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Calculation of Nuclear Spin–Spin Coupling Constants with *ab Initio* Molecular Orbital Wave Functions

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We investigate the use of *ab initio* molecular wave functions to evaluate the Fermi contact contribution to nuclear spin–spin coupling constants $^nJ_{AB}$ (A, B = C, H) for a data set of 19 molecules having well-defined experimental geometry and coupling values. We critically examine the theoretical and numerical problems associated with the Dirac δ function operator and its perturbation–theoretic treatment. We show that the common approximation of neglecting basis orbitals not centered on the coupled nuclei is a major source of error in previous calculations. By using the Pople–Santry sum-over-states expression in conjunction with modest *ab initio* MO basis sets (i.e., 3-21G, 6-31G*), we find that calculated values of $^3J_{HH}$, $^2J_{HH}$, and $^1J_{CC}$ show high correlation with experiment ($r^2 \simeq 0.96$–0.99). Calculated $^nJ_{CH}$ values are less highly correlated with experiment, probably resulting from neglect of contributions other than the Fermi contact term. On the basis of these comparisons, we conclude that vicinal and geminal proton–proton coupling constants can be estimated with ~ 1-Hz absolute accuracy by applying modest levels of *ab initio* molecular orbital theory.

I. Introduction

Nuclear magnetic resonance (NMR) spectroscopy yields chemical shifts (σ_A) and nuclear spin–spin coupling constants (J_{AB}) for magnetic nuclei A and B, arising from magnetic and spin interactions that are absent in nonrelativistic (Schrödinger) theory but appear naturally in relativistic quantum field theory. Although these NMR parameters potentially provide a wealth of information about molecular structure and dynamics, the theoretical situation with respect to their accurate calculation is still far from satisfactory.

Considerable effort has been devoted to calculating coupling constants (for reviews see refs 1–6), but quantitative prediction of J_{AB} remains problematic. Among the more promising techniques currently available for calculating J_{AB} are the polarization propagator methods developed by Oddershede and co-workers.[7] These techniques have often been successful in reproducing experimental couplings in small molecules, but as pointed out by Oddershede,[8] large molecules must still be treated at a semiempirical level, such as the INDO-MO (intermediate neglect of differential overlap molecular orbital) method.[9,10] Kowalewski and co-workers have made progress in including effects of electron correlation in calculations of J_{AB},[11,12] but these calculations, like the polarization propagator methods, are computationally intensive and thus not readily applicable to larger molecules. In short, methods that work well for small molecules, such as methane or ethane, must commonly be compromised with semiempirical or INDO-type approximations when applied to larger molecules. Early attempts to calculate J_{AB} with MO sum-over-states (SOS) perturbaton expressions[13] revealed the notorious sensitivity of these expressions to "cancellation of large terms of opposite sign."[14] This sensitivity led to the development of coupled methods[14] and to a near-abandonment of SOS techniques.

Here we examine the theoretical basis of SOS perturbation methods based on the fundamental Ramsey theory[15] and develop a modified SOS approach that incorporates *ab initio* wave functions. These calculations are relatively modest in computational cost and can be carried out with readily available electronic structure packages. As a result, they are practical for amino acids and small model peptides and can be used to extend the types of structural inferences available from modern NMR data.

The plan of the paper is as follows. In section II we critically review the basic Ramsey expression[15] for nuclear spin coupling constants and the corresponding MO treatment (due to Pople and Santry[13]) and point out some mathematical pathologies of the underlying theory. In section III, we describe an *ab initio* MO procedure for calculating the Fermi contact contribution to J_{AB} that includes terms commonly omitted in earlier MO treatments but avoids pathologies of the Ramsey formula. We present results (section IV) at a variety of *ab initio* Hartree–Fock basis set levels for $^nJ_{AB}$ (n = 1–3; A, B = C, H) in a representative data set of 19 hydrocarbons for which accurate experimental coupling constants and geometrical parameters are known. These results reveal a high degree of correlation ($r^2 \simeq 0.96$–0.99) with experimental vicinal and geminal proton–proton couplings ($^{2,3}J_{HH}$) and single-bond carbon–carbon couplings ($^1J_{CC}$) but somewhat lower correlations for C–H couplings. The correlations, which are achieved despite the need for linear scaling to overcome rather large errors in absolute magnitude, are indicative of the useful chemical content of SOS expressions. In section IV we also investigate the numerical effect of neglecting non-valence-s AO contact contributions from adjacent nuclei, apparently a large source of error in previous calculations. Further discussion is presented in section V, where we briefly compare our results with previous methods. Section VI concludes with a discussion of future prospects for theoretical analysis of spin coupling constants in biologically significant molecules.

II. Ramsey's Theory of Spin Coupling Constants in Molecular Orbital Approximation

A. Physical Basis of Ramsey's Formula. In 1953, Ramsey presented a classic treatment of J_{AB} in the framework of quantum-mechanical Rayleigh–Schrödinger perturbation theory.[15] Ramsey identified three distinct physical contributions to nuclear spin coupling: (i) the "orbital" contribution, due to polarizations induced by a magnetic nucleus in the electronic orbital motion which create magnetic fields at other nuclei; (ii) the "spin-dipolar"

contribution, due to polarizations induced in the electron spin distribution which create similar fields at coupled nuclei; and (iii) the "Fermi contact" contribution, due to electrons occupying orbitals that have simultaneous nonzero amplitudes at both nuclei. The orbital and spin-dipolar contributions (which vary as the inverse third power of electron–nuclear separation) are usually considered to be small compared to the Fermi contact term and will be ignored here. From the reduction of the relativistic Dirac equation to its nonrelativistic limit (see, e.g., ref. 16 and section 38, p 170, of ref 17), the Fermi contact term may be associated with a perturbation operator $\mathcal{H}^{(1)}$ of the form

$$\mathcal{H}^{(1)} = \mathcal{H}_{fc} = \frac{4\mu_0\mu_B\hbar}{3}\sum_N \gamma_N \sum_k \delta(\mathbf{r}_{kN})\hat{\mathbf{S}}_k\cdot\hat{\mathbf{I}}_N \qquad (1)$$

where $\delta(\mathbf{r}_{kN})$ is Dirac's δ function for electron k evaluated at nucleus N (with nuclear charge $Z_N e$), μ_0 is the permeability of a vacuum, μ_B is the Bohr magneton, and γ_N is the magnetogyric ratio of nucleus N. $\hat{\mathbf{S}}_k$ and $\hat{\mathbf{I}}_N$ are electron (k) and nuclear (N) spin operators, respectively. The unperturbed $\mathcal{H}^{(0)}$ is taken to be the usual nonrelativistic molecular electronic Hamiltonian $\mathcal{H}_{nr}$ in the Born–Oppenheimer approximation

$$\mathcal{H}^{(0)} = \mathcal{H}_{nr} = -\sum_i\left(\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_\alpha \frac{Z_\alpha e^2}{r_{\alpha i}}\right) + \sum_{i,j}'\frac{e^2}{r_{ij}} \qquad (2)$$

where the symbols have their usual meaning.[18] Operators 1 and 2 are added to give a relativistically corrected Hamiltonian $\mathcal{H}_r$ of Breit–Pauli[17] form

$$\mathcal{H}_r = \mathcal{H}^{(0)} = \mathcal{H}^{(1)} \qquad (3)$$

and a standard Rayleigh–Schrödinger perturbation theory treatment of this operator leads to the Ramsey equation for the Fermi contact contribution to the second-order spin–spin coupling between nuclei A and B[15]

$$J_{AB} = -(16\hbar/27\pi)\mu_0^2\mu_B^2\gamma_A\gamma_B \times$$
$$\sum_n \frac{1}{{}^3E_n - {}^1E_0}\langle 0|\sum_k \delta(\mathbf{r}_{kA})\hat{S}_k|n\rangle\langle n|\sum_j \delta(\mathbf{r}_{jB})\hat{S}_j|0\rangle \qquad (4)$$

where the ground singlet state $|0\rangle$ and excited triplet states $|n\rangle$ have respective energies ${}^1E_0$, ${}^3E_n$. Equation 4 forms the basis for all subsequent developments.

B. Formal Difficulties of the Ramsey Expression. Significant formal and numerical difficulties are associated with perturbation theory expressions based on eq 3:

It is known[17] that reduction of the relativistic quantum field theory to a Schrödinger-type equation with effective Breit–Pauli Hamiltonian $\mathcal{H}_r$ is valid *only* for first-order correction of the nonrelativistic energy by using the nonrelativistic zeroth-order eigenfunction $\Psi^{(0)} = \Psi_{nr}$

$$E_r = E_{nr} + \langle\Psi_{nr}|\mathcal{H}^{(1)}|\Psi_{nr}\rangle = E^{(0)} + E^{(1)} \qquad (5)$$

or, equivalently, by evaluating $\mathcal{H}_r$ with the nonrelativistic $\Psi^{(0)}$

$$E_r = \langle\Psi^{(0)}|\mathcal{H}_r|\Psi^{(0)}\rangle \qquad (6)$$

As pointed out by Bethe and Salpeter,[19] it is generally *incorrect* to associate E_r with the solution $\tilde{E}_r$ of the eigenvalue equation for $\mathcal{H}_r$

$$\mathcal{H}_r\Psi = \tilde{E}_r\Psi \qquad (7)$$

or with a variational expectation value $(\Phi \neq \Psi^{(0)})$

$$\tilde{E}_r = \langle\Phi|\mathcal{H}_r|\Phi\rangle \qquad (8)$$

Although this restriction is usually stated for the relativistic mass increase (p^4) correction, it apparently applies to the Fermi contact

term as well, since the Dirac delta function introduces arbitrarily large momentum components. Pending derivation of higher-order magnetic corrections from relativistic quantum field theory, it appears that the second-order Ramsey expression has only heuristic justification.

A further difficulty associated with perturbative treatment of the Dirac δ function is manifested in the fact that the operator $\mathcal{H} = \mathcal{H}_r = \mathcal{H}^{(0)} + \mathcal{H}^{(1)}$ of the formal eigenvalue equation (eq 7) cannot satisfy the formal mathematical requirements of Schrödinger-type operators in Hilbert space. The fundamental theory of such operators (cf. Kato)[20] requires that $\mathcal{H}\Phi$ be square integrable for all functions Φ in the Hermitian domain of $\mathcal{H}$. This requirement cannot be satisfied by the highly singular Dirac δ function. The non-square-integrability of $\mathcal{H}_r\Phi$ in turn implies that $(\Delta\mathcal{H}_r)^2 = \langle\mathcal{H}_r^2\rangle - \langle\mathcal{H}_r\rangle^2$ is divergent, the spectrum of $\mathcal{H}_r$ becomes unbounded, and the usual variational theorems for eigenvalues of $\mathcal{H}_r$ are inapplicable. The corresponding perturbative (and variation–perturbation) treatments of $\mathcal{H}_r$ are similarly invalid, since corrections beyond the first order in $\mathcal{H}_{fc}$ are formally divergent. Hiller and co-workers[21] have proposed an alternative integral representation of the contact operator, but the numerical behavior would presumably be ill-conditioned whether $\delta(\mathbf{r})$ or its finite representation is employed.

Since the Ramsey equation was heuristically justified on physical grounds, and since it appears (on the basis of previous numerical studies) to correlate with the physical spin coupling, we shall follow previous workers in adopting a truncated form of this expression. In defense of this procedure, one may cite apparently analogous cases in which a truncated form of a divergent expression furnishes a valid approximation for an underlying finite quantity, as, e.g, in the well-known theory of asymptotic series. A somewhat analogous situation seems to occur in the second-order perturbation treatment of the Stark effect, where the electric field perturbation fundamentally alters the nature of the eigenvalue spectrum (converting the bound-state spectrum to a pure continuum) and where the Rayleigh–Schrödinger perturbation expansion is formally invalid;[22] nevertheless, as shown by Titchmarsh,[23] the familiar second-order polarizability expression furnishes a valid approximation to the real part of the complex pole of the Green's function that properly describes the Stark-shifted resonance state. In a similar spirit, we shall conjecture that Ramsey's formula has some "asymptotic" validity and retains a degree of *correlation* with the physical spin coupling, even if its formal mathematical justification is obscure at present.

C. Molecular Orbital Sum-over-States Treatments. In practice, one cannot solve for the exact eigenfunctions of the nonrelativistic $\mathcal{H}^{(0)}$ that would be needed to formally evaluate the higher order Rayleigh–Schrödinger corrections in (8). The Hartree–Fock MO approximation provides the most practical way of describing the wave functions of large molecules at a useful level of chemical accuracy. The Ramsey equation (eq 4) can be simplified by introducing the Hartree–Fock approximation in two distinct theoretical ways ("uncoupled" or "coupled").[24] Many reviews[3,4,6] offer excellent descriptions of coupled methods, so we will not consider them further here.

In the uncoupled Hartree–Fock treatment of Pople and Santry,[13] the unperturbed $\mathcal{H}_{nr}$ is replaced by $\mathcal{H}_{HF}$, the sum of one-electron Fock operators $\mathcal{F}_i$

$$\mathcal{H}^{(0)} = \mathcal{H}_{HF} = \sum_i \mathcal{F}_i \qquad (9)$$

whose exact eigenfunctions are the complete set of determinantal wave functions D_K constructed from Hartree–Fock orbitals, with corresponding unperturbed eigenvalues E_K equal to the sum of

Hartree–Fock orbital energies ϵ_r of orbitals occupied in D_K

$$\mathcal{H}_{HF}D_K = E_K D_K, \quad E_K = \sum_r \epsilon_r \quad (10)$$

In this case the first-order wave function is a linear combination (formally, infinite in number) of Slater determinants built from unperturbed Hartree–Fock orbitals. The exact second-order sum-over-states (SOS) expression for J_{AB} can then be written in the form first derived by Pople and Santry[13]

$$J_{AB} = -(8\hbar/9\pi)\mu_0{}^2\mu_B{}^2\gamma_A\gamma_B\sum_i^{occ}\sum_j^{virt}\frac{1}{\epsilon_j-\epsilon_i}\langle\psi_i|\delta(\mathbf{r}_A)|\psi_j\rangle$$
$$\langle\psi_j|\delta(\mathbf{r}_B)|\psi_i\rangle \quad (11)$$

where ψ_i and ψ_j are occupied and virtual molecular orbitals with corresponding orbital energies ϵ_i and ϵ_j. Certain difficulties with this equation (and its usual approximations) will now be summarized.

The ill-conditioned nature of the SOS expression (11) for J_{AB} can be demonstrated by the following thought experiment: Suppose J_{AB} is evaluated with a basis set of n_o occupied and n_v virtual orbitals. One could now augment the basis with an artificial orbital ϕ_{v+1} having arbitrary finite amplitude in infinitesimal regions around nuclei A and B, with its remaining amplitude concentrated, say, 1 km from any nucleus in the molecule. Such an artificial basis function merely contributes another orbital to the virtual space (as a contribution to the unphysical Hartree–Fock continuum) and makes no physical contribution to the HF energy, wave function, or any observable ground-state property. Yet this function could make an arbitrarily large change in the SOS value for J_{AB}, since it has an arbitrarily large value at the single point sampled by $\mathcal{H}_{fc}$, obviously an unphysical result. We should anticipate on physical grounds that only virtuals corresponding to physical low-lying triplet states (rather than, e.g., background continuum) can contribute significantly to J_{AB}. The example suggests that pathologies of SOS expressions might be reduced at the minimal or near-minimal basis level, where the correspondence between virtuals and physical excited states is nearly one-to-one. This may account for the partial success of INDO-type methods, which are intrinsically formulated in a minimal basis "effective valence space" framework.

Another problem with the SOS method lies in the choice of excitation energy. It has been recognized[2] that an improved estimate of the excitation energy $^3E_n - ^1E_0$ is obtained by replacing the "Koopmans' theorem" estimate ($\epsilon_j - \epsilon_i$) of eq 11 by the difference

$$\epsilon_j - \epsilon_i - J_{ij} \quad (12)$$

where J_{ij} is the Coulomb integral. This replacement increases the calculated J_{AB} values (tending to bring them closer to experiment), but it introduces a slight inconsistency between $\mathcal{H}^{(0)}$, eq 9, and the unperturbed energy differences appearing in eq 12, corresponding to a reordered summation of terms in the formal Rayleigh–Schrödinger perturbation expansion. We retain the original Pople–Santry expression in the present treatment.

In earlier times, a still more drastic "average energy approximation" was commonly introduced which obviates the underlying mathematical difficulties but severs any link to *ab initio* theory. While such a procedure might be formally justified for a convergent perturbation expansion where the corresponding average energy is finite, it is improper for the J_{AB} expression. Nevertheless, when the average energy ΔE_{av} was treated as an adjustable empirical parameter, considerable success was achieved in describing qualitative features of J_{AB} coupling. Such an approximation underlies McConnell's[25] MO treatment as well as the Karplus equation[26] (derived in a related valence-bond framework), which gives the most widely used functional form for fitting the conformational dependence of experimental J_{AB} values. The qualitative empirical success of these procedures

supports the notion of approximate proportionality between a truncated form of eq 11 and the correctly formulated relativistic J_{AB}. But the average energy approximation has an uncontrolled empirical character that is inconsistent with *ab initio* evaluation of molecular properties and will not be considered further.

D. Other Difficulties of Molecular Orbital Methods. As remarked above, partial numerical success was achieved with semiempirical INDO methods, but attempts to refine this approach with extended *ab initio* MO methods met with failure (or erratic, unpredictable success),[14] and the divergencies underlying these instabilities were recognized by several workers.[4,14,27] Later numerical studies suggested extreme sensitivity to correlation effects or other small energy changes, contradicting the apparent success of INDO-based methods. The excellent series of reviews by Oddershede[3] provides a good chronological account of the virtual abandonment of attempts to use the SOS approach to calculate more accurate J_{AB} values following the initial successes of minimal basis INDO methods.

As discussed below, a severe difficulty may arise from the usual neglect of contributions to J_{AB} from atomic orbitals other than the valence s-orbitals on A or B ("valence-s approximation"). The diffuse outer regions of AOs of nonzero angular momentum would be expected to extend to adjacent nuclei, making potentially significant contributions to spin coupling between nuclei. One of the goals of the present work is to investigate (section IV) the numerical effect of non-s-type contributions to J_{AB} coupling. Such contributions, if important, may necessitate flexible valence-shell description, e.g., of double-ζ quality or beyond.

Still another difficulty arises in connection with the routine use of Gaussian-type basis sets in standard electronic structure packages. As is well-known, these functions fail to satisfy the nuclear cusp conditions[20] in the region sampled by the Fermi contact operator. Although large Gaussian basis sets could in principle improve the approximation of the nuclear cusp, in practice the variational energy is notoriously insensitive to accurate treatment of the cusp region. Properties associated with the contact operator $\mathcal{H}_{fc}$ are therefore expected to be poorly represented in absolute terms.[28] However, from a practical perspective it is only important that the Gaussian expansions accurately represent the *changes* in the cusp region due to chemical changes in the valence region. Thus, we may hope that modest Gaussian-type basis sets can lead to $\mathcal{H}_{fc}$ results *proportional* to experimental values, even if the absolute errors are large.

III. *Ab Initio* SOS Method for Nuclear Spin Coupling Constants

In the present work we follow the general approach of Pople and Santry[13] by adopting their starting molecular orbital SOS expression (eq 11) for J_{AB}. However, our approach differs in the avoidance of three steps that Pople and Santry (and subsequent workers) employed for their numerical evaluations:

(1) Avoidance of the INDO Approximation. Whereas Pople and Santry introduced the semiempirical INDO approximation for the LCAO-MO wave functions, we employ standard *ab initio* techniques to evaluate the ground-state restricted Hartree–Fock (RHF) wave function in a nonempirical manner. The subsequent evaluation of the SOS summation for J_{AB} is also carried out exactly over the full set of occupied and virtual MOs. In this approach, each molecular orbital ψ_i is obtained in standard LCAO (linear combination of atomic orbitals) form as a linear combination of basis functions ϕ_μ, with coefficients $c_{i\mu}$

$$\psi_i = \sum_\mu c_{i\mu}\phi_\mu \quad (13)$$

The contracted-Gaussian atomic orbitals are, in turn, formed

from linear combinations of Gaussian primitive orbitals g_s

$$\phi_\mu = \sum_s d_{\mu s} g_s \tag{14}$$

and each primitive Gaussian g_s is analytically evaluated at the positions of coupled nuclei.

(2) Avoidance of LCAO Expansions. Pople and Santry introduced the LCAO expansion (eq 13) into the expression for J_{AB}, leading to four-fold nested summations of the form

$$\langle \psi_i | \delta(\mathbf{r}_A) | \psi_j \rangle \langle \psi_j | \delta(\mathbf{r}_B) | \psi_i \rangle = \sum_\lambda \sum_\mu \sum_\nu \sum_\sigma c_{i\lambda} c_{j\mu} c_{j\nu} c_{i\sigma}$$
$$\langle \phi_\lambda | \delta(\mathbf{r}_A) | \phi_\mu \rangle \langle \phi_\nu | \delta(\mathbf{r}_B) | \phi_\sigma \rangle \tag{15}$$

Instead, we employ relationships of the form

$$\langle \psi_i | \delta(\mathbf{r}_A) | \psi_j \rangle = \psi_i(A) \psi_j(A) \tag{16}$$

to evaluate each ψ_i at the position of each nucleus once and for all. This greatly reduces the effort of evaluating the terms in (11), whether or not one approximates the evaluation of integrals $\langle \phi_\lambda | \delta(\mathbf{r}_A) | \phi_\mu \rangle$, $\langle \phi_\nu | \delta(\mathbf{r}_B) | \phi_\sigma \rangle$ over basis functions.

(3) Avoidance of the Valence-s Approximation. Pople and Santry discarded integrals $\langle \phi_\lambda | \delta(\mathbf{r}_A) | \phi_\mu \rangle$ in which either ϕ_λ or ϕ_μ were not both centered at nucleus A. (This goes beyond the usual ZDO approximation, where ϕ_λ and ϕ_μ could both be on center B without zeroing the integral.) In this case, only the s-type atomic orbitals of the valence shell contribute to spin coupling

$$\langle \phi_\lambda | \delta(\mathbf{r}_A) | \phi_\mu \rangle = |s_A(0)|^2 \tag{17}$$

In contrast, we include the exact contributions of all basis functions to all integrals by evaluating each $\psi_i(A)$ in the form

$$\psi_i(A) = \sum_\mu c_{i\mu} \phi_\mu(A) \tag{18}$$

and each $\phi_\mu(A)$ exactly in terms of its explicit representation (eq 14) in Gaussian primitives. This builds in the (relatively constant) error associated with the incorrect behavior of Gaussians in the cusp regions, but it allows incorporation of the important physical effect of the hydrogenic orbital expanding or contracting in the molecular environment, relative to its free-atom counterpart. For example, it is known that an optimal 1s-type hydrogenic basis function has Slater exponent $\zeta \simeq 1.2$ (rather than 1.0), reflecting the more contracted character of this orbital in the molecular environment.

In view of the formal and numerical difficulties cited in section II, we expect that the theoretical value J_{AB}^{theor} calculated by the procedure sketched above can have at most an approximate *proportionality* to experimental J_{AB} coupling constants. This conclusion is reinforced by recalling that we are systematically ignoring certain significant contributions, including the following: (1) orbital and spin–dipole terms, which provide a background contribution even if the principal dihedral dependence of J_{AB} arises from Fermi contact interactions; (2) possible differences between uncoupled and coupled Hartree–Fock treatments; and (3) electron correlation effects. By using contracted-Gaussian basis functions we also incur a systematic error in the Fermi contact contribution, shifting the calculated value away from experiment (by what is hoped to be a relatively constant difference). For these reasons, we seek empirical proportionality coefficients a and b by which the calculated theoretical values J_{AB}^{theor} can be related to experimental data through an equation of the form

$$J_{AB}^{\text{fit}} = a J_{AB}^{\text{theor}} + b \tag{19}$$

Such a and b values are expected to vary with the level of theoretical treatment, the relative contribution of neglected orbital and spin–dipolar terms for different nuclei, and other factors. An
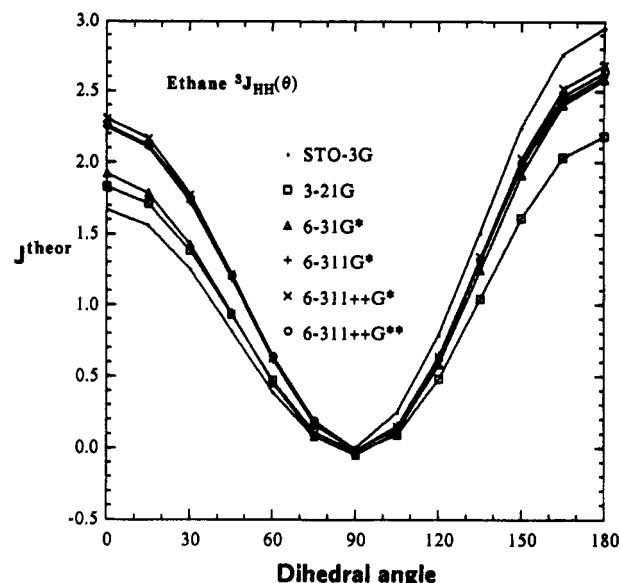

Figure 1. "Karplus-like" dihedral dependence of $^3J_{HH}$ (Hz) for ethane at various *ab initio* basis set levels: STO-3G (dot), 3-21G (box), 6-31G* (triangle), 6-311G* (plus), 6-311++G* (X), 6-311++G** (open circle). Idealized Pople–Gordon rigid-rotor geometry is used in each case.

approach based on eqs 11 and 19, although falling short of usual *ab initio* (nonempirical) criteria, can be of considerable value in analyzing measured J_{AB} values for complex molecules.

IV. Results

Our strategy has been to use eq 11 to evaluate the Fermi contact contribution to J_{AB} for cases that could lead to optimal parameters a and b in the empirical fitting, eq 19. Therefore, we restricted these calculations to well-studied molecules with known geometries, little or no conformational flexibility, and experimentally measured J_{AB} values.

We report our results in three categories. First, we examined the effect of basis set size on $^3J_{HH}$ couplings in ethane, both to determine the convergence properties of SOS methods and to select an optimal basis set for further studies. Second, with basis sets established from the ethane exercise, we calculated six different types of J_{AB} couplings for a wide range of hydrocarbons to examine the dependence on electronegativity, hybridization, bond length, and other variations. Finally, we examined the effects of neglect of non-valence-s AOs on the value of $^3J_{HH}$, by testing the validity of approximations that were commonly adopted in previous work.

A. Dihedral Angle Dependence of $^3J_{HH}$ in Ethane. The dihedral angle dependence of $^3J_{HH}$ in ethane[26] was examined with a variety of standard basis sets (STO-3G, 3-21G, 6-31G*, 6-311G*, 6-311++G*, and 6-311++G**)[29] to address the question of convergence with respect to increasing numbers of virtual orbitals (section II.C). Points were calculated at 15-deg increments of rotation about the dihedral angle θ (θ ranging from 0° to 60°), with idealized rigid-rotor geometry[30] at all basis set levels. Results are shown in Figure 1.

Figure 1 demonstrates the well-known "Karplus-like"[26] behavior of the dihedral dependence, which is recovered at all basis set levels. It is also seen that $^3J_{HH}$ appears to converge satisfactorily as the basis set is expanded within this range, despite the inherent instability of eq 11 as manifested in results (discussed below) for other types of couplings.

B. Substituent and Hybridization Effects. Effects of substituents and the hybridization of the carbon atom framework are well-known.[31,32] We chose a large number of molecules from a previous study by André and co-workers,[33] where the authors calculated the Fermi contact contribution to J_{AB} with semiempirical and minimal *ab initio* wave functions. In addition to molecules from André and co-workers, we have included, among
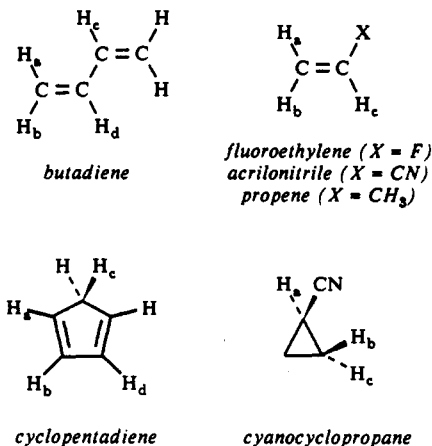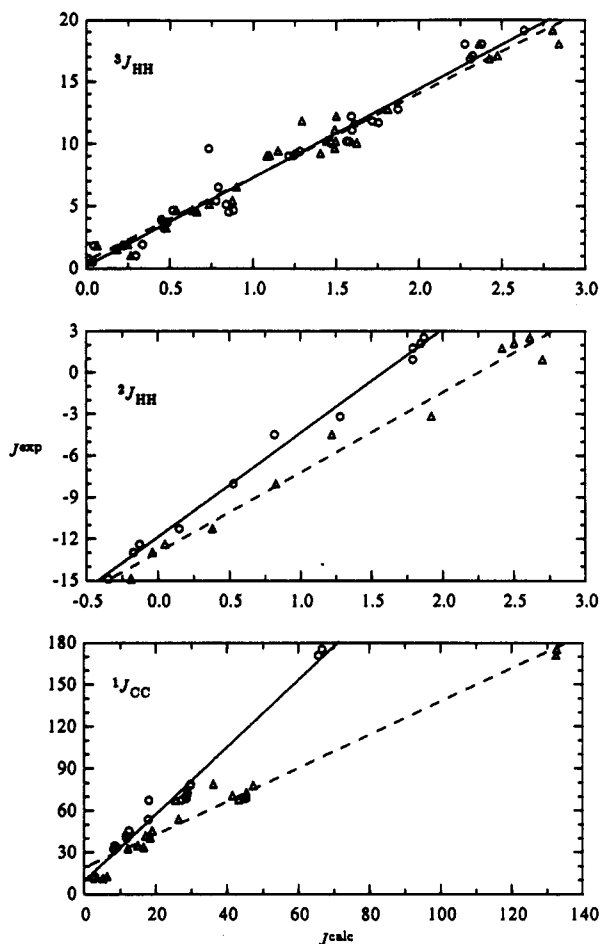
butadiene

fluoroethylene (X = F)
acrilonitrile (X = CN)
propene (X = CH₃)

cyclopentadiene   *cyanocyclopropane*

Figure 2. Atomic labels identifying coupled nuclei in Table I.

Figure 3. Comparison of calculated and experimental like-atom spin coupling constants $^nJ_{AA}$ (cf. Table I) for vicinal (n = 3, upper panel) and geminal (n = 2, middle panel) H–H coupling and directly bonded (n = 1, lower panel) C–C coupling at two basis set levels: 3-21G (circles), 6-31G* (triangles). Also shown are the optimal regression lines (cf. Table II) for 3-21G (solid) and 6-31G* (dashed) basis sets.

Figure 4. Comparison of calculated and experimental spin coupling constants $^nJ_{CH}$ (cf. Table I) for vicinal (n = 3, upper panel), geminal (n = 2, middle panel), and directly bonded (n = 1, lower panel) CH interactions at two basis set levels: 3-21G (circles), 6-31G* (triangles). Also shown are the optimal regression lines (cf. Table II) for 3-21G (solid) and 6-31G* (dashed) basis sets.

Table I at 3-21G (circles) and 6-31G* (triangles) are plotted against experimental values in Figures 3 and 4. The lines (solid and dashed for 3-21G and 6-31G*, respectively) correspond to best linear fits of the data.

Statistical results from a linear regression analysis for each coupling type at each basis set are shown in Table II. The statistics are valuable, since they set confidence limits for future work and establish a linear relationship between experiment and theory, eq 19. The results from Table II show that the slope and intercept of eq 19 are dependent upon both coupling type and basis set.

C. Previous Approximations. As remarked in section III., the full molecular orbital expression, eq 11, is often approximated by neglecting the contributions of orbitals other than s_A and s_B, the valence-s AOs on the two coupled nuclei. This leads to a simplified expression of the form

$$J_{AB} = (2\hbar/9\pi)\mu_0^2\mu_B^2\gamma_A\gamma_B|s_A(A)|^2|s_B(B)|^2\Pi_{A,B} \quad (20a)$$

where

$$\Pi_{A,B} = 4\sum_i^{occ}\sum_j^{virt}\frac{c_{is_A}c_{js_A}c_{js_B}c_{is_B}}{\epsilon_i - \epsilon_j} \quad (20b)$$

is the mutual atom–atom polarizability of Coulson and Longuet-Higgins.[35] Equation 20 is tantamount to truncating eq 18 to a single term of the LCAO expansion

$$\psi_i(A) \simeq c_{is_A}\phi_{s_A}(A) \quad (21)$$

At the INDO-type level, eq 20 can be partially justified in terms of general consistency with the ZDO approximation. However,

others, norbornane and norbornene. These molecules, first investigated by Marshall and co-workers,[34] have received a great deal of attention owing to the nonequivalence of *exo–exo* and *endo–endo* couplings in norbornane and the near equivalence of the same couplings in norbornene. Molecules and couplings included in this study are listed in Table I (cf. Figure 2 for atomic labeling).

Our calculations were performed at 3-21G and 6-31G* basis sets with full geometry optimization at each basis unless otherwise noted. We have examined $^3J_{HH}$, $^2J_{HH}$, $^1J_{CC}$, $^1J_{CH}$, $^2J_{CH}$, and $^3J_{CH}$ couplings in the 19 molecules included for study. Table I lists the results from the various calculations. Calculated data from
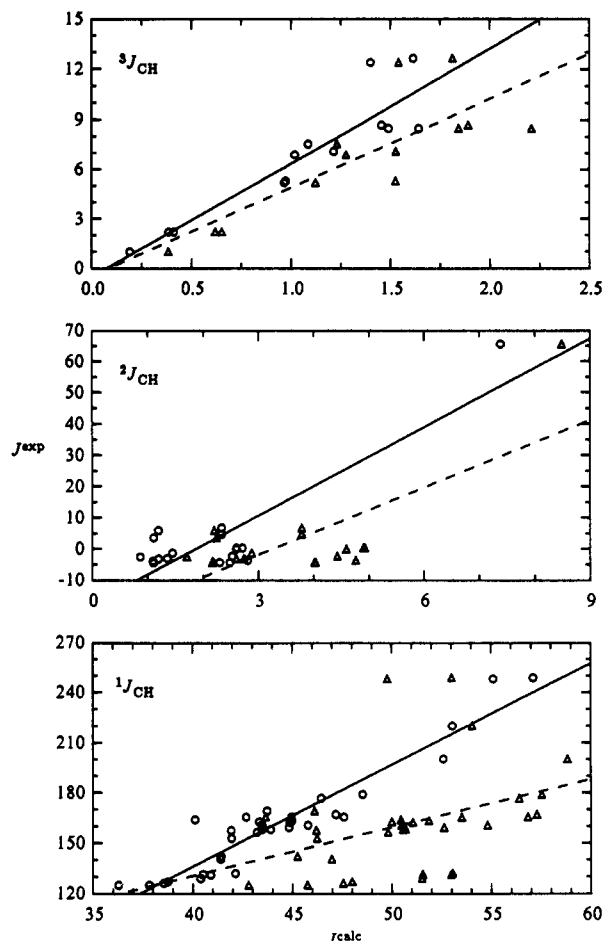
TABLE I: Calculated and Experimental Couplings Used in this Study

$^3J_{HH}$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornane (exo–exo)^{a,b}	11.47	10.66	12.2	34	propene (H$_a$—H$_c$)^c	16.60	16.86	16.81	33
norbornane (endo–endo)^{a,b}	9.01	7.94	9.05	34	propene (H$_b$—H$_c$)^c	11.28	10.26	10.2	33
norbornane (exo–endo)^{a,b}	3.84	4.19	4.62	34	propene (CH$_3$—H$_c$)^c	5.77	6.62	6.5	33
norbornene (exo–exo)^{a,b}	9.28	8.29	9.40	34	cyclopropane (cis)	9.08	10.02	9.2	33
norbornene (endo–endo)^{a,b}	8.79	7.83	9.02	34	cyclopropane (trans)	5.68	6.45	5.4	33
norbornene (exo–endo)^{a,b}	3.35	3.64	3.87	34	cyclopropene (HC=CH)	2.26	2.36	1.0	33
norbornene (1–2endo)^{a,b}	0.41	0.79	0.55	43	cyclopropene (HC—CH)	0.48	1.00	1.8	33
norbornene (1–2exo)^{a,b}	3.60	3.73	3.66	43	butadiene (H$_a$—H$_d$)^c	16.70	17.20	17.05	33
norbornene (1–7anti)^{a,b}	1.42	1.80	1.51	43	butadiene (H$_b$—H$_d$)^c	11.39	10.64	10.17	33
norbornene (1–7syn)^{a,b}	1.75	1.98	1.83	43	butadiene (H$_c$—H$_d$)^c	10.60	11.49	10.04	33
ethane (trans)	16.36	19.69	18.0	44	fluoroethylene (trans)	13.48	12.74	12.75	33
ethane (gauche)	3.46	3.78	3.2	44	fluoroethylene (cis)	6.43	4.84	4.65	33
ethylene (trans)	18.92	19.44	19.1	33	trans-1-fluoropropene (HC=CH)	11.50	10.59	11.1	45
ethylene (cis)	12.64	11.37	11.7	33					
acrylonitrile (trans)	17.08	16.46	18	33	cis-1-fluoropropene (HC=CH)	6.22	5.03	4.5	45
acrylonitrile (cis)	12.39	9.26	11.8	33	cyclopentadiene (H$_a$—H$_b$)^c	6.12	5.52	5.1	33
acetylene	5.36	10.60	9.6	33	cyclopentadiene (H$_b$—H$_d$)^c	2.55	2.23	1.9	33

$^2J_{HH}{}^d$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornene (2,2)^{a,b}	-10.77	-10.81	-11.29	43	propene (CH$_2$)	1.95	1.41	2.08	33
norbornene (7,7)^{a,b}	-7.92	-8.24	-8.03	43	cyclopropane	-5.76	-5.98	-4.5	33
methane	-12.85	-12.72	-12.4	33	butadiene (CH$_2$)	1.53	0.91	1.74	33
ethane	-13.16	-13.22	-13	33	fluoroethylene	-2.29	-1.95	-3.2	33
ethylene	2.12	2.04	2.5	33	acetone	-14.48	-14.08	-14.9	33
acrylonitrile	1.53	2.55	0.91	33					

$^1J_{CC}$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornane (2,3)^{a,b}	31.28	38.50	33.4	46	propene (C—C)	39.23	41.36	45.5	33
norbornane (3,4)^{a,b}	29.08	33.29	32.5	46	cyclopropane	16.31	26.35	12.4	46
ethane	26.65	36.55	34.6	33	cyanocyclopropane (C—CC)	15.80	24.93	10.9	33
ethylene	75.01	70.01	67.6	33	cyanocyclopropane (C—CN)	80.13	74.92	77.9	33
acrylonitrile (C=C)	77.98	68.02	70.6	33	butadiene (C=C)	77.63	71.76	68.8	46
acrylonitrile (C—C)	80.63	61.64	78.6	33	butadiene (C—C)	52.20	50.10	53.7	46
acetylene	166.59	176.07	170.6	33	1,1-dimethylethylene (C=C)	78.52	72.63	72.6	46
propyne (C—C)	52.54	49.11	67.4	33	1,1-dimethylethylene (C—C)	37.27	39.17	41.8	46
propyne (C≡C)	169.15	176.28	175	46	acetone	37.61	40.74	40.1	33
propene (C=C)	77.38	72.56	70	33					

$^1J_{CH}$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornane (1,1)^{a,b}	144.36	150.38	140.4	47	propyne (CH)	227.68	158.47	248	33
norbornane (7,7)^{a,b}	138.97	163.56	131.4	47	propene (H$_a$)^c	156.13	159.06	162.6	33
norbornane (2–2exo)^{a,b}	138.28	163.45	128.9	47	propene (H$_b$)^c	156.98	160.50	160.6	33
norbornane (2–2endo)^{a,b}	141.37	167.65	131.0	47	propene (H$_c$)^c	147.58	148.11	157.4	33
norbornene (1,1)^{a,b}	144.53	140.70	142	48	cyclopropane	171.00	172.94	160.5	33
norbornene (2,2)^{a,b}	152.10	140.78	165.5	48	cyclopropene (C=C)	215.21	170.77	220	33
methane	122.62	146.84	125	33	cyanocyclopropane (H$_a$)^c	187.71	180.79	179	33
ethane	113.28	138.32	125	33	cyanocyclopropane (H$_b$)^c	181.94	178.78	165.5	33
ethylene	155.43	158.52	156.2	33	cyanocyclopropane (H$_c$)^c	179.48	180.08	167	33
fluoroethylene (H$_a$)^c	165.17	166.66	159.2	33	butadiene (H$_a$)^c	156.98	160.69	158	48
fluoroethylene (H$_b$)^c	165.51	162.14	162.2	33	butadiene (H$_b$)^c	159.59	161.12	158	48
fluoroethylene (H$_c$)^c	212.47	184.52	200.2	33	butadiene (H$_d$)^c	147.66	148.22	152.7	48
acrylonitrile (H$_a$)^c	166.08	164.47	163.2	33	2-methylpropene (CH$_3$)	127.04	152.02	126	48
acrylonitrile (H$_b$)^c	165.93	169.21	165.4	33	acetone (average)	128.28	153.33	127	33
acrylonitrile (H$_c$)^c	174.99	177.53	176.7	33	cyclopentadiene (H$_a$)^c	158.55	147.86	169.11	49
acetylene	239.81	167.80	248.7	33					
propyne (CH$_3$)	148.88	167.90	132.0	33	cyclopentadiene (H$_c$)^c	136.62	160.38	163.86	49

$^2J_{CH}$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornane (1–2exo)^{a,b}	-4.93	-3.87	-3.1	47	propene (H$_a$)^c	6.86	11.85	0.3	33
norbornane (1–2endo)^{a,b}	-6.46	-4.87	-3.2	47	propene (H$_b$)^c	5.72	5.30	-4.4	33
norbornane (2–3exo)^{a,b}	-7.43	-7.93	-4.0	47	propene (H$_c$)^c	8.77	10.66	-3.7	33
norbornane (2–3endo)^{a,b}	-4.07	-2.89	-1.4	47	cyclopropane	-9.56	-11.30	-2.6	33
ethane	-7.27	-8.00	-4.5	33	butadiene (H$_c$)^c	6.84	9.43	-0.05	33
ethylene	6.08	8.25	-2.4	33	acetone (average)	-6.45	-7.77	5.9	33
acrylonitrile (H$_b$)^c	3.96	5.43	-4.4	33	cyclopentadiene (H$_c$)^c	-7.29	-7.45	3.56	49
acrylonitrile (H$_a$)^c	7.83	11.64	0.3	33	cyclopentadiene (C2–H3)^c	4.31	3.62	6.73	49
acetylene	51.97	37.48	65.5	33	cyclopentadiene (C2–H1)^c	4.31	3.62	4.66	49

$^3J_{CH}$

molecule	3-21G	6-31G*	exp	ref	molecule	3-21G	6-31G*	exp	ref
norbornane (C1,H3endo)^{a,b}	2.29	3.02	2.2	47	norbornane (C2,H7anti)^{a,b}	9.71	9.39	8.5	47
norbornane (C1,H3exo)^{a,b}	0.77	1.57	1.0	47	norbornane (C2,H7syn)^{a,b}	2.11	2.84	2.2	47
norbornane (C1,H4)^{a,b}	10.75	11.35	8.5	47	propene (H$_b$)^c	10.56	9.22	12.65	49
norbornane (C7,H3endo)^{a,b}	7.81	7.70	7.1	47	propene (H$_a$)^c	6.92	6.11	7.55	49
norbornane (C3,H5exo)^{a,b}	9.46	9.64	8.7	47	2-methylpropene (CH$_2$ trans)	9.08	7.78	12.4	49
norbornane (C3,H5endo)^{a,b}	6.16	7.69	5.3	47	2-methylpropene (CH$_2$ cis)	6.11	5.54	5.2	49
norbornane (C3,H1)^{a,b}	6.47	6.36	6.9	47					

^{a} Norbornane and norbornene geometries were coptimized at 3-21G only. ^{b} For numbering conventions see ref 34. ^{c} See Figure 2 for labeling. ^{d} $^2J_{HH}$ from propyne was not included in this table, Figure 3, or the statistics in Table II owing to a large deviation from other data. Scuseria has shown[50] that electron correlation significantly influences couplings in molecules with triple bonds. However, we have included results from acetylene and propyne in all the other relevant categories of coupling constants reported.

TABLE II: Statistics of Correlation of Experimental and Theoretical J_{AB} Values, Showing the Least-Squares Slope (a), Intercept (b), Linear Regression Coefficient (r^2), and Standard Deviation about the Regression (s_r) at RHF/3-21G and RHF/6-31G* Theoretical Levels[a]

J_{AB}	3-21G			6-31G*		
	a	b	r^2 (s_r)	a	b	r^2 (s_r)
$^3J_{HH}$	7.12	0.15	0.958 (1.13)	6.73	0.57	0.971 (0.94)
$^2J_{HH}$	7.49	-11.87	0.991 (0.64)	5.75	-12.99	0.980 (0.99)
$^1J_{CC}$	2.39	9.50	0.979 (6.44)	1.19	18.90	0.966 (8.22)
$^1J_{CH}$	6.07	-106.94	0.893 (10.25)	2.88	15.02	0.148 (28.97)
$^2J_{CH}$	9.43	-17.69	0.749 (8.27)	7.19	-23.54	0.525 (11.39)
$^3J_{CH}$	6.87	-0.53	0.839 (1.51)	5.36	-0.48	0.662 (2.19)

[a] Data from propyne for $^2J_{HH}$ were not included in the statistics.
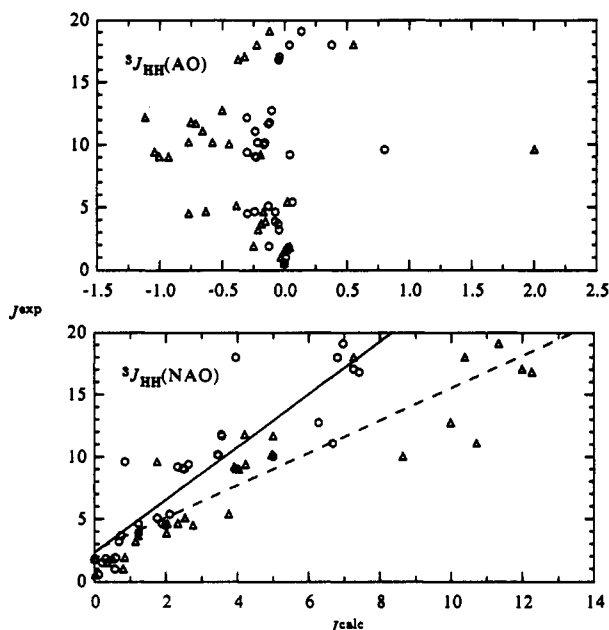

Figure 5. Alternative calculations of $^3J_{HH}$ with the valence-s approximation in terms of AOs (upper panel) or NAOs (lower panel), showing the significantly lower correlation with experiment (cf. upper panel of Figure 3; full calculation). Weak regression coefficients of 0.799 and 0.800 are found for the valence-s_{NAO} approximation to 3-21G (circles; solid regression line) and 6-31G* (triangles; dashed regression line) data, respectively, but the corresponding valence-s_{AO} approximations of the upper panel are essentially uncorrelated with experiment.

the approximate eq 20 has become standard even for wave functions beyond the INDO level.

Figure 5 shows plots of $^3J_{HH}$ from the same data employed in Figure 3 but calculated with eq 20. In one case (upper panel), s_A was taken as the ordinary 1s basis AO, and in the other case (lower panel), s_A was taken as the 1s natural atomic orbital (NAO).[36] As seen in Figure 5, the use of NAOs improves the correlation somewhat (leading to r^2 confidence values of 0.80 and 0.76 for 3-21G and 6-31G*, respectively), compared to results for standard AOs (which show essentially no correlation with experiment). However, when compared with r^2 values of 0.96 and 0.97 (cf. Table II) for the full calculation, it is clear that the valence-s approximation severely degrades the accuracy of the theoretical result.

To better understand the source of the errors in eq 20, we have listed in Table III the amplitudes of some AOs and NAOs at an *exo* proton of norbornane. Clearly, the valence-s orbitals are dominant, but orbitals centered on adjacent nuclei can have amplitudes greater than 20% of the valence-s contribution. Large basis sets obviously have more overlapping AOs or NAOs contributing to this error, but even for a minimal basis (data not shown), the problem is evident. It should be noted that an orthogonal basis (such as the NAO set) does not avoid this problem, because the orthogonality refers to an integration over

TABLE III: Amplitudes (in atomic units) for Atomic Orbitals (AOs) and Natural Atomic Orbitals (NAOs) Evaluated at an *exo* Proton in Norbornane[a]

orbital	3-21G		6-31G*	
	AO(H_{exo})	NAO(H_{exo})	AO(H_{exo})	NAO(H_{exo})
H(1s)	0.955	0.809	0.995	0.905
H(2s)	0.200	0.769	0.181	0.745
C(2s)	0.028	-0.090	0.053	-0.099
C($2p_x$)	-0.012	0.016	-0.018	0.027
C($2p_y$)	0.038	-0.016	0.056	-0.021
C($2p_z$)	0.059	-0.040	0.086	-0.062
C(3s)	0.092	0.144	0.092	0.287
C($3p_x$)	-0.029	-0.009	-0.027	-0.002
C($3p_y$)	0.088	0.133	0.083	0.229
C($3p_z$)	0.139	0.161	0.129	0.260
C(d_{z^2})			0.073	0.096
C($d_{x^2-y^2}$)			-0.035	0.071
C($d_{3z^2-r^2}$)			0.030	-0.186
C(d_{xy})			-0.026	0.072
C(d_{xz})			-0.041	0.076
C(d_{yz})			0.124	-0.247

[a] Only the top two orbitals [H(1s), H(2s)] are centered on the proton, while the remaining orbitals are centered on the directly bonded carbon atom [amplitudes of other nonbonded atoms (not shown) decrease rapidly with distance]. Note that although the largest contribution arises from the valence-s orbital on H, neighboring orbitals contribute amplitudes as much as 20% of this value.

all space and therefore indicates nothing above relative orbital amplitudes at a single point.

One might suppose that the errors in coupling constants would correlate with the neighboring orbital overlap ($\sim 20\%$). However, the actual situation is far worse. When the MOs are formed using the LCAO expansion, eq 18 or 21, the errors in J_{AB} are compounded by errors of the individual MO amplitudes acting in concert. The relatively small errors in individual MO amplitudes are therefore amplified in the final J_{AB} values, as shown in Table IV for the *exo* proton in norbornane. An interesting feature of Table IV is the systematic change of MO amplitude errors with respect to either AO or NAO basis. When using the AO basis, the amplitudes of the occupied and some low-lying unoccupied MOs *decrease* and the higher energy unoccupied MOs *increase* relative to MOs obtained by the full LCAO expansion (eq 18). With the NAO basis, an opposite trend is observed (with significantly lower percentage errors). At the bottom of Table IV, values of the *exo–exo* coupling constant $^3J_{HH}(exo)$ with and without the valence-s approximation are given, showing the essentially uncontrolled nature of this approximation.

V. Discussion

The most obvious problem with results calculated directly from eq 11 is that the magnitudes are too low. A perfect theoretical model, when its results are plotted against experiment, would produce slopes (a) and regression coefficients (r^2) equal to 1 and intercepts (b) equal to 0. Typically, the low values are manifested as slopes much greater than unity. The absolute values of the couplings calculated by SOS methods seem to vary systemically with basis set. In every result shown in Figures 3 and 4, the 3-21G slopes are larger than the slopes from 6-31G* basis sets. André and co-workers[33] obtained similar, but opposite, trends with slopes increasing with higher levels of treatment (from extended Hückel to CNDO to STO-3G). Along with Figure 1, this suggests that the SOS expression for J_{AB} may be oscillating with basis set size, with a minumum near the 3-21G basis. Independent of the oscillatory behavior is the increased uncertainty of the convergence with increasing basis set (section II.C), making results from 6-31G* often less correlated with experiment than those from 3-21G. It is interesting to note that the valence-s approximation with NAOs, eq 20, consistently produces larger values than eq 11. However, the larger values are still too low (in agreement with previous results[33]), and the increase in absolute

TABLE IV: Absolute Values of Some Molecular Orbital (MO) Amplitudes $\psi_i(0)$ (with Corresponding Orbital Energies ϵ_i) Evaluated at an *exo* Proton in Norbornane by Using the Full LCAO Expansion ("full") or the Valence-s Approximation (with Associated Percentage Errors) for Either AOs ("Valence-s_{AO}") or NAOs ("Valence-s_{NAO}") at Two *ab Initio* Basis Set Levels[a]

	MO amplitude $|\psi_i(0)|$				
ϵ_i (au)	full	valence-s_{AO}	error (%)	valence-s_{NAO}	error (%)
		RHF/3-21G			
−0.630	0.127	0.085	−33	0.141	+11
−0.544	0.182	0.123	−32	0.200	+10
−0.412	0.170	0.117	−32	0.185	+9
+0.275	0.065	0.038	−41	0.176	+170
+0.881	0.237	0.303	+28	0.045	−81
+1.048	0.197	0.258	+31	0.039	−80
+1.096	0.232	0.272	+17	0.085	−63
+1.897	0.325	0.498	+53	0.050	−85
[$^3J_{HH}^{calc}$]	[1.59]	[−0.30]		[3.33]	
		RHF/6-31G*			
−0.628	0.137	0.095	−31	0.159	+16
−0.543	0.184	0.129	−30	0.212	+15
−0.414	0.179	0.128	−28	0.209	+17
+0.257	0.056	0.034	−39	0.177	+216
+0.702	0.227	0.265	+17	0.053	−77
+0.791	0.137	0.163	+19	0.051	−63
+0.856	0.105	0.108	+3	0.056	−47
+1.561	0.318	0.443	+39	0.061	−81
[$^3J_{HH}^{calc}$]	[1.50]	[−1.12]		[5.45]	

[a] The selected orbitals are representative of occupied ($\epsilon_i < 0$) and virtual ($\epsilon_i > 0$) MOs at each level. Note that the valence-s approximation tends to systematically overestimate the amplitudes of low-energy MOs and underestimate the amplitudes of high-energy MOs. Also shown for comparison is the calculated value of the *exo-exo* vicinal proton–proton coupling constant $^3J_{HH}^{calc}$ (experimental value, 12.2 Hz) corresponding to each approximation, illustrating the large errors associated with use of the valence-s approximation.

magnitude is accompanied by a *significant* decrease in r^2 (Figure 5). We were surprised to find that the AO basis failed completely with this approximation at even the modest 3-21G basis set. At the STO-3G level (data not shown), we obtained valence-s_{AO} results somewhat similar to the valence-s_{NAO} results for 3-21G or 6-31G* but still significantly inferior to those obtained with the full expression (eq 11). This indicates that the valence-s_{AO} approximation, already poor at the minimal STO-3G level, becomes increasingly untenable as attempts are made to improve the description with a more flexible valence-shell basis.

When the coupling constant is evaluated with explicit forms of the Gaussian orbitals, an error is introduced into the calculation by the lack of cusps at the nuclei (section II.D). For proton–proton couplings, this "Gaussian" coupling constant, $\tilde{J}$ for example, can be adjusted by assuming that the error is proportional to the fourth power of the ratio of the analytical wave function to the occupied orbital wave function for a hydrogen atom at a particular basis set.

$$J = \left(\frac{\pi^{-1/2}}{\phi(0)}\right)^4 \tilde{J} \qquad (22)$$

This correction amounts to 1.62 for 3-21G and 1.14 for 6-31G* basis sets; it is a help, but the values are still too low. As discussed in section II.C, use of the modified eq 12 for the excitation energy would also lead to values of J_{AB} that are larger but probably still far too small compared to the physical value. We believe that the fundamental difficulties of eq 11 go beyond such corrections.

The intercept *b* is close to zero for both basis sets for $^3J_{HH}$ but large and negative for $^2J_{HH}$. Kowalewski and co-workers,[2,11,12] concluded that electron correlation effects are substantial for geminal couplings. Lee and Schulman[37] found that the spin orbit term can contribute substantially (47% of the total coupling in H_2O) to $^2J_{HH}$. According to Kowalewski (Table 3 of ref 2) both of these effects introduce positive contributions to the coupling and would make our agreement with experiment worse. It is

worth noting that our results for $^2J_{HH}$ are in qualitative agreement with the study of André and co-workers.[33] The high quality ($r^2 \simeq 0.99$) of our RHF/3-21G fit for $^2J_{HH}$ suggests that electron correlation, other spin–spin coupling mechanisms, and differences in Hartree–Fock treatment (*viz.*, coupled vs uncoupled) can affect the absolute magnitude of the coupling but that the present level of theory is sensitive to important chemical *trends* (such as geometry, substituents, and hybridization changes).

Despite the problems with the absolute magnitudes, the linear correlation with experimental data is quite high for most of the H–H or C–C couplings. This fact leads us to conclude that the principal chemical effects are qualitatively reproduced with even modest split valence basis sets. For geminal or vicinal proton–proton couplings, the standard deviation about the regression (s_r) is in the range 0.6–1.1 Hz, indicating a highly useful level of absolute accuracy in this important case.

However, the $^1J_{CH}$ and $^3J_{CH}$ couplings have considerable scatter, and $^2J_{CH}$ values have low correlation with experiment. More disturbing is the (sometimes dramatic) decrease in linear correlation of $^nJ_{CH}$ when going from 3-21G to 6-31G* basis sets. These problems with $^nJ_{CH}$ couplings could have at least two causes. First, as described in section II.B, the non-square-integrability of functions perturbed by the Dirac δ function operator presumably leads to divergence of eq 11 as the basis set is expanded. However, all of our attempts to reduce the number of virtual orbitals in the 6-31G* basis to physically significant ones (i.e., those with nonvanishing natural occupancies) resulted in poorer results than those calculated with the full eq 11. Second, there is presumably a large error associated with neglect of spin–orbit and spin–dipolar terms in the calculations. These terms are known to be more important for carbon nuclei than for protons, since the former have electronic orbitals with nonvanishing angular momenta. Moreover, because of the inverse distance dependence of these terms, $^2J_{CH}$ should be affected more than $^3J_{CH}$.

Many previous studies that used *ab initio* wave functions to calculate J_{AB} met with limited success.[33,38–40] The work of André and co-workers,[33] which evaluated many of the same molecules employed in this study, provides a useful comparison. The general features of $^1J_{CC}$ and $^2J_{HH}$ are similar to our results. André and co-workers reported higher experimental correlations with some basis sets for $^1J_{CH}$ and $^2J_{CH}$ than ours, but they also note that points with mean deviations greater than 3σ were neglected. Their plotted data for $^1J_{CH}$ and $^2J_{CH}$ do not seem to support the relatively high reported values of *r* (not r^2). The major improvement in our work is in $^3J_{HH}$. We obtained results similar to those of André and co-workers when we used the valence-s approximations (Figure 5), but with the full eq 11 our results were in much better agreement with experiment (Figure 3).

VI. Conclusion

The Ramsey-type expression employing a Dirac δ function in a second-order perturbation correction (coupled or uncoupled, correlated or uncorrelated) exhibits pathological numerical behavior. Numerically, however, we find that when eq 11 is truncated by a finite basis set expansion of approximately 3-21G level, chemically significant results can be obtained that have high linear correlation with experiment, particularly for proton–proton couplings. This high correlation can only be achieved by evaluating the full equations (eq 11), without the usual approximation (eq 21) of neglecting non-valence-s atomic orbitals. We specifically recommend the 3-21G basis set for such calculations. The methods employed here can be readily applied to molecules as large as amino acids or dipeptides, as will be demonstrated in forthcoming work.[41] This can provide a better understanding and utilization of coupling constants in large, biologically important molecules.

[The FORTRAN program used to calculate the Fermi contact term from NBO archive files[42] is available upon request.]

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(19) For example, Bethe and Salpeter state (ref 17, p 173), "The Breit equation is thus a good approximation (for a weak external field) as long as the small [Breit–Pauli correction operator] is only treated by first order perturbation theory... However, one would get quite wrong results if one solved [eq 7] exactly or treated [$\mathcal{H}^{(1)}$ and other Breit–Pauli corrections] in higher order perturbation theory"; similarly, on p 179, they state, "In the relativistic region $p \gg mc$, both the operators and wave functions are quite wrong (operators too large, wave functions too small)...For instance, spurious divergences in the integrals are encountered if [eq 7] is treated in higher order perturbation theory."

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