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The dynamical correlation in spacer-mediated electron transfer couplings

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The dynamical correlation effect in electron transfer (ET) coupling was studied in this work, for cases where electrons tunnel through a many-electron environment. The ET couplings for three different bridge-mediated model systems were calculated: (I) *trans*-alkyl chains $[H_2C-(CH_2)_n-CH_2, n=2-10]$, (II) two isomers of *trans*-1,4-dimethylenecyclohexane, and (III) two ethylenes spaced by a saturated ethane molecule. The couplings were calculated as half energy gaps of the two lowest adiabatic states. The dynamical correlation was included with spin-flip (SF) and ionization potential or electron affinity coupled-cluster singles and doubles (SF-CCSD and IP/EA-CCSD) and a ΔCCSD scheme. The direct coupling (DC) scheme is also used as a way to obtain a solution with nondynamical correlation, since DC uses approximated eigenstates that are symmetry-restoring linear combinations of two symmetry-broken unrestricted Hartree-Fock configurations. For all cases tested except for one, results from the DC scheme closely follow the CCSD data, indicating that the dual-configuration solutions can be a good approximation of wave functions with nondynamical correlation included, but there exist exceptions. Comparing the DC results with SF-CCSD and IP or EA-CCSD data, we concluded that the dynamical correlation effect is small for most of the cases we tested. © *2006 American Institute of Physics*.
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I. INTRODUCTION

In classical Marcus electron transfer (ET) theory,[1] electron transfer reaction rates are determined by three factors: the standard free energy difference (ΔG_0), reorganization energy (λ), and the electronic coupling (H_{RP}, the off-diagonal matrix element for the Hamiltonian of the reactant and product states). It is possible to estimate ΔG_0 from redox potentials in electrochemistry experiments. The reorganization energy can be estimated from a classical solvent model (for the *outer* reorganization energy, λ_{out})[2] and a set of quantum mechanical calculations (for the *inner* reorganization energy, λ_{in}).[3–5] In the weak-coupling limit, the ET rate is proportional to the amplitude square of electron coupling. Accurately estimating the coupling is important for many applications—for example, ET across biological molecules such as proteins and DNA molecules[6–10] and charge carrier mobilities in polymeric and organic materials.[11–14]

To calculate ET coupling using quantum chemistry methods, one can use a resonant condition at the transition state—the energy gap of the symmetric and antisymmetric states formed by the reactant and product diabatic states are twice the coupling value, under the two-state approximation. The widely used Hartree-Fock Koopmans theorem (HF-KT) scheme is based on this energy-gap principle in a one-electron model. Beyond one-electron theory, accurately calculating two adiabatic states at the transition state is not seen frequently because the electronic states are near degenerate in ET systems. The small energy difference between symmetric and antisymmetric adiabatic states is directly proportional to the ET coupling. A proper theoretical treatment for the nondynamical correlation is necessary for this situation. Traditionally, multiconfigurational self-consistent field (MC-SCF) or complete active space SCF (CASSCF) methods are suitable for this type of problem—both make use of a linear combination of a set of near-degenerate configurations as a zero-order wave function to recover nondynamical correlations.[15–18]

We have previously developed the spin-flip (SF) scheme for calculating adiabatic state energy gaps in determining ET couplings.[19] In SF, a high-spin configuration is used as a reference state and the desired low-spin configurations are generated as spin-flipping excitations.[20–22] With the high-spin reference, the active molecular orbitals (MOs) can be treated in a balanced manner, and therefore, it is possible to account for the nondynamical correlation without choosing active spaces or configurations. The SF approach can be combined with density-functional theory,[21] configuration interaction, or coupled-cluster theoretical models. SF-configuration interaction singles (CIS) is the SF variant of the traditional spin-conserving CIS method. Higher order excitations can be included via SF-CIS(D), SF-CISD, equation-of-motion (EOM) SF-CCSD, or SF-optimized doubles (OD) methods.[20]

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We have previously shown that SF-CIS is an accurate and robust *ab initio* scheme for calculating ET coupling strengths, without requiring one to choose active space or important configurations.[19] The dynamical correlation effects were included via SF-CCSD or SF-OD methods. In that work, the intermolecular ET couplings were found to be insensitive to the inclusion of dynamical correlation. For example, for the cation radical diethylene, SF-OD values were 10%–15% smaller than that of HF-KT, and 20%–30% lower than SF-CIS values. However, this observation is not sufficient to conclude the role of dynamical correlation in the ET couplings since it was limited to through-space systems. For bridge-mediated ET, an electron tunnels through a many-electron environment and the coupling values may be more pronouncedly affected by electronic correlation.

Another way to start with a proper HF reference and avoid nondynamical correlation is to use the ionization potential (IP) or electron affinity (EA) variants of the equation-of-motion coupled-cluster (EOM-CC) method in obtaining final states of one less or one more electrons,[23–25] where the cationic states (or anionic states) are obtained using a neutral HF reference. For many ET systems, the near-degenerate orbitals can be treated in a balanced manner with a neutral state. In the present study, we included IP-CCSD for the hole transfer (HT) studies, and EA-CCSD for ETs. By comparing these results with SF-CCSD values, we can access the effect of using different references.

The direct coupling (DC) scheme is also widely used to calculate the ET coupling.[26–29] In the DC scheme, the coupling matrix element is calculated directly using charge-localized determinants (the "diabatic states" in ET literatures[30]). In ET systems, it has been shown that such charge-localized states can be approximated by symmetry-broken unrestricted Hartree-Fock (UHF) solutions.[26,27,31] The adiabatic eigenstates are assumed to be the symmetric and antisymmetric linear combinations of the two symmetry-broken UHF solutions. Therefore, DC data can be viewed as a result of two-configuration solutions that may recover the nondynamical correlation.

In fundamentally characterizing ET through a bridge fragment, the electronic coupling between the two terminal CH_2 groups in the *trans*-alkyl chains $H_2C-(CH_2)_n-CH_2$ was studied.[27,32–39] Methylene-substituted cyclohexanes were also used as model systems.[16,37–40] The distance dependence and pathway analysis of ET among the two π orbitals of the methylenes through such σ-bonded spacers were analyzed. Orbital relaxation effects were treated by the ΔHF method, and correlation effects were included via ΔMP2 or ΔDFT models, presumably from the energy difference of two ground-state solutions with different symmetries.[34] The authors found that ΔMP2 may change the coupling from ΔHF by a factor as large as 2–3, but the distance dependence was unaffected. Using a similar approach at the CCSD level, Cukier and Cave[36] studied the through-bond and through-space contributions to the electronic couplings. This ΔCCSD approach could potentially treat the nondynamical situation properly, but it relies on the symmetry of the system. CASSCF was used to include the nondynamical correlation arising from the problems created by nearly degenerate
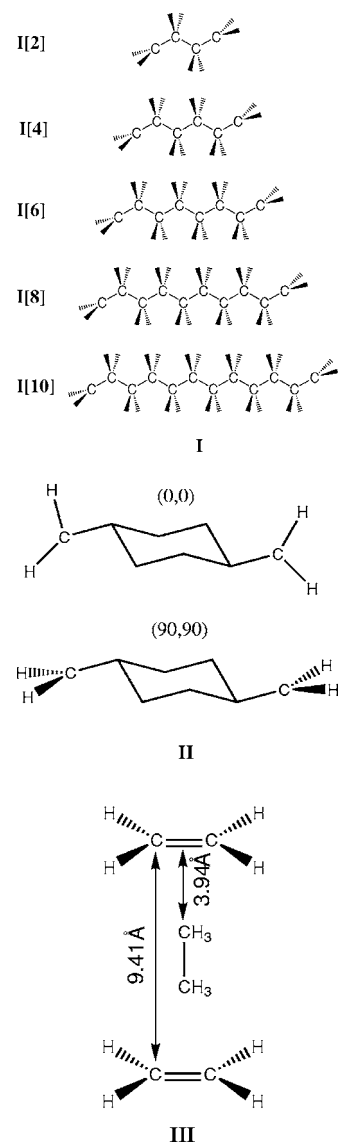

FIG. 1. Molecules studied.

orbitals.[16] For cyclohexane spaced methylenes, the variational symmetry breaking followed by a symmetry-restoring configuration interaction (CI) yielded energy splitting values close to HF-KT results.[16]

In bridge-mediated systems where a spacer fragment lies between the electron donor and acceptor, the electron tunnels through a many-electron environment. Therefore, the dynamical correlation effects may be important. We tested the effect of dynamical correlation in ET coupling for three different bridge-mediated systems (Fig. 1): (I) *trans*-alkyl chains [$H_2C-(CH_2)_n-CH_2$, $n=2-10$], (II) two isomers of *trans*-1,4-dimethylenecyclohexane, and (III) two ethylenes spaced by a saturated ethane molecule. Using symmetry-restrained solutions, we calculated ΔCCSD couplings. A consistency among SF-CCSD, IP/EA-CCSD, and/or ΔCCSD data indicates an insensitivity towards different reference states, a desirable sign of treating the nondynamical correlation properly. We further accessed the extent of spin contamination of the SF-CCSD data using restricted open-shell HF-CCSD (ROHF-CCSD). We then compared the CCSD results with those from DC, HF-KT, and SF-CIS, which are
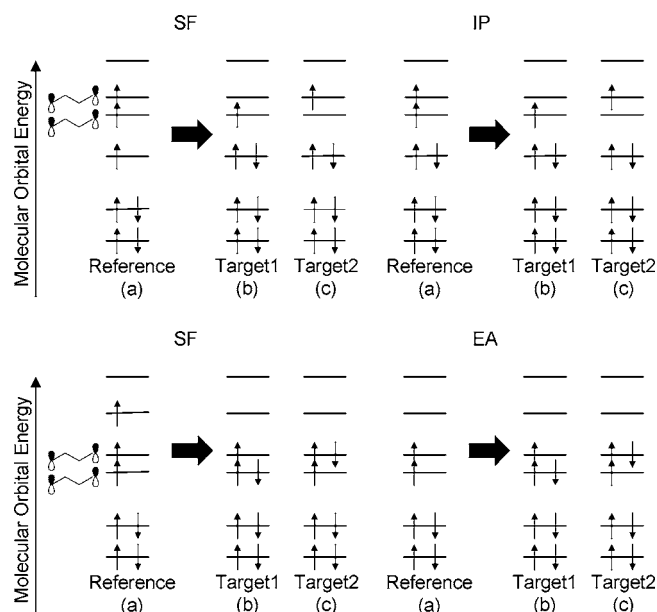
FIG. 2. Spin-flip (SF), ionization potential (IP), and electron affinity (EA)–equation-of-motion CCSD schemes, with I^2 as an example. Shown in (A) is for a cation, and (B) is for an anion. Configurations (a) are the charged quartet (for SF) or neutral triplet (IP and EA) reference states. (b) and (c) are the target charged, doublet configurations. The two π orbitals involved in ET are depicted with a small MO graph.

models with different reference configurations but without double excitations. We inferred the effects of dynamical correlations by the smallest difference between CCSD values and the DC, HF-KT, or SF-CIS data. For most cases tested the dynamical correlation effects were no larger than 10%. Most of the discrepancies among values derived from different theoretical models can be attributed to the effect of employing a different reference, or the nondynamical correlation effect. With the molecules tested, we found that there is no universal way to treat the nondynamical correlation.

II. METHOD

Both ET and HT coupling values were calculated for all molecules studied. In the following, HT (ET) indicates the case where the two electroactive groups exchange an extra positive (negative) charge, and the energy gap of the two lowest cationic (anionic) doublet states was calculated. In SF schemes, a quartet UHF state was used as the reference. For IP or EA-CCSD calculations, the starting reference state was a neutral triplet state for molecules I and II, and for III, a singlet state was used. Schematic representations for SF, IP, and EA-CCSD are included in Fig. 2. For I[2] and III, ΔCCSD data was included in the comparison, in which the difference of two ground-state CCSD energies was calculated. The UHF references were the conventional doublet states, while the symmetries of the states were constrained by choosing the occupied orbitals in the initial guesses.

In this paper, we have studied ET couplings in three series of molecules. The first system is intramolecular charge transfer, through *trans*-alkyl chains [H$_2$C−(CH$_2$)$_n$−CH$_2$, n =2−10]. The second system is constituted by two isomers of *trans*-1,4-dimethylenecyclohexane, as shown in Fig. 1. For both systems, the molecules were optimized in their neutral

triplet states with B3LYP/6−311+G*.[41] In the optimization of system I, the hydrogens of the terminal CH$_2$ were constrained to be perpendicular to the plane of reflection symmetry of the molecule. For *trans*-1,4-dimethylenecyclohexane (II), the two methylene groups were in the equatorial position. We considered two isomers: the (0,0) orientation corresponds to the hydrogens of the terminal groups placed on the symmetry plane of mirror reflection, while the terminal CH$_2$ groups of the (90,90) isomer formed a plane that is perpendicular to the symmetry plane. The third case (III) we studied is composed of a pair of ethylenes with an ethane molecule in between. The ethylene structure was from an averaged geometry of optimized structures (B3LYP/DZP) in ionic and neutral states. The ethane molecule in the middle was optimized at the B3LYP/6−31 ++G** level. In order to maximize the van der Waal's interaction between the ethane and ethylene molecules, we optimized intermolecular distances with MP2/6−31++G**, keeping all other degrees of freedom fixed. The distances are as indicated in Fig. 1 (III). All calculations were performed with a developmental version of Q-CHEM,[42] except for most IP (EA)-CCSD values, which were obtained with ACESII.[43]

The geometry of all molecules studied was constrained to the C_{2h} point group. While the signs of couplings depend on the phases of the states involved, the convention is to assign a negative coupling where the symmetrically linear combined orbital is lower in energy.[37] We list the signs of couplings of all molecules in Table I. For molecules I and II we followed the phases of the atomic p orbitals on the two terminal carbon atom, and for system III the molecular π (for HT, or π^* for ET) orbital of each ethylene was the corresponding zero-order orbital. As shown and discussed previously, the symmetric orbital may not be always lower in energy.[37]

III. RESULTS AND DISCUSSION

A. Electron transfer through *trans*-alkyl chains

1. The I [2] molecule

For the smallest molecule of this series (n=2), couplings using a number of basis sets are shown in Table II. For the HT (cation) case, the coupling values from different basis sets were very similar. Different theoretical schemes, however, led to very different results. HT couplings derived from CCSD schemes are decreased by 35%–45%, compared with SF-CIS results, or 14%–18% when compared with HF-KT data. Compared with CCSD data, DC values are only 2%–5% smaller. SF-CCSD values are very similar to those from IP-CCSD, spin-conserving CCSD, or ΔCCSD. The consistency among CCSD couplings with different refer-

TABLE I. The signs of ET and HT couplings. A negative sign was given for cases where the symmetrical orbital is lower in energy, and vice versa (Ref. 37).

	I[n]	II (0,0)	II (90,90)	III
HT	−	+	+	+
ET	−	+	−	−

TABLE II. ET and HT couplings of I[2] (listed are absolute values of couplings in units of eV).

Basis sets	HF-KT	SF-CIS	SF-CIS(D)	SF-CCSD	IP(EA)-CCSD	DC	ΔCCSD
				HT			
3-21G	0.711	0.915	0.551	0.587	0.581	0.563	0.587
6-31G*	0.653	0.872	0.490	0.554	0.542	0.527	0.550
DZP	0.635	0.855	0.483	0.540[a]	0.527	0.511	0.533
TZP	0.637	0.863	0.478	0.533	0.526	0.515	0.533
cc-pVDZ	0.643	0.866	0.481	0.549	0.535	0.522	0.543
cc-pVTZ	0.635	0.866	0.457	0.542	0.523	0.517	0.532
cc-pVQZ	0.634	0.866				0.521	
				ET			
3-21G	0.386	0.396	0.427	0.418	0.416	0.408	0.428
6-31G*	0.288	0.296	0.390	0.365	0.363	0.353	0.380
DZP	0.219	0.241	0.327	0.322[b]	0.317	0.305	0.334
TZP	0.157	0.173	0.286	0.286	0.282	0.276	0.296
cc-pVDZ	0.221	0.241	0.400	0.342	0.336	0.325	0.355
cc-pVTZ	0.118	0.141	0.377	0.297	0.295	0.287	0.314
cc-pVQZ	0.033	0.073			0.270[c]	0.261[d]	

[a]With the conventional spin-conserving EOM-CCSD and DZP basis set, the coupling value is 0.517 eV. The coupling from ROHF-SF-CCSD/DZP is 0.532 eV.
[b]Corresponding EOM-CCSD/DZP value is 0.336 eV. With ROHF-SF-CCSD/DZP, the value is 0.322 eV.
[c]Extrapolation gives an infinite basis set estimate of 0.23 eV.
[d]Extrapolation gives an infinite basis set estimate of 0.19 eV.

ences indicates that the nondynamical correlation effect is essentially diminished in these calculations. The equation-of-motion formalism diagonalizes the effective coupled-cluster Hamiltonian directly. Thus, in principle, the nondynamical correlation problem can be treated. In this case, even starting with a doublet HF reference where the active MOs were not treated in a balanced manner, the coupling from the conventional EOM-CCSD energy gap (0.517 eV, with DZP basis set) was very close to that of SF-CCSD (0.540 eV) and IP-CCSD (0.527 eV). Similar consistency is also seen in ΔCCSD data. SF-CCSD with a restricted open-shell HF (ROHF) reference yielded a value of 0.538 eV, indicating very little spin-contamination problem.

For ET, (Table II) the couplings increased from SF-CIS to SF-CIS(D), and decreased slightly from SF-CIS(D) to SF-CCSD. In increasing the number of basis functions, we observed a *decrease* in the coupling magnitudes, and the differences between schemes with (SF-CCSD, IP/EA-CCSD, or ΔCCSD) and without dynamical correlation (SF-CIS or HF-KT) increase with an increasing basis set size. In all basis sets tested, DC results closely follow the SF or EA-CCSD results, with DC's data only 2%–5% lower than those from double excitation models. With DZP basis, ΔCCSD coupling is very similar to that of spin-conserving CCSD, and both are slightly larger than SF-CCSD and EA-CCSD data. This possibly indicates a residual nondynamical correlation effect in these CCSD results.

While it is hard to obtain a converged result with large basis sets, we can extrapolate for the basis set limit. With the correlation-consistent basis sets, we assume that the error arising from incomplete basis sets systematically decreases as in the case of total energy,[44]

$$V_n = V_\infty + a \exp(-bn), \tag{1}$$

where V_n is the coupling calculated using the nth basis set in the correlation-consistent sets, and V_∞ is the basis set limit of the coupling. There are three unknown parameters to solve, but at present we have only two SF-CCSD numbers. Since the EA-CCSD and DC results closely follow those of SF-CCSD, we have used these data to fit Eq. (1), and obtained V_∞ as 0.23 and 0.19 eV for EA-CCSD and DC, respectively. The extrapolated difference in the two schemes was increased, which is partially due to the numerical operation in the fitting that increases uncertainty.

For both ET and HT, a very interesting result we observed is the close agreement between DC and the two EOM-CCSD variants. DC is based on a symmetry-restoring linear combination of charge-localized UHF symmetry-broken solutions.[16,26,45] The eigenfunctions in DC are dual configuration in nature, and possibly an essential part of the nondynamical correlation is corrected this way. Compared to SF-CIS, a scheme that is aimed at treating the nondynamical correlation effect arising from the near-degenerate π orbitals, DC offers a greatly improved alternative approach.

In this case, we found that the perturbative inclusion of double excitation in SF-CIS(D) does not offer a systematic, gradual correction. Instead, for the HT, the SF-CIS(D) values were the smallest among all methods. For ET, the SF-CIS(D) values exceeded all other values and the extent of overestimation increased in large basis sets.

To see whether the coupling is through space or through bond in nature, we have calculated a truncated I[2] system where the $-CH_2-CH_2-$ fragment in the middle was replaced by two bond-capping hydrogen atoms. Results are shown in Table III. We found that in HT couplings, the through-space model contributes only 8%–10% of the full coupling, and for ET couplings, 13%–23%. Base on this observation, we conclude that the couplings for I[2] are dominated by bridge-mediated coupling, with a non-negligible through-space contribution.

TABLE III. ET and HT couplings (in units of eV) of a truncated model of I[2], where the bridge fragment in the middle was removed.

Basis sets	SF-CCSD	IP(EA)-CCSD	DC
HT			
DZP	0.0484	0.0474	0.0451
TZP	0.0464	0.0450	0.0434
cc-pVDZ	0.0536	0.0513	0.0520
cc-pVTZ	0.0558	0.0533	0.0520
ET			
DZP	0.0412	0.0673	0.0690
TZP	0.0494	0.0408	0.0409
cc-pVDZ	0.0456	0.0503	0.0471
cc-pVTZ	0.0456	0.0465	0.0387

2. The I[n] series

The ET and HT couplings for I[n], n=4,6,8,10 were also calculated and results were shown in Fig. 3(A), where the molecules were optimized in the neutral triplet states. For a proper comparison, we have used the structure employed previously[34] to calculate couplings with the SF scheme, and results were included in Fig. 3(B).

ΔHF and ΔMP2 data from Ref. 34 were also included for comparison. It is seen that HT coupling is sensitive to a change in the structure. The neutral triplet optimized structure is shown in Fig. 4, where I[2] is depicted as an example. Compared with the previously used structure,[34] where all CC bond distances were set to 1.54 Å, C–H 1.116 Å, HCC angles, 109.5°, and H_tCH_t angles, 120° (H_t denotes the terminal hydrogen atoms), the C–C bond length constitutes the major difference in these two structures. Therefore, the different HT coupling and distance dependency may be due to the difference in the C–C distances.

For HT couplings, our results with SF-CCSD are close to the ΔMP2 data reported before. We found that SF-CIS(D) cannot properly describe the couplings either, since the ex-
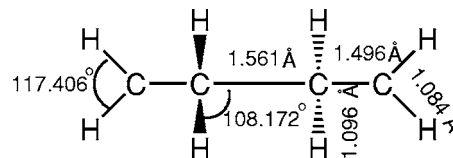
FIG. 4. Structure of I[2] optimized at the neutral triplet state using B3LYP/6−311+G*

pected exponential distance dependence is not observed. Results from HF-KT and SF-CCSD are similar, both exhibiting a smooth exponential decay.

For anions, results from different schemes fell within a small range. Couplings from HF-KT and SF-CIS exhibit a smaller slope for short chains than that for long bridges. Such a difference in slopes is decreased in SF-CCSD and SF-CIS(D) results, and therefore the data appeared to be closer to a straight line in the semilog plot.

When the coupling strengths decay exponentially with the length of the mediating bridge, the decay rate β, can be obtained by fitting to the definition

$$|V|^2 = |V_0|^2 \exp(-\beta r), \qquad (2)$$

where r is the distance of two carbon atoms in the terminal groups. Fitting our data with Eq. (2) gives β values around 0.4 Å^{-1} for cations, 0.6–0.7 Å^{-1} for anions, in the previously used structure. Fitting coupling data from an optimized neutral triplet structure gives β values varying between 0.4 and 0.5 Å^{-1} for cations, and about 0.7 Å^{-1} for anions, as shown in Table IV. Compared with an experimentally studied system such as the norbornane spaced series of molecules which has a β value of 0.98 Å^{-1},[46,47] the smaller β values for trans-alkyl chains are probably due to the smaller energy difference of the frontier electrons in the donor (acceptor) and the bridge fragment. β's derived from HF-KT data are very close those from the SF-CCSD scheme. Therefore, it appears that the dynamical correlation does not play an important role in determining the exponential decay factor β.
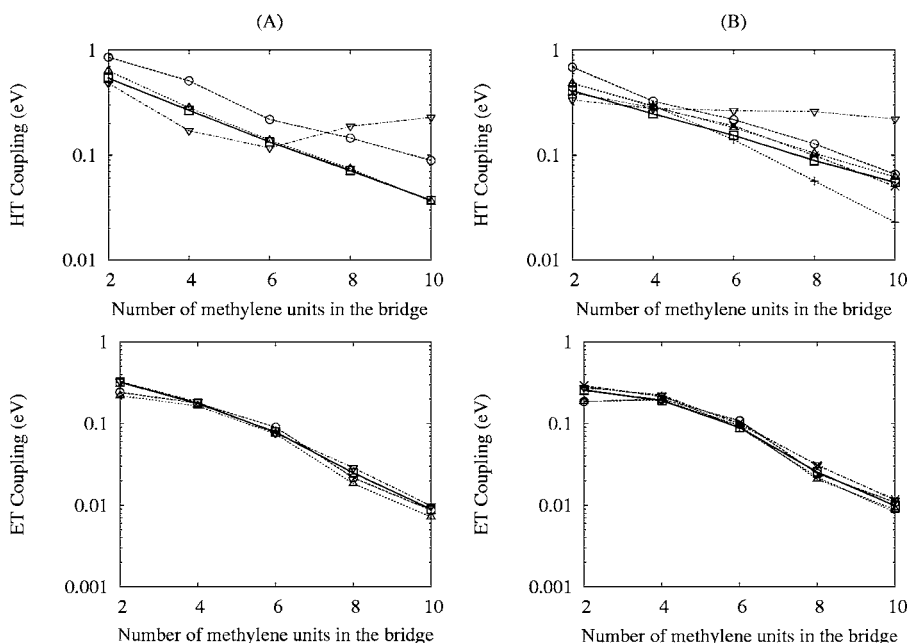

FIG. 3. HT and ET couplings for the I series, using two different structures: a fully optimized structure in the neutral triplet state (A), and a structure follows that of Ref. 34 (B). Basis sets used are DZP (A) and 6−31G* (B, for a consistent comparison.). The models used are HF-KT (triangles), SF-CIS (circles), SF-CIS(D) (inverse triangles), SF-CCSD (squares with solid line), and in (B), (D). ΔHF ("+") and ΔMP2 ("×") data from Ref. 34.

TABLE IV. The exponential decay coefficients β (in Å^{-1}) of series I[n].

Type	Structure	HF-KT	SF-CIS	SF-CIS(D)	SF-CCSD
HT	As in Ref. 34[a]	0.412	0.452	$\cdots$[b]	0.404
	Neutral triplet[c]	0.556	0.445	$\cdots$[b]	0.526
ET	As in Ref. 34	0.668	0.624	0.668	0.684
	Neutral triplet	0.710	0.688	0.697	0.718

[a]6-31G* basis set was used for this structure.
[b]Nonexponential dependence observed.
[c]DZP basis set was used for this structure.

As a summary, for electron tunnels through an all-*trans* alkyl chain, the couplings derived from SF-CCSD are close to those from IP or EA-CCSD, a consistency that implies both a charged quartet configuration and a neutral triplet state could serve as suitable references in calculations using EOM-CCSD. For both anions and cations, differences of DC and SF-CCSD results are only 2%–5%, implying a very small influence of dynamical correlation on the coupling values. DC is based on wave functions composed of two charge-localized configurations, which is potentially able to account for the nondynamical correlation effect. Therefore, DC may be a very useful low-cost alternative method for a precise estimate of electronic couplings.

B. *trans*-1,4-dimethylenecyclohexane

The ET and HT couplings for the two isomers of *trans*-1,4-dimethylenecyclohexane are included in Table V. As shown previously,[26,33] the couplings are highly dependent on the relative orientation of the donor and acceptor fragments to the bridge. Both the ET and HT couplings for the (0,0) conformer are an order of magnitude higher than in the (90,90) isomer.

Contrary to the previous *trans*-alkyl bridge case, the HT couplings for both isomers were drastically increased with a perturbative inclusion double excitation [SF-CIS(D)] and then decreased when a full account of double excitation was included (SF-CCSD). Compared with the one-electron model HF-KT, the SF-CCSD values were increased (by about 20%–60%) for the (0,0) isomer but they were decreased (by about

TABLE V. ET and HT couplings in two isomers of 1,4-*trans*(e,e)-dimethylenecyclohexane (absolute coupling values in units of eV).

Basis sets	HF-KT	SF-CIS	SF-CIS(D)	SF-CCSD	IP(EA)-CCSD	DC	ΔCCSD
			HT - (0,0) isomer				
6-31G	0.0745	0.005 15	0.148	0.119	0.123	0.132	0.131
6-31G*	0.104	0.039 6	0.158	0.126	0.130	0.143	0.140
DZP	0.110	0.045 4	0.164	0.134[a]	0.138	0.143	0.146
TZP	0.109	0.041 2	0.160	0.130	0.135	0.147	0.145
cc-pVDZ	0.109	0.042 1	0.168	0.135	0.139	0.146	0.148
			HT - (90,90)				
6-31G*	0.0223	0.013 9	0.0447	0.011 4	0.010 7	0.002 34	0.007 67
DZP	0.0182	0.011 2	0.0397	0.007 07[b]	0.006 10	0.001 47	0.002 94
TZP	0.0169	0.009 47	0.0403	0.006 05	0.005 08	0.002 31	0.001 41
cc-pVDZ	0.0248	0.017 4	0.0427	0.012 7	0.011 1	0.003 64	0.008 33
			ET - (0,0)				
6-31G*	0.303	0.323	0.232	0.237	0.234	0.209	0.235
DZP	0.285	0.292	0.241	0.232[c]	0.230	0.208	0.231
TZP	0.277	0.266	0.253	0.229	0.230	0.213	0.232
cc-pVDZ	0.297	0.314	0.266	0.241	0.239	0.213[d]	0.240
			ET - (90,90)				
6-31G*	0.0519	0.056 6	0.0341	0.030 3	0.030 6	0.032 1	0.030 3
DZP	0.0803	0.075 6	0.0512	0.047 1[e]	0.047 4	0.046 3	0.046 8
TZP	0.0589	0.061 3	0.0559	0.042 3	0.042 8	0.041 7	0.041 8
cc-pVDZ	0.0206	0.021 6	0.0467	0.020 8	0.021 2	0.022 7[f]	0.020 7

[a]With the conventional spin-conserving EOM-CCSD and DZP basis set, the coupling value is 0.115 eV.
[b]Corresponding EOM-CCSD/DZP value is −0.0235 eV. With ROHF-SF-CCSD/DZP, the value is 0.006 98 eV.
[c]Corresponding EOM-CCSD/DZP value is 0.219 eV.
[d]Values using cc-pVTZ and cc-pVQZ are 0.210 and 0.210 eV, respectively. Extrapolation to infinite basis sets gives 0.21 eV.
[e]Corresponding EOM-CCSD/DZP value is 0.0383 eV, ROHF-SF-CCSD/DZP gives 0.0468 eV.
[f]Values using cc-pVTZ and cc-pVQZ are 0.0277 and 0.0307 eV, respectively. Extrapolation to infinite basis sets gives 0.035 eV.

TABLE VI. HT and ET couplings of III where charge transfer between two ethylenes is mediated by a saturated ethane (absolute coupling values in units of eV).

Basis sets	HF-KT	SF-CIS	SF-CIS(D)	SF-CCSD	IP(EA)-CCSD	DC	ΔCCSD
				HT			
6-31G*	0.012 8	0.011 3	0.009 39	0.011 3	0.015 7	0.011 1	0.014 8
DZP	0.011 7	0.009 92	0.009 15	0.011 3[a]	0.016 5	0.010 3	0.015 2
TZP	0.012 0	0.010 2	0.009 28	0.011 4	0.016 7	0.010 6	0.015 5
cc-pVDZ	0.012 8	0.011 2	0.009 57	0.011 5	0.016 4	0.011 2	0.014 9
				ET			
6-31G*	0.013 4	0.005 06	0.008 23	0.007 10	0.009 74	0.007 10	0.009 98
DZP	0.005 55	0.004 09	0.004 35	0.004 81[b]	0.005 02	0.004 35	0.005 04
TZP	0.009 86	0.004 52	0.006 50	0.008 13	0.008 82	0.007 37	0.008 87
cc-pVDZ	0.024 1	0.006 13	0.007 09	0.011 8[c]	0.015 9	0.010 6[d]	0.015 9

[a]With the conventional spin-conserving EOM-CCSD and DZP basis set, the coupling value is 0.006 98 eV. The coupling from ROHF-SF-CCSD is 0.0113 eV.
[b]The corresponding EOM-CCSD/DZP value is 0.000 933 eV. With ROHF-SF-EOMCCSD/DZP, the value is 0.004 86 eV.
[c]The corresponding EOM-CSD/cc-pVDZ value is 0.002 05 eV.
[d]Values using cc-pVTZ and cc-pVQZ are 0.0155 and 0.0185 eV, respectively. Extrapolating to infinite basis sets gives 0.023 eV.

50%–60%) for the (90,90) one. For anions, in both structures, SF-CCSD values were smaller than HF-KT [18%–20% for (0,0) and 1%–40% for (90,90)] or the single excitation theory SF-CIS [14%–27% for (0,0) or 4%–47% for (90,90)].

In Ref. 16 the ET energy-gap values of 0.367, 0.403, and 0.440 eV were reported with CASSCF or RASSCF for the (0,0) isomer, using symmetric or symmetry-broken references. SF-CCSD yields 0.266 eV (cc-PVDZ) or 0.241 eV (DZP) for the ET coupling, which is in rough agreement with previous results.

In Table V, it can be seen that IP/EA-CCSD results agree well with SF-CCSD values for all four cases, with differences smaller than 5 meV. For anions, ΔCCSD results are very close to SF and EA-CCSD values, while for HT(0,0) they are close to DC data. DC data are 6%–16% above or below the corresponding SF-CCSD results, except for HT in the (90,90) isomer, where the DC results are much smaller than the CCSD values. This close agreement between DC and SF-CCSD again indicates a small dynamical correlation effect.

The case of HT coupling in the (90,90) isomer remains unclear. There is a lack of consistency among data from different schemes. SF-CIS and HF-KT results are very different from other data, and spin-conserving CCSD data are from the other two CCSD based schemes, both indicating the large influence of references. The rough agreement among SF-CCSD, ROHF-SF-CCSD, and IP-CCSD implies that the consistency is only achieved at the double excitation level. Both DC and ΔCCSD values are much smaller than SF or IP-CCSD data, and they barely agree with each other. It is possible that such dual-configuration solutions are not correct in this case, and there may exist a large dynamical correlation effect, but we do not have enough supporting data to conclude quantitatively.

Another interesting phenomenon is that, for HT in the (0,0) isomer, the coupling with HF-KT/6-31G is much smaller than the data with polarized basis functions, indicating that the polarized functions are important in this case.

In sum, for the cyclohexane-spaced model molecules, couplings at CCSD levels can be obtained quite reliably with SF-CCSD, as judged by their consistency with the corresponding IP or EA-CCSD and ΔCCSD values. The effect of dynamical correlation can be determined to be small in general, except for the HT coupling of (90,90), where DC and ΔCCSD coupling values are different from SF-CCSD results.

C. Ethane-mediated coupling between two ethylenes

The third test case we studied (denoted as III) is a direct extension from the previously studied ethylene dimer to a bridge-mediated system.[19] A saturated ethane molecule is now placed in the middle of a pair of ethylene molecules where charge exchanging takes place, a strategy similar to that used in Ref. 48. Electron tunneling between the ethylenes is increased by the presence of the ethane since the effective potential barrier is lowered from that in a vacuum. Coupling values derived from energy gaps are shown in Table VI.

SF schemes were previously shown to be robust in the use of large or diffusive basis sets.[19] This property is also seen here, since the anionic HF-KT/cc-pVDZ coupling was very large, but not in the SF derived data. However, with larger basis sets the discrepancies among results obtained from different schemes were increased. The numbers for ET are varied in a larger range than that of HT.

In Table VI, many IP- and EA-CCSD results deviate from the SF-CCSD data by about 2%–19%, which is not seen in previous cases. Using ROHF as the reference, the ROHF-SF-CCSD couplings are quite close to the SF-CCSD result, seemingly indicating that spin contamination is *not* a problem in the SF-CCSD calculations. Conventional CCSD results are very different from the SF-CCSD or IP/EA-CCSD values. For ET couplings, spin-conserving CCSD couplings are one order of magnitude smaller than other CCSD data, indicating a high sensitivity on reference configurations.

TABLE VII. HT and ET couplings (in units of eV) for a pair of face-to-face stacked ethylenes with an intermolcular distance of 3.5 Å.

Basis sets	HF-KT	SF-CIS	SF-CCSD	IP(EA)-CCSD	DC
			HT		
DZP	0.586	0.633	0.515[a]	0.522	0.523
cc-pVDZ	0.583	0.624	0.515	0.519	0.515
cc-pVTZ	0.584	0.641	0.517	0.520	0.520
cc-pVQZ	0.584	0.645		0.522	0.522[b]
			ET		
DZP	0.701	0.541	0.581	0.585	0.582
cc-pVDZ	0.674	0.530	0.549	0.551	0.598
cc-pVTZ	0.299	0.525	0.562	0.571	0.572
cc-pVQZ	0.0720	0.516			

[a]With the conventional spin-conserving EOM-CCSD, the coupling value is 0.507 eV. The coupling from ROHF-SF-CCSD is 0.514 eV.
[b]Extrapolating to infinite basis sets gives 0.54 eV.

For both ET and HT, there exists a good agreement between DC results and SF-CCSD data. With cc-pVDZ basis, we found that the DC coupling value is only 10% less than that of SF-CCSD. In this case, the consistency of DC and SF-CCSD is likely an indication for a small dynamical correlation effect, although we cannot rule out the possibility of a mere coincidence. On the other hand, the ΔCCSD results closely follow IP/EA-CCSD values and some of them are 40% more than corresponding SF-CCSD values. Such disagreement among CCSD data indicates that the nondynamical correlation may still exist in the results.

Increasing the number of basis functions in the correlation-consistent series, the couplings were increased as seen in DC and SF-CCSD data. The intermolecular nature requires using large basis sets. In Table VI we report extrapolated values from the DC scheme.

1. A comparison with through-space coupling

For a fair comparison of the dynamical correlation effect for ET/HT between the through-space situation and the ethane-mediated case, in Table VII we list the results of ET and HT couplings of two ethylenes using correlation-consistent basis sets. It is shown that IP/EA-CCSD and DC results are close to the SF-CCSD data. The DC and SF-CCSD values differed by 3% for HT and by 9% or ET. This difference is generally smaller than the corresponding values in the ethane-mediated case.

We note that the signs of the ET and HT couplings were all negative. The HT couplings were different from the ethane-mediated case (Table I). Electronic tunneling paths carry phases and, as a result, constructive and destructive interferences may lead to different signs and magnitudes.

D. Superexchange model

Bridge-mediated ET is typically contributed by the superexchange mechanism. The coupling between the donor and acceptor fragments is increased by their coupling to the bridge in between. With the bridge fragment, the transfer matrix element (or the *effective* Hamiltonian matrix element) is given by[49–52]

$$T = V + VGV, \tag{3}$$

where G is the Green's function associated with the Hamiltonian H, composed of an unperturbed H^0 and a perturbation V. It is convenient to define the zero-order space as noninteracting donor, bridge and acceptor states, while V contains the interaction among them.

When the donor and acceptor are separated by a relatively large distance, the direct interaction between them vanishes. Therefore, the overall effective coupling arises from the second term in Eq. (3),

$$H_{DA}^{\text{eff}} = T_{DA} \approx [V(E1 - H)^{-1}V]_{DA} \approx \sum_B \frac{V_{DB}V_{BA}}{E - E_B}. \tag{4}$$

The superexchange terms arising from each bridge level (B) are, therefore, inversely proportional to the energy gaps given by the energy of the electron being transferred (E) and the energy of bridge states (E_B). To see whether there exists a shift in energy that dominates the final coupling values, we model the smallest denominator in Eq. (4) with the difference of IPs (for HT, i.e., cations) or electron affinities (EAs) (for ET, i.e., anions) between the donor (acceptor) and the bridge fragments. In calculating such IP or EA, neutral molecules resembling the donor (bridge) part were formed by removing the acceptor and bridge (donor and acceptor) fragments. Hydrogen atoms were added to fill broken covalent bonds when necessary, with their positions optimized (at HF/6-31G* level) while keeping all other atoms fixed.

In Fig. 5, we plotted differences in IP (for HT) or EA (for ET) between the bridge and the donor/acceptor fragments with respect to their coupling values, with each pair of data calculated at roughly the same level of theory. Energy differences in the HF level were plotted against two coupling values determined by HF-KT and SF-CIS schemes. CCSD energy differences were plotted together with couplings derived from IP(EA)-CCSD or SF-CCSD. From Fig. 5, there is a very little correlation among the quantities plotted.

From Eq. (4), the factors influencing bridge-mediated coupling include changing of the near-neighbor couplings in addition to changes in the energy gaps. The results in Fig. 5 show that the overall coupling strength is *not* correlated with
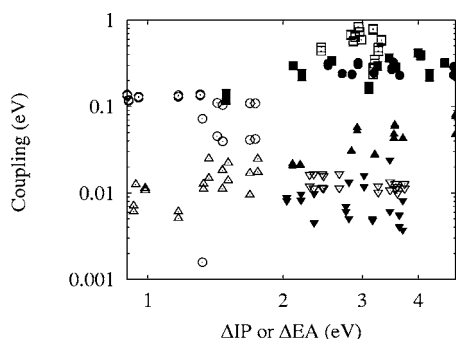
FIG. 5. The correlation in changes in IP or EA energies vs the final coupling values. Open symbols are for HTs, and closed symbols are for ETs. Data from four molecules are included: I[2] (squares), II(0,0) (triangles), II(90,90) (circles), and III (inverse triangles).

a shift in energy levels; instead, correlation might affect near-neighbor couplings, or it might be a sum of contributions mediated by a number of different local orbitals of the bridge, as analyzed before.[40] Since each contribution has a phase, there exists cancellation of different terms. Therefore, there is no simple rule to explain the effects in ET couplings when double excitation is included in the theoretical framework.

E. General remarks

Based on a two-state model, we have assigned half of the energy gaps as electron transfer couplings. The large energy gaps observed in I[2] and in the (0,0) isomer of II could be speculated as unfavorable situations, since with large energy gaps, it is more likely to have a third state nearby, and the energy gaps may be affected. While it is hard to verify the two-state model in general, the agreement between DC and energy-gap derived values is a positive sign. DC does not depend on any other state, as long as the two UHF states it uses can properly represent the space of the eigenstates. Therefore, the general agreement between DC and CCSD couplings observed in most cases implies that the energy gaps are not affected by other (excited) states of the system.

To account for the dynamical correlation effect properly, it would be desirable to have a list of full configuration interaction values to compare with, which is not possible given the size of the systems studied. At present we have assumed that an agreement among CCSD-derived values ensured the quality of the answers. The agreement between SF-CCSD and IP/EA-CCSD indicates an insensitivity toward the choice of reference, which is necessary but not sufficient for a correct answer. For example, if any of the bridge orbitals were close to the active donor/acceptor orbital energies, then both SF and IP/EA-CCSD suffer a similar nondynamical situation, and their answer may be similar. On the other hand, the previously used ΔCCSD scheme has the advantage of employing separate optimized references in the two states. So an agreement of ΔCCSD and other EOM-CCSD values enhances the validity of these CCSD answers, as seen in I[2] and the ET of both isomers in II. But again these agreements are good indicators but not sufficient for exact values.

IV. CONCLUSION

We have investigated the dynamical correlation effects in ET coupling for cases where electrons tunnel through a bridge fragment. For many cases we were able to access the quality of coupling values at the CCSD level by the consistency of SF-CCSD, IP/EA-CCSD, and ΔCCSD data. We found that most results from the DC, a scheme that is based on a symmetry-restoring linear combination of two UHF symmetry-broken configurations, followed closely the corresponding SF-CCSD results, indicating a sign of small dynamical correlation effects for ET couplings. Perturbative inclusion of double excitation models such as SF-CIS(D) could not systematically improve the coupling values. We also showed that a change of coupling from different theoretical models is not correlated with the changes in energy gaps between the donor (acceptor) and the bridge fragment.

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