

Distance Dependence of Electronic Coupling through Trans Alkyl Chains: Effects of Electron Correlation

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Electronic coupling between CH₂ π donor/acceptor groups at the termini of trans alkyl chains [H₂C–(CH₂)_{n–2}–CH₂, *n* = 4–16] was investigated using Hartree–Fock (HF) theory, second-order Moller–Plesset perturbation theory (MP2), and density functional theory (DFT). For each method the couplings in the ions were calculated in two ways: (1) the difference in donor/acceptor orbital energies [Koopmans' theorem (KT)] and (2) the difference between the ground state and first excited state energy of the ions (ΔE). The distance dependence of the coupling in anions was found to be independent of the method used, indicating that electron correlation has little effect. In contrast, the distance dependence of the couplings in cations was very dependent on the method used. For cations, couplings from Δ DFT calculations have a weak distance dependence ($\beta < 0.4$) similar to that found previously for KT couplings from HF ($\beta \sim 0.4$), while couplings from KT(DFT) and Δ MP2 calculations have a stronger distance dependence ($\beta \sim 0.6–0.7$) similar to that found previously from Δ HF calculations. When energetics are examined, it appears that the weak distance dependence for some of the methods may arise from small energy differences between the donor/acceptor levels and the energies of the filled orbitals. This was confirmed by calculations on a series of trans alkyls with different donor/acceptor groups (NH₂, SiH₂, PH₂). The couplings for the anions have a stronger distance dependence ($\beta \sim 0.6–0.7$) in all of the methods. Finally, it is found that the inclusion of diffuse functions in the basis set does not introduce problems for the calculation of anion couplings by density functional theory, in contrast to ab initio molecular orbital calculations where erratic results are obtained.

I. Introduction

Electronic coupling (*V*), with its exponential dependence on distance,

$$V = V(0)e^{-\beta r/2} \quad (1)$$

governs much of the distance and orientation dependence of long-distance electron-transfer (ET) rates. The idea that the material between the donor and acceptor has a major role in promoting the electronic coupling interaction is well established.^{1–8} Experiments in our laboratories measured the exponential attenuation parameter, β , to be 1.2 Å^{–1} through a rigid glass⁹ and slightly less than 1.0 Å^{–1} in intramolecular ET when the donor and acceptor are attached to a spacer group through a connected series of saturated bonds.¹⁰ Measurements by Paddon-Row,^{11–13} Chidsey,^{14,15} C. Miller,¹⁶ Finklea,¹⁷ Mallouk,¹⁸ McLendon,¹⁹ and co-workers supported these values, although experiments of Kuhn,^{20,21} Moebius,²² Isied,²³ and Barton^{24,25} suggested the possibility of much smaller values.

Theoretical studies^{26–45} have used methods from semiempirical to ab initio molecular orbital theory including Koopmans' theorem (KT) applied to Hartree–Fock (HF) orbital energies, Δ HF (which is often called Δ SCF), Δ MP2, and direct calculation from charge-localized, diabatic states. Of these methods, KT has been most widely applied. It is the least computationally demanding and can sometimes supply better results than Δ HF due to a tendency for cancellation of errors from relaxation and correlation. The KT method also makes the exciting prediction that hole-transfer couplings are especially efficient for long

hydrocarbon spacers.^{32,38} This is in contrast to Δ HF calculations which compute a stronger distance dependence (larger β). The KT method has also been used in calculations that predict that constructive interference can result in “superbridges” which enhance the transmission of electronic coupling by orders of magnitude.^{44,45}

If there are special principles that can selectively improve the efficiency of desirable long-distance charge-transfer processes, they could have great value in the design of molecular devices for energy storage and a variety of other purposes. They could, for example, enable chemists to design arrays of molecular groups in which electrons are transferred over large distances and directed to a desired location. Therefore, the predictive ability of theoretical methods for long-distance electron transfer is of great interest, especially given that the experimental situation is unclear. The purpose of this paper is to investigate the effect of inclusion of electron correlation on the distance dependence of electronic couplings through simple, saturated hydrocarbon spacers. Electron correlation effects are included using both perturbation theory and density functional theory (DFT). The use of newer theoretical methods such as DFT to examine electronic couplings is definitely desirable.

Density functional theory (DFT)^{46–48} has recently become widely used in quantum chemistry for the calculation of structures, reaction energies, and other properties of molecules. Density functional methods have been found to yield results of quality comparable to second-order Moller–Plesset (MP2) perturbation theory or higher.⁴⁷ Since DFT methods include correlation effects and are computationally less demanding than comparable correlation level ab initio methods, it is of interest

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to determine the reliability of these methods for the calculation of electronic couplings. Kim et al.⁴⁹ have used both local spin density (LSD) and nonlocal spin density (NLSD) functional theory to study electronic coupling in a series of rigid nonconjugated polynorbornyl dienes. The local density calculations were done with the exchange potential of Dirac⁵⁰ and the correlation functional of Vosko, Wilkes, and Nusair.⁵¹ Kim et al. performed their nonlocal spin density calculations with the gradient-corrected exchange and correlation functionals of Becke⁵² and Perdew.⁵³ Several basis sets from minimal to split-valence plus polarization were used. They found the couplings from density functional theory to be appreciably smaller than those from MP2 theory and to fall off somewhat less rapidly with increasing bridge length than those from MP2 theory.⁴⁹

In this study we have investigated electronic coupling in straight-chain alkyls [$\text{H}_2\text{C}-(\text{CH}_2)_{n-2}-\text{CH}_2$, $n = 4-16$] using density functional theory and second-order perturbation theory. We hoped to learn whether inclusion of correlation effects would confirm the strongly enhanced hole-transfer couplings through long, straight-chain hydrocarbons predicted by KT, but not by the ΔHF methods,³² and whether DFT is a useful alternative to ab initio molecular orbital theory for calculation of couplings. In the present study we have used three density functional theories, including a hybrid method that combines Hartree-Fock with exchange-correlation functionals. Hybrid methods have been found to produce results in better agreement with experiment than do the pure density functional methods for calculation of some molecular properties.^{54,55} The dependence of the density functional couplings on basis set size was also investigated. The results are compared to couplings from ab initio molecular orbital theory using KT, ΔHF , and ΔMP2 methods. The theoretical methods are presented in section II, and results are presented and discussed in section III.

II. Theoretical Methods

The ab initio molecular orbital methods used to calculate the electronic couplings have been described in detail in previous work.³² The methods include Koopmans' theorem (KT), ΔHF , and ΔMP2 . Koopmans' theorem is based on energy differences between orbitals containing symmetric and antisymmetric combinations of the donor and acceptor groups, whereas ΔHF and ΔMP2 are based on the energy differences (ΔE) between the corresponding states, which are usually the ground and first excited states of the molecular ions. The KT and ΔHF methods are at the Hartree-Fock level, whereas ΔMP2 method includes correlation effects based on second-order perturbation theory. The wave functions have delocalized donor/acceptor orbitals, that is, an equal electron distribution on the terminal CH_2 groups. Some of the ab initio results have been reported previously, but we include them here for completeness in the comparison with the DFT results.

Three density functional methods are used in this study. The first is the local spin density functional SVWN which includes the Slater exchange functional⁵⁶ and the uniform gas approximate correlation functional of Vosko, Wilkes, and Nusair.⁵¹ Next we examined the more sophisticated BLYP density functional method which includes the Becke (B) exchange functional⁵² and the Lee, Yang, Parr (LYP) correlation functional.⁵⁷ The Becke part involves a single parameter that fits the exchange functional to accurate computed atomic data. Both parts involve local density gradients as well as densities. The third is the B3LYP density functional method, a functional that is a linear combination of Hartree-Fock exchange, 1988 Becke exchange, and LYP correlation. The B3LYP functional is

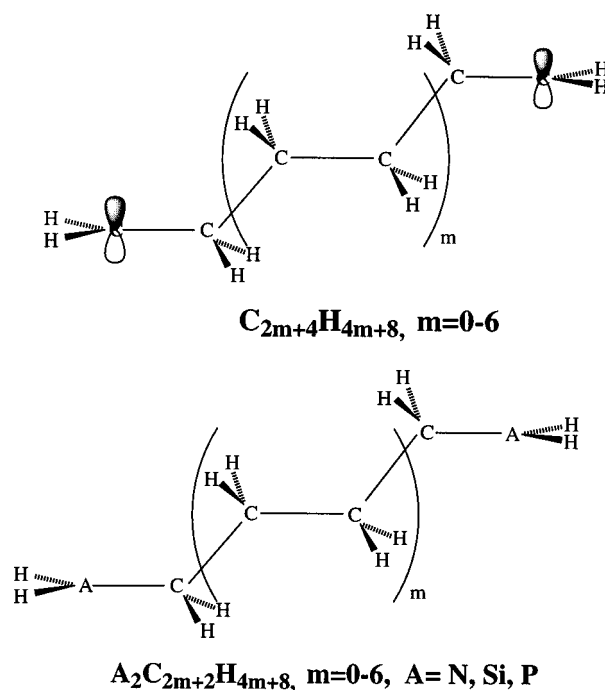


Figure 1. Structure of the trans alkyl chain ($R(\text{C}-\text{H}) = 1.11 \text{ \AA}$, $R(\text{C}-\text{C}) = 1.54 \text{ \AA}$, $\angle\text{HCC} = 109.5^\circ$, $\angle\text{H}_i\text{CH}_i = 120^\circ$), where H_i represents terminal hydrogens.

referred to as a hybrid functional, an idea introduced by Becke.⁵⁸ In a recent assessment of density functional methods the B3LYP functional gave the best agreement with experiment for 148 enthalpies of formation.⁵⁵ Although it did not attain quite as good agreement with experiment as high-level ab initio methods such as G2 theory,⁵⁹ the average absolute deviation from experiment was a reasonable 3 kcal/mol. It has also been found to perform well for computation of structures and vibrational frequencies.⁵⁴

We have calculated couplings in two ways from density functional theory. The first is based on differences in orbital energies of the neutral triplet and is analogous to the use of Koopmans' theorem (KT) for calculation of couplings from orbital energies in ab initio calculations. Formally Koopmans' theorem does not apply to density functional theory. While the eigenvalues from the Kohn-Sham⁶⁰ equations have no exact physical significance,⁶¹ they may have semiquantitative value since they reflect correlation effects.⁶¹ The couplings from the three DFT methods will be referred to as KT(SVWN), KT(BLYP), and KT(B3LYP). The second way is based on the difference between the energy of the ground and first excited state of the donor/acceptor molecule (ΔE), similar to what is done in the ΔHF and ΔMP2 methods. We refer to it as a ΔDFT calculation. The ΔDFT calculations are done using the BLYP and B3LYP methods and are referred to as ΔBLYP and ΔB3LYP . All of the DFT calculations were done with the self-consistent Kohn-Sham procedure with an expansion of molecular orbitals in terms of an orbital basis.⁶²

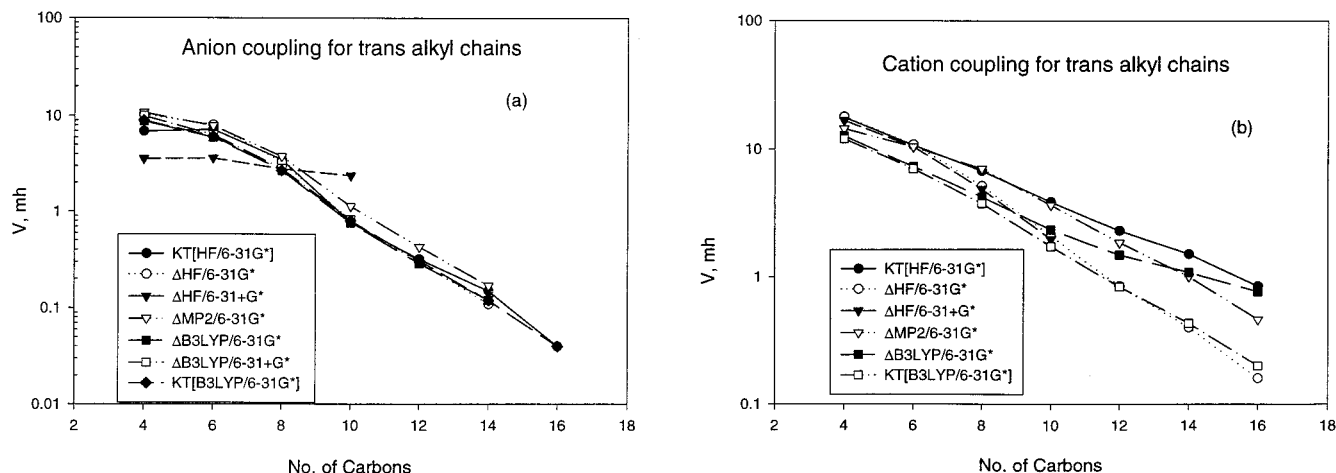
The structures of the chain alkyls are illustrated in Figure 1. Standard values are used for the bond distances and bond angles. In addition, we also calculated some of the couplings using HF/3-21G optimized geometries of the ground state cation to assess effects of nuclear relaxation. The basis sets used in this work are the 3-21G, 6-31G(d), and 6-31+G(d) basis sets.⁶³ The latter basis set includes diffuse functions on the carbons. All of the calculations were done with the Gaussian 94 computer program, and open-shell systems were done with spin-unrestricted methods.⁶⁴

TABLE 1: Couplings in Anions of $\text{H}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_2$ Trans Alkyl Chains (in mhartrees)

method ^a	<i>n</i>						
	4	6	8	10	12	14	16
KT[HF/6-31G(d)]	-6.89	-7.16	-3.49	-0.77	-0.32	-0.15	-0.04
$\Delta\text{HF}/6-31\text{G(d)}$	-10.29	-8.02	-3.28	-0.81	-0.30	-0.11	
$\Delta\text{HF}/6-31+\text{G(d)}$	-3.56	-3.60	-2.78	-2.37			
$\Delta\text{MP2}/6-31\text{G(d)}$	-10.76	-7.86	-3.75	-1.13	-0.43	-0.17	
$\Delta\text{MP2}/6-31+\text{G(d)}$	-2.92	-2.07	0.91	2.98			
KT[SVWN/6-31G(d)]	-9.04	-5.74	-2.65	-0.89	-0.36	-0.15	-0.08
KT[BLYP/6-31G(d)]	-8.64	-5.63	-2.54	-0.82	-0.32	-0.14	-0.05
KT[B-null/6-31G(d)]	-8.30	-5.58	-2.55	-0.79	-0.30	-0.13	-0.05
KT[B3LYP/6-31G(d)]	-8.92	-6.10	-2.68	-0.80	-0.31	-0.12	-0.04
$\Delta\text{BLYP}/6-31\text{G(d)}$	-5.69	-4.69	-2.25	-0.65			
$\Delta\text{B3LYP}/3-21\text{G}$	-8.23	-5.38	-2.37	-0.58			
$\Delta\text{B3LYP}/6-31\text{(d)}$	-9.91	-6.32	-2.80	-0.82			
$\Delta\text{B3LYP}/6-31+\text{G(d)}$	-8.78	-5.95	-2.68	-0.76	-0.29	-0.12	

^a See section II for a description of methods and structures.**TABLE 2: Couplings in Cations of $\text{H}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_2$ Trans Alkyl Chains (in mhartrees)**

method ^a	<i>n</i>						
	4	6	8	10	12	14	16
KT[6-31G(d)]	-17.68	-10.70	-6.73	-3.86	-2.30	-1.51	-0.84
$\Delta\text{HF}/6-31\text{G(d)}$	-17.86	-10.86	-5.14	-2.08	-0.84	-0.40	-0.16
$\Delta\text{HF}/6-31+\text{G(d)}$	-16.73	-10.38	-4.86	-1.96			
$\Delta\text{MP2}/6-31\text{G(d)}$	-14.42	-10.40	-6.99	-3.64	-1.85	-1.00	-0.46
KT[SVWN/6-31G(d)]	-10.74	-6.29	-3.25	-1.38	-0.63	-0.32	-0.14
KT[BLYP/6-31G(d)]	-10.74	-6.24	-3.24	-1.41	-0.66	-0.33	-0.15
KT[B-null/6-31G(d)]	-11.28	-6.71	-3.66	-1.72	-0.86	-0.47	-0.22
KT[B3LYP/6-31G(d)]	-12.03	-7.00	-3.75	-1.72	-0.83	-0.43	-0.20
$\Delta\text{BLYP}/6-31\text{G(d)}$	-11.54	-6.46	-3.87	-2.21			
$\Delta\text{B3LYP}/3-21\text{G}$	-13.23	-7.55	-4.23	-2.32			
$\Delta\text{B3LYP}/6-31\text{G(d)}$	-12.65	-7.27	-4.23	-2.33	-1.48	-1.08	-0.76
$\Delta\text{B3LYP}/6-31+\text{G(d)}$	-12.20	-7.18	-4.18	-2.30			

^a See section II for a description of methods and structures.**Figure 2.** Computed couplings in anions and cations for trans alkyls (standard geometry) as a function of the number of carbons.

III. Results and Discussion

The couplings for anions and cations of the trans alkyls $\text{H}_2\text{C}-(\text{CH}_2)_{n-2}-\text{CH}_2$, $n = 4-16$, calculated from DFT and ab initio molecular orbital theory are listed in Tables 1 and 2 and are plotted as a function of n in Figure 2. Computed values of β from eq 1 for successive pairs (n even) of the trans alkyls are given in Tables 3 and 4 for anions and cations, respectively.

A. Anions. The distance dependence of the couplings for anions at long distances ($n > 10$) is computed to be similar ($\beta \sim 0.7-1.0$) by all the methods (see Table 4 and Figure 2). Electron correlation does not contribute significantly to the coupling in the anions. The inclusion of diffuse functions in the basis set [6-31+G(d)] slightly decreases the magnitudes of

the couplings in the ΔB3LYP calculations, especially at the shorter distances, but the rate of falloff with distance remains almost unchanged. For the shortest chain the inclusion of diffuse functions has the largest effect—a decrease of 35% compared to less than 15% for the other chains. The larger effect in the $n = 4$ chain may be due to the direct interaction. Inclusion of a diffuse function in the 6-31+G(d) basis set causes the HF-based methods [KT(HF), ΔHF , and ΔMP2] to produce erratic and unrealistic couplings in the anions. This problem has been noted in previous ΔHF and KT calculations.^{32,35} Density functional theory does not have the same problem with continuum states, in part because it gives positive electron affinities for the triplet trans alkyl diradicals when diffuse

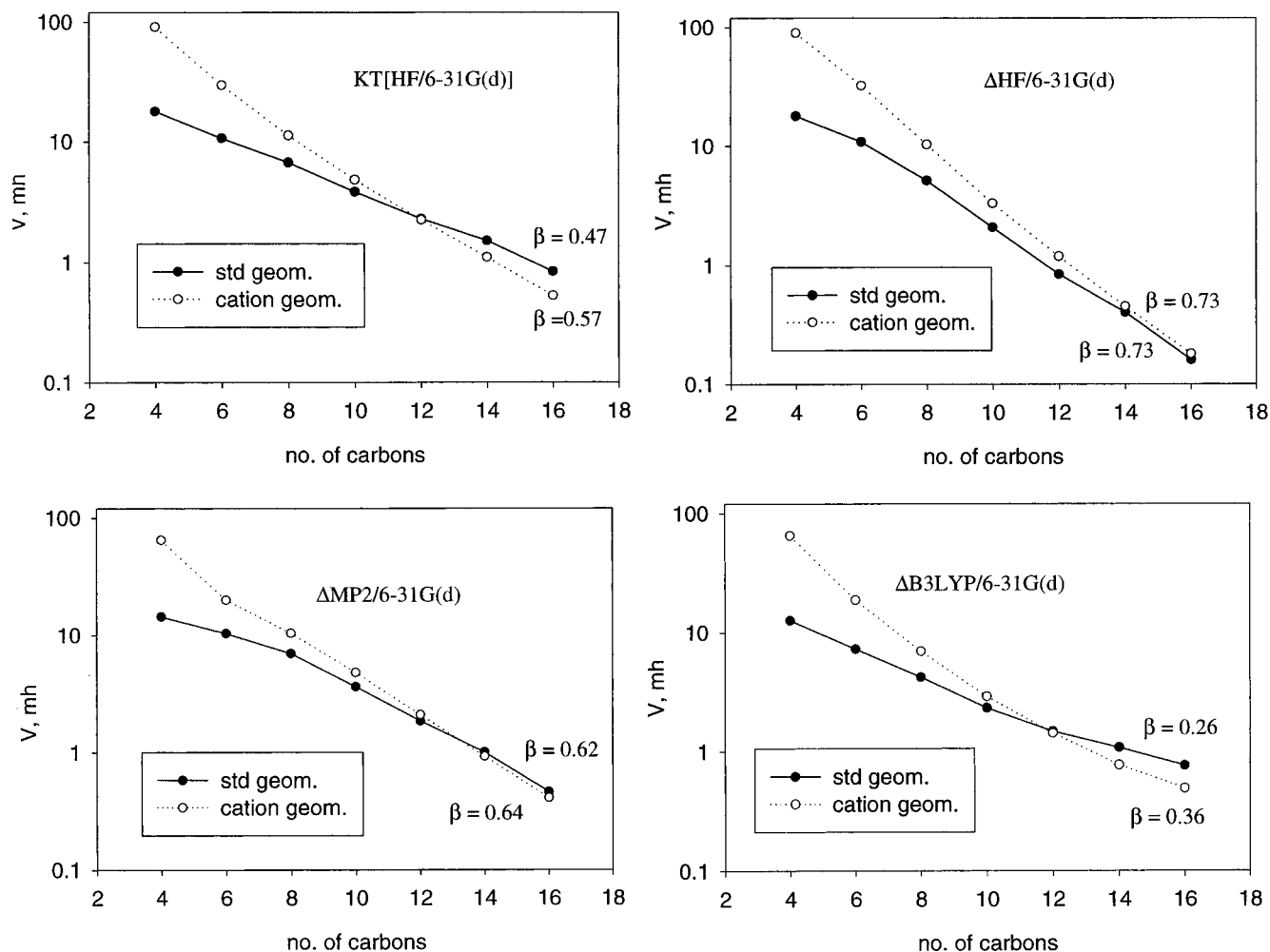


Figure 3. Comparison of computed couplings in cations for trans alkyls using the HF/3-21G optimized geometry of the ground state cation and the standard geometry.

TABLE 3: Values of β (\AA^{-1}) of Coupling in Anions of $\text{H}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_2$ from Exponential Fits to the Couplings for Successive Pairs (n Even) in Table 1

method	n					
	4, 6	6, 8	8, 10	10, 12	12, 14	14, 16
KT[HF/6-31G(d)]	-0.03	0.57	1.19	0.70	0.61	1.0
Δ HF/6-31G(d)	0.20	0.71	0.78	0.79	0.80	
Δ MP2/6-31G(d)	0.25	0.81	0.96			
KT[SVWN/6-31G(d)]	0.36	0.61	0.86	0.72	0.70	
KT[BLYP/6-31G(d)]	0.36	0.61	0.86	0.72	0.70	
KT[B-null/6-31G(d)]	0.32	0.63	0.94	0.78	0.69	0.77
KT[B3LYP/6-31G(d)]	0.30	0.48	0.62	0.58	0.52	0.61
Δ BLYP/6-31G(d)	0.34	0.66	1.12			
Δ B3LYP/3-21G	0.34	0.65	1.12			
Δ B3LYP/6-31G(d)	0.31	0.64	1.00	0.77	0.71	
Δ B3LYP/6-31+G(d)	0.16	0.59	0.99			

functions are included in the basis set. In contrast, Hartree–Fock level calculations give strongly negative electron affinities (~ -2 eV) for the trans alkyls as shown in Table 5. Examination of the wave functions suggests that the failure of the HF method is due to continuum states, which mix strongly into the donor/acceptor energy levels. The DFT wave functions have much less of this mixing.

B. Cations. In contrast to the anions, the distance dependence of the couplings in the cations varies with the method used. The KT (HF) results give surprisingly slow falloffs, $\beta \sim 0.4$, with distance for the coupling in cations, as noted in our previous study.³² The Δ HF couplings ($\beta \sim 0.6$ – 0.7), Δ MP2 ($\beta \sim 0.5$ –

TABLE 4: Values of β (\AA^{-1}) of Coupling in Cations of $\text{H}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_2$ Trans Alkyl Chains from Exponential Fits to the Couplings for Successive Pairs (n Even) in Table 2

method	n					
	4, 6	6, 8	8, 10	10, 12	12, 14	14, 16
KT[6-31G(d)]	0.40	0.37	0.44	0.41	0.34	0.47
Δ HF[6-31G(d)]	0.40	0.60	0.72	0.72	0.59	0.73
Δ HF[6-31+G(d)]	0.38	0.61	0.72			
Δ MP2/6-31G(d)	0.26	0.32	0.52	0.53	0.49	0.62
KT[SVWN/6-31G(d)]	0.42	0.52	0.68	0.62	0.54	0.66
KT[BLYP/6-31G(d)]	0.43	0.52	0.66	0.88	0.55	0.62
KT[B-null/6-31G(d)]	0.41	0.49	0.60	0.55	0.73	0.61
KT[B3LYP/6-31G(d)]	0.43	0.48	0.62	0.58	0.52	0.61
Δ BLYP/6-31G(d)	0.46	0.41	0.45			
Δ B3LYP/3-21G	0.45	0.46	0.48			
Δ B3LYP/6-31G(d)	0.44	0.44	0.48	0.36	0.25	0.26
Δ B3LYP/6-31+G(d)	0.42	0.43	0.47			

0.6), and KT (DFT) ($\beta \sim 0.6$) all fall off more rapidly, but still less so than computed values for anions or most of the experiments. The Δ DFT (Δ B3LYP and Δ BLYP) couplings give $\beta \sim 0.45$ for 10 or fewer carbon atoms and $\beta \sim 0.25$ – 0.35 for 10 or more carbon atoms. The slower falloff for some density functional methods at long distances has also been noted by Kim et al.⁴⁹ in their study of dienes. At long distances (> 10 carbon atoms) the magnitudes of the Δ MP2 couplings are 2–3 times the magnitudes of the Δ HF couplings, although the distance dependence is similar. The effect of correlation is thus larger than the 10–25% effect found by Newton³⁰ for shorter chains. The discrepancy between the Δ MP2 and Δ DFT results

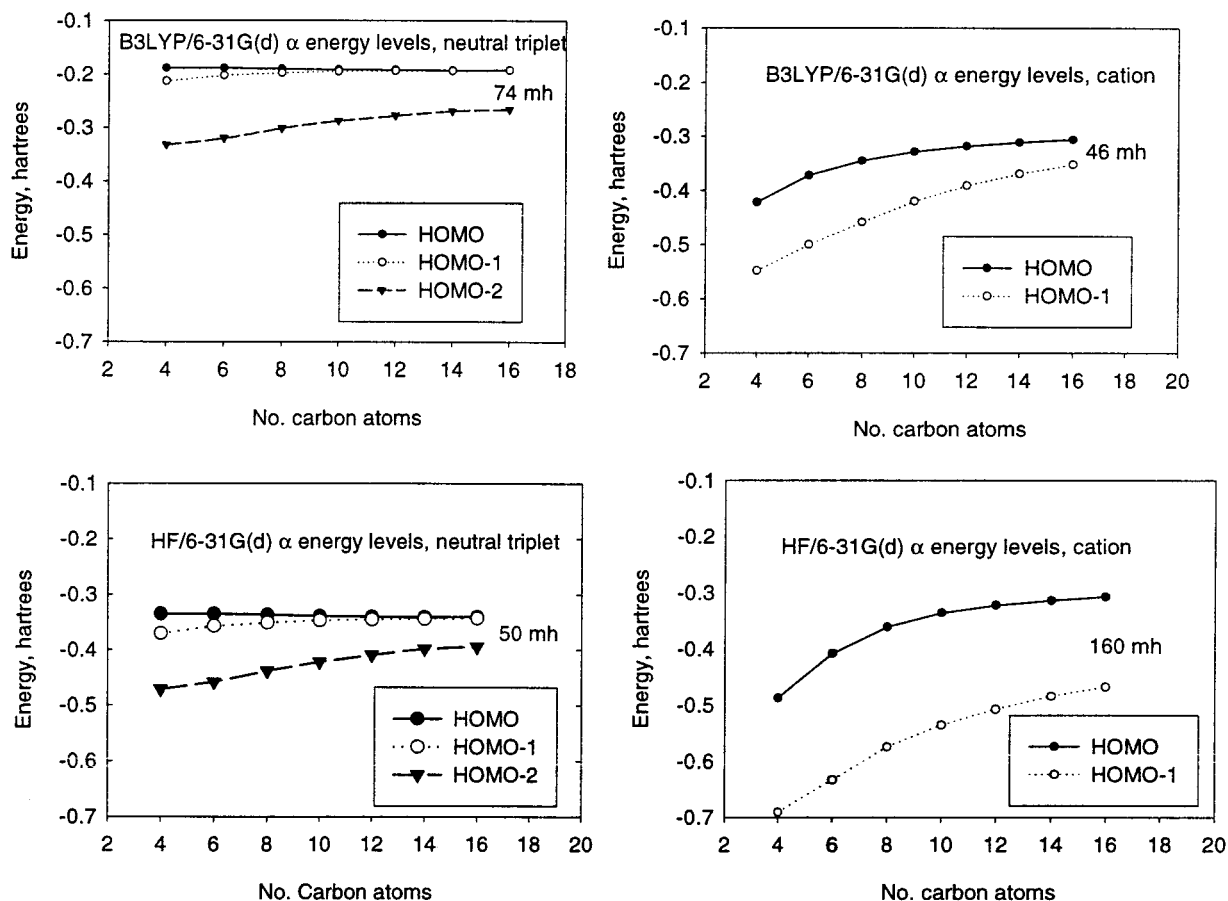


Figure 4. HOMO, HOMO-1, and HOMO-2 energy levels for trans alkyls from B3LYP/6-31G(d) and HF/6-31G(d) calculations on the neutral triplet and the cation.

for couplings in the cations needs to be resolved by CCSD(T) or QCISD(T) methods, but at the present time this is feasible only on the shorter chains which do exhibit the discrepancy.

We investigated the effect of using other geometries by carrying out HF/3-21G geometry optimization of the ground state cations. The effect of using the cation geometries for the calculation of the couplings as opposed to the standard geometries is shown in Figure 3. Some of the couplings change, especially at the short distances, but at the long distances there is little difference in the β values.

The summary of results in Table 6 does not provide evidence for a relationship between the distance dependence and inclusion of either electronic relaxation or correlation effects. We also examined the distance dependence of DFT couplings for cations using only the exchange functional. Results from KT calculations based on the Becke exchange functional,⁵² KT(B-null/6-31G*), are given in Tables 2, 4, and 6. Comparison of the KT(B-null/6-31G*) and KT(BLYP/6-31G*) results indicates that inclusion of correlation does not significantly change the distance dependence of the couplings. Similar results are also obtained for coupling in the anions when only the exchange functional is used (see Tables 1 and 3).

An examination of the energy levels computed by the different methods indicates that the small values of β for the cation couplings from the Δ DFT and KT methods are at least partially due to a smaller energy difference, B , between the donor/acceptor levels and the energies of the filled orbitals of the spacer. On the basis of a superexchange picture of coupling^{33,65} or Larsson's partitioning method,⁶⁶ one would expect that smaller values of B will result in larger couplings and a more gradual decrease with distance (small β). The

TABLE 5: Comparison of Electron Affinities (in eV) of Trans Alkyl Straight-Chain Diradicals from HF and B3LYP Methods^a

n	HF		B3LYP	
	6-31G*	6-31+G*	6-31G*	6-31+G*
4	-3.40	-2.11	-0.90	0.06
6	-3.64	-2.12	-0.76	0.17
8	-3.79	-2.10	-0.69	0.22
10	-3.84	-2.08	-0.64	0.25

^a Calculated from difference in energy of the neutral triplet and the ground state of the anion at the same standard geometry.

TABLE 6: Summary of Electron Correlation and Electronic Relaxation Effects on Couplings in Cations of $\text{H}_2\text{C}(\text{CH}_2)_{n-2}\text{CH}_2$ Trans Alkyl Chains

method	correlation	relaxation	distance dependence
KT[HF/6-31G(d)]	no	no	weak ($\beta \sim 0.4$)
Δ HF/6-31G(d)]	no	yes	intermediate ($\beta \sim 0.7$)
Δ MP2/6-31G(d)]	yes	yes	intermediate ($\beta \sim 0.6$)
KT[B-null/6-31G(d)]	no	no	intermediate ($\beta \sim 0.7$)
KT[BLYP/6-31G(d)]	yes	no	intermediate ($\beta \sim 0.6$)
Δ BLYP/6-31G(d)]	yes	yes	weak ($\beta \sim 0.3$)

energy difference, B , between the donor/acceptor orbital and the highest occupied orbital of the spacer is plotted as a function of chain length in Figure 4 for the cation and neutral triplet used in the ab initio and DFT calculations. From the KT[HF/6-31G(d)] neutral triplet results, B decreases by more than a factor of 2, becoming about 50 mhartrees (1.4 eV) at the longest chain length. Both the small B and its decrease with length will contribute to the softening of β . In contrast, Δ HF/6-31G(d) computes a larger B (160 mhartrees), which does not depend

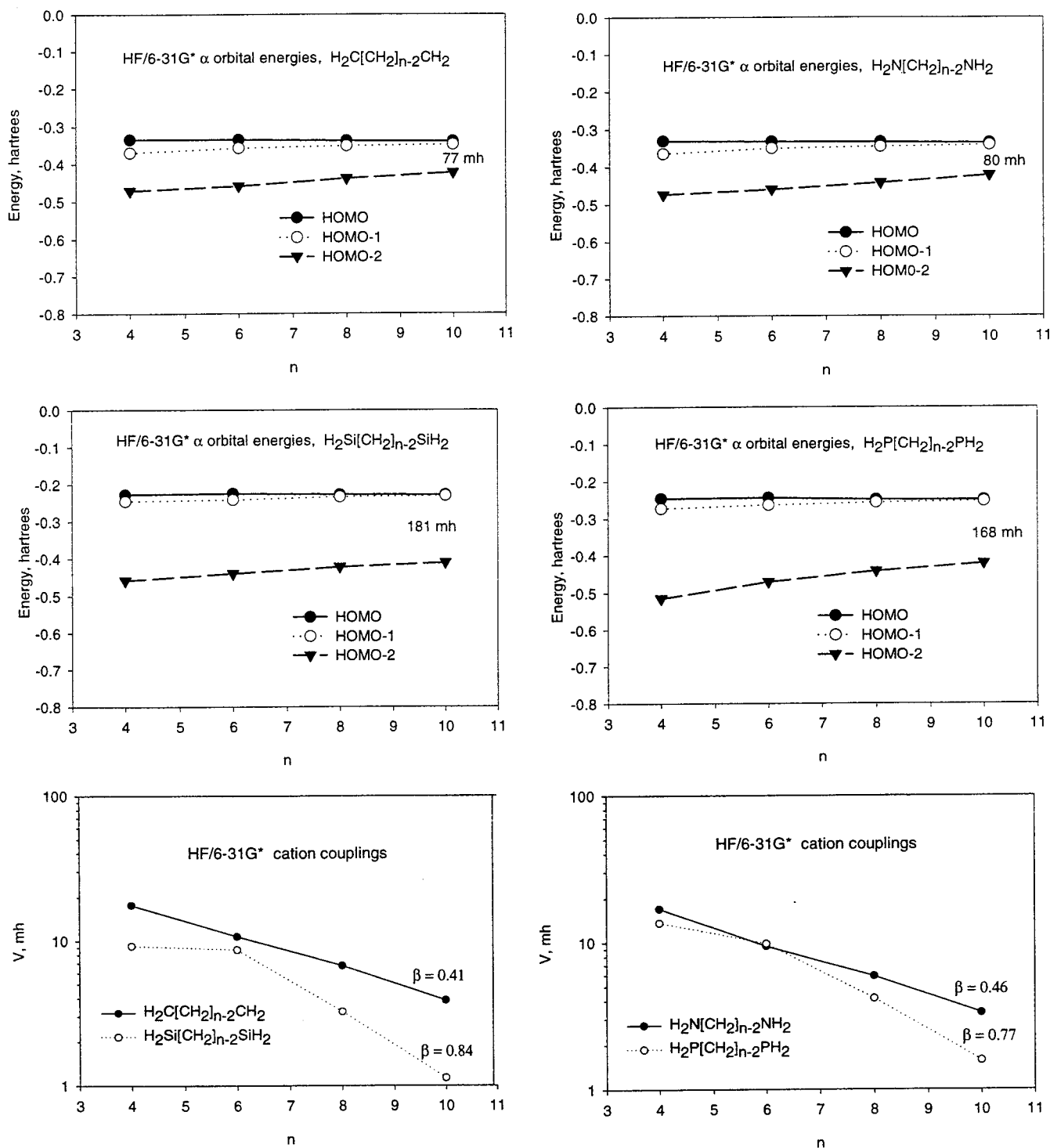


Figure 5. HOMO, HOMO-1, and HOMO-2 energy levels for trans alkyls with CH₂, NH₂, SiH₂, and PH₂ terminal, donor-acceptor groups from HF/6-31G(d) calculations on the neutral triplet.

strongly on chain length. The methods that give very small values of β have small values of B (HF/6-31G(d) neutral triplet and B3LYP/6-31G(d) cation) whereas the method with the largest value of B (HF/6-31G(d) cation) has the largest β .

We have tested the idea that the energy difference B influences the falloff rate by changing the terminal donor/acceptor groups of the HF/6-31G(d) neutral triplet to increase the energy difference B . In Figure 5, the HOMO, HOMO-1, and HOMO-2 energy levels are plotted for the chain alkyls with CH₂, NH₂, SiH₂, and PH₂ donor/acceptor groups as a function of chain length. The CH₂- and NH₂-terminated chains have a small energy difference (80 mhartrees) between the occupied

levels and the donor/acceptor levels whereas for the SiH₂ and PH₂ terminated chains the gap is much larger (160–180 mhartrees). Also shown in the figure are the couplings in the cation as a function of chain length. The results indicate that chains with the large gap (SiH₂ and PH₂ terminal groups) have β values of around 0.8, while the chains with the small gap (CH₂ and NH₂ terminal groups) have β values of around 0.4. This is consistent with the hypothesis that a small value of the energy difference B is responsible for a surprisingly slow dropoff (small β values) for the KT and Δ DFT cation couplings, and leaves open the possibility that there is no special mechanism of coupling peculiar to cations, but that long-range coupling

(small β) can occur whenever donor/acceptor levels are close to spacer levels (small B). If so, then very long-range ET (very small β) might be expected for either anions or cations if B is small. This observation is consistent with an earlier study by Shepard, Paddon-Row, and Jordan,⁴¹ who found couplings in cations to be governed by the energy of the donor/acceptor groups in a study of a series of trans alkyls having OH, SH, CH₂, vinyl, and ethynyl terminal groups.

Although not explicitly shown in this paper, it seems plausible that such small β 's can occur for anions with tunneling energies close to the σ^* states of the spacer and that β will not vary greatly from 1.0 at any energy except near the spacer states. Such behavior was predicted in Huckel-like calculations by Beratan.^{67,68} In most real chemical systems, small B will not, however, be readily attained.

The basis set dependence of the DFT cation couplings was investigated at the $\Delta B3LYP$ level of theory. The inclusion of diffuse functions has little effect (<5%) on couplings in the cation from the $\Delta B3LYP$ calculations, and the smaller 3-21G basis set gives couplings that are similar to those computed with large basis sets. This insensitivity of the couplings for through-bond couplings is similar to what we found in previous ab initio calculations. The couplings from the hybrid DFT method, $\Delta B3LYP$, are slightly larger than those from the pure DFT method ($\Delta BLYP$) but have similar values of β (see Table 3).

C. Comparison with Experiment. The distance-dependence parameter β through straight hydrocarbon chains on electrodes has been measured in several groups following the work by Chidsey^{14,15} and co-workers and the much earlier monolayer assembly measurements, principally by Kuhn and Moebius.^{20–22} Chidsey,^{14,15} Finklea,¹⁷ and Miller¹⁶ attached alkyl chains to gold electrodes and covalently bonded redox groups to the opposite ends of the chains to increase the integrity of their structures. Their data are therefore expected to be less sensitive to defects and pinholes, which might affect the monolayer assembly results. The presence of pinholes would make β appear too small. Even with anchored redox groups, Finklea found that pinholes can be an issue. All three groups obtained $\beta \sim 1.0 \text{ \AA}^{-1}$, a value supported by Mallouk's¹⁸ measurements of ET rates between ruthenium complexes and viologens in solution with connecting alkane chains confined by cyclodextrins. However, there are reports of exceptionally smaller values. Waldeck and co-workers⁶⁹ found that $\beta \sim 0.5$ for transfer through alkyls on an InP surface. They attributed the small β to small B but acknowledged that effects of pinholes could not be definitely excluded, particularly because their Fe(CN)₆^{3–/4–} redox couple was not attached to the chains.

IV. Conclusions

The following conclusions can be drawn from this study of long-range electronic coupling in chain alkyls [H₂C–(CH₂)_{*n*–2}–CH₂, $n = 4–16$], including electronic correlation effects:

1. The distance dependence of the computed couplings in anions is independent of method used (i.e., KT or ΔE), and inclusion of electron correlation (via MP2 theory or density functional theory) has little effect. The distance dependence of the couplings in cations from ab initio molecular orbital theory using KT and ΔHF methods is very different. Inclusion of electron correlation by MP2 theory alters the magnitudes of ΔHF couplings by factors as large as 2–3, but there is little effect on the distance dependence.

2. In cations of trans alkyl chains the ΔDFT method gives a weak distance dependence ($\beta \sim 0.3$) similar to that from KT based on Hartree–Fock orbital energies. In contrast, couplings

from ΔHF , $\Delta MP2$, and KT (DFT) have a stronger distance dependence ($\beta \sim 0.6–1.0$). Most experimental results support these larger values. Small energy differences between donor/acceptor levels and the filled spacer levels appear to be the cause of the weak distance dependence from KT (HF) and ΔDFT calculations. It occurs with CH₂ and NH₂ donor/acceptor groups, but not with SiH₂ and PH₂ donor/acceptor groups, which have energies farther from the spacer levels.

3. From the above it seems likely that shallow distance dependence (small β) is not an inherent property of cations or of coupling via the filled σ orbitals. Instead, it arises because the energies of some donor/acceptor groups are close to the highest orbitals of the spacers.

4. Inclusion of diffuse functions in basis sets in DFT calculations on the trans alkyl anions does not lead to erratic and unrealistic couplings as is found for couplings calculated from Hartree–Fock-based methods. The ΔDFT results indicate that inclusion of diffuse functions decreases the couplings by 5–10% except for short distances, where it is up to 35%, but has little effect on the distance dependence.

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