. By contrast, the second term in eq 35 arises as a product of two geminal bond orders, $p^0(h,\sigma)$ and $p^0(\sigma',h')$ which can have no dependence on dihedral angle. It is well known from experiment and confirmed by calculations that the vicinal coupling varies with dihedral angle approximately as in eq 38; thus we can write[37]

$$J_{HH'} \cong 4185(\Delta E)^{-1}p^0(h,h') =$$

$$A'\cos^2\phi + B'\cos\phi + C' \quad (39)$$

Because $K(h,h')$ has been neglected in eq 37 for $p^0(h, h')$, there is no pure through-space contribution to $J_{HH'}(vic)$. Furthermore, $p^0(h,h')$ and, therefore, $J_{HH'}(vic)$ as written in eq 39, contains no pure "through-bond" term since $K(c,c')$ involves an interaction between the nonbonded orbitals c and c', and skips the intervening bond $\sigma-\sigma'$.

The constants A, B, C in eq 38 and A', B', C' in eq 39 depend on a number of parameters; they vary with the C–C distance, the hybridization of c and c', etc.[37] As $K(c,c')$ can be resolved into a sum of exchange integrals over s and p orbitals on the carbons, so can the constants A, B, C.[7,27] The largest contribution comes from the 2p orbitals which are π orbitals with respect to the C–C' bond. This term is the main part of the coefficient A of the $\cos^2\phi$ dependence in eq 38 and 39 and was used to relate the esr hyperfine interactions to the vicinal coupling in section IIA (see eq 31). The $\cos\phi$ term in the vicinal interaction, which was neglected in eq 31, leads to the fact that $J_{HH'}(trans) > J_{HH'}(cis)$ and is regulated by $\sigma-\pi$ exchange interactions. Of course, for particular dihedral angles ($\phi \cong 90°$), the values of $K(c,c')$ and $p^0(h,h')$ are small, so that the through-bond term $p^0(h,\sigma)p^0(\sigma',h')$ may make a significant contribution. This produces a small change in the constant C' in eq 39, relative to the value obtained from $p^0(h,h')$ above.

For general saturated hydrocarbons, "through-bond" couplings correspond to paths involving each σ bond in the intervening chain of atoms. This type of contribution has been emphasized by Koide and Duval[4] in their Dirac vector-model formulation of the coupling problem.[3,45] These authors neglected all exchange interactions except those which correspond to the alternating intraatomic Hund coupling and covalent binding in the path connecting the coupled nuclei. For the vicinal case, the resulting contribution is just the small term $p^0(h,\sigma)p^0(\sigma',h')$ discussed above. For longer range coupling, the Duval–Koide "through-bond" term, which is now of third or higher order, remains independent of the dihedral angles of the system. Again, the bulk of the experimental evidence indicates that the dihedral angles are important, so that the through-bond contribution appears to be negligible with respect to other terms for the couplings of protons separated by no more than five bonds.[35]

As to the "through-space" mechanism, it is, of course, possible that protons, which are separated by many bonds, might be so close together that the coupling can be approximated by

$$J_{HH'} \cong 4185(\Delta E)^{-1}p^0(h,h') \cong$$

$$4185(\Delta E)^{-1}\left\{\frac{K(h,h')}{2[K(c,h) + K(c',h')]}\right\} \quad (40)$$

where the orbitals are defined as in the ethanic fragment. Such a "through-space" coupling is most likely to be found in an "overcrowded molecule,"[46] but experimental evidence for its existence seems to be lacking. For the coupling between fluorines, it has been suggested[2,43] that a corresponding "through-space" mechanism is the dominant term, but even here the experimental evidence is not compelling.

Appendix

A "mean excitation energy" in the second-order perturbation sum (eq 3) has been used in this paper as in most previous VB calculations of coupling constants. Justification[3,47] of the mean energy formula has been based on the assumption that, for molecular systems in which deviations from a localized bond description are small, the triplets which are of importance in the perturbation sum are localized triplets, *i.e.*, those which can be expressed as functions which differ from the perfect pairing structure by having the spins of one electron pair coupled to give a triplet bond function instead of a singlet bond function. A theoretical treatment of this type has been given by Duval[48] in terms of the Dirac vector formalism. The resulting perturbation expressions are almost identical with those based on the mean energy approximation.[7,44] Since larger magnitudes of coupling constants are obtained in a theoretical VB treatment[8] which includes both the localized and delocalized triplets, it now appears that the latter may be significant. The delocalized triplets differ from the nonperfect pairing singlets by having the spin of a "long-bonded" pair coupled to give a triplet. To clarify the effect of summation over VB triplets, we carry out a four-electron perturbation treatment. It results in an expression for the coupling constant which is proportional to that obtained in the mean energy approximation. Although the calculated magnitudes are greater, the discussion of the coupling mechanism is not affected.

In correspondence with eq 1, we write the triplet VB wave function, $^3\Psi_\kappa$, as

$$^3\Psi_\kappa = \sum_l c_{\kappa l}{}^3\psi_l \quad (A1)$$

(44) P. Chandra and P. T. Narasimhan, *Mol. Phys.*, 11, 189 (1966).
(45) H. M. McConnell, *J. Chem. Phys.*, 23, 2454 (1955).

(46) M. A. Ali and C. A. Coulson, *J. Chem. Soc.*, 1558 (1959); F. A. L. Anet, A. J. R. Bourn, P. Carter, and S. Winstein, *J. Amer. Chem. Soc.*, 87, 5249 (1965).
(47) M. Karplus, *J. Chem. Phys.*, 33, 941 (1960).
(48) E. Duval, *ibid.*, 45, 2855 (1966).

where the $^3\psi_i$'s are sets of canonical triplet structures; and the $c_{\kappa i}$'s are expansion coefficients for state $^3\Psi_\kappa$.[49] Introducing the $^3\Psi_\kappa$ and $^1\Psi_0$ into the second-order perturbation summation formula for the coupling constant[10] and making use of the appropriate superposition diagrams, one finds[8]

$$J_{NN'} = -(2h)^{-1}(16\pi\beta\hbar/3)^2\gamma_N\gamma_{N'}\phi_t{}^2(N)\phi_u{}^2(N') \times$$

$$\sum_\kappa[E_\kappa - E_0]^{-1}\sum_{jklm}(1/2)^{2n-i_{jl}-i_{km}}c_jc_{\kappa l}c_kc_{\kappa m}f_{jl}{}^tf_{km}{}^u \quad (A2)$$

In eq A2, $\phi_t{}^2(N)$ and $\phi_u{}^2(N')$ denote the densities of orbitals t and u at nuclei N and N', respectively. In the superposition diagram of the singlets and triplets, i_{jl} is the number of islands, and $f_{jl}{}^t$ equals $+1$ or -1 if t occupies an even (β spin) or an odd (α spin) position, respectively, in the Rumer diagrams and if t is in an island which contains a broken bond. If t is an island which does not contain a broken bond, the factor $f_{jl}{}^t$ is zero.

For the four-electron, two-bond fragment (r–r', s'–s) with $K(r,r') = K(s,s')$, the assumption that deviations from perfect pairing are small leads to the following approximate ground-state wave function and energy (see eq 18–21)

$$\left.\begin{array}{c} {}^1\Psi_0 = c_1{}^1\psi_1 + c_2{}^1\psi_2 \\[4pt] c_1 \cong 1 \\[6pt] c_2 \cong \dfrac{K(r,s) + K(r',s') - K(r,s') - K(r',s)}{4K(r,r')} \end{array}\right\} \quad (A3)$$

and

$$^1E_0 \cong 2K(r,r') = 2K(s',s) \quad (A4)$$

There are three triplet canonical structures[49]

$$^3\psi_1(r\text{---}r',s'\text{--}s); \quad ^3\psi_2(r\text{---}s, r'\text{--}s');$$
$$^3\psi_3(r\text{--}r',s'\text{---}s) \quad (A5)$$

which can be combined to give a symmetric triplet

$$^3\Psi_s = (1/\sqrt{2})(^3\psi_1 - {}^3\psi_3) \quad (A6)$$

with energy

$$^3E_s = -[K(r,s) + K(r',s')] \quad (A7)$$

and two antisymmetric triplets

$$^3\psi_I = (1/\sqrt{2})(^3\psi_1 + {}^3\psi_3) \quad (A8)$$

$$^3\psi_{II} = {}^3\psi_2 \quad (A9)$$

For the latter, the Hamiltonian and overlap matrix elements are

$$H(I,I) = -[K(r,s') + K(r',s)] \quad (A10a)$$

$$H(II,II) = -K(r,r') + K(r',s') - K(r,s) - (1/2)K(r,s') - (1/2)K(r',s) \quad (A10b)$$

$$H(I,II) = (1/\sqrt{2})[K(r',s') - K(r,s) - K(r,s') - K(r',s)] \quad (A10c)$$

$$S(I,I) = S(II,II) = 1 \quad (A10d)$$

$$S(I,II) = (1/\sqrt{2}) \quad (A10e)$$

Assuming that the interbond exchanges are small in

(49) A. D. McLachlan, *J. Chem. Phys.*, **33**, 663 (1960).

comparison with the intrabond exchanges, the following approximate antisymmetric energies are obtained

$$^3E_{A1} \cong -[K(r,s') + K(r',s)] \quad (A11)$$

$$^3E_{A2} \cong -2K(r,r') \quad (A12)$$

and the lowest triplet-state wave function is

$$^3\Psi_{A1} = c_{A1,1}{}^3\psi_I + c_{A1,2}{}^3\psi_{II}$$

where

$$\begin{array}{c} c_{A1,1} \cong [K(r,r')]^{-1}\{(1/2)\{[K(r,r')]^2 + q\}\}^{1/2} \\[4pt] c_{A1,2} \cong -q[K(r,r')]^{-1}\{2\{[K(r,r')]^2 + q\}\}^{-1/2} \end{array} \quad (A13)$$

in which q contains terms linear and quadratic in the interbond exchange integrals.

With neglect of the negligible contributions from the highest energy triplet and terms of second order or higher in $c_{A1,2}$ and c_2, the approximate expression for the contact coupling is obtained from eq A2

$$J_{NN'}(S + A1) \cong -a\left[\left(\frac{(1/2)c_1{}^2}{^3E_s - {}^1E_0}\right) - \left(\frac{(1/2)c_{A1,1}c_1{}^2 + (1/2)c_{A1,1}c_{A1,2}c_1{}^2 + c_1c_2c_{A1,1}{}^2}{^3E_{A1} - {}^1E_0}\right)\right] \quad (A14)$$

where $a = -(18h)^{-1}(16\pi\beta\hbar)^2\gamma_N\gamma_{N'}\phi_r{}^2(N)\phi_s{}^2(N')$. With the ground-state energy and coefficients given in eq A3 and A4, the excited-state energies in eq A7 and A11, first-order coefficients

$$c_{A1,1} = 1 - (1/2)\left[\frac{K(r',s') - K(r,s)}{K(r,r')}\right]$$

$$c_{A1,2} = \frac{1}{\sqrt{2}}\left[\frac{K(r',s') - K(r,s)}{K(r,r')}\right] \quad (A15)$$

and energy denominators expanded to first order, e.g.

$$\frac{1}{^3E_s - {}^1E_0} = \frac{1}{-[K(r,s) + K(r',s')] - 2K(r,r')} \cong$$
$$-\frac{1}{2K(r,r')}\left\{1 - \frac{[K(r,s) + K(r',s')]}{2K(r,r')}\right\} \quad (A16)$$

we obtain

$$J_{NN'}(S + A1) \cong$$
$$-a\left[\frac{K(r,s) + K(r',s') - K(r,s') - K(r',s)}{4\{K(r,r')^2\}}\right] \quad (A17)$$

In deriving eq A17, it is to be noted that all the contributions due to delocalization in the function $^3\psi_{A1}$ have cancelled to first order. Thus the coupling constant is given by eq A17 even if *localized* triplets are used with coefficients

$$c_{A1,1} = c_s = 1; \quad c_{A1,2} = 0 \quad (A18)$$

and energies given by eq A7 and A12. However, if one assumes that $\Delta E = {}^3E_{A1} - {}^1E_0 = {}^3E_s - {}^1E_0$.

$$J_{NN'}(S + A1) =$$
$$a(\Delta E)^{-1}\left[\frac{K(r,s) + K(r',s') - K(r,s') - K(r',s)}{4K(r,r')}\right] \quad (A19)$$

If ΔE in eq A19 is taken to be $-2K(r,r')$ as was done by Duval,[48] the coupling constants calculated from eq A17 are twice those based on eq A19. It is important to

note that the difference between eq A17 and A19 need not be interpreted as a consequence of delocalization of the $^3\Psi_{A1}$ state; instead, as outlined above, it results in this simple case from the splitting of the excited-state degeneracy in forming the correct localized $^3\Psi_s$ and $^3\Psi_{A1}$ functions. Moreover, the dependence on the exchange parameters is the same in any case. Thus the qualitative considerations of mechanisms of contact coupling

do not depend on whether a sum over excited states or an average energy is employed. Which approach is better for deriving quantitative results is not clear and will require detailed calculations on simple systems for its elucidation.[50]

(50) For some discussion of the difficulties, see D. S. Bartow and J. W. Richardson, *J. Chem. Phys.*, **42**, 4018 (1965); and Y. Kato and A. Saika, *ibid.*, **46**, 1975 (1967).

Structures and Conformations of the Cyclohexadienes

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Abstract: The structures of 1,3-cyclohexadiene and 1,4-cyclohexadiene in the gas phase were determined by electron diffraction. Interatomic distances and mean-square amplitudes of vibration were evaluated. In neither molecule are the carbon atoms coplanar; the structure found for the 1,3 isomer is in good agreement with the available microwave data. Of particular interest was the magnitude of the dihedral angle in the 1,4 isomer; it was found to be 159.3°. Here the copolanar conformation was expected from estimates of nonbonded repulsions. This pair of isomers provides critical test structures for the several sets of empirically parametrized potential functions proposed for calculating strain energies of cyclic hydrocarbons.

Conclusions regarding the structure of 1,4-cyclohexadiene are contradictory. Raman and ir spectra[1] have been interpreted in terms of a conformation which deviates only slightly from planar (D_{2h}). Crystal-structure analyses of two compounds which incorporate 1,4-C_6H_8 rings have been reported. In 9,10-dihydroanthracene[2] the ring is folded about the axis through the methylene carbon atoms with a dihedral angle of about 145°. On the other hand, the crystallographic data for 9,10-dihydro-1,2:5,6-dibenzoanthracene[3] show a centrosymmetric structure which eliminates the possibility of a folded 1,4-C_6H_8 ring. Dipole moment measurements of 1,4-dichloro-1,4-cyclohexadiene[4] led to reduced values of $\mu = 0.3$ or 0.42 D, depending on the correction assumed for atomic polarization; from these, dihedral angles of 152 and 160°, respectively, were derived. Dipole moment measurements on 1,4-C_6H_8[5] suggested a small dipole moment, $\mu = 0.13$ D, but the experimental error is too large to distinguish between the planar and boat conformations. Herbstein[6] concluded from semiempirical calculations that angle strain and steric interactions (H···H only) should lead to a minimum energy at a dihedral angle of 140°.

On the basis of chemical arguments Beckett and Mulley[7] suggested a nonplanar structure for the 1,3-cyclohexadiene ring in 9,10-dihydrophenanthrene. Butcher[8] reported microwave absorption data for 1,3-

cyclohexadiene, using the normal isotopic species. When he assumed generally accepted bond lengths and angles, he could deduce a torsional angle τ (the angle by which one ethylene group is rotated relative to the other ethylene group about the C_2-C_3 bond; see Figure 7). From his experimental value for $(I_a + I_b - I_c)/2$, he found $\tau = 17.5 \pm 2°$.

Experimental Section

A very pure sample of 1,4-C_6H_8 was obtained from Dr Michael Gorfinkel, Institute of Organic Chemistry, University of Novosibirsk, to whom sincere thanks are due. Additional material and the 1,3 isomer were purchased from the K & K Laboratories (99% purity for 1,3-C_6H_8 and 95-99% for 1,4-C_6H_8). Single-step distillations from samples maintained at -35 and $-25°$, respectively, corresponding to the sample temperatures used for the electron diffraction photographs, gave material which was better than 99%, as checked by vpc.

For each compound three sets of photographs were taken: one at low voltage (*ca.* 25 kV) and at a long sample–plate distance (*ca.* 26 cm), and two sets at high voltage (*ca.* 75 kV) at the same distance and at a shorter distance (*ca.* 13 cm). The vapor pressures were kept at 3–4 torr. With liquid nitrogen cooled cryopumps situated above the gas nozzle the ambient pressure in the diffraction chamber was maintained at about 1.5×10^{-5} torr during the exposures. The sample–plate distance (L) and wavelength (λ) were determined by a least-squares fit on six measured ring diameters of several MgO calibration photographs. The maximum standard deviation in q(ring) was 0.0012 in the case of high voltage–short distance: $q = (40/\lambda) \sin (\theta/2)$.

Density–Intensity Calibration. Each set of photographs consisted of four plates. Two plates of each set, with a time–exposure ratio of about 1/1.5 were selected for the density–intensity calibration, following the procedure proposed by Bauer and Kimura.[9] The optical densities of the selected plates were between 0.5 and 1.5. The first two coefficients of the power series, $I = D(1 + B_1D + B_2D^2)$, where D is the optical density and I the corresponding intensity, were determined by a least-squares procedure. The B_i's

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