

Proton Fermi-Contact Coupling Constants from Local-Density-Functional Theory: Application to the Soliton in Polyacetylene

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We show that the first-principles local-density-functional $X\alpha$ method reliably predicts proton Fermi-contact coupling constants for planar, neutral, organic π radicals. Results for the radical soliton in polyacetylene yield -0.39 for the ratio of the two observed proton Fermi-contact constants, close to the experimental value of -0.33 . These studies also justify use of McConnell's relation to analyze the polyacetylene proton ENDOR spectrum. Our theoretical value of McConnell's constant for polyacetylene is -26 G, in good agreement with classical estimates of this quantity.

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Thomann *et al.*¹ recently reported electron-nuclear double-resonance (ENDOR) experiments that associate the neutral free radical in *cis*- and *trans*-polyacetylene composites with two magnetically inequivalent proton sites. These sites have small isotropic hyperfine coupling constants, consistent with a mobile² Su-Schrieffer-Heeger³ (SSH) soliton. Additional studies established that the two coupling constants have opposite signs,⁴ and indicated that the radical resides in the *trans* segments of the composite.⁵ The existence of two magnetically inequivalent proton sites is also consistent² with the SSH model³ of radical solitons but shows that their picture^{1,2,4,5} must be generalized to include electron correlations explicitly.

Prior theoretical analyses^{1,2,4,6} of the polyacetylene proton ENDOR data have been limited to studies that use simplified, highly parametrized Hamiltonians. These models include the SSH model, the Heisenberg model, the SSH-Hubbard model, and the Pariser-Parr-Pople model. Such models explicitly treat only the π electrons, preventing direct calculation of the isotropic hyperfine coupling constants.⁷ They must rely instead on the McConnell relation⁸ $a_H = QP_C^\pi$ relating the $2p\pi$ spin population⁹ P_C^π on a carbon atom to the hyperfine coupling constant a_H of an adjacent proton, where Q is a parameter assumed independent of P_C^π . This state of the theory is not surprising. Highly delocalized neutral π radicals like the one in polyacetylene have so far proved too large for traditional *ab initio* methods to treat. We show below, however, that first-principles local-density-functional (LDF) methods can accurately predict proton Fermi-contact coupling constants for planar, neutral, organic π radicals, and can treat the radical in polyacetylene.

Our work is based on the spin-unrestricted LDF theory.¹⁰ This theory leads to the set of one-electron equations,

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{Coul}} + V_{X\sigma}\right]\phi_{i\sigma} = \epsilon_{i\sigma}\phi_{i\sigma}, \quad (1)$$

for an electron of spin σ in the spin orbital $\phi_{i\sigma}$ with eigenvalue $\epsilon_{i\sigma}$. The potential, V_{Coul} , includes both the

electron-nuclear attraction and the classical interelectron Coulomb repulsion; we assume the Slater¹¹ $X\alpha$ form for the spin-dependent local-exchange potential,

$$V_{X\sigma}(\mathbf{r}) = -3\alpha[3\rho_\sigma(\mathbf{r})/4\pi]^{1/3},$$

with¹² $\alpha = 0.7$. The quantity $\rho_\sigma(\mathbf{r})$ denotes the charge density for an electron of spin σ at the position \mathbf{r} .

The discrete-variational method¹³ (DVM), a linear combination of atomic orbitals (LCAO) technique, is used to solve the differential equations (1) self-consistently. The calculations are implemented by use of an atomic basis set consisting of numerical LDF- $X\alpha$ solutions for atomic C and H ($1s$ through $2p$ for C and $1s$ for H). These atomic solutions are obtained by use of Herman-Skillman¹⁴ methods. In contrast to an LCAO Gaussian basis, this numerical basis automatically incorporates the cusp in the hydrogen $1s$ wave function at the proton where a_H is evaluated. The calculations are further simplified by freezing of the carbon $1s$ core. Having obtained the spin-unrestricted solutions to Eqs. (1), we determine the Fermi-contact coupling constant, $a_H(\mathbf{r}^H)$ (in gauss), for a proton at the position \mathbf{r}^H using the expression¹⁵

$$a_H(\mathbf{r}^H) = 17.04(8\pi/3)g_p g_e \rho_{\text{spin}}(\mathbf{r}^H), \quad (2)$$

where the spin density (in electrons per cubic bohr) at the proton is $\rho_{\text{spin}}(\mathbf{r}^H) = [\rho_\uparrow(\mathbf{r}^H) - \rho_\downarrow(\mathbf{r}^H)]$, and the constants g_p (5.5856) and g_e (≈ 2.0) denote the proton and electron g factors, respectively.

We have checked the present methods by comparing our results for a_H for several small molecules to corresponding results obtained from Eqs. (1) and (2) by the Gaussian-basis LCAO- $X\alpha$ techniques of Dunlap, Connolly, and Sabin.¹⁶ The analytic-basis results for a_H had converged with respect to the size of the Gaussian basis set. These Gaussian-basis-set results were found to agree within (2-5)% with those obtained by use of the present methods.

In Table I we compare our calculated proton Fermi-contact coupling constants to the corresponding experimental data¹⁷⁻²⁰ for several planar, conjugated, neu-

tral, organic π radicals. For simplicity, no geometry optimization was attempted; the calculations were made on the assumption that all C-C bond lengths are 1.40 Å and all C-H bond lengths are 1.08 Å. For the allyl and phenalenyl radicals, all bond angles were taken to be 120°, while for cyclopentadienyl and tropylium, the bond angles were obtained by the assumption of D_{5h} and D_{7h} symmetry, respectively. Note that the signs of the experimental values of a_H in Table I were not experimentally determined but have been assigned on the basis of the calculations. In contrast to predictions based on McConnell's relation (but in agreement with experiment¹⁷), the theory predicts two different Fermi-contact coupling constants for the protons in positions 1 and 2 in allyl. Experiment has not determined which of these two similar coupling constants is associated with which terminal proton, and so the Table I assignments for this molecule are based on the calculations.

For the cyclopentadienyl and tropylium radicals, we find positive $2p\pi$ spin populations at all the carbon atoms. However, for allyl and phenalenyl, we find negative $2p\pi$ spin populations at the starred carbon atoms of Table I and positive $2p\pi$ spin populations at the un-

starred carbon atoms. Negative P_C^π 's cannot be accounted for by use of tight-binding or extended Hückel theories that neglect correlation effects. Such semiempirical theories predict extremely small or exactly zero spin populations at the starred carbons²¹ and hence through McConnell's relation very little, if any, Fermi-contact coupling at the adjacent protons, contrary to experiment. On the other hand, our theoretical predictions in Table I are all within $\approx 25\%$ of the experimental results, and almost half of the calculated values are accurate within $\approx 10\%$.

Having established the predictive character of the theory, we now consider the radical in polyacetylene. Experiment⁵ suggests that this radical resides on the all-*trans* segments present in the *cis-trans* composite. We define the *trans*-polyacetylene chain geometry, including the defect, by adopting the SSH³ soliton model. Successive (CH) groups along the chain are labeled by subscripts n ; $n=0$ for the central (CH) group. The coordinate system is oriented so that the planar polyacetylene chain lies entirely in the xy plane, with the x axis along the chain and the origin of the coordinate system at the central carbon atom. Then the positions of the C and H atoms in the n th (CH) group are defined by the vectors

$$\mathbf{r}_n^C = [nR_{CC} \cos(\theta_{HCC} - \pi/2) + (-1)^n \mu_0 \tanh(n/l)] \hat{\mathbf{x}} + [1 - (-1)^n] R_{CC} \times \frac{1}{2} \cos(\theta_{CCC}/2) \hat{\mathbf{y}},$$

and

$$\mathbf{r}_n^H = \mathbf{r}_n^C - (-1)^n R_{CH} \hat{\mathbf{y}},$$

respectively, where $\theta_{HCC} = \theta_{CCC} = 120^\circ$, $R_{CH} = 1.08$ Å and $R_{CC} = 1.40$ Å, and $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are unit vectors along the x and y axes. The chain dimerization is defined by μ_0 and the soliton width by l .

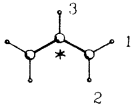
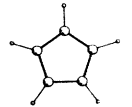
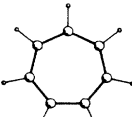
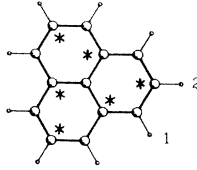
Assuming the experimentally derived²² $\mu_0 = 0.03$ Å and the commonly accepted $l = 7$, we find that the soliton induces the spin density at the polyacetylene protons shown in Fig. 1. These results were obtained from a long but finite chain terminated with CH_2 groups. However, this chain is long enough (49 carbons) that the reported results have converged with respect to increasing chain length. This spin density immediately yields the corresponding a_H 's through Eq. (2). We find negative P_C^π 's adjacent to the protons with positive a_H 's. These carbons with negative $2p\pi$ populations (n odd) alternate along the chain with carbons with positive $2p\pi$ populations (n even). As before, negative P_C^π 's and the corresponding positive a_H 's must arise from correlation effects.

In contrast to the large number of magnetically inequivalent protons that might be anticipated from Fig. 1, Thomann *et al.* observe only two distinct proton sites. However, Fig. 1 represents a single, stationary position of the soliton. Heeger and Schrieffer² suggest that during the lifetime of the nuclear Zeeman state, T_1 , the soliton diffuses rapidly along the chain leading

to motional averaging over sites. If during T_1 the soliton diffuses along a $2N$ -carbon-atom segment of the chain, there will be only two magnetically inequivalent protons,^{1,2} with the motionally averaged Fermi-contact coupling constants given approximately by $a_H^+ = (1/N) \sum_+ a_H(\mathbf{r}^H)$ and $a_H^- = (1/N) \sum_- a_H(\mathbf{r}^H)$. The symbol \sum_+ (\sum_-) denotes a restricted sum over the protons adjacent to the odd (even) carbon sites. Although each of a_H^+ and a_H^- depends on N , their ratio, $R = a_H^+ / a_H^-$, does not. Additional calculations made with the assumption of $l = 0.01, 4, \text{ and } 9$ show that R depends insignificantly on the assumed static soliton width. Our calculated value of R (-0.39) can then be compared directly to the most recent experimental value of R (-0.33). Given the theoretical and experimental uncertainties inherent in arriving at these ratios, the agreement between theory and experiment is very good. Comparing the theoretically predicted NaH^- (-49 G) to the experimentally derived a_H (-1.36 G), we find a diffusion length of $2N = 72$ carbons.²³ A similar estimate with use of a_H^+ instead of a_H^- leads to $2N = 90$ carbons. These results are close to Thomann *et al.*'s³ estimate that the polyacetylene radical affects approximately fifty carbons.

Our results show that a diffusing soliton with small l accounts for the experimentally observed R . In view of the insensitivity of R to l , this result does not exclude the possibility that a static soliton with very large

TABLE I. Comparison of the theoretically predicted to experimentally determined proton Fermi-contact coupling constants for several planar, neutral, organic π radicals.

RADICAL	POSITION	COUPLING CONSTANT (GAUSS)		
		1	2	3
ALLYL 	EXP. ^a	(-)13.93	(-)14.83	(+)4.06
	THEORY	-17.67	-18.14	+3.91
CYCLOPENTADIENYL 	EXP. ^b	(-)6.20 \pm 1	-	-
	THEORY	-6.85	-	-
TROPYL 	EXP. ^c	(-)3.95 \pm .25	-	-
	THEORY	-4.98	-	-
PHENALENYL 	EXP. ^d	(-)6.27	(+)1.83	-
	THEORY	-6.67	+1.38	-

^aReference 17.

^bReference 18.

^cReference 19.

^dReference 20.

l could also account for the data: For large l , the a_H in the interior of the defect could alternate between effectively two values, with edge effects becoming unimportant. Experiment indicates² that motional averaging does occur for higher temperatures, but such a static model could ultimately prove important in the understanding of recent polyacetylene ENDOR data⁵ below 4 K.

Prior to our work, all analyses of the polyacetylene proton ENDOR spectrum have relied on McConnell's relation, $a_H = QP_C^{\pi}$. Because we calculate both a_H and P_C^{π} , we can test this relation for polyacetylene. Our results do show an excellent linear correlation between a_H and P_C^{π} . Although the calculated values of a_H and P_C^{π} for the static $l=7$ soliton vary widely along the chain, the average value of $a_H - QP_C^{\pi}$ is only 0.13 G with a standard deviation of just 0.11 G for the least-squares fit $Q = -26$ G. This first-principles-derived Q (-26 G) is close to the value of ~ -23 G evident-

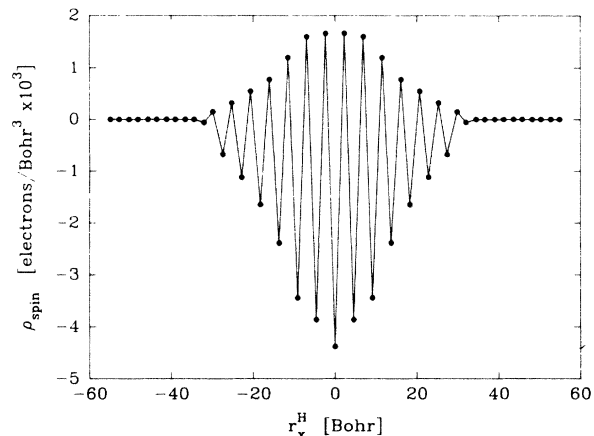


FIG. 1. Calculated spin density induced by the $l=7$ soliton at the protons along the polyacetylene chain. The proton positions, designated by dots, are measured from the soliton center.

ly assumed by Thomann *et al.*⁴ in analyzing their polyacetylene data. This Q also lies within the range of values (-22 to -27 G) long used²⁴ to analyze electron spin-resonance data for small organic radicals.

We have shown that LDF methods can reliably predict proton Fermi-contact constants for planar, neutral, organic π radicals. Our polyacetylene results show that a diffusing soliton can account for the ratio of the two observed proton Fermi-contact coupling constants, justify application of McConnell's relation to this polymer, and yield a reasonable value of Q . The approach used here is not restricted to neutral hydrocarbons, but is perfectly general and should be applicable to the calculation of isotropic proton-coupling constants in a wide variety of molecular environments.

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⁷Because the protons lie in the nodal plane of the carbon π orbitals, these states make no direct contribution to the spin density or Fermi-contact coupling constants at the protons.

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⁹The DVM- $X\alpha$ method includes interatomic overlap explicitly: $P\bar{c}$ is calculated as the difference between weighted spin-up and spin-down Mulliken populations. If the two-center atomic-basis overlap integrals were all zero, this way of calculation of $P\bar{c}$ would reduce to the difference between spin-up and spin-down local carbon $2p\pi$ densities of states integrated up to the Fermi level.

¹⁰See, e.g., J. W. D. Connolly, in *Modern Theoretical Chemistry*, edited by G. A. Segal (Plenum, New York, 1976), Vol. 7, and references therein.

¹¹See, e.g., J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 2, pp. 323 ff.

¹² $\alpha = 0.7$ is in common use for molecular calculations [e.g., B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. **71**, 4993 (1979)]. This α is close to the Kohn-Sham value of $\frac{2}{3}$ [W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965)]: Variation of α between $\frac{2}{3}$ and 0.7 has an insignificant effect on our results. Test calculations we made using the Hedin-Lundqvist exchange-correlation potential

[L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971)] show that inclusion of the correlation correction term consistently leads to slightly smaller a_H 's than the $X\alpha$ potential, giving a little better agreement with experiment at high spin densities, a little worse at low spin densities.

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²¹Exactly zero spin populations are predicted if only nearest-neighbor interactions are included. Longer-range one-electron interactions can lead to finite small spin populations of the wrong sign.

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²³Although the derived value of N implies that the soliton diffuses along a chain longer than that used to model the static defect, this poses no problem: The longer chain will give practically identical static results.

²⁴See, e.g., J. E. Wertz and J. R. Bolton, *Electron Spin Resonance* (McGraw-Hill, New York, 1972), and references therein.