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Spin−Orbit Coupling in Biradicals. 1. The 2-Electrons-in-2-Orbitals Model Revisited

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Abstract: The two-electrons-in-two-orbitals active space model of electronic structure of biradicals and biradicaloids is extended to a Hamiltonian that incorporates the usual kinetic and electrostatic energy terms, and also outside electric and magnetic fields, spin−spin dipolar terms, and one- and two-electron spin−orbit coupling terms. It leads to a more rigorous version of the Salem−Rowland rules for the dependence of T_1−S_0 spin−orbit coupling (SOC) in biradicals and biradicaloids on molecular structure and conformation. For large T_1−S_0 SOC in a bitopic biradical, (i) the localized orbitals *A* and *B* that are singly occupied in the T_1 state either interact covalently or one of them is sufficiently lower in energy to have nearly double occupancy in the S_0 state, (ii) on at least one atom of reasonably high atomic number one p orbital contributes strongly to *A* and another to *B*, and (iii) the atomic contributions add constructively rather than destructively. The nature of this addition is such that inverse heavy atom effects on SOC are possible. Through-bond coupling is essential and its effects are apparent from simple resonance structures, illustrated on α,ω-alkanediyl biradicals. Implications for the zero-field splitting parameters of triplet states are noted.

Introduction

In triplet photochemical reactions,[1,2] excitation of organic molecules from the ground state (S_0) into the lowest triplet state (T_1) triggers geometrical changes, followed by intersystem crossing (ISC) to S_0 and by further geometrical changes associated with thermal equilibration. The structure and efficiencies of formation of the products depend on (i) the nature of the motions executed in the T_1 state, (ii) the probability of ISC at the various geometries reached in T_1, and (iii) the motions executed after return to the S_0 state.

Factors (i) and (iii) are governed by the shapes of the T_1 and S_0 energy hypersurfaces, the temperature, and the rate of vibrational equilibration with the environment. In solutions, vibrational equilibration with the solvent is fast. Transition state theory can be used for the description of motion on the T_1 surface, and steepest descent for the description of the final motion on the S_1 surface.[3] In the low-pressure gas phase, vibrational equilibration with the environment is slow and RRKM theory can be used to describe the fate of the very energetic S_0 molecules produced by the ISC, almost independently of the geometry at which ISC occurred (hot ground state reactions). Our present interest is in solution reactions, in which the geometry of return to the S_0 state plays a paramount role.

Much effort has gone into the calculation of the T_1 and S_0 surfaces and into the rationalization of their shapes (e.g., using correlation diagrams).[4] The T_1 surface tends to have low-energy regions at three types of geometries:[3,4] those where S_0 also has a minimum, those of triplet exciplexes, and "biradicaloid geometries", with two roughly nonbonding molecular orbitals (MOs) each occupied by one electron. In solution photochemistry, ISC at biradicaloid geometries is particularly important, since it provides access to new S_0 minima and therefore frequently leads to photochemical transformations.

Factor (ii), the T_1−S_0 ISC rate as a function of molecular geometry, is less well understood. In biradicals with well separated radical centers, hyperfine interactions provide the main ISC mechanism.[5,6] However, in those with radical centers close together, of most interest to us presently, spin−orbit coupling[7−9] (SOC) is believed to be dominant. Among the factors that determine the ISC rate, the Franck−Condon weighted density of states plays a similar role as it does in S_1−S_0 internal conversion, but the ISC rate from a triplet sublevel T_u to a singlet S_j is also proportional to the square of the SOC matrix element $\langle T_u|\hat{H}^{SO}|S_j\rangle$.

If the populations of the three sublevels are in rapid equilibrium on the time scale of triplet lifetime, the T_1 to S_j ISC rate is dictated by the scalar

$$SOC_j = (|\langle T_x|\hat{H}^{SO}|S_j\rangle|^2 + |\langle T_y|\hat{H}^{SO}|S_j\rangle|^2 + |\langle T_z|\hat{H}^{SO}|S_j\rangle|^2)^{1/2}$$

This can be thought of as the length of a vector $\boldsymbol{SOC}_j$ with components $\langle T_u|\hat{H}^{SO}|S_j\rangle$ (the "spin−orbit coupling vector" for T_1−S_j).

The present basis for qualitative understanding of the structural dependence of $\langle T_u|\hat{H}^{SO}|S_0\rangle$ at biradicaloid geometries is an analysis by Salem and Rowland[10] performed for the 2-in-2 model of biradical electronic structure (active space: two electrons in two orbitals, also known as the 3×3 CI model[10−15]). Assuming that the biradical has two completely localized

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(1) (a) Turro, N. J *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991. (b) Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, FL, 1991. (c) Kopecky, J. *Organic Photochemistry*; VCH: New York, NY, 1992.

(2) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH: New York, NY, 1995.

(3) Michl, J. *Top. Current Chem.* **1974**, *46*, l.

(4) Michl, J.; Bonačić-Koutecký, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, NY, 1990.

(5) Turro, N. J.; Kraeutler, B. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 259. Forbes, M. D. E.; Ruberu, S. R. *J. Phys. Chem.* **1993**, *97*, 13223. See also: Buchachenko, A. L. *Chem. Rev.* **1995**, *95*, 2507.

(6) Closs, G. L.; Forbes, M. D. E.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285.

(7) Richards, W. G.; Trivedi, H. P.; Cooper, D. L. *Spin−Orbit Coupling in Molecules*; Clarendon Press: Oxford, 1981.

(8) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

(9) Ellis, R. L.; Jaffé, H. H. In *Modern Theoretical Chemistry*; Segal, G., Ed.; Plenum: New York, 1977; Vol. 8, p 74.

(10) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(11) Michl, J. *Mol. Photochem.* **1972**, *4*, 257.

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radical-carrying orbitals *A* and *B* with some p character, they found that strong SOC was favored by three factors: (i) orthogonality of the axes of the two p orbitals, in keeping with the El-Sayed rules[16] for ISC in aromatics, (ii) "ionic" (zwitterionic, hole-pair) character in the S_0 wave function, and (iii) spatial proximity of the orbitals *A* and *B*.

A fair amount of theoretical work on spin−orbit coupling in biradicals and biradicaloids followed Salem and Rowland's original paper. Shaik and Epiotis[17] analyzed qualitatively various reaction paths involving biradicaloid geometries but their assumption of a closed-shell (single determinant) S_0 wave function appears hard to justify. The *ab initio* results of Carlacci et al.[18] for the trimethylene biradical were compatible with the Salem−Rowland rules. Additional computational results have been obtained for 1,2,[19−24] 1,3,[21,22,24−26] and 1,4[21,25,27] biradicals.

In the present paper, we elaborate and illustrate our restatement[2,4,22,28] of the Salem−Rowland rules. Regarding the need for "ionic" character, we show that only the introduction of the symmetrized hole-pair structure ($A^2 + B^2$) into the S_0 wave function of a perfect biradical is helpful for SOC (in all but axial[13] biradicals, a weak polarization of the S_0 state fails to introduce the symmetrized hole-pair structure and does not help). The effect of the two-electron part of the SOC operator, ignored by Salem and Rowland,[10] is found to be negligible.

We also consider explicitly the delocalization of *A* and *B* into the saturated skeleton and the resulting vectorial one- and two-center contributions from orbital pairs on individual atoms,[2,4,22,28] which can interfere constructively or destructively. The mode of interference can often be discerned from molecular symmetry. Numerical results demonstrate that this through-bond mechanism dominates SOC in biradicals. Against the original expectations,[10] the through-space distance between *A* and *B* plays a subordinate role. We illustrate the results on α,ω-alkanediyl biradicals. Finally, we caution that the 2-in-2 model, on which the rules are based, is only valid for bitopic biradicals.

Subsequent papers in this series describe *ab initio* computations of spin−orbit coupling in a wide variety of biradicals and biradicaloids, and analyze the results for the bitopic ones in terms of the presently discussed algebraic 2-in-2 model.

Results and Discussion

States of an Electron Pair. We first summarize the states of two electrons confined to two orbitals in the absence of spin-orbit coupling.[4,12−14,28,29]

(a) One-Electron Functions. The spin space is spanned by the orthonormal spin functions α and β, and the orbital space by the two most localized orthonormal orbitals *A* and *B* (minimal interorbital and maximal intraorbital electron−electron repulsion). The two spaces are isomorphic, and we use the symbol *a* when either α or *A* is meant, and the symbol *b* when either β or *B* is meant.

The equivalence of any two-level problem to the problem of a particle of spin $^1/_2$ in magnetic field[30] results from the fact that any Hermitean 2×2 matrix is fully characterized by its four complex elements. The average of the diagonal elements is chosen as the energy zero h_0, and their difference as well as the real and imaginary parts of the off-diagonal element can be thought of as three components of a real vector $\boldsymbol{h}$, h_x, h_y, and h_z:

$$h_0 = (\{a|\hat{h}_1|a\rangle + \langle b|\hat{h}_1|b\rangle)/2$$

$$h_x = \mathrm{Re}\langle a|\hat{h}_1|b\rangle$$

$$h_y = \mathrm{Im}\langle a|\hat{h}_1|b\rangle$$

$$h_z = (\langle a|\hat{h}_1|a\rangle - \langle b|\hat{h}_1|b\rangle)/2$$

In the spin space, $\boldsymbol{h} = (g\beta_e/2)\boldsymbol{B}$, where the *g* factor is close to 2, β_e is the Bohr magneton, and $\boldsymbol{B}$ is external magnetic field, with components B_x, B_y, and B_z in real space. In an unperturbed system, $\boldsymbol{B} = \boldsymbol{h} = 0$, both eigenstates have zero energy, and are described by the functions α and β or their arbitrary linear combinations.

In orbital space, $\boldsymbol{h}$ vanishes for an unperturbed perfect biradical, which has two orbitals of zero energy, described by the functions *A* and *B* or their arbitrary linear combinations. Analogous to the three components of $\boldsymbol{B}$, one-electron perturbations of a perfect biradical come in three distinct flavors, and these correspond to the three components of vector $\boldsymbol{h}$ in the abstract space of biradicaloid structure.

The one-electron part of covalent perturbation, $h_x = \mathrm{Re}\langle A|\hat{h}_1|B\rangle$, produces a homosymmetric biradicaloid.[13,14,31] This perturbation can be introduced only by a change in molecular structure, not by introduction of an outside field. It is equivalent to the Hückel resonance integral between the localized orbitals *A* and *B*. An example is the untwisting of ethylene away from the 90° twist angle.

The magnetizing perturbation, $h_y = \mathrm{Im}\langle A|\hat{h}_1|B\rangle$, produces a magnetized biradical. It cannot be introduced by a change in molecular structure, but only by introduction of an outside magnetic field. An example is an O_2 molecule placed in magnetic field directed along the molecular axis.

The one-electron part of polarizing perturbation, $h_z = (\langle A|\hat{h}_1|A\rangle - \langle B|\hat{h}_1|B\rangle)/2$, produces a heterosymmetric biradicaloid.[13,14,31] It can be introduced either by a change in the molecular structure of the biradical or by imposition of an

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[12] Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 1.

[13] Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170.

[14] Michl, J.; Bonačić-Koutecký, V. *Tetrahedron* **1988**, *44*, 7559.

[15] Michl, J. *J. Mol. Struct. (Theochem.)* **1992**, *260*, 299.

[16] El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834. Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199.

[17] Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*,18; **1980**, *102*, 122. Shaik, S. *J. Am. Chem. Soc.* **1979**, *101*, 3184.

[18] Carlacci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323.

[19] Caldwell R. A.; Carlacci, L.; Doubleday, C. E. J.; Furlani, T. R.; King, H. F.; McIver, J. W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6901.

[20] Caldwell, R. A.; Jacobs, L. D.; Furlani, T. R.; Nalley, E. A.; Laboy, J. *J. Am. Chem. Soc.* **1992**, *114*, 1623.

[21] Helms, A. M.; Caldwell, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 358.

[22] Michl, J., U. S.−Japan Binational Seminar *New Aspects of Molecular Photochemistry in Photoconversion*; University of Tsukuba, Japan, April 13−17, 1992. Michl, J.; Downing, J. W. *Book of Abstracts*; IAPS 5th Winter Conference, Clearwater Beach, FL, January 2−6, 1993; p 10.

[23] Minaev, B. F.; Jonsson, D.; Norman, P.; Ågren, H. *Chem. Phys.* **1995**, *194*, 19.

[24] Böckmann, M.; Klessinger, M.; Zerner, M. C. *J. Phys. Chem.* **1996**, in press.

[25] Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 9795.

[26] Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577.

[27] Morita, A.; Kato, S. *J. Phys. Chem.* **1993**, *97*, 3298.

[28] Michl, J. In *Theoretical and Computational Models for Organic Chemistry*; Formosinho, S. J., Csizmadia, I. G., Arnaut, L. G., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 207.

[29] For additional detail, see refs 15 and 28.

[30] Cohen-Tannoudji, C.; Diu, B.; Laloë, F. *Quantum Mechanics*; Wiley: New York, NY, 1977.

[31] Our definitions[13,14] of homosymmetric, heterosymmetric, and nonsymmetric biradicaloids differ slightly from those originally introduced by Salem and Rowland.[10]

[32] E.g.: Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper and Row: New York, 1967.

[33] Weltner, W., Jr. *Magnetic Atoms and Molecules*; Van Nostrand Reinhold: New York, 1983.

[34] We could have equally well chosen to rotate to the most delocalized orbitals instead, and this would have only had the effect of interchanging the significance of the labels *x* and *z* in the singlet subspace.

outside electric field with a nonvanishing component along the line that connects the centers of the orbitals A and B. Both of these perturbations make the energies of these localized orbitals different, and a polarizing perturbation is equivalent to the introduction of a difference between the Hückel Coulomb integrals of orbitals A and B. Examples are 90° twisted aminoborane, or similarly twisted ethylene placed in an electric field with a non-zero component along the CC axis.

In general, more than one of the perturbations may be present simultaneously (in nonsymmetric[13,14,31] biradicaloids both covalent and polarizing structural perturbations are present).

(b) Two-Electron Functions. Both in spin space and in ordinary space, the two-electron function space is spanned by the four products, $a(1)a(2)$, $a(1)b(2)$, $b(1)a(2)$, and $b(1)b(2)$. Following the usage that is standard for spin space,[32,33] we choose the basis function

$$T \text{ or } \Sigma = 2^{-1/2}[a(1)b(2) - b(1)a(2)]$$

in the subspace that is antisymmetric relative to electron label permutation, and the functions

$$S[x] \text{ or } \Theta[x] = -2^{-1/2}[a(1)a(2) - b(1)b(2)]$$

$$S[y] \text{ or } \Theta[y] = 2^{-1/2}i[a(1)a(2) + b(1)b(2)]$$

$$S[z] \text{ or } \Theta[z] = 2^{-1/2}[a(1)b(2) + b(1)a(2)]$$

in the subspace that is symmetric. For T and S, $a = A$, $b = B$, and for Σ and Θ, $a = \alpha$, $b = \beta$. The phase factors on the right secure cyclic permutation properties with regard to x, y, and z (Appendix).

The total wave functions in the 2-in-2 model are elements in the direct product of the spin space and the orbital (geminal) space. Pauli principle restricts their number to those that are antisymmetric with respect to electron interchange: three singlet levels ($S[u]\Sigma$, $u = x, y, z$) and the three sublevels of a triplet ($T\Theta[u]$, $u = x, y, z$).

The average energy $E(\mathrm{T}_1)$ of the triplet sublevels is

$$\begin{aligned} E(\mathrm{T}_1) = \langle A|\hat{h}_1|A\rangle + \langle B|\hat{h}_1|B\rangle + \\ \langle AB|e^2/r_{12}|AB\rangle - \langle AB|e^2/r_{12}|BA\rangle \\ = h_A + h_B + J_{AB} - K_{AB} \end{aligned}$$

The Hamiltonian matrix simplifies if we first make judicious use of the two available degrees of rotational freedom (Appendix). One of these is the freedom of orbital rotation in the one-electron function space. For a general choice of A and B, the elements $\langle S[x]\Sigma|\hat{H}_2|S[z]\Sigma\rangle$ and $\langle S[z]\Sigma|\hat{H}_2|S[x]\Sigma\rangle$ are nonzero. After rotation in the orbital space to the most localized orthogonal orbitals possible,[34] they vanish. A simple algorithm for finding these orbitals is available.[13] The other degree of freedom is the rotation of the molecular coordinate system in real space. By choosing x, y, and z to coincide with the principal axes of the spin−spin dipolar coupling tensor, we diagonalize its contribution to the triplet block.

With $E(\mathrm{T}_1)$ as the energy zero, the Hamiltonian matrix (1) for the active space of the 2-in-2 model then is

For the moment, we neglect the elements of $\hat{H}^{\mathrm{SO}}$. The matrix then separates into two completely analogous 3×3 blocks, one for the singlets and one for the triplets. We treat them in parallel in order to bring out the formal identity of the results.

We first redefine a structurally perfect biradical as one for which $\gamma_{AB} = \delta_{AB} = 0$. In an unperturbed ($\boldsymbol{E} = \boldsymbol{B} = 0$) perfect biradical, the Hamiltonian matrix is then diagonal, and the six functions $S[u]\Sigma$ and $T\Theta[u]$, $u = x, y, z$, describe the eigenstates.

The energies of the triplet levels are split by up to a cm^{-1} or so by the magnetic dipole−magnetic dipole interaction of the two electrons,

$$D_u = (g^2\beta_{\mathrm{e}}{}^2/2)\langle T|(r_{12}^2 - 3u_{12}^2)/r_{12}^5|T\rangle$$

where $u = x$, y, or z, and r_{12} is the interelectronic distance. The D_x, D_y, and D_z values measure the anisotropy of the electron distribution and add up to zero (we neglect the small electron−electron contact term, which shifts all three levels equally). The molecular axes are usually labeled so as to produce the order $D_z > D_y > D_x$. However, the analogy between the singlet and the triplet subspace is illustrated best if we adopt $D_z > D_x > D_y$, with $T\Theta[z]$ the lowest in energy, and $T\Theta[y]$ the highest.

The energies of the singlet levels are split by ca. 10^3 to 10^4 cm^{-1} by electric charge−charge interactions of the two electrons. The exchange integral K_{AB} between the two localized orbitals A and B is the self-repulsion of their overlap charge density and measures their interpenetration,

$$K_{AB} = \langle AB|e^2/r_{12}|BA\rangle$$

whereas the integral K'_{AB} is related to the separation of their centroids [it is equal to the exchange integral between the two most delocalized orbitals, $2^{-1/2}(A \pm B)$]

$$\begin{aligned} K'_{AB} = [(\langle AA|e^2/r_{12}|AA\rangle + \langle BB|e^2/r_{12}|BB\rangle)/2 - \\ \langle AB|e^2/r_{12}|AB\rangle]/2 \\ = [(J_{\mathrm{AA}} + J_{\mathrm{BB}})/2 - J_{\mathrm{AB}}]/2 \end{aligned}$$

The energy of the $S[z]$ state lies above that of the average of the three nearly degenerate triplet sublevels, and is followed by $S[x]$, with $S[y]$ at the highest energy ($K'_{AB} \geq K_{AB} \geq 0$). In pair biradicals ($K'_{AB} > K_{AB} \simeq 0$),[13] such as orthogonally twisted ethylene, A and B are well separated, the triplet sublevels are nearly degenerate with $S[z]$, and the much higher lying states $S[x]$ and $S[y]$ are also very close in energy to each other. In axial biradicals ($K_{AB} = K'_{AB}$),[13] such as linear carbene, the triplet sublevels lie well below $S[z]$, which is degenerate with $S[x]$, and $S[y]$ is much higher. Most among the perfect biradicals are intermediate between the pair and axial limits.

Perturbation of a perfect biradical by a structural change or by an external field introduces off-diagonal elements into the Hamiltonian matrix. In the triplet subspace, they represent the Zeeman perturbation by the x, y, and z components of an outside magnetic field $\boldsymbol{B}$. In the singlet subspace, they represent a generalization of the one-electron perturbations introduced above, and are due to the covalent interaction between the orbitals A and B (γ_{AB}, analogous to B_x in the spin space), to the

$$\begin{array}{lllllll}
 & S[x]\Sigma & S[y]\Sigma & S[z]\Sigma & T\theta[x] & T\theta[y] & T\theta[z] \\
S[x]\Sigma & 2K'_{AB} & (\delta_{AB} - e\boldsymbol{E}\cdot\mathbf{r}_{AB})/i & 2i\beta_{\mathrm{e}}\boldsymbol{B}\cdot(\hat{\mathbf{r}}\times\nabla)_{AB} & ih_{2xx}^{\mathrm{SO}} & ih_{2xy}^{\mathrm{SO}} & ih_{2xz}^{\mathrm{SO}} \\
S[y]\Sigma & i(\delta_{AB} - e\boldsymbol{E}\cdot\mathbf{r}_{AB}) & 2(K'_{AB} + K_{AB}) & \gamma_{AB}/i & h_{1x}^{\mathrm{SO}} + h_{2yx}^{\mathrm{SO}} & h_{1y}^{\mathrm{SO}} + h_{2yy}^{\mathrm{SO}} & h_{1z}^{\mathrm{SO}} + h_{2yz}^{\mathrm{SO}} \\
S[z]\Sigma & 2\beta_{\mathrm{e}}\boldsymbol{B}\cdot(\hat{\mathbf{r}} \times \nabla)_{AB}/i & i\gamma_{AB} & 2K_{AB} & h_{2zx}^{\mathrm{SO}}/i & h_{2zy}^{\mathrm{SO}}/i & h_{2zz}^{\mathrm{SO}}/i \\
T\theta(x] & h_{2xx}^{\mathrm{SO}}/i & h_{1x}^{\mathrm{SO}} + h_{2yx}^{\mathrm{SO}} & ih_{2zx}^{\mathrm{SO}} & -D_x & g\beta_{\mathrm{e}}B_z/i & ig\beta_{\mathrm{e}}B_y \\
T\theta[y] & h_{2xy}^{\mathrm{SO}}/i & h_{1y}^{\mathrm{SO}} + h_{2yy}^{\mathrm{SO}} & ih_{2zy}^{\mathrm{SO}} & ig\beta_{\mathrm{e}}B_z & -D_y & g\beta_{\mathrm{e}}B_x/i \\
T\theta[z] & h_{2xz}^{\mathrm{SO}}/i & h_{1z}^{\mathrm{SO}} + h_{2yz}^{SO} & ih_{2zz}^{\mathrm{SO}} & g\beta_{\mathrm{e}}B_y/i & ig\beta_{\mathrm{e}}B_x & -D_z
\end{array} \qquad (1)$$

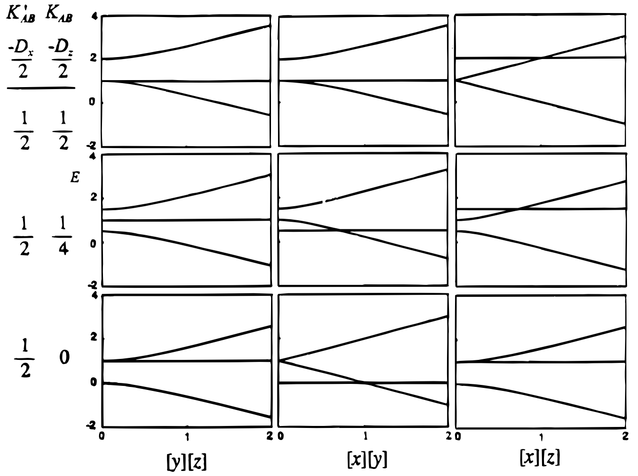

Figure 1. Energies of either (i) the three singlet states or (ii) the three triplet states of the 2-in-2 model of biradical structure in arbitrary units, as a function of the absolute value of the off-diagonal Hamiltonian matrix element, [*y*][*z*] (covalent perturbation for singlets, or magnetic field in *x* direction for triplets), [*x*][*y*] (polarizing perturbation for singlets, or magnetic field in *z* direction for triplets), or [*x*][*z*] (magnetizing perturbation for singlets, or magnetic field in *y* direction for triplets). Top, center, and bottom rows show results for three choices of (i) K_{AB}, K'_{AB} (top, axial biradical, and bottom, pair biradical) or (ii) $-D_z/2$, $-D_x/2$, in the same arbitrary units. The energy labeled zero is (i) equal to or (ii) $-2D_y/3$ below the average triplet energy.

magnetizing perturbation by an outside magnetic field $\boldsymbol{B}$ $[2\beta_e \boldsymbol{B}\cdot(\boldsymbol{r} \times \nabla)_{AB}$, analogous to B_y in the spin space], and to the polarizing perturbation (analogous to B_z in the spin space), induced by molecular structure (δ_{AB}) and/or an outside electric field $\boldsymbol{E}$ ($-e\boldsymbol{E}\cdot\boldsymbol{r}_{AB}$):

$$\gamma_{AB} = \langle A|\hat{h}_1|B\rangle + \langle B|\hat{h}_1|A\rangle + \langle AA|e^2/r_{12}|AB\rangle + \langle BB|e^2/r_{12}|BA\rangle$$

$$\delta_{AB} = \langle A|\hat{h}_1|A\rangle + \langle AA|e^2/r_{12}|AA\rangle/2 - (\langle B|\hat{h}_1|B\rangle + \langle BB|e^2/r_{12}|BB\rangle/2)$$

$$\boldsymbol{r}_{AB} = \langle A|\hat{\boldsymbol{r}}|A\rangle - \langle B|\hat{\boldsymbol{r}}|B\rangle$$

$$(\hat{\boldsymbol{r}} \times \nabla)_{AB} = \langle A|\hat{\boldsymbol{r}} \times \nabla|B\rangle = (i/\hbar)\langle A|\hat{\boldsymbol{l}}|B\rangle$$

with $\hat{\boldsymbol{r}}$ standing for the position operator (the zero differential overlap approximation is used), $e < 0$ for electron charge, $\hat{\boldsymbol{l}}$ for the angular momentum operator, and ∇ for the gradient operator. The three components of $\hat{\boldsymbol{r}} \times \nabla$ are the differential rotations around *x*, *y*, and *z*: $\partial/\partial\xi$, $\partial/\partial\eta$, and $\partial/\partial\zeta$.

The expressions for the energies and eigenfunctions of the Hamiltonian as a function of the three types of perturbation are formally identical in the singlet and the triplet subspace.[15,28] If only one of the three possible perturbations is present, the energies plotted in Figure 1 apply, and are valid equally for the three triplet and the three singlet states, with vastly different energy scales. If two or all three perturbations are present, the curve crossings are generally avoided. The significance of the crossings for singlet photochemistry ("funnels" in S_1), "sudden polarization",[35] orbital angular momentum quenching ("sudden magnetization"), etc., has been discussed.[28]

The lowest singlet state S_0 of an unperturbed perfect biradical is described by the function $S[z]$ (in perfectly axial biradicals, degenerate with $S[x]$). It will be important for spin−orbit coupling that S_0 can acquire partial $S[y]$ character in two linearly independent ways (Figure 1): (i) a covalent perturbation of arbitrary strength causes the "dot−dot" structure $S[z]$ and the "symmetrized hole−pair" structure $S[y]$ to mix through the off-diagonal element γ_{AB}, and (ii) a polarizing perturbation by an off-diagonal element δ_{AB} larger than a critical threshold value δ_0 brings about a state crossing and causes the S_0 state to be described by an uneven mixture of the "symmetrized" and "antisymmetrized" hole−pair structures $S[x]$ and $S[y]$. Since[13]

$$\delta_0 = 2[K'_{AB}(K'_{AB} - K_{AB})]^{1/2}$$

we have $\delta_0 = 0$ in the limit of an exactly axial biradical. In this special case, an arbitrarily small polarizing perturbation will stabilize the $S[x]$ component of the initially degenerate S_0 state by acquisition of some $S[y]$ character. Combinations of the two kinds of perturbation are also possible.

In the way of examples, we note that the S_0 state of orthogonally twisted ethylene, a perfect biradical that is nearly exactly of the pair type (K_{AB} very small), can acquire $S[y]$ character (i) by twisting away from orthogonality and (ii) by polarization in a very strong electric field (e.g., by placing a positive charge of more than 1.735 elementary units on the CC axis at a distance of 1.85 Å from a C atom[13]) or by heteroatom replacement (e.g., going at least to an orthogonally twisted formaldiminium cation or more surely, to aminoborane[13]). Along similar lines, the S_0 state of bent carbene, a heterosymmetric biradicaloid ($\delta > 0$, since orbital *B* has some s character and lower energy), has considerable $S[y]$ character (a weak heterosymmetric perturbation is sufficient since linear carbene is a perfectly uniaxial biradical, with $K'_{AB} = K_{AB}$). The existence of two distinct types of perturbed biradicals for which SOC can be large was noted originally by Salem and Rowland.[10]

Spin−Orbit Coupling. The matrix elements $\langle T_x|\hat{H}^{SO}|S_j\rangle$, $\langle T_y|\hat{H}^{SO}|S_j\rangle$, and $\langle T_z|\hat{H}^{SO}|S_j\rangle$ are responsible for the weak interaction between the singlet and triplet subspaces in the Hamiltonian matrix. The operator $\hat{H}^{SO} = \hat{H}_1^{SO} + \hat{H}_2^{SO}$ describes the interaction of the spin magnetic moments of electrons with the magnetic moments caused by their own orbital motion $[\hat{H}_1^{SO} = \sum_i \hat{h}_1^{SO}(i)]$, and with that of other electrons, as well as the shielding effects of the latter $[\hat{H}_2^{SO} = \sum_{i,j} \hat{h}_2^{SO}(i,j),\ i \neq j]$. Ignoring the presumably negligible effect of an external electric field on this operator, it has the form[36]

$$\hat{h}_1^{SO}(i) = (g\beta_e^2/\hbar^2)\sum_\kappa Z_\kappa |\boldsymbol{r}_\kappa|^{-3}\hat{\boldsymbol{l}}_i^\kappa\cdot\hat{\boldsymbol{s}}_i$$

$$\hat{h}_2^{SO}(i,j) = -(g\beta_e^2/\hbar^2)\, r_{ij}^{-3}[(\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j) \times \hat{\boldsymbol{p}}_i]\cdot(\hat{\boldsymbol{s}}_i + 2\hat{\boldsymbol{s}}_j)$$

where the sum runs over all nuclei κ, Z_κ is the atomic number of nucleus κ, $\hat{\boldsymbol{r}}_\kappa$ is the position operator of the electron relative to nucleus κ, $\hat{\boldsymbol{l}}_i^\kappa$ is the angular momentum operator with nucleus κ taken as the origin, $\hat{\boldsymbol{s}}$ is the spin angular momentum operator, and $\hat{\boldsymbol{p}}$ is the linear momentum operator.

Evaluation of the elements of $\hat{H}^{SO}$ in the Hamiltonian matrix gives

$$h_{1u}^{SO} = g\beta_e^2\sum_\kappa Z_\kappa\langle A||\boldsymbol{r}_\kappa|^{-3}(\hat{\boldsymbol{r}}^\kappa \times \nabla)_u|B\rangle$$

$$h_{2xu}^{SO} = (g\beta_e^2/2)[\langle AB|g_u|AA\rangle - \langle AB|g_u|BB\rangle]$$

$$h_{2yu}^{SO} = (g\beta_e^2/2)i[\langle AB|g_u|AA\rangle + \langle AB|g_u|BB\rangle]$$

$$h_{2zu}^{SO} = (g\beta_e^2/2)\langle AB|g_u|BA\rangle$$

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[35] Bonačić-Koutecký, V.; Bruckmann, P.; Hiberty, P.; Koutecký, J.; Leforestier, C.; Salem, L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 575.

[36] McWeeny, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*; Academic Press: New York, 1969; p 214.

where $u = x, y, z$ and

$$\hat{\boldsymbol{g}} = r_{12}{}^{-3}(\hat{\boldsymbol{r}}_2 - \hat{\boldsymbol{r}}_1) \times (\hat{\nabla}_1 + \hat{\nabla}_2)$$

i.e.,

$$\langle AB|g_u|AA\rangle = \langle A(1)B(2)|r_{12}{}^{-3}[(\hat{\boldsymbol{r}}_2 - \hat{\boldsymbol{r}}_1) \times (\hat{\nabla}_1 + \hat{\nabla}_2)]_u|A(1)A(2)\rangle$$

etc.

All the elements of $\hat{H}_2^{\mathrm{SO}}$ that occur in the Hamiltonian matrix for the active space depend on the overlap density of the localized orbitals A and B and would be neglected in the zero differential overlap approximation. In the case of h_{2zu}^{SO} the overlap density appears twice and this integral is particularly small. The elements h_{2xu}^{SO} vanish exactly in a perfect biradical, in which A and B are equivalent. Our numerical *ab initio* calculations for selected examples with polarized basis sets and configuration interaction of reasonable size[22,37] confirmed that the size of the elements of $\hat{H}_2^{\mathrm{SO}}$ within the active space matrix is indeed negligible and we ignore them in the following. In contrast, the elements of $\hat{H}_2^{\mathrm{SO}}$ that involve both the active space and inner shells are large. After all, $\hat{H}_2^{\mathrm{SO}}$ is primarily due to the shielding of nuclei by inner shell electrons, and provides a contribution that is roughly half the size of that of $\hat{H}_1^{\mathrm{SO}}$ and has the opposite sign. We shall return to this issue below.

To evaluate the elements of $\hat{H}_1^{\mathrm{SO}}$, the orbitals A and B are expressed in terms of an AO basis:

$$|A\rangle = \sum_{\mu} c_{A\mu}|\mu\rangle$$

$$|B\rangle = \sum_{\nu} c_{B\nu}|\nu\rangle$$

and h_{1u}^{SO} becomes a triple sum over atom labels κ and orbital labels μ and ν:

$$h_{1u}^{\mathrm{SO}} = g\beta_{\mathrm{e}}^2 \sum_{\kappa} Z_{\kappa} \sum_{\mu}\sum_{\nu} c_{A\mu}c_{B\nu}\langle\mu||\boldsymbol{r}_{\kappa}|^{-3}(\boldsymbol{r}_{\kappa} \times \nabla)_u|\nu\rangle$$

For the atomic basis set we use the pre-orthogonal natural hybrid orbitals introduced by Weinhold.[38] Each of these is strictly localized on a single atom and orthogonal to other hybrid orbitals located on the same atom but not to hybrid orbitals located on other atoms.

As shown by numerical evaluation[37] for selected examples, the contributions to h_{1u}^{SO} provided by nucleus κ and those pairs of natural hybrid orbitals that are not both centered on κ are very small due to the factor $|\boldsymbol{r}_{\kappa}|^{-3}$ in the integral, and we shall neglect them. Since the operator $\hat{\boldsymbol{r}}^{\kappa} \times \nabla$ annihilates an s orbital located on κ, the summation is then restricted to non-hydrogen atoms κ only.

In evaluating the remaining terms, in which $|\mu>$ and $|\nu>$ are both located on atom κ, the presence of core electrons, and specifically, the electrons of the inner shells, cannot be ignored. Since the two-electron two-orbital model only deals explicitly with the active space, it is appropriate to account for the effect of the electrons of the fixed core by replacing the factor $g\beta_{\mathrm{e}}^2 Z_{\kappa}|\boldsymbol{r}_{\kappa}|^{-3}$ in the integral by the empirical value of the atomic spin−orbit coupling constant ζ_{κ} for the valence p orbitals on atom κ.[39] Since we are primarily interested in organic molecules, we ignore any contributions to the natural hybrid orbitals made by d AOs and those of an even higher angular momentum. The spin−orbit coupling constant increases rapidly with increasing atomic number Z_{κ}.

Disregarding Rydberg-type orbitals with very low occupancies, each atom κ that carries four valence orbitals contributes a sum over the twelve ordered non-diagonal pairs of its four natural hybrid orbitals. Adding up the two contributions from any of the only six possible hybrid orbital pairs, taken in one and the other order, then produces six numbers:

$$h_{1u}^{\mathrm{SO}} = \sum_{\kappa} \zeta_{\kappa} \sum_{[\mu\nu]\kappa} (c_{A\mu}c_{B\nu} - c_{A\nu}c_{B\mu})\langle\mu|(\hat{\boldsymbol{r}}^{\kappa} \times \nabla)_u|\nu\rangle$$

where κ runs over non-hydrogen atoms and the hybrid orbital pair label $[\mu\nu]\kappa$ ($\mu < \nu$) runs over all six orbital pairs μ,ν on atom κ. Numerical evaluation[22,37] shows that on most atoms, the coefficient products in the parentheses are small, and all contributions are negligible. On some atoms, one and occasionally two or more are large, making a qualitative interpretation of the results facile.

Atomic Vectorial Contributions to SOC. It appears most convenient to base qualitative understanding on the consideration of the vectorial contributions $\zeta_{\kappa}\sum_{[\mu\nu]\kappa}(c_{A\mu}c_{B\nu} - c_{A\nu}c_{B\mu})\langle\mu|\hat{\boldsymbol{r}}^{\kappa} \times \nabla|\nu\rangle$ ($\mu < \nu$) provided by each atom. We therefore view h_{1x}^{SO}, h_{1y}^{SO}, and h_{1z}^{SO} as components of a vector $\boldsymbol{h}^{\mathrm{SO}}$, equal to the sum of all these atomic vectorial contributions. Once the orbitals A and B are known, each atomic vector is readily evaluated, since for orbitals located on atom κ, $(\hat{\boldsymbol{r}} \times \nabla)_z p_x = -p_y$, $(\hat{\boldsymbol{r}} \times \nabla)_z p_y = p_x$, $(\hat{\boldsymbol{r}} \times \nabla)_z p_z = (\hat{\boldsymbol{r}} \times \nabla)_z s = 0$, etc., by cyclic permutation of indices.

The vector $\langle\mu|\boldsymbol{r}^{\kappa} \times \nabla|\nu\rangle$ with components $\langle\mu|(\boldsymbol{r}^{\kappa} \times \nabla)_x|\nu\rangle$, $\langle\mu|(\boldsymbol{r}^{\kappa} \times \nabla)_y|\nu\rangle$, and $\langle\mu|(\boldsymbol{r}^{\kappa} \times \nabla)_z|\nu\rangle$ is perpendicular to the axes of the two hybrid orbitals μ and ν. To determine its sense, the hybrid orbitals are represented by p orbitals drawn with their signs as they appear in the orbitals A and B. Then, ν is rotated so as to make it coincide with μ. When the direction of this rotation is indicated with the curved fingers of the left hand, its thumb points in the direction of $\langle\mu|\boldsymbol{r}^{\kappa} \times \nabla|\nu\rangle$. The absolute direction depends on the arbitrary choice of phase of orbitals A and B, but the relative directions of the atomic contributions, and thus their constructive or destructive interference as they add to form $\boldsymbol{h}^{\mathrm{SO}}$, are independent of this choice. The length of the vector $\langle\mu|\boldsymbol{r}^{\kappa} \times \nabla|\nu\rangle$ is unity if both μ and ν are pure p orbitals with axes at 90° to each other. As s orbital contributions to μ and ν increase, the vector becomes shorter.

A Reformulation of Salem−Rowland Rules for Spin−Orbit Coupling in Biradicals. In terms of state wave functions based on the most localized orbital set A, B, with molecular axes chosen as the principal axes of the spin−spin dipolar coupling tensor, in the absence of outside fields, with the neglect of $\hat{h}_2^{\mathrm{SO}}$, and with the usual definition of triplet zero-field splitting parameters $D = 3D_z/2$ and $E = (D_x - D_y)/2$, the Hamiltonian matrix for the active space of the two-electron two-orbital model takes a simplified form (2) suitable for a discussion of the structural dependence of SOC.

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(37) Havlas, Z.; Downing, J. W.; Michl, J. Unpublished results.

(38) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(39) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.

$$\begin{array}{c|cccccc} & S[x]\Sigma & S[y]\Sigma & S[z]\Sigma & T\theta[x] & T\theta[y] & T\theta[z] \\ \hline S[x]\Sigma & 2K'_{AB} & \delta_{AB}/i & 0 & 0 & 0 & 0 \\ S[y]\Sigma & i\delta_{AB} & 2(K'_{AB}+K_{AB}) & \gamma_{AB}/i & h^{\mathrm{SO}}_{1x} & h^{\mathrm{SO}}_{1y} & h^{\mathrm{SO}}_{1z} \\ S[z]\Sigma & 0 & i\gamma_{AB} & 2K_{AB} & 0 & 0 & 0 \\ T\theta[x] & 0 & h^{\mathrm{SO}}_{1x} & 0 & D/3-E & 0 & 0 \\ T\theta[y] & 0 & h^{\mathrm{SO}}_{1y} & 0 & 0 & D/3+E & 0 \\ T\theta[z] & 0 & h^{\mathrm{SO}}_{1z} & 0 & 0 & 0 & -2D/3 \end{array} \qquad (2)$$

(a) Perfect Biradicals. Consider first a perfect biradical, in which the covalent (γ) and polarizing (δ) structural perturbations vanish. Only the highest energy singlet state, $S[y]\Sigma$, mixes with the triplet sublevels, and its interaction with the *u*th sublevel is dictated by h^{SO}_{1u}.

Since the wave function of the lowest state S_0 is $S[z]\Sigma$ (in axial biradicals, degenerate with $S[x]\Sigma$), we obtain the Salem and Rowland result[10] that in perfect biradicals the triplet sublevels do not couple to S_0 at all. Triplet to lowest singlet conversion by the spin−orbit coupling mechanism requires that the biradical be perturbed to a biradicaloid in order for its S_0 state to acquire at least some and preferably a large amount of $S[y]\Sigma$ character.

(b) Biradicaloids. When γ or δ or both are different from zero, the eigenfunctions of the Hamiltonian, S_j ($j = 0, 1, 2$), acquire the form

$$S_j = C_{jx}S[x]\Sigma + C_{jy}S[y]\Sigma + C_{jz}S[z]\Sigma$$

Using the previously introduced notation, the final general formulas of the 2-in-2 model for the spin−orbit matrix elements, the spin−orbit coupling vector ***SOC***, and the scalar coupling *SOC* between S_0 and the sublevels of T_1 are

$$\langle T_u|\hat{H}^{\mathrm{SO}}|S_0\rangle = C_{0y}h^{\mathrm{SO}}_{1u} = C_{0y}\sum_{\kappa}\zeta_{\kappa}\sum_{[\mu\nu]\kappa}(c_{A\mu}c_{B\nu} - c_{A\nu}c_{B\mu}) \times \langle\mu|(\hat{\boldsymbol{r}}^{\kappa} \times \nabla)_u|\nu\rangle$$

$$\boldsymbol{SOC} = C_{0y}\boldsymbol{h}^{\mathrm{SO}} = C_{0y}\sum_{\kappa}\zeta_{\kappa}\sum_{[\mu\nu]\kappa}(c_{A\mu}c_{B\nu} - c_{A\nu}c_{B\mu}) \times \langle\mu|\hat{\boldsymbol{r}}^{\kappa} \times \nabla|\nu\rangle$$

$$SOC = C_{0y}|\boldsymbol{h}^{\mathrm{SO}}|$$

For a large value of *SOC* between S_0 and T_1, (i) perturbation of the perfect biradical needs to be such as to make the coefficient C_{0y} large. Two ways of achieving this have been described above. The other requirement is for the vector $\boldsymbol{h}^{\mathrm{SO}}$ to be long. This requires (ii) large individual atomic vectorial contributions and (iii) constructive rather than destructive addition of these contributions. A large atomic contribution is provided when one of the orbitals *A* and *B* contains a large contribution from a p orbital on an atom of a relatively high atomic number Z_κ and thus atomic spin−orbit constant ζ_κ, and the other, a large contribution from a different p orbital on the same atom. The constructive or destructive mode of addition of atomic contributions is often apparent from symmetry or approximate symmetry.

The direction of the final vector $\boldsymbol{h}^{\mathrm{SO}}$ normally is of lesser importance: the squares of its projections into the principal axes *x*, *y*, and *z* determine the relative rates at which the individual triplet sublevels T_x, T_y, and T_z convert to S_0.

These results permit a revised formulation of the Salem−Rowland rules for spin−orbit coupling in a general perturbed biradical:

In order for SOC between S_0 and T_1 to be large, the most localized orthogonal orbitals A and B singly occupied in T_1 should be as follows:

(i) They either interact covalently through a non-zero resonance integral and/or are sufficiently different in energy for one to have electron occupancy near two in S_0.

(ii) The biradical contains one or more high-Z atoms at which one p orbital contributes strongly to A and another to B.

(iii) These p orbitals enter into A and B in a manner such that the contributions on all such atoms add rather than cancel.

Condition (i) is a more rigorous statement of the Salem and Rowland's requirement[10] of "ionic character" in S_0. For systems with *A* and *B* at equal or similar energies, it is met at the expense of increasing the energy of T_1 above its minimum.

If the condition is to be met by making the energies of *A* and *B* different enough for the hole-pair structure to dominate S_0, it is essential to go beyond the critical threshold value of the heterosymmetric perturbation δ_0 discussed above. This value is smallest when *A* and *B* are located at the same atom and generally increases with their increasing separation. Thus, in a carbene, already a small difference in the content of s character in the two nonbonding orbitals is sufficient, whereas in a twisted ethylene, one of the carbons needs to be replaced by an atom at least as electronegative as a positively charged nitrogen. In 1,3 biradicals the required electronegativity difference is even larger, and indeed, there is experimental evidence[40] that a moderate degree of polarization does not enhance the rate of intersystem crossing in 1,3-diaryl-1,3-cyclopentanediyls.

Condition (ii) effectively requires the principal parts of the orbitals *A* and *B* to be represented by p orbitals whose axes are orthogonal or close to it, and thus often runs directly counter to condition (i) if their energies are similar.

Through-Bond Coupling. In order to evaluate properly the above condition (ii), it is essential to work with a reasonably realistic representation of the localized orbitals *A* and *B* that includes any partial delocalization through the saturated chain that is due to through-bond interactions. Even though the extent of such delocalization is small, the numerical *ab initio* results reported in the following papers of this series show that through-bond interactions normally dominate SOC in saturated biradicals (since numerical results were not available, this was not appreciated by Salem and Rowland in their pioneering study[10]). The insignificance of through-space interactions is due to the factor $|\boldsymbol{r}_\kappa|^{-3}$ in the matrix element, which causes them to fall off very rapidly with the distance between the orbitals involved. Since two-center terms hardly ever play an important role, we have neglected them in the simplest formulation of the 2-in-2 model.

For instance, even in twisted ethylene (Chart 1), the dominant interaction is not provided by the two-center term involving

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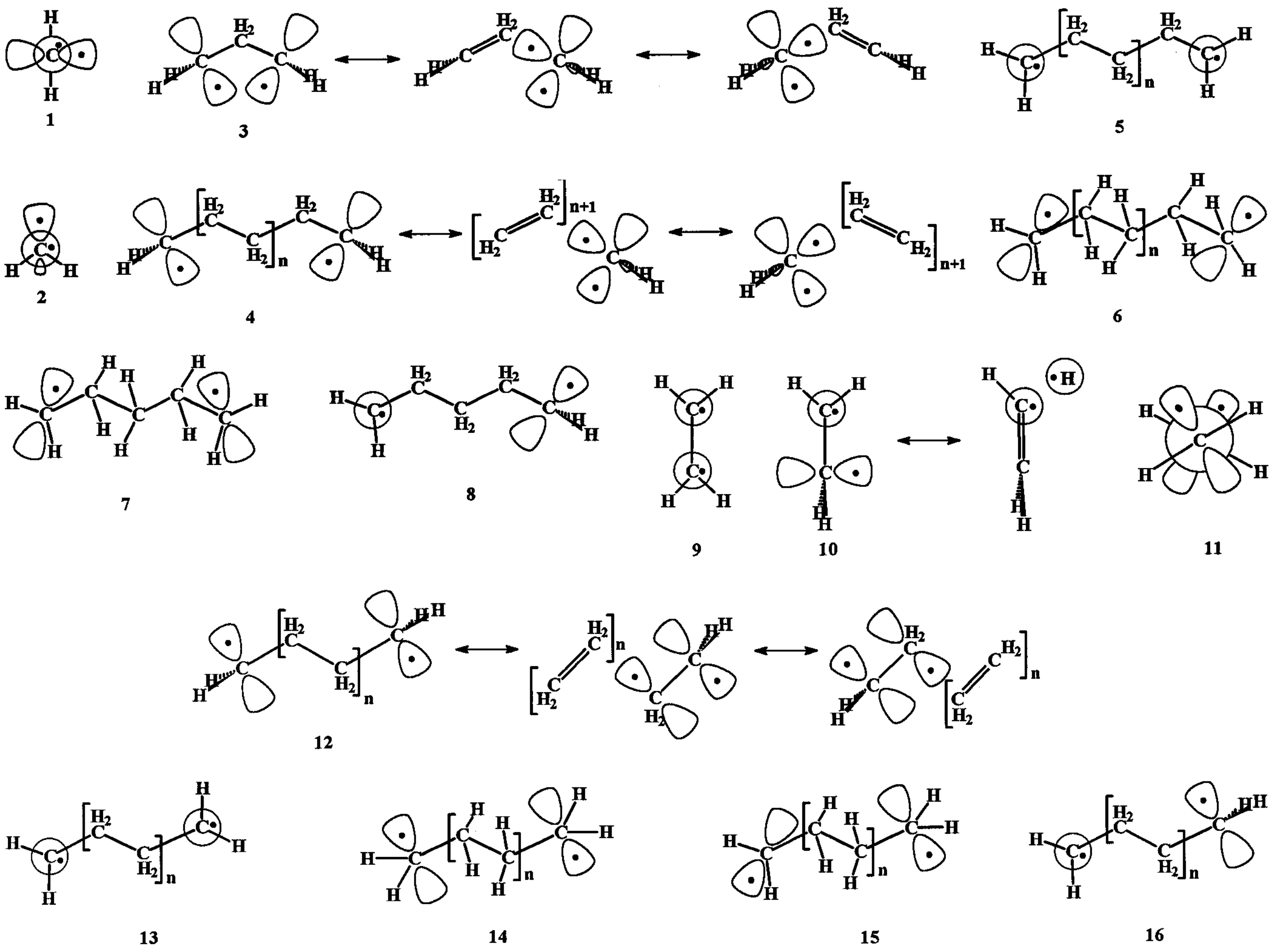
(40) Kita, F.; Nau, W. M.; Adam, W.; Wirz, J. *J. Am. Chem. Soc.* **1995**, *117*, 8670.

(41) Langhoff, S. R. *J. Chem. Phys.* **1974**, *61*, 3881.

Chart 1



the singly occupied p orbitals on the two neighboring CH_2carbons, but by the (oppositely signed) sum of the terms involving one of these p orbitals at a time along with the small portion of the other singly occupied orbital that is delocalized by hyperconjugation onto the adjacent CH_2 group.[22,37] For more distant carbons, the two-center terms are even less important.

Use of Symmetry. In symmetrical biradicaloids, condition (iii) is the longest recognized and most obvious in that it follows immediately from group theory. It is more difficult to apply to biradicaloids whose geometries lack any helpful symmetry elements.

The use of group theory in the evaluation of SOC in molecules[8] in general and biradicaloids[17] in particular has been common. In our case, the irreducible representations to which the space parts of S_0 and T_1 belong are readily identified once the symmetries of orbitals *A* and *B* or their symmetry-adapted combinations are determined. In biradicaloids, the energies of *A* and *B* or their symmetry-adapted combinations are different, and the space part of S_0 in σ,σ and π,π biradicaloids, but not σ,π biradicaloids, typically belongs to the totally symmetric representation. Since the singlet spin function Σ is also totally symmetric, the overall symmetry of S_0 of typical biradicaloids is usually easily determined. In perfect biradicals, the energies of *A* and *B* are equal since they normally belong to a degenerate representation. The symmetry determination then tends to be a little more complicated, but is not needed for our purposes, since *SOC* vanishes as noted above.

The space part of T_1 belongs to the product of irreducible representations of the two symmetry-adapted singly occupied orbitals. Its three possible spin parts $\Theta[x]$, $\Theta[y]$, and $\Theta[z]$ transform like the rotations R_x, R_y, and R_z, and the overall symmetries of the total functions $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ are thus again easily determined. Only those of the three that belong to the same irreducible representation as S_0 can be mixed with it by action of the totally symmetric spin−orbit coupling operator. For others, *SOC* vanishes.

Illustrations. To illustrate the qualitative use of the revised rules for SOC in biradicals and biradicaloids, consider the all-anti (planar zigzag) conformations of α,ω-alkanediyl biradicals (Chart 1, Table 1, whose footnote *c* states the directions of molecular axes).

(a) Odd Number of Carbon Atoms. In its hypothetical linear geometry (**1**), carbene has the orbitals *A* and *B* represented by the p_x and p_y AOs on carbon. Since the resonance integral between them vanishes by symmetry, and since their energies are equal by symmetry, it is a perfect biradical and S_0 will not be mixed with T_1 by SOC. Note that linear carbene violates condition (i) while it satisfies condition (ii). Since it contains only one non-hydrogen center, condition (iii) is not applicable. The vanishing *SOC* also follows directly from symmetry: the degenerate S_0 belongs to Δ_g and T_1 belongs to Σ_g^-. Therefore, $T\Theta[x]$ and $T\Theta[y]$ belong jointly to Π_g, and $T\Theta[z]$ to Σ_g^+. These are both different from Δ_g. Note that symmetry permits the *z* sublevel of T_1 to spin−orbit couple with the excited singlet Σ_g^+ (in our notation, $S[y]\Sigma$), as expected from the 2-in-2 model.

In the realistic bent geometry of carbene (**2**), *A* and *B* still have a zero resonance integral, but their energies are different since one contains an admixture of s character. Since linear carbene is an axial biradical ($\delta_0 = 0$), already a small energy

Table 1. Symmetry Aspects of Spin−Orbit Coupling in All-Anti α,*ω*-Alkanediyl Biradicals[a]

no.[b]	point grp[c]	(*A*) *A*+*B*	(*B*) *A*-*B*	T_1	$\Theta[x]$	$\Theta[y]$	$\Theta[z]$	$T\Theta[x]$	$T\Theta[y]$	$T\Theta[z]$	S_0	allowed sublevel[d]
1	$D_{\infty h}$	(π_u)		Σ_g^-	Π_g	Π_g	Σ_g^-	Π_g	Π_g	Σ_g^+	Δ_g	
2	C_{2v}	(b_1)	(a_1)	B_1	B_2	B_1	A_2	A_2	A_1	B_2	A_1	*y*
3, 4	C_{2v}	a_1	b_2	B_2	B_2	B_1	A_2	A_1	A_2	B_1	A_1	*x*
5	C_{2v}	b_1	a_2	B_2	B_2	B_1	A_2	A_1	A_2	B_1	A_1	*x*[e]
6, 15	C_2	b	a	B	B	B	A	A	A	B	A	*x,y*
7	C_s	a′	a″	A″	A″	A″	A′	A′	A′	A″	A′	*x,y*
8, 16	C_s	(a″)	(a′)	A″	A″	A″	A′	A′	A′	A″	A″	z[f]
9	D_{2h}	b_{3u}	b_{2g}	B_{1u}	B_{3g}	B_{2g}	B_{1g}	B_{2u}	B_{3u}	A_u	A_g	
10	D_{2d}	e		A_2	E	E	A_2	E	E	A_1	B_1	
11	D_2	b_3	b_2	B_1	B_3	B_2	B_1	B_2	B_3	A	A	*z*
12	C_{2h}	b_u	a_g	B_u	B_g	B_g	A_g	A_u	A_u	B_u	A_g	
13	C_{2h}	a_u	b_g	B_u	B_g	B_g	A_g	A_u	A_u	B_u	A_g	
14	C_i	a_u	a_g	A_u	A_g	A_g	A_g	A_u	A_u	A_u	A_g	

[a] Irreducible representations for the symmetry-adapted one-electron functions singly occupied in T_1 [localized, *A* and *B*, in parentheses, or delocalized, $A \pm B$], the two-electron triplet space function T_1, the two-electron triplet spin functions $\Theta[x]$, $\Theta[y]$, and $\Theta[z]$, the total two-electron triplet wave functions $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$, and the total two-electron singlet wave function S_0. [b] Only biradical geometries that have at least some symmetry elements are included. For the others, $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ are all allowed by symmetry to spin−orbit couple with S_0. [c] Point group, with the *z* axis vertical and the *y* axis horizontal in the formula as drawn in Chart 1 (carbon atoms in the plane of the paper). Exceptions: **6**, **7**, **14**, and **15** are drawn in perspective (in **6**, *z* is the 2-fold symmetry axis and *y* is the other in-plane axis, and in **7**, *xy* is the symmetry plane), in **11** *z* is the C−C line, perpendicular to the plane of the paper, *y* is horizontal and *x* vertical, and in **8** and **12**−**16** *z* is perpendicular to the plane of carbon atoms, while *x* and *y* lie in this plane. [d] Labels of triplet sublevels that are symmetry allowed to mix with S_0. [e] Although $T\Theta[x]$ is symmetry allowed to couple with S_0, in the present approximation this spin−orbit coupling vanishes. [f] Although $T\Theta[z]$ is symmetry allowed to couple with S_0, in the present approximation this spin−orbit coupling vanishes.

difference is sufficient to guarantee an electron occupancy close to two in the lower energy orbital in the S_0 state. Conditions (i) and (ii) are now both fulfilled, while condition (iii) is still irrelevant. We expect *SOC* to increase strongly as the HCH valence angle decreases from 180°. It should stop increasing as C_{0y} approaches its limiting value of $2^{-1/2}$. Probably even before then, it will start dropping as the valence angle approaches 90°, at which point the more stable orbital *B* loses nearly all of its p character and becomes an essentially pure s orbital, violating condition (ii). The triplet sublevel that mixes with S_0 is selected by the direction of $\boldsymbol{h}^{SO}$, which lies along *y* (i.e., along the H−H line), perpendicular to the axes of the two carbon p orbitals involved in *A* and *B*. Most of these results also follow from symmetry: in the C_{2v} point group, *A* belongs to b_1 and *B* to a_1, the space part of T_1 to B_1, and the overall symmetry of $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ to A_2, A_1, and B_2, respectively. Since S_0 transforms like A_1, only $T\Theta[y]$ will spin−orbit couple to it. Numerical calculations[37,41] agree with these conclusions.

The 90,90 conformations of α,*ω*-alkanediyls with an odd number of carbon atoms (**3**, **4**, axes of both singly occupied p orbitals in the plane of the carbon atoms) are "ethanologous" carbenes in the sense that no-bond resonance structures containing a triplet carbene substructure can be written as minor contributors to the valence-bond description of their triplet states (the importance of such structures will decrease with the increasing number of lost bonds, i.e., with the length of the carbon chain). These resonance structures can be viewed as shorthand symbols indicating the delocalization of the two nonbonding orbitals by *σ* hyperconjugation through antiperiplanar interactions familiar from the usual interpretation of electron transfer, photoelectron spectra, Grob fragmentation, spin−spin and hyperfine coupling constants, etc., in terms of through-bond coupling.

In these structures, the energies of *A* and *B* are equal, and condition (i) can be satisfied only by the presence of a nonzero resonance integral between them. This is easily provided in 1,3-propanediyl (**3**) by direct through-space interaction between the main portions of these two orbitals at carbons 1 and 3 for all realistic CCC valence angles, but cannot be provided in this way for the longer-chain biradicals **4**. In chains of all lengths, through-bond coupling provides an additional opportunity for covalent interaction. This, too, will fall off with chain length, but less rapidly, and it will depend on the CCC valence angle. For 1,5-pentanediyl and longer chains (**4**), condition (i) will be satisfied rather poorly in this conformation, and much better in more folded conformations that bring *A* and *B* into through-space interaction. These will be considered in a later paper.

Condition (ii) is satisfied on both terminal carbon atoms. On one, *A* has a large amplitude on the in-plane p orbital of the radical center and *B* has some, albeit small, amplitude on the p orbital participating in the formation of the CC bond. On the other terminal carbon, the roles of *A* and *B* are interchanged. The direction of the atomic vectorial contributions is along *x*, perpendicular to the plane of the carbon atoms. The internal carbon atoms are likely to make smaller contributions, since there, the coefficients of *A* and *B* are both small.

Since we now have more than one contributing atomic center, condition (iii) needs to be considered. Do the out-of-plane vectors provided by the terminal carbons add, or do they cancel? In the former case, S_0 will spin−orbit couple to the $T\Theta[x]$ sublevel, in the latter, *SOC* will vanish. Working out the directions from the rules given above shows that the two contributions add. An easier way to reach this conclusion is to use group theory, starting with the symmetry-adapted orbitals $2^{-1/2}(A \pm B)$: in the C_{2v} point group, $A + B$ belongs to a_1 and $A - B$ to b_2, the space part of T_1 therefore belongs to B_2, and the overall symmetry of $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ belongs to A_1, A_2, and B_1, respectively. Since S_0 transforms like A_1, symmetry permits $T\Theta[x]$ to spin−orbit couple to it, but the other two sublevels cannot.

Note that the conclusion that all three conditions are satisfied and *SOC* will not vanish (but will fall off with the chain length) was reached for reasons different from those applicable to the previous example of carbene, even though the presence of carbene-like resonance structures was important. The inherent orthogonality of the axes of the singly occupied orbitals of carbene provided large one-center contributions and permitted condition (ii) to be satisfied in both cases, but in carbene itself the only way to satisfy condition (i) was to introduce inequivalence between *A* and *B* by bending, whereas in 1,3-propanediyl it was achieved by introducing a resonance integral (making the ends interact).

The 0,0 conformation of the odd-carbon biradical chains (**5**, both p orbital axes perpendicular to the plane of carbon atoms) satisfies condition (i) by through-space interaction and hyperconjugation for all chain lengths (these two contributions to the resonance integral have opposite signs and cancel for certain CCC valence angles in the case of 1,3-propanediyl[42]), but it does not satisfy condition (ii) since A and B are both of π symmetry and cannot each comprise a different p orbital on any one center. Condition (iii) does not need to be examined to reach the conclusion that SOC vanishes.

This result does not follow from symmetry alone: in the C_{2v} point group, $A + B$ belongs to b_1 and $A - B$ to a_2, the space part of T_1 to B_2, and the overall symmetry of $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ to A_1, A_2, and B_1, respectively. Since S_0 transforms like A_1, $T\Theta[x]$ is symmetry allowed to spin−orbit couple to it, but the other two sublevels are not. However, the allowed coupling depends on the very small two-center terms only, and these have been neglected in the present model.

At the partially twisted symmetric conformations, ϕ,ϕ (**6**, conrotatory, C_2) and $\phi,-\phi$ (**7**, disrotatory, C_s), conditions (i), (ii), and (iii) are all satisfied. For **6**, the overall symmetries of the triplet sublevels are A for the x and y directions, so these two couple to S_0 (for $T\Theta[z]$ the symmetry is B and it does not couple). For **7**, the symmetries are A′ for the x and y directions, so these sublevels again couple to S_0 (for $T\Theta[z]$ the symmetry is A″ and it does not couple).

Among less symmetrical configurations, the "semirotatory" C_s 0,90 geometry **8** fails to satisfy condition (i). One of the localized orbitals is of π and the other of σ symmetry, so their resonance integral must vanish, and their energies are not sufficiently different for one of them to acquire both electrons in S_0 at the cost of substantial charge separation. We conclude that *SOC* vanishes within the present model, even though the coupling of S_0 to $T\Theta[z]$ is allowed by symmetry: at C_s geometry, the overall symmetries of the $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ sublevels are A′, A′, and A″, respectively, and that of S_0 is A″.

At partial twist angles (0,ϕ or ϕ,90 geometries), all three conditions are satisfied, and *SOC* does not vanish.

(b) Even Number of Carbon Atoms. Ethylene satisfies condition (i) but violates condition (ii) when it is planar (**9**), and violates condition (i) but satisfies condition (ii) when it is orthogonally twisted (**10**), so in both limiting cases, *SOC* vanishes (at the latter geometry, ethylene is a perfect biradical and this result is obvious *a priori*). This agrees with group theory: the overall symmetries of the three triplet sublevels of the planar D_{2h} molecule are B_{2u}, B_{3u}, and A_u, and none can couple to the S_0 state (A_g). In the orthogonally twisted D_{2d} molecule, the symmetries are E for the degenerate pair of sublevels $T\Theta[x]$ and $T\Theta[y]$, and A_1 for $T\Theta[z]$. Since S_0 transforms according to B_1, it cannot spin−orbit couple with any of the three triplet sublevels.

In partially twisted ethylene (**11**), however, conditions (i), (ii), and (iii) are all fulfilled and S_0 spin−orbit couples with $T\Theta[z]$, which is of A symmetry in the D_2 group, while $T\Theta[x]$ transforms like B_2 and $T\Theta[y]$ like B_3. As mentioned above, condition (ii) is satisfied by delocalization of the p orbital of each carbon atom of the twisted π bond into the orbitals of the CH_2 group on the other carbon. The degree of such hyperconjugative delocalization is small, and the net resulting *SOC* is also relatively small.

In a fashion entirely analogous to what we have seen for odd-carbon α,ω-alkanediyls, longer even-carbon triplet α,ω-alkanediyls can be viewed as "ethanologous" triplet ethylenes for the purpose of understanding the delocalization of their unpaired electrons. In order to contribute to the fulfilment of condition (ii), these ethylene substructures need to be at geometries other than planar ethylene, and preferably close to orthogonal ethylene.

At 90,90 (C_{2h}) conformations (**12**), 1,4-butanediyl and its longer analogues satisfy conditions (i) and (ii), but fail condition (iii). This is immediately obvious from symmetry: $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ transform like A_u, A_u, and B_u, respectively, and cannot couple with S_0, which transforms according to A_g. At 0,0 (C_{2h}) conformations (**13**), these biradicaloids satisfy condition (i) but fail condition (ii). Sublevel symmetries are the same as in **12**, and *SOC* again vanishes.

At partially twisted conrotatory ϕ,ϕ (C_i) conformations **14** with parallel A and B orbital axes, condition (i) is clearly fulfilled and condition (ii) may be met, but condition (iii) is not. All three triplet sublevels are of A_u symmetry and cannot couple with S_0, which is of A_g symmetry. In contrast, at partially twisted disrotatory $\phi,-\phi$ (C_2) conformations **15**, all three conditions are satisfied. The sublevels $T\Theta[x]$, $T\Theta[y]$, and $T\Theta[z]$ transform like A, A, and B, respectively, so the first two spin−orbit couple to S_0, which also transforms like A.

The "semirotatory" C_s 0,90 geometry **16** does not satisfy condition (i), since one of the orbitals is of π and the other of σ symmetry, causing their resonance integral to vanish, and since their energies are similar. At this C_s geometry, the overall symmetries of the triplet and singlet levels are the same as in **8**. Once again, the coupling between S_0 and $T\Theta[z]$ is symmetry allowed, but is due only to terms neglected in the simple model.

At partial twist angles (0,ϕ or ϕ,90 geometries), all three conditions of the model are satisfied, and *SOC* does not vanish.

Normal and Inverse Heavy Atom Effects. Like other properties of biradicals and biradicaloids, their *SOC* can be affected by the introduction of inductive and/or conjugating substituents. These operate by the usual modes of action, primarily by changing the shapes and energies of the orbitals A and B and modifying the CI mixing coefficients C_{ju}. They can affect the size of *SOC* in either direction.

In addition, unlike most properties, SOC is known to respond to the "heavy atom effect" of the substituent, specifically due to the introduction of a "heavy" (large Z_κ and ζ_κ) atom into the molecule.[1,2,4,8] Obviously, such substitution offers an opportunity to provide a new atomic contribution with a very large weight ζ_κ, if A delocalizes onto one and B onto another p orbital on the heavy atom. If Z_κ, and thus ζ_κ, are sufficiently large, even a very moderate degree of participation by the p orbitals of the heavy atom in A and B may be sufficient for its vectorial contribution to dominate those from the lower atomic number atoms originally present. Often, the introduction of a heavy atom therefore greatly increases the total length of the ***SOC*** vector, and changes its direction as well. This is the origin of the normal "heavy atom effect".

However, the vectorial atomic contribution from the heavy atom substituent to ***SOC*** may also be merely comparable in size to the sum of contributions already present. If it happens to be pointed approximately in the opposite direction, the introduction of the heavy atom can actually decrease the resulting length of ***SOC***. Such an "inverse heavy atom effect" is rare but known and has been considered puzzling.[43] We suspect that a systematic search, guided by the simple model outlined here, would probably rapidly uncover additional instances of this predictable "anomaly".

In addition to the "internal heavy atom effect" discussed so far, an "external heavy atom effect" is also well recognized.[1,2,4,8] It is due to the presence of atoms of high Z_κ, and ζ_κ in molecules that are in immediate contact with the substrate, usually

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(42) Doubleday, C. D., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. Goldberg, A. H.; Dougherty D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

(43) Turro, N. J.; Kavarnos, G.; Fung, V.; Lyons, A. L., Jr.; Cole, T., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 1392.

molecules of solvent, and represents an extremely sensitive probe of the delocalization of the singly occupied orbitals *A* and *B* onto neighboring molecules.

Application of the Results. In conclusion, we comment on two applications of the results that have been obtained.

(a) Limits of Applicability. While the 2-in-2 model is likely to represent most bitopic[44] biradicals adequately, there are many important photochemical processes that involve biradicals of higher topicity, i.e., those in which the radical centers also carry lone pairs, empty valence orbitals, or multiple bonds. For these, the model should not be applied.

(b) Intersystem Crossing (ISC) in Biradicals. A desirable description of a process in which a triplet biradical wanders through a variety of conformations before finally converting to a stable singlet molecule would call for a molecular dynamics study in which the variable strength of spin−orbit coupling is considered continuously and the probability of product formation is evaluated at all times.[27] A knowledge of SOC as a function of structure is an essential prerequisite.

In many cases, the presently common description,[6] based on the sudden approximation, is probably adequate. In this picture, the triplet biradical goes through a large number of conformations in which the T_1 and S_0 states are nearly degenerate and its wave function is a rapidly oscillating mixture of singlet and triplet character, with the triplet dominant at all times. A decision as to whether the triplet or the singlet potential energy surface will be followed needs to be taken only when the biradical reaches a geometry in which the two surfaces separate in energy. Typically, this is a geometry at which there is either through-space or through-bond covalent interaction between the orbitals *A* and *B*. After that, the triplet surface most likely will dictate the molecular motions (with a probability given by the average weight of the triplet in the wave function at the time of decision), but occasionally, the singlet surface will do so (with the complementary probability given by the weight of the singlet). After many attempts, the decision will eventually fall in favor of the singlet, the singlet surface will be followed, and a stable molecule will be formed.

In many saturated biradicals, the energies of the *A* and *B* orbitals are fairly close, and according to the present model, the only likely geometries at which SOC will be strong are those at which there is a significant covalent interaction between the two radical centers, i.e., just those at which a decision is likely to be taken. This interaction destabilizes the T_1 state and stabilizes the S_0 state, and this has two important consequences. First, a small but non-zero activation energy should be needed for the triplet biradical to reach the best geometries for ISC. Second, immediately after the transition from the T_1 to the S_0 state, the molecule should find itself part way down a deep abyss in the S_0 potential energy surface, into which it is very likely to fall immediately. In that sense, T_1 to S_0 ISC in triplet biradicals should be concerted with the formation of a new bond. Experimental evidence for this has been accumulating.[45]

(c) Zero-Field Splitting Parameters in Triplet States of Biradicals. A side benefit of the present analysis is insight into the effect of spin−orbit coupling on the *D* and *E* parameters that are frequently measured to characterize the triplet state of organic biradicals. They are determined by the energy differences among the three triplet sublevels in zero magnetic field and are often interpreted in terms of the spin−spin dipolar interactions alone, i.e., using only the triplet block of the Hamiltonian matrix given above. This procedure is correct only if the effects of spin−orbit coupling matrix elements, also present in the matrix, are negligible. Although it appears to be justified in the absence of heavy atoms in the very few cases of biradicals for which calculations have been reported,[33] such as carbene,[41] and also in the cases that we have examined so far,[37] it is not yet clear just when the correction for SOC will be significant.

The proper procedure is to diagonalize the whole Hamiltonian matrix with the elements of $\hat{H}^{SO}$ included, and only then evaluate *D* and *E* from the energies of the predominantly triplet resulting levels. In ordinary organic molecules, the SOC elements are small relative to the triplet−singlet energy difference and their effects are adequately described by second-order perturbation theory. It is then seen that they will have no detectable influence on the ordinarily quite large separations of the singlet levels. However, the three triplet sublevels are spaced so close together that even very small differential effects of their coupling to the singlet states may affect the size of the resulting *D* and *E* parameters.

In perfect biradicals, this is particularly likely if the $S[y]\Sigma$ state is low in energy. For this, the sum $K'_{AB} + K_{AB}$ needs to be small, and this is most likely when *A* and *B* are delocalized over the same atoms. For instance, in the O_2 molecule, where the $S[y]\Sigma$ state lies only 1.64 eV above the T_1 state, spin−orbit coupling provides the dominant contribution to *D*.[33] Large effects might also be found in those biradicaloids in which S_0 has large $S[y]\Sigma$ character and is nearly degenerate with T_1.

Using second-order perturbation theory, assuming that T_1 lies below S_0 in energy, and returning to the usual labeling of the axes, such that $D > 0$, $E < 0$ (i.e., $D_z > D_y > D_x$, T_z lowest and T_x highest in energy), the correct values of the zero-field splitting parameters, D' and E', are related to the values *D* and *E* calculated from the triplet part of the Hamiltonian matrix alone (spin dipole−dipole coupling without SOC) by

$$D' = D + \sum_j [E(S_j) - E(T)]^{-1} C_{jy}^2 \{(h_{1z}^{SO})^2 - [(h_{1y}^{SO})^2 + (h_{1x}^{SO})^2]/2\}$$

$$E' = E + \sum_j [E(S_j) - E(T)]^{-1} C_{jy}^2 [(h_{1x}^{SO})^2 - (h_{1y}^{SO})^2]/2$$

where $E(S_j) - E(T)$ is the difference between the energy of the *j*th singlet S_j and the average energy of the triplet sublevels.

These expressions show explicitly the three factors that control the size of the SOC contributions from each singlet S_j to zero-field splitting in biradicals and biradicaloids: (i) the S_j-T_1 gaps, (ii) the lengths of the $\boldsymbol{SOC}_j$ vectors that describe coupling with the various singlet states S_j, and (iii) the directions of these vectors in the molecular frame defined by the principal axes of the spin dipole−dipole coupling tensor. If $\boldsymbol{SOC}_j$ makes equal angles with all three axes, *x*, *y*, and *z*, its contribution to the total effect on the zero-field splitting parameters is nil, regardless of its length. If it is inclined toward *z* and away from the *xy* plane, it will increase *D*, and if it is inclined toward *x* and away from *y*, it will make *E* less negative. The overall effect is deduced by summing over the contributions from all singlet states, weighted by their inverse energies relative to *E*(T).

Conclusion

The 2-in-2 model of electronic structure deals with the most localized orbitals *A* and *B* singly occupied in the T_1 state and describes spin−orbit coupling in bitopic biradicals and biradicaloids in terms of S_j-T_1 spin−orbit coupling vectors $\boldsymbol{SOC}_j$, whose components describe the coupling of S_j to T_x, T_y, and T_z. The length of $\boldsymbol{SOC}_0 \equiv \boldsymbol{SOC}$ defines the overall S_0-T_1 SOC strength.

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[44] Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

[45] De Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759. Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83. Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B.-S. *J. Am. Chem. Soc.* **1991**, *113*, 9630.

In the 2-in-2 model, ***SOC*** is given by a product of a scalar C_{0y} that is characteristic of the CI wave function of the S_0 state and a vector $\boldsymbol{h}^{SO}$, characteristic of the orbitals A and B.

The scalar C_{0y} is the amplitude of the symmetrized hole-pair structure $S[y]$ in the S_0 wave function. It vanishes in perfect biradicals. Two types of perturbation can mix $S[y]$ into S_0, make C_{0y} non-zero, and induce spin−orbit coupling of S_0 with T_1: a covalent interaction of A and B, and a polarization that causes one of the hole-pair structures, A^2 or B^2, to dominate the S_0 state.

The vector $\boldsymbol{h}^{SO}$ is a sum of atomic vectors. Each of these is provided by a non-hydrogen atom that carries a contribution from A on one p orbital and from B on another, is proportional to the atomic spin−orbit coupling constant ζ_κ, and is a sensitive function of the through-bond delocalization of A and B, as well as geometrical symmetry. These vectors are readily visualized from the form of the orbitals A and B, and from a consideration of standard resonance structures. In addition to ordinary heavy-atom effects, the vectorial nature of the sum provides for inverse heavy atom effects.

These concepts are illustrated on the case of α,ω-alkanediyl biradicals at various conformations, and their application to intersystem crossing in biradicals and to the evaluation of zero-field splitting parameters in EPR spectra of triplets is discussed. Finally, we point out formal similarities in the quantum mechanical description of the three singlets permitted in the model and the three sublevels of the triplet, which allow the use of angular momentum algebra in both cases.

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Note Aded in Proof: Results of spin−orbit coupling calculations for α,ω-alkanediyls were discussed in a very recent communication: Zimmerman, H. E.; Kutateladze, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 249.

Appendix

It is frequently necessary to translate the full two-electron wave function from an initially chosen one-electron basis set to another, e.g., from a localized to a delocalized choice of orbitals, etc. This transformation is most readily accomplished using the well-developed apparatus of angular momentum algebra. This is commonly used for this purpose in the spin space, but is just as useful in the isomorphic geminal space of the two electrons.

One-Electron Space. Any operator acting in the two-dimensional one-electron function space spanned by a and b (where a is α or A and b is β or B) can be written as a linear combination of the unit matrix ($\hat{\boldsymbol{\sigma}}^2/3$) and the three Pauli matrices $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$. E.g., the Hamiltonian is

$$\hat{h}_1 = h_0(\hat{\boldsymbol{\sigma}}^2/3) + \boldsymbol{h} \cdot \hat{\boldsymbol{\sigma}}$$

By definition of the Pauli matrices, the functions a and b are eigenfunctions of $\hat{\sigma}_z$, i.e., are adapted to the z axis. This could be indicated explicitly by calling them a^z and b^z. For spin space, this z axis lies in real three-dimensional Cartesian space, and for orbital space, z is the direction of the polarizing perturbation in the three-dimensional abstract space of perturbations of a perfect biradical. In order to guarantee cyclic permutation properties with respect to the indices x, y, and z, the y- and x-adapted basis functions a^y, b^y and a^x, b^x are derived from a^z and b^z by application of a $+2\pi/3$ and a $-2\pi/3$ rotation, respectively, around an axis $\boldsymbol{n}$ with directional cosines $n_x = n_y = n_z = 3^{-1/2}$. The directions y and x are the directions of axes in real Cartesian space when a and b are taken to be spin functions, and they are the directions of the magnetizing perturbation and the covalent perturbation in the abstract space of perfect biradical perturbations when a and b are taken to be orbitals.

Using the standard form[46] of the rotation operator for a particle of spin $^1/_2$,

$$R_n^{1/2}(\omega) = \cos(\omega/2) - i\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{n} \sin(\omega/2)$$

where ω is the angle of rotation and the components of the unit vector $\boldsymbol{n}$ are the direction cosines of the axis of rotation, one obtains for the functions adapted to the axes y and x

$$a^y = [(1 + i)/2](a^z + ib^z)$$

$$b^y = [(1 + i)/2](a^z - ib^z)$$

$$a^x = [(1 - i)/2](a^z + b^z)$$

$$b^x = [-(1 + i)/2](a^z - b^z)$$

In orbital space, the functions adapted to the z axis (the polarizing operator) are the most localized orbital set, those adapted to the y axis (the magnetizing operator) are the most delocalized complex orbital set, and those adapted to the x axis (the covalent perturbation operator) are the most delocalized "real" (constant complex phase) orbital set.

Two-Electron Space. The two-electron spin and geminal function spaces are obtained as direct products of the one-electron spaces of the first and the second electron. Permutational symmetry permits a factorization of each of these four-dimensional direct product spaces into a direct sum of a three-dimensional subspace with elements symmetric with respect to an interchange of electron labels ($[x]$, $[y]$, and $[z]$, corresponding to a particle of spin one), and a one-dimensional space with an element that is antisymmetric with respect to this interchange ($[o]$, corresponding to a particle of spin zero). In geminal space, where a is A and b is B, $[x] = S[x]$, $[y] = S[y]$, $[z] = S[z]$, $[o] = T$, and in spin space, where a is α and b is β, $[x] = \Theta[x]$, $[y] = \Theta[y]$, $[z] = \Theta[z]$, $[o] = \Sigma$.

These two-electron bases have been built from the z-adapted one-electron functions $a = a^z$ and $b = b^z$ and could be labeled $[x]^z$, etc. Starting with a^y and b^y or a^x and b^x instead, one can similarly construct the analogous two-electron bases $[x]^y$, etc., or $[x]^x$, etc. The standard rotation operators for particles of spin zero and one show how the two-electron basis set responds to any rotation of the one-electron basis set:

$$R_{\boldsymbol{n}}^0(\omega) = 1$$

$$R_{\boldsymbol{n}}^1(\omega) = 1 - i\boldsymbol{n}\cdot\hat{\boldsymbol{J}} \sin\omega - (\boldsymbol{n}\cdot\hat{\boldsymbol{J}})^2 (1 - \cos\omega)$$

where the dimensionless operator $\hat{\boldsymbol{J}}$ is defined by

$$\hat{\boldsymbol{J}}(1,2) = [\hat{\boldsymbol{\sigma}}(1) + \hat{\boldsymbol{\sigma}}(2)]/2$$

($\hat{\boldsymbol{J}}^2/2$ is the unit operator and $\hbar\hat{\boldsymbol{J}}$ is the angular momentum operator).

For instance, applying rotations by $+2\pi/3$ and $-2\pi/3$ about an axis $\boldsymbol{n}$ with directional cosines $n_x = n_y = n_z = 3^{-1/2}$, we obtain $[o]^x = [o]^y = [o]^z$, $[x]^x = [z]^y = [y]^z$, $[y]^x = [x]^y = [z]^z$, $[z]^x = [y]^y = [x]^z$ and note that cyclic permutation symmetry of the three indices is preserved as expected.

Any operator acting in the one-dimensional two-electron function space spanned by $[o]$ is a simple scalar, and any

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(46) Altmann, S. L. *Rotations, Quaternions, and Double Groups*, Clarendon Press: Oxford, 1986.

Hermitean operator acting in the three-dimensional two-electron function space spanned by [x], [y], and [z] can be written as a linear combination of the three operators $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$, their squares $\hat{J}_x^2$, $\hat{J}_y^2$, and $\hat{J}_z^2$, and their anticommutators, $(\hat{J}_y\hat{J}_z + \hat{J}_z\hat{J}_y)$, $(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z)$, and $(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x)$.

The Hamiltonian for the full two-electron problem without spin−orbit coupling can be written in terms of angular momentum operators in a way that is completely analogous for the singlets (geminal space) and the triplets (spin space). Using the principal axes of the spin−spin dipolar coupling tensor, and using the most localized set of orbitals A, B, we have

$$\hat{H} = \sum_u (W_u \hat{J}_u + \mathbf{W}_{uu} \hat{J}_u^{\,2}), \qquad u = x, y, z$$

where in the spin space, $W_u = g\beta_{\mathrm{e}} B_u$, $\mathbf{W}_{xx} = -D/3 + E$, $\mathbf{W}_{yy} = -D/3 - E$, $\mathbf{W}_{zz} = 2D/3$, and in the geminal space, $W_x = \gamma_{AB}$, $W_y = 2\beta_e \boldsymbol{B}\cdot(\mathbf{r} \times \nabla)_{AB}$, $W_z = \delta_{AB} - e\boldsymbol{E}\cdot\boldsymbol{r}_{AB}$, $\mathbf{W}_{xx} = 2K_{AB}$, $\mathbf{W}_{\mathrm{yy}} = 0$, $\mathbf{W}_{\mathrm{zz}} = 2K'_{AB}$.

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