Vicinal NMR Proton−Proton Coupling Constants. An NBO Analysis

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A method of natural bond orbital (NBO) interactions between bonds and antibonds, $\sigma_m \rightarrow \sigma_n^*$, has been developed for analyzing vicinal proton−proton coupling constants, ${}^3J_{HH}$. The contribution to ${}^3J_{HH}$ from such an interaction $\sigma_m \rightarrow \sigma_n^*$ is defined as J_{mn^*} and is obtained following these three steps: (i) the SOS scheme is used to calculate ${}^3J_{HH}$; (ii) the same calculation is repeated after deleting the relevant off-diagonal elements in the NBO Fock matrix; (iii) J_{mn^*} is obtained as the difference between those calculated in steps i and ii. Application of this method to the ethane and fluoroethane molecules shows that the main contribution to ${}^3J_{HH}$ comes from the through space term while the substitution of a hydrogen in ethane by a fluorine changes this through space term and, in addition, gives a direct contribution to ${}^3J_{HH}$.

Introduction

The vicinal proton−proton coupling constants ${}^3J_{HH}$ in fragments H−N−M−H are a powerful tool for structural elucidation and conformational analysis of molecules in solution[1] because of its Karplus-type dependence on the dihedral angle ϕ between the N−H and M−H vectors.[2,3] A lot of empirically parametrized equations describing this dependence have been published over the years.[1,3] Recently, accurate ab initio calculations for the angular dependence of ${}^3J_{HH}$ in the ethane molecule have been carried out at the multiconfiguration self-consistent-field (MCSCF) level of theory with the inclusion of the four contributions to ${}^3J_{HH}$[4,5] as well as using the second-order polarization approximation with coupled cluster singles and doubles amplitudes (SOPPA-CCSD).[6] Sekino and Bartlett calculated the dominant Fermi contact contribution to ${}^3J_{HH}$[7] using the equation of motion coupled cluster (EOM(CCSD)) theory. Extension of this kind of quantitative calculations to the study of the angular dependence of ${}^3J_{HH}$ in ethane derivatives is a very hard task.[6,8,9] Therefore, ab initio calculations of ${}^3J_{HH}$ for ethane derivatives have been restricted to the SCF level[10−12] except those recently performed by Provasi, Aucar, and Sauer using the second-order polarization propagator approximation (SOPPA).[9] On the other hand, there are many experimental trends of the ${}^3J_{HH}$ coupling constants that can be adequately reproduced resorting to much more modest calculations which, furthermore, yield trends that are surprisingly close to those obtained with more sophisticated calculations. In fact, the angular dependence of ${}^3J_{HH}$ coupling constants can readily be estimated for large molecules within 1 Hz by applying a modified sum over states, SOS, approach developed by Edison, Markley, and Weinhold[13] that incorporates ab initio wave functions. Using that approach, these authors performed calculations of one-, two-, and three-bond coupling constants in a model peptide as functions of the backbone dihedral angles ϕ and ψ.[14] The calculated coupling ${}^3J_{HH}$ shows an obvious "Karplus-like" behavior along the dihedral angle H−N−C−H and is closely related to the vicinal NBO interaction of the C−H bond with the N−H antibond ($\sigma_{C-H} \rightarrow \sigma_{N-H}^*$). However, the cis orientation has a much smaller vicinal interaction that is apparent in the coupling constants (see Figure 5 in ref 14). These striking results prompted us to probe the relationships between the ${}^3J_{HH}$ couplings and the $\sigma_m \rightarrow \sigma_n^*$ interactions involving the σ_m bond and σ_n^* antibond with the aim of improving the understanding of electronic interactions and factors affecting this type of couplings.

In this paper, the contribution of the interaction $\sigma_m \rightarrow \sigma_n^*$, J_{mn^*}, to ${}^3J_{HH}$ is defined as the difference between the J_{HH} value calculated using the total Fock matrix and that obtained performing the same calculation but where the corresponding off-diagonal elements of the Fock matrix, $\langle\sigma_m|\hat{F}|\sigma_n^*\rangle$ and $\langle\sigma_n^*|\hat{F}|\sigma_m\rangle$, were deleted ($\hat{F}$ is the Fock operator). This modified version of the Edison et al. SOS method is applied in this work to calculate all J_{mn^*} contributions to ${}^3J_{HH}$ in ethane and fluoroethane as functions of the dihedral angle ϕ = H−C−C−H between the coupled protons.

The sum $J_{\sigma\sigma^*}$ of all the calculated J_{mn^*} contributions reproduces satisfactorily the empirical trends of angular dependence and substituent effects for the ${}^3J_{HH}$ couplings. This fact allows us to ascribe a semiquantitative meaning to the J_{mn^*} contributions. On the other hand, the J_{mn^*} terms can be conveniently grouped in sets corresponding to through space and through C−C bond contributions to $J_{\sigma\sigma^*}$ and to direct and

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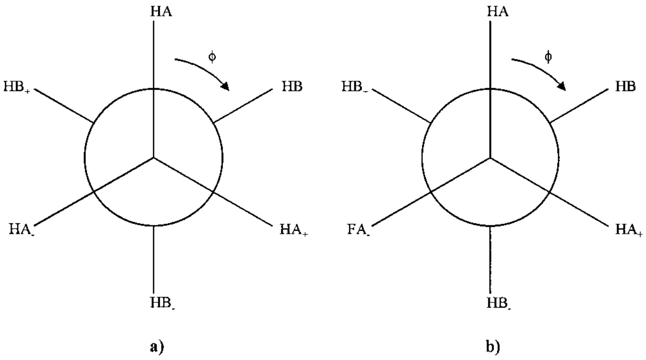

Figure 1. Notation for ethane (a) and fluoroethane (b). The dihedral angle between the coupled protons HA and HB is denoted by ϕ.

indirect substituent effects upon $J_{\sigma\sigma^*}$. The information about the transmission mechanisms through the molecular electronic system that produce the $^3J_{\mathrm{HH}}$ coupling differs, in part, from that provided by the inner projections of the polarization propagator contributions from localized orbitals within the PP approach method (IPPP-CLOPPA).[3,15,16]

Methods and Calculations

A complete description of the method by Edison et al. for calculating $^3J_{\mathrm{HH}}$ coupling constants can be found elsewhere.[13] The Fermi contact contribution to the coupling constants is calculated using the SOS method,[17,18]

$$^3J_{\mathrm{HH}} = k\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{virt}}[1/(\epsilon_j - \epsilon_i)]\langle\Psi_i|\delta(r_{\mathrm{H}})|\Psi_j\rangle\langle\Psi_j|\delta(r_{\mathrm{H'}})|\Psi_i\rangle \quad (1)$$

where k is a constant that involves, among others, the magnetogyric ratios of the coupled nuclei and $\delta(r_{\mathrm{H}})$ is the Dirac delta function, which selects the value of occupied (unoccupied) molecular orbital $\Psi_{i(j)}$ (with eigenvalue $\epsilon_{i(j)}$) at nucleus H. The used ab initio molecular orbital (MO) procedure includes terms commonly omitted in earlier MO treatments and avoids pathologies of the Ramsey formula. The results of the Edison et al. calculations for a series of small molecules with known geometry show a high correlation with experiment although the absolute magnitudes are too small. For this reason, the calculated theoretical values J^{calc} may be related to experimental data through an equation of the form

$$J^{\mathrm{fit}} = aJ^{\mathrm{calc}} + b \quad (2)$$

where a and b are determined from a linear regression analysis with experimental data. By using the modest 6-31G* basis set, Edison et al. found $a = 6.73$ and $b = 0.57$ with a linear regression coefficient of 0.971 and a standard deviation of 0.94 Hz.[13] A Fortran program was used to calculate the Fermi contact term from NBO archive files[19,20] provided by the NBO analysis program.[21,22]

In the present work, single-point ab initio RHF/6-31G* calculations have been carried out for ethane and fluoroethane, Figure 1. Rotation of the dihedral angle ϕ between the coupled protons at 30° increments was done by using idealized rigid rotor geometry.[23] The calculations were performed with the Gaussian package of programs.[24] The Fermi contact contributions to $^3J_{\mathrm{HH}}$ were calculated from the "archive" NBO file (FILE 47),[25] the AO → NBO transformation matrix (FILE 37), and the Fock matrix in the NBO set (FILE 49), using the Fortran program by Edison et al.[13,14] conveniently modified. The original program reads the Fock matrix **F** and the overlap matrix **S** in atomic orbital (AO) basis and solves the Roothaan−Hall equations $(\mathbf{F} - \mathbf{ES})\mathbf{C} = \mathbf{0}$, where **E** is the diagonal matrix of eigenvalues ϵ_i and **C** is the matrix of eigenfunctions necessary for calculating $^3J_{\mathrm{HH}}$, eq 1. The modified program reads the Fock matrix **F'** in NBO basis from FILE 49 and, after deleting the relevant off-diagonal elements, solves the equation $(\mathbf{F'} - \mathbf{ES})\mathbf{C'} = \mathbf{0}$, where **C'** is the matrix of eigenfuntions in NBO basis, which is transformed into the matrix of eigenfunctions **C** in AO basis by means of the AO → NBO transformation matrix (FILE 37).

Results and Discussion

Ethane. *Angular Dependence.* The NBO m bonds for C−HA, C−HB, C−C, C−HA$_+$, C−HA$_-$, C−HB$_+$, and C−HB$_-$ (see Figure 1) are denoted by A, B, C, HA$_+$, HA$_-$, HB$_+$, and HB, respectively. The same symbols with an asterisk are used for the corresponding antibonds, n*. The sum of all $J^0_{\mathrm{mn}^*}$ contributions to the coupling J^0 between the protons HA and HB in ethane is denoted by $J^0_{\sigma\sigma^*}$,

$$J^0_{\sigma\sigma^*} = \sum J^0_{\mathrm{mn}^*} \quad (3)$$

The total $J^0_{\sigma\sigma^*}$ contribution to the calculated J^0 coupling of ethane shows a "Karplus-like" behavior similar to that of J^0, as can be seen in Figure 2a where both parameters are plotted against the dihedral angle ϕ between the coupled protons. The largest difference between J^0 and $J^0_{\sigma\sigma^*}$ is 3.0 Hz for $\phi = 0°$. This difference decreases when ϕ increases from 0° to 90°. For $90° < \phi < 180°$, the agreement between both curves is very good, the largest difference being 0.5 Hz for $\phi = 180°$. On the basis of this satisfactory agreement between J^0 and $J^0_{\sigma\sigma^*}$ the $J^0_{\mathrm{mn}^*}$ contributions may be taken as physically meaningful.

The $J^0_{\sigma\sigma^*}$ parameter may be decomposed into different contributions,

$$J^0_{\sigma\sigma^*} = J^0_{\mathrm{TS}} + J^0_{\mathrm{TB}} + \sum_{\mathrm{i}} J^0_{\mathrm{H_i}} + \sum_{\mathrm{i,j}} J^0_{\mathrm{H_iH_j}} \quad (4)$$

$$\mathrm{i, j} = \mathrm{A_-, A_+, B_-, B_+} \quad (5)$$

where J^0_{TS} denotes the through space contribution to $J^0_{\sigma\sigma^*}$, because it is equal to the sum of the two contributions from interactions between the NBO orbitals corresponding to the C−H bonds of the coupled protons HA and HB,

$$J^0_{\mathrm{TS}} = J^0_{\mathrm{AB}^*} + J^0_{\mathrm{BA}^*} \quad (6)$$

Because of symmetry reasons, for $^3J_{\mathrm{HH}}$ in ethane both terms must be a fortiori equal to each other. For other compounds or for different types of coupled nuclei, both terms may be very different. The through space interactions between NBO orbitals corresponding to the C−H bonds are very different from the corresponding through space interactions between the isolated atoms H at the same separation.[26]

The term J^0_{TB} represents the through C−C bond contribution to $J^0_{\sigma\sigma^*}$ since it is equal to the sum of the four contributions from interactions between the NBO orbitals corresponding to the C−C bond and to the C−H bonds of the coupled protons,

$$J^0_{\mathrm{TB}} = J^0_{\mathrm{AC}^*} + J^0_{\mathrm{BC}^*} + J^0_{\mathrm{CA}^*} + J^0_{\mathrm{CB}^*} \quad (7)$$

The term $J^0_{\mathrm{H_i}}$ is equal to the sum of the four contributions from interactions between the NBO orbitals corresponding to

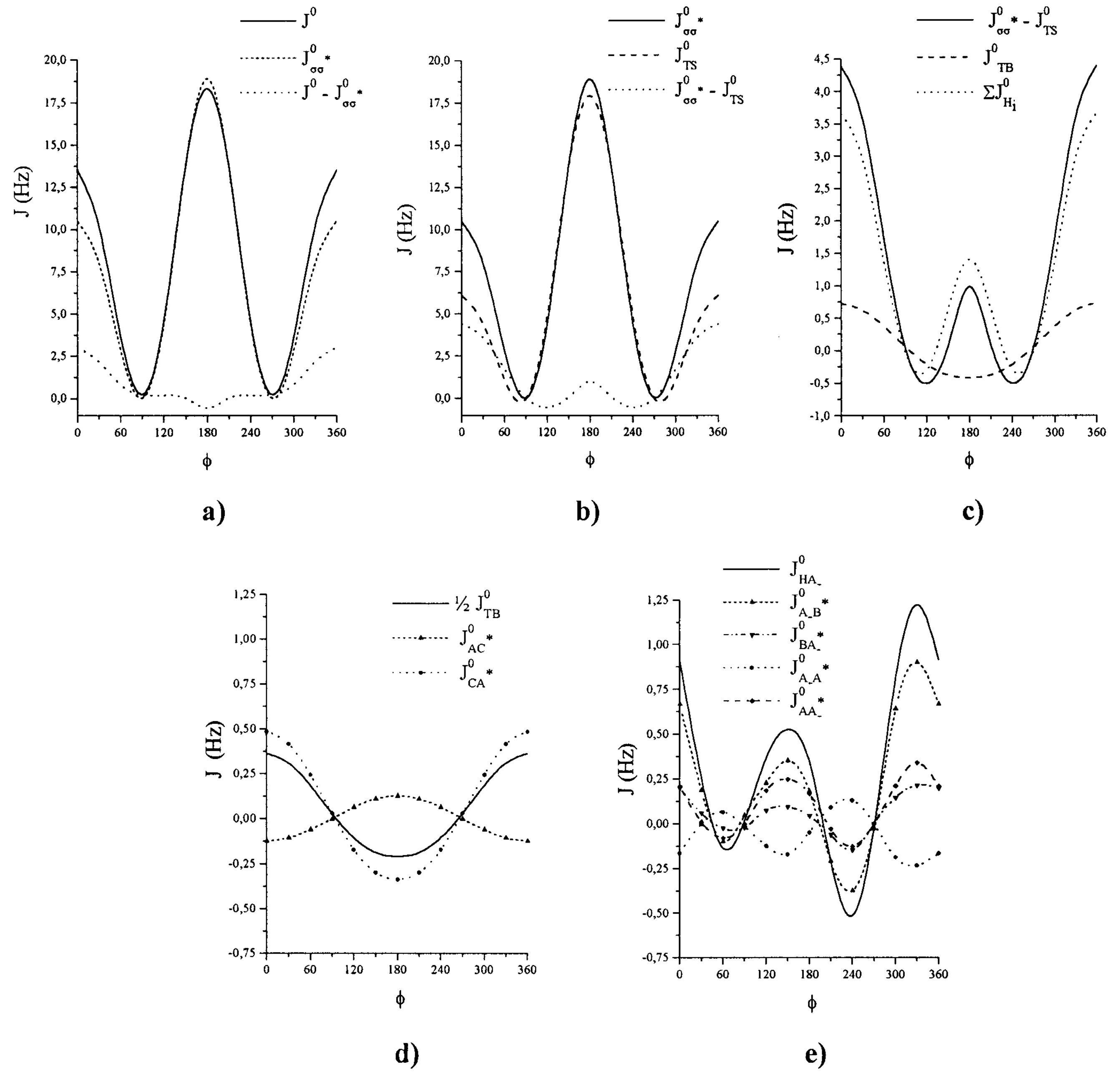

Figure 2. Angular dependence in ethane: (a) comparison of the calculated J^0 coupling with the sum $J^0_{\sigma\sigma^*}$ of the $J^0_{\mathrm{mm}^*}$ contributions; (b) comparison of $J^0_{\sigma\sigma^*}$ with the through space contribution J^0_{TS}; (c) contributions other than the through space J^0_{TS} (sum of these contributions $J^0_{\sigma\sigma^*} - J^0_{\mathrm{TS}}$, through C−C bond contribution J^0_{TB} and sum of hydrogen contributions $\sum J^0_{\mathrm{H_i}}$); (d) through C−C bond contribution J^0_{TB} and its components $J^0_{\mathrm{AC}^*}$ and $J^0_{\mathrm{CA}^*}$; (e) the hydrogen HA₋ contribution $J^0_{\mathrm{HA}_-}$ and its components $J^0_{\mathrm{A\_B}^*}$, $J^0_{\mathrm{BA\_}^*}$, $J^0_{\mathrm{A\_A}^*}$, and $J^0_{\mathrm{AA\_}^*}$.

either the C−H$_i$ bonds or antibonds (H$_i$ = H$_{A+}$, H$_{A-}$, H$_{B+}$, H$_{B-}$) with the C−H antibond or bond containing the coupled protons,

$$J^0_{\mathrm{H_i}} = J^0_{\mathrm{H_iA^*}} + J^0_{\mathrm{H_iB^*}} + J^0_{\mathrm{AH_i^*}} + J^0_{\mathrm{BH_i^*}} \qquad (8)$$

The term $J^0_{\mathrm{H_i}}$ will be dubbed the contribution (or effect) of the H$_i$ hydrogen upon $J^0_{\sigma\sigma^*}$.

Finally, the term $J^0_{\mathrm{H_iH_j}}$ is equal to the sum of the two contributions from interactions between the NBO orbitals corresponding to the C−H$_i$ and C−H$_j$ bonds,

$$J^0_{\mathrm{H_iH_j}} = J^0_{\mathrm{H_iH_j^*}} + J^0_{\mathrm{H_jH_i^*}} \qquad (9)$$

The term $J^0_{\mathrm{H_iH_j}}$ will be named the effect of the interaction between the hydrogens H$_i$ and H$_j$.

The main contribution to $J^0_{\sigma\sigma^*}$ is the through space J^0_{TS} which, together with $J^0_{\sigma\sigma^*}$, are plotted in Figure 2b against ϕ where for the sake of comparison, their difference is also displayed. The largest differences between $J^0_{\sigma\sigma^*}$ and J^0_{TS} appear for angles ϕ between 0° and 90°. For ϕ equal to 0° the contribution J^0_{TS} amounts 6.1 Hz, while the sum of the remaining contributions in eq 4 amounts 4.4 Hz.

The sum of all the other contributions than J^0_{TS} to $J^0_{\sigma\sigma^*}$, i.e., $J^0_{\sigma\sigma^*} - J^0_{\mathrm{TS}}$, is plotted in Figure 2c together with the through bond contribution J^0_{TB}, eq 7, and the sum $\sum J^0_{\mathrm{H_i}}$ of the substituent hydrogen effects, eq 8. The $\sum J^0_{\mathrm{H_i}}$ values are close to $J^0_{\sigma\sigma^*} - J^0_{\mathrm{TS}}$ but there is a small contribution from J^0_{TB} that changes from 0.7 Hz for ϕ equal to 0° to −0.4 Hz for ϕ equal to 90°. The contribution to $J^0_{\sigma\sigma^*}$ from interactions between pairs of hydrogens, eq 9, does not appear plotted in Figure 2c because it is always smaller than 0.3 Hz in magnitude.

According to eq 7 the through C−C bond contribution J^{0}_{TB} is equal to the sum of four terms being $J^{0}_{\mathrm{AC}*} = J^{0}_{\mathrm{BC}*}$ and $J^{0}_{\mathrm{CA}*} = J^{0}_{\mathrm{CB}*}$. The terms $J^{0}_{\mathrm{AC}*}$ and $J^{0}_{\mathrm{CA}*}$ are plotted in Figure 2d together with the sum of both, which is equal to $^{1}/_{2}J^{0}_{\mathrm{TB}}$. The signs of $J^{0}_{\mathrm{AC}*}$ and $J^{0}_{\mathrm{CA}*}$ are different. As a consequence, the sum of both terms, i.e., $^{1}/_{2}J^{0}_{\mathrm{TB}}$, is smaller in magnitude than the main term $J^{0}_{\mathrm{CA}*}$.

Each of the four hydrogen effects, $J^{0}_{\mathrm{H_i}}$, is given by the combination of four terms, eq 8. The effect $J^{0}_{\mathrm{HA\_}}$, for i = A_{-}, of the hydrogen HA_{-} is plotted in Figure 2e together with its four contributions. The main contribution $J^{0}_{\mathrm{A\_B}*}$ is reinforced by $J^{0}_{\mathrm{AA\_}*}$ and $J^{0}_{\mathrm{AB\_}*}$ but weakened by $J^{0}_{\mathrm{A\_A}*}$. The four $J^{0}_{\mathrm{H_i}}$ effects are related by

$$J^{0}_{\mathrm{HA\_}}(\phi) = J^{0}_{\mathrm{HB\_}}(\phi) = J^{0}_{\mathrm{HA_+}}(-\phi) = J^{0}_{\mathrm{HB_+}}(-\phi) \quad (10)$$

These relations can be derived from the invariance of the $^{3}J_{\mathrm{HH}}$ coupling under reflections and rotations of the nuclear coordinates.[27] Likewise, the contributions to the $J^{0}_{\mathrm{H_i}}$ effects are related by

$$J^{0}_{\mathrm{A\_B}*}(\phi) = J^{0}_{\mathrm{B\_A}*}(\phi) = J^{0}_{\mathrm{A_+B}*}(-\phi) = J^{0}_{\mathrm{B_+A}*}(-\phi) \quad (11)$$

$$J^{0}_{\mathrm{A\_A}*}(\phi) = J^{0}_{\mathrm{B\_B}*}(\phi) = J^{0}_{\mathrm{A_+A}*}(-\phi) = J^{0}_{\mathrm{B_+B}*}(-\phi) \quad (12)$$

$$J^{0}_{\mathrm{BA\_}*}(\phi) = J^{0}_{\mathrm{AB\_}*}(\phi) = J^{0}_{\mathrm{BA_+}*}(-\phi) = J^{0}_{\mathrm{AB_+}*}(-\phi) \quad (13)$$

$$J^{0}_{\mathrm{AA\_}*}(\phi) = J^{0}_{\mathrm{BB\_}*}(\phi) = J^{0}_{\mathrm{AA_+}*}(-\phi) = J^{0}_{\mathrm{BB_+}*}(-\phi) \quad (14)$$

Taking into account eqs 10−14, the plots in Figure 2e for $J^{0}_{\mathrm{HA\_}}(\phi)$ and its contributions can be used for the remaining $J^{0}_{\mathrm{H_i}}$ effects after changing conveniently the notation in the case of $J^{0}_{\mathrm{HB\_}}(\phi)$, and also the abscissa sign in the cases of $J^{0}_{\mathrm{HA_+}}(\phi)$ and $J^{0}_{\mathrm{HB_+}}(\phi)$. The change of the abscissa sign is equivalent to changing the abscissa scale from 360° to 0° instead of from 0° to 360°. This fact explains why the curve for the sum of the $\sum J^{0}_{\mathrm{H_i}}$ effects is symmetrical with respect to $\phi = 180°$ (see Figure 2c), while the curve for $J^{0}_{\mathrm{HA\_}}$ is clearly asymmetrical.

The dependence upon the angle ϕ = H−C−C−H of the J^{0} coupling of ethane is far different from the dependence on ϕ of the NBO second-order perturbation interaction $\Delta E^{(2)}$ between $\sigma_{\mathrm{A}} \rightarrow \sigma^{*}_{\mathrm{B}}$ (or $\sigma_{\mathrm{B}} \rightarrow \sigma^{*}_{\mathrm{A}}$), as Figure 3 shows. Like in the case of the dependence upon the angle ϕ = H−N−C−H of the $^{3}J_{\mathrm{HH}}$ coupling of a model peptide[3], the relation $J^{0}/\Delta E^{(2)}$ is much larger for the cis orientation, $\phi = 0°$, than for the trans orientation, $\phi = 180°$. The reason for this difference of behavior between the cis and the trans orientations is triple. The first of these reasons is the fact that the contribution to $J^{0}_{\sigma\sigma*}$ of the $\sigma_{\mathrm{A}} \rightarrow \sigma^{*}_{\mathrm{B}}$ and $\sigma_{\mathrm{B}} \rightarrow \sigma^{*}_{\mathrm{A}}$ interactions is not proportional to $\Delta E^{(2)}$. This contribution correspond to the through space J^{0}_{TS} term plotted in Figure 2b against ϕ. The term J^{0}_{TS} explains most of the $J^{0}(180°)$ value and a half of $J^{0}(0°)$. Therefore, the relation $J^{0}_{\mathrm{TS}}/\Delta E^{(2)}$ is ca. 2.5 times greater for the cis than for the trans orientation. The two other reasons are the facts that other terms than J^{0}_{TS} fairly contribute to $J^{0}_{\sigma\sigma*}(0°)$, see Figure 2b, and that for ϕ equal to 0°, $J^{0}_{\sigma\sigma*}$ is smaller than J^{0}, see Figure 2a.

Fluoroethane. *Substituent Effects.* Comparison of the calculated contributions to $^{3}J_{\mathrm{HH}}$ in fluoroethane and in ethane allow us to analyze the effect upon the vicinal coupling of substituting an atom of H in the ethane molecule by an atom of F. The F substituent is placed in the A_{-} position, Figure 1b, and the NBO filled orbital for the C−F bond is denoted by FA_{-}. Expressions for a F atom in other positions can be deduced from those in the A_{-} position by means of eqs 10−14 after changing the symbols A_{-}, A_{+}, B_{-}, and B_{+} in sub index by FA_{-}, FA_{+}, FB_{-}, and FB_{+}, respectively.

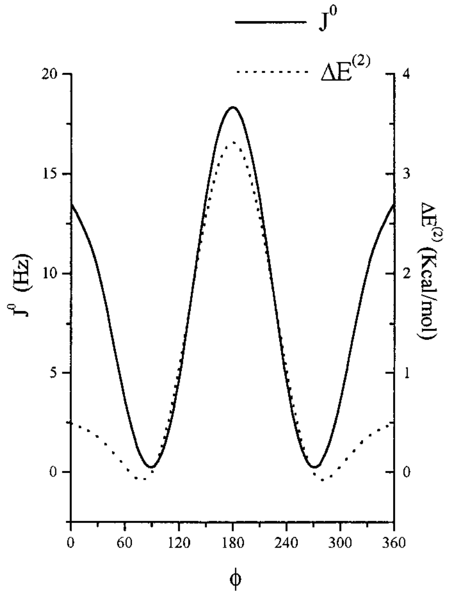

Figure 3. Comparison of the angular dependence in ethane for the calculated J^{0} coupling and for the NBO second-order perturbation interaction $\Delta E^{(2)}$ between $\sigma_{\mathrm{A}} \rightarrow \sigma^{*}_{\mathrm{B}}$.

The parameter $J^{\mathrm{F}}_{\sigma\sigma*}$ for fluoroethane may be decomposed into different contributions, like $J^{0}_{\sigma\sigma*}$ for ethane was in eq 4,

$$J^{\mathrm{F}}_{\sigma\sigma*} = J^{\mathrm{F}}_{\mathrm{TS}} + J^{\mathrm{F}}_{\mathrm{TB}} + J^{\mathrm{F}}_{\mathrm{FA\_}} + \sum_{\mathrm{k}} J^{\mathrm{F}}_{\mathrm{H_k}} + \sum_{\mathrm{k}} J^{\mathrm{F}}_{\mathrm{FH_k}} + \sum_{\mathrm{k,l}} J^{\mathrm{F}}_{\mathrm{H_kH_l}} \quad (15)$$

$$\mathrm{k, l} = \mathrm{A}_{+}, \mathrm{B}_{-}, \mathrm{B}_{+} \quad (16)$$

The terms in this equation with the same sub indexes than in eq 4, i.e., $J^{\mathrm{F}}_{\mathrm{TS}}$, $J^{\mathrm{F}}_{\mathrm{TB}}$, $J^{\mathrm{F}}_{\mathrm{H_k}}$, and $J^{\mathrm{F}}_{\mathrm{H_kH_l}}$, are given by expressions 6−9 after changing the J^{0}_{X} symbols to the respective $J^{\mathrm{F}}_{\mathrm{X}}$. Therefore, the interactions $\sigma_{\mathrm{m}} \rightarrow \sigma^{*}_{\mathrm{n}}$ making up these terms are the same in fluoroethane as in ethane. In addition, there are other interactions in fluoroethane that are not in ethane, i.e., those related with the C−F bond and with the lone pairs of electrons in the F atom.

The $J^{\mathrm{F}}_{\mathrm{FA\_}}$ term in eq 15 corresponds to the F effect and is given by the combination of a term $J^{\mathrm{F}}_{\mathrm{CF}}$ related with the C−F bond and a term $J^{\mathrm{F}}_{\mathrm{FP}}$ related with the F lone pairs,

$$J^{\mathrm{F}}_{\mathrm{FA\_}} = J^{\mathrm{F}}_{\mathrm{CF}} + J^{\mathrm{F}}_{\mathrm{FP}} \quad (17)$$

$$J^{\mathrm{F}}_{\mathrm{FA\_}} = \sum_{\mathrm{p}} (J^{\mathrm{F}}_{\mathrm{F_pA}*} + J^{\mathrm{F}}_{\mathrm{F_pB}*}) + \sum_{\mathrm{q}} (J^{\mathrm{F}}_{\mathrm{AF_q}*} + J^{\mathrm{F}}_{\mathrm{BF_q}*}) \quad (18)$$

where p indexes the NBO filled orbitals of F, i.e., the C−F bond and the lone pairs, and q the unfilled ones. Sums for the σ_{CF} and σ^{*}_{CF} orbitals give rise to the $J^{\mathrm{F}}_{\mathrm{CF}}$ term. Sums involving lone pairs give rise to the $J^{\mathrm{F}}_{\mathrm{FP}}$ term.

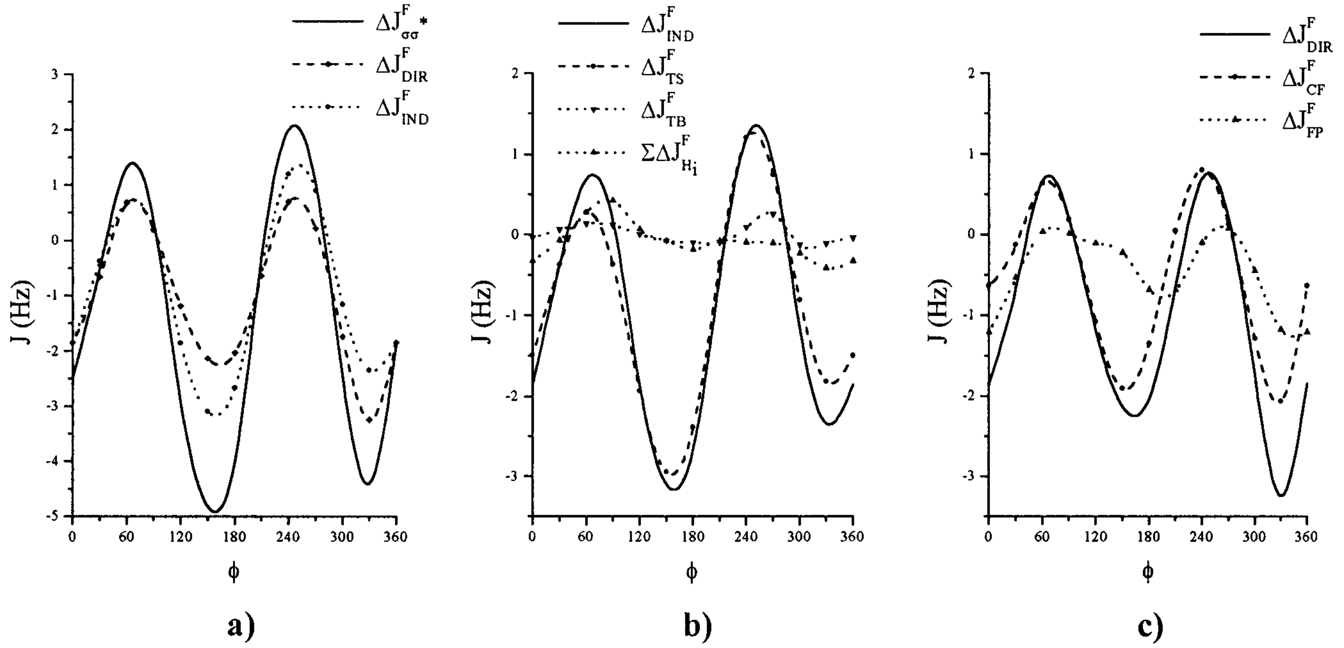

Figure 4. Angular dependence in fluoroethane: (a) the substituent effect $\Delta J^{F}_{\sigma\sigma^*}$ and of its direct ΔJ^{F}_{DIR} and indirect ΔJ^{F}_{IND} components; (b) indirect contribution ΔJ^{F}_{IND} and its components ΔJ^{F}_{TS}, ΔJ^{F}_{TB}, and $\sum\Delta J^{F}_{H_k}$; (c) direct contribution ΔJ^{F}_{DIR} and its components ΔJ^{F}_{CF} and ΔJ^{F}_{FP}.

The $J^{F}_{FH_k}$ terms in eq 15 correspond to the effect of interactions between the F and the H_k hydrogens,

$$J^{F}_{FH_k} = \sum_{p} J^{F}_{F_pH_k^*} + \sum_{q} J^{F}_{H_kF_q^*} \qquad (19)$$

Substitution of a hydrogen H in position A_- of ethane by a fluorine F (see Figure 1) changes the parameter $J^{0}_{\sigma\sigma^*}$ of ethane by an amount $\Delta J^{F}_{\sigma\sigma^*}$ equal to the difference between $J^{F}_{\sigma\sigma^*}$ of fluoroethane and $J^{0}_{\sigma\sigma^*}$,

$$\Delta J^{F}_{\sigma\sigma^*} = J^{F}_{\sigma\sigma^*} - J^{0}_{\sigma\sigma^*} \qquad (20)$$

This substituent effect $J^{F}_{\sigma\sigma^*}$ can be decomposed in a direct ΔJ^{F}_{DIR}, an indirect ΔJ^{F}_{IND}, and an interaction ΔJ^{F}_{INT} contributions,

$$\Delta J^{F}_{\sigma\sigma^*} = \Delta J^{F}_{DIR} + \Delta J^{F}_{IND} + \Delta J^{F}_{INT} \qquad (21)$$

The direct contribution J^{F}_{DIR} is equal to the difference between the contribution J^{F}_{FA-} to $J^{F}_{\sigma\sigma^*}$ of the F, given by eq 17, and the contribution J^{0}_{HA-} to $J^{0}_{\sigma\sigma^*}$ of the H in position A_-, given by eq 8

$$\Delta J^{F}_{DIR} = J^{F}_{FA} - J^{0}_{HA\_} \qquad (22)$$

Taking into account the second member in eq 17 the term J^{F}_{DIR} can be decomposed into a contribution ΔJ^{F}_{CF} related to the C−F bond,

$$\Delta J^{F}_{CF} = J^{F}_{CF} - J^{0}_{HA\_} \qquad (23)$$

and another contribution ΔJ^{F}_{FP} from the lone pairs of F,

$$\Delta J^{F}_{DIR} = \Delta J^{F}_{CF} - \Delta J^{F}_{FP} \qquad (24)$$

The indirect contribution ΔJ^{F}_{IND} is given by

$$\Delta J^{F}_{IND} = \sum_{X} \Delta J^{F}_{X}, \qquad X = TS, TB, H_k, H_kH_l \qquad (25)$$

with

$$\Delta J^{F}_{X} = J^{F}_{X} - J^{0}_{X} \qquad (26)$$

These represent the changes in the through space (ΔJ^{F}_{TS}), through C−C bond (ΔJ^{F}_{TB}), H_k ($\Delta J^{F}_{H_k}$), and H_kH_l ($\Delta J^{F}_{H_kH_l}$) contributions due to the substitution of the H in position A_- of ethane by a F atom.

Finally, the interaction contribution ΔJ^{F}_{INT} is given by

$$\Delta J^{F}_{INT} = \sum_{k} (J^{F}_{FH_k} - J^{0}_{H_{A\text{-}}H_k}) \qquad (27)$$

This represents the sum of the differences between the contributions from interactions of the F with the H_k hydrogens in fluoroethane and from interactions of the H in position A_- of ethane with the remaining H_k hydrogens.

The direct ΔJ^{F}_{DIR} and indirect ΔJ^{F}_{IND} contributions to the substituent effect $\Delta J^{F}_{\sigma\sigma^*}$ show a similar angular dependence on ϕ (see Figure 4a), with positive maxima near 60° and 240° and negative minima near 160° and 330°. The ΔJ^{F}_{INT} contribution, with magnitude smaller than 0.3 Hz, is not plotted in Figure 4a. Only the interaction of the lone pairs of F with the σ^*_{A+} orbital gives noteworthy contributions to ΔJ^{F}_{INT}.

The indirect contributions ΔJ^{F}_{IND} and its components ΔJ^{F}_{TS}, ΔJ^{F}_{TB}, and $\sum J^{0}_{H_k}$, see eqs 25 and 26, are plotted against the angle ϕ in Figure 4b. The change in the through space term ΔJ^{F}_{TS} is the main component of ΔJ^{F}_{IND}. The change in the through bond term ΔJ^{F}_{TB} and the sum of the changes in the H_k terms $\Delta J^{F}_{H_k}$ are very small. The changes $\Delta J^{F}_{H_kH_l}$, not plotted in Figure 4b, are negligible.

The direct contribution ΔJ^{F}_{DIR} and its components ΔJ^{F}_{CF} and ΔJ^{F}_{FP} (see eqs 22−24) are plotted in Figure 4c against the angle ϕ. The term $\Delta J^{\mathrm{F}}_{\mathrm{CF}}$ related to the C−F bond is the main component of $\Delta J^{\mathrm{F}}_{\mathrm{DIR}}$, but the negative contribution of the lone pairs $\Delta J^{\mathrm{F}}_{\mathrm{FP}}$ is appreciable with minima near 200° and 340°.

Conclusion

The analysis of the $^3J_{\mathrm{HH}}$ coupling constant in ethane based upon the NBO interactions $\sigma_{\mathrm{m}} \rightarrow \sigma^*_{\mathrm{n}}$ shows that the through-space J^{0}_{TS} term is the main contribution to $^3J_{\mathrm{HH}}$ (see Figure 2b). Nevertheless, the contribution to $^3J_{\mathrm{HH}}$ from the substituent hydrogens $\sum J^{0}_{\mathrm{H_i}}$ is also important, particularly for angles ϕ close to 0° (see Figure 2c). On the contrary, according to the IPPP−CLOPPA method the $^3J_{\mathrm{HH}}$ coupling constant is completely transmitted through-space by only the bonds and antibonds containing the coupled protons.[28] The structure of these bonds is influenced by the remaining bonds in the molecule which, however, do not take part in any of the coupling pathways.[28] Therefore, the IPPP-CLOPPA method embodies in the through-space transmission pathway the substituent effects calculated using the method of NBO interactions developed in this paper or using the NNBI (neglect of nonbonded interactions) approach.[29] Consequently, the meaning of the terms through-space, through-bond, and substituent effect depends on the method used, reflecting that this division of the total coupling has a certain degree of arbitrariness. Only the total coupling is amenable to measurement.

In the IPPP-CLOPPA method localized molecular orbitals (LMOs) are obtained by applying a unitary transformation to the canonical MOs arising from a RHF calculations. Then, the $^3J_{\mathrm{HH}}$ coupling is decomposed into a sum of individual terms (coupling pathways), each one depending on at most four LMOs. On the other hand, in our NBO method a standard calculation is compared with a modified calculation in which the elements of the Fock matrix associated with the interactions of interest are set equal to zero. The difference between the calculated values for $^3J_{\mathrm{HH}}$ is attributed to the effect upon $^3J_{\mathrm{HH}}$ of the bonds involved in the deleted interactions. In this way, the effect upon $^3J_{\mathrm{HH}}$ of any molecular fragment can be easily estimated which may be useful in the derivation of generalized Karplus equations.[27]

The elucidation of the origin for the differences between the decompositions of $^3J_{\mathrm{HH}}$ into sums of individual terms provided by the methods of NBO interactions and IPPP-CLOPPA is difficult. In addition to the fact that both methods are, in principle, physically different, the IPPP-CLOPPA method uses LMOs, which differ in localizability and transferability from the NBOs.[30] Furthermore, in the case of the IPPP-CLOPPA method, the $^3J_{\mathrm{HH}}$ couplings are calculated from semiempirical INDO wave functions using the polarization propagator technique to calculate the second-order corrections to the energy within the random phase approximation level,[3,15,16,28] while in the case of the NBO interaction method, the $^3J_{\mathrm{HH}}$ couplings are calculated from ab initio 6-31G* wave functions using the Pople Santry sum over states expression.[18] Each of these differences between methods can contribute to the differences between both decompositions of $^3J_{\mathrm{HH}}$.

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References and Notes

(1) Thomas, W. A. *Prog. NMR Spectrosc*. **1997**, *30*, 183.
(2) Karplus, M. *J. Chem. Phys*. **1959**, *30*, 11.
(3) Contreras, R. H.; Peralta, J. E. *Prog. NMR Spectrosc.*, in press.
(4) Guilleme, J.; San Fabián, J.; Casanueva, J.; Díez, E. *Chem. Phys. Lett.* **1999**, *314*, 168.
(5) Pecul, M.; Jaszuñski, M.; Sadlej, J. *Chem. Phys. Lett.* **1999**, *305*, 139.
(6) Grayson, M.; Sauer, S. P. A. *Mol. Phys.* **2000**, *98*, 1981.
(7) Sekino, M.; Bartlett, R. J. *Chem. Phys. Lett.* **1994**, *225*, 486.
(8) Guilleme, J.; San Fabián, J. *J. Chem. Phys.* **1998**, *109*, 8168.
(9) Provasi, P. F.; Aucar, G. A.; Sauer, S. P. A. *J. Chem. Phys.* **2000**, *112*, 6201.
(10) San Fabián, J.; Guilleme, J.; Díez, E.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Chem. Phys. Lett.* **1993**, *206*, 253.
(11) San Fabián, J.; Guilleme, J.; Díez, E.; Lazzeretti, P.; Malagoli, M.; Zanasi, R.; Esteban, A. L.; Mora, F. *Mol. Phys.* **1994**, *82*, 913.
(12) San Fabián, J.; Guilleme, J.; Díez, E. *Mol. Phys.* **1997**, *91*, 343.
(13) Edison, A. S.; Markley, J. L.; Weinhold, F. *J. Phys. Chem.* **1993**, *97*, 11657.
(14) Edison, A. S.; Markley, J. L.; Weinhold, F. *J. Biomol. NMR* **1994**, *4*, 519.
(15) Diz, A. C.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *Int. J. Quantum Chem.* **1990**, *37*, 663.
(16) Contreras, R. H.; Peralta, J. A.; Giribet, C. G.; Ruiz de Azúa, M. C.; Facelli, J. C. *Annu. Rep. NMR Spectrosc.* **2000**, *41*, 55.
(17) Ramsey, N. F. *Phys. Rev.* **1953**, *91*, 303.
(18) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.
(19) Glendenig, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *QCPE Bull.* **1990**, *10*, 58.
(20) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.
(21) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.
(22) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.
(23) Pople, J. A.; Gordon, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 4253.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.
(25) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO Version 3.1*.
(26) Becskey, G. B. *Chem. Phys. Lett.* **1995**, *242*, 507.
(27) Diez, E.; San Fabian, J.; Guilleme, J.; Altona, C.; Donders, L. A. *Mol. Phys.* **1989**, *68*, 49.
(28) Cavasotto, C. N.; Giribet, C. G.; Ruiz de Azúa, M. C.; Contreras, R. H. *J. Comput. Chem.* **1991**, *12*, 141.
(29) Barfield, M. *J. Am. Chem. Soc.* **1980**, *102*, 1.
(30) Carpenter, J. E.; Weinhold, F. *J. Am. Chem. Soc.* **1988**, *110*, 368.