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Multistate Density Functional Theory for Effective Diabatic Electronic Coupling

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Abstract

Multistate density functional theory (MSDFT) is presented to estimate the effective transfer integral associated with electron and hole transfer reactions. In this approach, the charge-localized diabatic states are defined by block localization of Kohn–Sham orbitals, which constrain the electron density for each diabatic state in orbital space. This differs from the procedure used in constrained density functional theory that partitions the density within specific spatial regions. For a series of model systems, the computed transfer integrals are consistent with experimental data and show the expected exponential attenuation with the donor–acceptor separation. The present method can be used to model charge transfer reactions including processes involving coupled electron and proton transfer.

Graphical abstract

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ASSOCIATED CONTENT

Supporting Information

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Numerical values of computed transfer integrals; brief description of the local monomer calculations; and results for He₄⁺ excited states (PDF)

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The charge transfer integral or effective electronic coupling between electron (or hole) donor and acceptor groups is a key parameter that controls the rate of electron transfer (ET) as well as electronic excitation energy transfer.^{1,2} In most theoretical methods, a prerequisite for computing transfer integrals is a suitable definition of the electronically localized donor and acceptor configurations, called diabatic states, which distinguish the initial and final locations of the charge or excitation.³ Because diabatic states are not uniquely defined,^{4–8} a plethora of techniques have been developed to model diabatic configurations^{1,8–22} and the corresponding charge transfer matrix elements.²³ Broadly speaking, methods for constructing diabatic states may be grouped into two categories; the first relies on a suitable transformation of the relevant adiabatic states to produce localized orbitals to form the corresponding diabatic states,²⁴ and the second approach determines diabatic states on the basis of the characteristic local features of the physical system as in valence bond theory.²⁵ Typically, the diabatic states generated in the first category are orthogonal and contain orthogonalization tails,²² whereas diabatic states in the second group do not have orthogonality constraint and are thus more intuitive for interpretation. One approach that has gained popularity for computing diabatic coupling in the past few years^{2,23} is constrained density functional theory with configuration interaction (CDFT-CI)^{26–28} because DFT can be applied to large systems with the inclusion of electron correlation. However, in a recent communication, Mavros and Van Voorhis highlighted some spectacular failures of their approach for some simple diatomic models as well as molecular systems, including the classic example of the $\text{Fe}^{2+}(\text{H}_2\text{O})_6/\text{Fe}^{3+}(\text{H}_2\text{O})_6$ pair for ET.²⁹ In this Letter, we illustrate that multistate density functional theory (MSDFT)^{30,31} can be conveniently used to determine transfer integrals associated with electron or hole transfer reactions and that it does not exhibit the problems encountered in CDFT as a consequence of a philosophically different way of constraining electron density.

Mavros and Van Voorhis showed that in some cases, the computed electronic coupling does not decay exponentially with distance and concluded that “it can be difficult to determine whether the CDFT-CI coupling for a particular system is trustworthy”.²⁹ The exponential attenuation of effective electronic coupling with distance was first recognized by Dexter in the study of excitation energy transfer,^{32–34} and it is approximately related to the overlap S_{12} between the donor (1) and acceptor states (2)

$$V_{12}=V^{\circ}S_{12}\propto e^{-\beta R/2} \quad (1)$$

where V° is a constant for a given system, β is the exponential factor, and R is the donor–acceptor distance. The relation has also been used to estimate the resonance integral³⁶ and applied to ET in biological systems in which β values of 0.9–1.6 Å⁻¹ have been found for various coupling zones.^{2,37} Thus, it is critical for a suitable diabatic coupling method to reproduce this fundamental property. Mavros and Van Voorhis²⁹ provided a lucid analysis and pointed out that the origin of the failure of CDFT is due to partial ET between the donor and acceptor states. In particular, because CDFT constrains electron density in spatial regions, the constrained density is in fact composed of “parts of multiple electrons” from the spatially delocalized orbitals that belong to other regions.²⁹ In other words, there is leakage of electrons between donor and acceptor groups because CDFT does not use local orbitals to produce the constrained density for a diabatic state,³⁰ although the constrained density happens to integrate to the desired number of electrons for that state.²⁶ Furthermore, it was shown that even for systems where the computed coupling exhibited correct behavior, the success was “only through fortuitous cancellation of errors”. These authors proposed a charge transfer metric based on the density difference matrix between donor and acceptor states as a diagnostic for predicting whether or not CDFT coupling is trustworthy, but the problem remains in the CDFT definition of diabatic states and its evaluation of transfer integrals.²⁹

In MSDFT,^{30,31} we begin by defining the charge-localized initial, $\Psi_1(\text{DA}^+)$, and final, $\Psi_2(\text{D}^+\text{A})$, diabatic configurations^{20,25,38,39} for an ET reaction (or hole transfer in the reverse direction) through fragmental block localization of Kohn–Sham (BLKS) orbitals (Figure 1), where D and A are, respectively, the electron donor and acceptor groups (also called fragments). The fragments in each diabatic state are partitioned according to the Lewis resonance structure as in valence bond (VB) theory,²⁵ and the BLKS orbitals are constructed using the basis functions on atoms within a given fragment. Furthermore, the electron density for a diabatic state, K ($K = 1$ or 2), is determined from the Slater determinant function of BLKS orbitals such that $\rho_K^{\text{BLKS}}(\mathbf{r}) = \rho_K^{\text{D}}(\mathbf{r}) + \rho_K^{\text{A}}(\mathbf{r})$,³⁰ with $\rho_K^{\text{D}}(\mathbf{r})$ and $\rho_K^{\text{A}}(\mathbf{r})$ being the electron densities of the donor and acceptor groups, respectively. Importantly, integration of the fragment density over all space, rather than a particularly constrained local region, yields naturally the number of electrons in the fragment (eq 2)³⁰

$$\int d\mathbf{r} \rho_K^a(\mathbf{r}) = N_K^a \quad (2)$$

where N_K^a is the number of electrons in the a th (D or A) fragment of diabatic state K (1 or 2). Therefore, block-localized density functional theory (BLDFT), that is, DFT with BLKS orbitals, for defining diabatic states in MSDFT corresponds to a strictly constrained density functional theory in orbital space.³⁰ This computational scheme is philosophically different from that of the CDFT approach by Van Voorhis and co-workers who constrain electron density in a spatial region from delocalized orbitals over both donor and acceptor fragments.

^{26–28} Consequently, the block localization method in MSDFT does not suffer from ET contamination of diabatic states found in spatial localization of density.²⁹ Diabatic states defined in MSDFT are nonorthogonal states and have a flavor of effective VB configurations.^{40–42}

The adiabatic ground state ($\Phi_g = c_{g1}\Psi_1 + c_{g2}\Psi_2$) associated with an ET reaction in MSDFT is obtained either by configuration interaction involving the variationally optimized diabatic states (VDC) or by the method of multiconfiguration self-consistent field (MCSCF) to optimize both orbital and configuration variables.²⁵ The diabatic states optimized in the latter approach are called consistent diabatic states (CDCs). MSDFT is a density functional representation of the mixed molecular orbital and valence bond (MOVB) theory^{25,38,39,43} that has been used in condensed-phase simulations as well as ET processes. When the system contains just one fragment, MSDFT reduces exactly to the conventional Kohn–Sham DFT. On the other hand, when BLKS orbitals are localized on atoms, MSDFT becomes an ab initio VB theory,^{41,44,45} which is equivalent to the complete active space (CASSCF) approach, but dynamic correlation is automatically included in MSDFT because the Hamiltonian matrix elements are determined by BLDFT.⁴⁶

The adiabatic ground and excited states show a splitting along the reaction coordinate at $z^\ddagger$ where the two diabatic states cross (Figure 1). The energy difference between the adiabatic surfaces, $\varepsilon = \varepsilon_e - \varepsilon_g$, gives a quantitative measure of the effective electronic coupling, the transfer integral, between $\Psi_1(\text{DA}^+)$ and $\Psi_2(\text{D}^+\text{A})$. In general, both ε and V_{12} are dependent on the reaction coordinate z

$$\Delta\varepsilon(z) = \sqrt{\frac{\Delta E_{12}^2(z)}{1 - S_{12}^2(z)} + 4V_{12}^2(z)} \quad (3)$$

where $\Delta E_{12} = H_{11}[\rho_1^{\text{BLKS}}(\mathbf{r})] - H_{22}[\rho_2^{\text{BLKS}}(\mathbf{r})]$ is the energy difference between the two diabatic states enumerated by BLDFT³⁰ and the transfer integral V_{12} is given by^{23,47}

$$V_{12}(z) = \frac{1}{1 - S_{12}^2} \left| H_{12} - \frac{H_{11}H_{22}}{2} S_{12} \right| \quad (4)$$

At medium and long-range separations between the donor and acceptor groups, the effective electronic coupling can be approximated by the implicit expression using the ground-state energy (referring to the generalized secular equation)³⁰

$$V_{12}^g(z) = |H_{12} - \varepsilon_g S_{12}| \quad (5)$$

Equationss 4 and 5 are related by an overlap-dependent factor $g(z)$,

$$V_{12}(z) = V_{12}^g(z)g(z) \quad (6)$$

$$g(z)=1+\frac{1}{2c_{g1}c_{g2}}\left\{\frac{S_{12}(z)}{1-S_{12}^2(z)}\right\} \quad (7)$$

where c_{g1} and c_{g2} are configuration coefficients for the adiabatic ground state. Although eq 4 is valid for all values of the reaction coordinate and overlap, the quantitative difference with eq 5 only becomes noticeable at short donor and acceptor separations (see below).

It is interesting to note the special situation at $z = z^\ddagger$, in which eq 5 corresponds to $V_{12}^g = H_{11} - \varepsilon_g$, whereas eq 4 represents the average in ground- and excited-state splitting, $V_{12} = \varepsilon/2$ (Figure 1), and they differ by an overlap denominator, $V_{12} = V_{12}^g/(1+S_{12})$.

Using MSDFT, we have examined the dependence of electronic coupling on donor–acceptor separation for a series of species, including He/He⁺, Zn/Zn⁺, Zn⁺/Zn²⁺, Fe²⁺/Fe³⁺, Fe²⁺ (H₂O)₆/Fe³⁺(H₂O)₆, and the cyclohexane pair *c*–C₆H₁₂⁺/*c*–C₆H₁₂. Several cases were shown to exhibit nonexponential attenuation with distance using CDFT-CI, while others appeared to behave normally.²⁹ For the cyclohexane system, the monomer structures were optimized using B3LYP/6-311G(d,p), and the structural variations accompanying the ET were represented using the linear reaction coordinate model.⁹ In each case, we partitioned the system into two blocks on the basis of the atomic or molecular fragment; (a) for the initial reactant state $\Psi_1(\text{DA}^+)$, the transferring electron is assigned to the D group, and (b) for the final product state $\Psi_2(\text{D}^+\text{A})$, the electron ends in the A block. The donor and acceptor group partitioning as well as the definition of the ET reactant (initial) and product (product) states are illustrated in Figure 1 for the ET between ethylene and the ethylene cation radical. Here, in the reactant state, one C₂H₄ molecule is treated as the donor fragment (yellow), and the C₂H₄⁺• ion is the acceptor group (purple); together, they form the reactant $\Psi_1(\text{DA}^+)$ block-localized determinant. For the product state, an electron is transferred from the donor group to the acceptor group, producing the corresponding determinant, $\Psi_2(\text{D}^+\text{A})$. Here, the notation, $\Psi_1(\text{DA}^+)$ and $\Psi_2(\text{D}^+\text{A})$, is used to emphasize that fragmental BLKS determinants are used to generate the electron densities for the corresponding diabatic states, $\rho_1^{\text{BLKS}}(\mathbf{r})$ and $\rho_2^{\text{BLKS}}(\mathbf{r})$. The latter is used in standard KS-DFT calculations to determine the constrained DFT energies H_{11} and H_{22} . In the present MSDFT calculations, the Perdew–Burke–Ernzerhof (PBE) functional⁴⁸ and the hybrid PBE0 model were used along with the 6-31+G(d) basis set except for the two metals (Fe and Zn) for which the TZV basis set was used. The electronic coupling for ET was computed using eq 4, except cases noted for comparison with eq 5. All MSDFT calculations were performed using a module implemented in a modified version of GAMESS(US).

The off-diagonal Hamiltonian matrix element H_{12} is not the ET coupling except when the overlap between the reactant and product diabatic states is zero.^{8,25} Strictly, there is currently no density functional to directly compute the off-diagonal Hamiltonian matrix element, $H_{12} = F_{\text{xc}}^{\text{TD}}[\rho_{12}]$, which is an implicit functional of the diabatic state densities and the transition density $\rho_{12}(\mathbf{r})$. On the other hand, H_{12} can be evaluated exactly in wave function theory (WFT)⁴⁹ as in MOVb.^{38,39} We have proposed two approaches to estimate

H_{12} in density functional theory,³⁰ which turn out to yield similar results. First, we directly apply the expression for nonorthogonal determinants in WFT using BLKS orbitals for the two diabatic states to obtain H_{12}^{BLKS} , where the superscript BLKS is to emphasize that the quantity is computed using WFT with BLKS orbitals. H_{12}^{BLKS} does not include explicitly correlation effects (although the orbitals are optimized using DFT with inclusion of the correlation potential). Electron correlation is included in an average sense from the two diabatic states at a given coordinate z (Figure 1). Thus, the off-diagonal matrix element in MSDFT is determined by

$$H_{12} = H_{12}^{\text{BLKS}} + S_{12} \frac{\Delta E_1^c + \Delta E_2^c}{2} \quad (8)$$

where $\Delta E_1^c = E_c^{\text{PBE}}[\rho_1^{\text{BLKS}}]$ and $\Delta E_2^c = E_c^{\text{PBE}}[\rho_2^{\text{BLKS}}]$ are the correlation energies for the two diabatic states, which can also be approximated by the energy difference between BLDFT and that of Hartree–Fock theory using BLKS orbitals.

Alternatively, we use the transition density directly to estimate $H_{12}[\rho_{12}(\mathbf{r})]$ in the standard Kohn–Sham exchange–correlation functional for the ground state.³⁰ This, of course, is not strictly valid, but interestingly, the numerical results seem to be very similar to that from eq 8 using PBE and PBE0 (as well as other functionals) in a number of applications.^{30,31,46,50–52} Nevertheless, in the absence of a well-defined transition density functional for electronic coupling, we recommend the use of eq 8 for applications, but it is also useful to compare the results from direct KSDFT calculations.

First, we examine the effect of mixing different fractions of Hartree–Fock (exact) exchange in the PBE functional on the V_{12} . Figure 2 shows the computed transfer integral for $\text{Fe}^{2+}(\text{H}_2\text{O})_6/\text{Fe}^{3+}(\text{H}_2\text{O})_6$ as a function of the iron–iron distance R (note that the coordinate z in Figure 1 corresponds to inner-sphere geometrical reorganization at a given R). Previously, it was noted that the computed electronic coupling for this system strongly depends on the percentage of exact exchange used, spanning as much as 5 orders of magnitude.²⁹ In MSDFT, the use of eq 8 corresponds to 100% Hartree–Fock exchange for the off-diagonal matrix element H_{12} , whereas PBE0 contains 25% exact exchange and PBE has no Hartree–Fock contribution. Figure 2 shows that the results from different portions of exact exchange do not show significant difference beyond $R = 6 \text{ \AA}$. At the shortest distance ($4.5 \text{ \AA}$) examined, where the water ligands on the two iron ions are in close contact, the difference in the computed transfer integrals between the use of 0 and 100% exact change is about 25 meV. The same trends (not shown) are found for all other cases examined here. Thus, we do not observe significant dependence of computed transfer integrals on the percentage of exact exchange included in a functional as it should be.

To investigate the difference between eqs 4 and 5 for computing electronic coupling, we present results for the Ne/Ne^+ and Zn/Zn^+ pairs in Figure 3. These two systems are shown because they exhibit the greatest differences between the two equations (the computed g factors, eq 7, along interfragment distances for all systems are given in the Supporting Information). Migliore pointed out that eq 4 is applicable for all situations,²³ including the

use of orthogonal or nonorthogonal diabatic states as well as a full range of donor–acceptor separations. At the B3LYP/6-31+G(d) level, both systems have a minimum, at 1.86 and 2.45 Å, respectively, where the effective electronic coupling is underestimated using eq 5 by a factor of 1.6 for Ne/Ne⁺ and of 4.5 for Zn/Zn⁺. At the minimum of the diatomic complex, electronic resonance delocalization is significant, and the meaning of electron or hole transfer in a complex at such a short distance is no longer well-defined. On the other hand, when the interatomic distance is stretched by 0.5 Å farther away from the minimum, the differences in the computed transfer integral are reduced to a factor of 1.0 and 1.8 for the two cases, respectively. Thus, for practical purposes, the results in Figure 3 indicate that for applications of electron and hole transfer reactions, there is no particular difference in using eq 4 or eq 5 to estimate the transfer integrals.

Figures 4 and 5 depict the computed transfer integrals for all systems as a function of the internuclear separation R using PBE and PBE0. With the PBE density functional, we have directly used the transition density of the reactant and product diabatic states in the standard functional, whereas eq 8 is used for computing the off-diagonal matrix element, corresponding to 100% Hartree–Fock exchange. In both methods, the energies for the diabatic states, that is, the diagonal matrix elements, are determined using the corresponding exchange and correlation functional for the ground state. The results shown in Figures 4 and 5 are virtually indistinguishable, suggesting that both eq 8 and the density functionals for the ground state can be used to estimate transfer integrals for charge transfer reactions.

Specifically, the cyclohexane dimer cation radical system was used in the study of Marros and Van Voorthuis to illustrate that CDFT-CI behaves sensibly when frontier orbitals in the donor and acceptor fragments are nondegenerate.²⁹ Indeed, for the most part, the attenuation of the computed coupling is exponentially dependent on the distance between the two rings. A decay exponent (-1.0 Å^{-1}) corresponding to $\beta = 4.6 \text{ Å}^{-1}$ ($R^2 = 0.97$) was obtained in the interval of 5–8 Å, which is identical to the MSDFT value (4.6 Å^{-1}). The absolute values of the computed effective coupling are also very similar (8.9 meV from MSDFT vs about 5 meV from CDFT at 5 Å); the slight difference is not surprising because the construction of the two diabatic states is not identical. For the diatomic cation Ne/Ne⁺, the computed electronic coupling from CDFT also decays exponentially with $\beta = 6.8 \text{ Å}^{-1}$ ($R^2 = 0.98$) in the range of 2.5–4 Å. On the other hand, the effective coupling from MSDFT decreases more slowly with a β value of 4.5 Å^{-1} ($R^2 = 0.999$), spanning from 2.6 to 6.0 Å.

For transition metal cases, the exponential decay factor β is about 3–5 Å⁻¹ from MSDFT calculations (Figures 4 and 5). In early studies, it was found that even in the case of zinc dimer, which showed an exponential attenuation of the computed electronic coupling, the result was, in fact, attributed to a fortuitous cancellation of errors. For the iron systems, Fe²⁺/Fe³⁺ and Fe²⁺(H₂O)₆/Fe³⁺(H₂O)₆, the computed effective electronic couplings neither attenuated exponentially with distance nor exhibited converged results with different fractions of the exact exchange mixed in PBE. In both cases, it was shown that there is significant charge transfer in the diabatic state. For comparison, the transfer integrals estimated using MSDFT both with PBE functional and with 100% Hartree–Fock exchange in calculation of the off-diagonal matrix element exhibited the expected behaviors. With the addition of six water molecules as ligands on each iron center, the computed effective

coupling decayed slightly slower at $\beta = 3.0 \text{ \AA}^{-1}$ ($R^2 = 0.996$). At $5.5 \text{ \AA}$ separation in $\text{Fe}^{2+}(\text{H}_2\text{O})_6/\text{Fe}^{3+}(\text{H}_2\text{O})_6$, the computed V_{12} was 7 meV, which decayed to about 1 meV at $7 \text{ \AA}$. Early studies by Newton provided electronic coupling values of 6 and 3 meV at the two distances (but different ligand configurations).⁵³ Similar values were obtained by Dupuis and co-workers, who reported β values of $2.5\text{--}3.1 \text{ \AA}^{-1}$ for different ligand orientations;⁵⁴ the agreement with the present results is good.

For comparison with a different diabaticization approach, we highlight results on the cationic cluster, $(\text{He}_4)^+$, involving four helium atoms in square geometry, in which the adjacent atoms are separated by $2 \text{ \AA}$. This elementary model was used by Subotnik et al. to test their diabaticization procedure based on Boys localization of adiabatic ground and excited states.²¹ In their approach, a CASSCF(7,8) calculation with the 6-31G(d) basis set was used to generate the adiabatic ground and excited states. Using three of the excited states, Subotnik et al. transformed these adiabatic configurations into four diabatic states of equal energy, each of which corresponds to the cation localized near one of the nuclear centers.²¹ In the present MSDFT approach, we first construct four diabatic states by block localization of the cationic charge on one of the He atoms with the remaining three grouped in a second block. These four diabatic states are analogous to those obtained from the adiabatic states in ref 21; however, the diabatic states in MSDFT are nonorthogonal. We then obtain the adiabatic ground and excited states in the second computational step through configuration interaction using the four diabatic states.

Table 1 lists the computed excitation energies, the resonance energy (the energy difference between the adiabatic ground state and the charge localized diabatic state), and the effective electronic coupling between two adjacently localized ions and between the diagonal pairs in the square-planar structure. We first evaluate the performance of MSDFT by comparison of observables—the excitation energies to the first two excited states. In particular, we obtained excitation energies of 1.17 eV for the degenerate S_1 and S_2 states and 2.53 eV for the S_3 state using MSDFT, which are in good accord with the corresponding CASPT2(7,8)/aug-cc-pVQZ values of 1.14 and 2.45 eV. Previously, Subotnik et al. reported values of 1.15 and 2.46 eV, respectively, from CASSCF(7,8)/6-31G(d). Thus, there is little effect due to basis and dynamic correlation in this system. Table S5 further shows that inclusion of diffuse functions slightly increases the excitation energy of the S_3 state by 0.04 eV relative to that from cc-pVQZ. This trend is also found in MSDFT when the diffuse functions are removed (Table 1). It is of interest to note here that the present MSDFT method provides an alternative procedure for the excited states without using time-dependent approaches.^{31,52} In this regard, TDDFT is not able to yield reasonable results for this system, with errors of about 100% or more in the computed excitation energies (2.07, 2.35, and 2.77 eV for the degenerate states and 3.10, 3.47, and 3.76 eV for the third excited state using M06-2X, Cam-B3LYP, and PBE, respectively, Table S5).

MSDFT yields a delocalization resonance energy of 1.14 eV, slightly smaller than that obtained in ref 21. Importantly, the computed electronic coupling from these two very different techniques is also in accord, though MSDFT produced a smaller coupling value (by 8 meV) in the diagonally localized states.²¹ When the same basis set (6-31G(d)) is used as in the work of Subotnik et al., the difference is 28 meV. There are two possible factors

contributing to this difference. First, the coupling energy from Boys diabatization states has contamination due to orthogonalization details, but nonorthogonal diabatic states are used in MSDFT. The second reason is that the four diabatic states from orthogonal transformation of multiple adiabatic excited states have not been reduced to a two-state representation associated with an ET reaction, whereas a two-state model was used to compute the transfer integral for ET in Table 1. Nevertheless, the overall agreement between the two approaches is quite reasonable. As a further comparison, we have examined the electronic coupling values for $(\text{He}_2)^+$ at 2 and $2\sqrt{2}$ Å separations, which are 0.619 and 0.081 eV, in excellent agreement with those (0.617 and 0.082 eV) obtained by Subotnik et al.²¹ In comparison with the effective electronic couplings at the two distances in $(\text{He}_4)^+$, both methods showed influence due to interactions with the environment (via the other two helium atoms through bond and through space).

Finally, we examine the performance of MSDFT on an all-trans polyene system to simulate a hole transfer between two gold atoms, one covalently connected to the polyene tip and the other noncovalently connected. Conjugated π -bridges in ET have been extensively studied experimentally and computationally.^{55–59} In this case, we have partitioned the system into three blocks, corresponding to $[\text{Au}][\text{S}-(\text{CH}=\text{CH})_n\text{H}][\text{Au}]$, in which the cation is localized on either of the Au atoms for the corresponding reactant and product states. The structures of $\text{AuS}(\text{CH}=\text{CH})_n\text{H}$, $n = 1–5$, are optimized using B3LYP/LanL2DZ, and the second gold atom is placed (on the right) along the terminal C=C bond at 2.5 Å from the carbon atom. The transition integrals depicted in Figure 6 are determined using PBE0/SBKJC, which shows a good linear dependence in the logarithm plot with the distance between the two gold atoms. However, compared with other intermolecular charge transfers through space, the transfer integral through the conjugated system decays more slowly with distance at a rate of $\beta = 0.22 \text{ Å}^{-1}$ ($R^2 = 0.987$). Importantly, this is in agreement with the experimental estimate of 0.2–0.3 Å^{−1} for all-trans polyene bridges.^{57,58} Strictly speaking, one notices a slight curvature in Figure 6 because of relatively large overlap in the conjugated bridge system, a feature also observed by Mo et al.⁵⁶ in the $(\text{CH}_2)(\text{CH}=\text{CH})_n(\text{CH}_2)$ model system. In the latter case, the p_z orbitals of the two terminal methylene groups are treated as the hole donor and acceptor site, and it was found that $\beta = 0.18 \text{ Å}^{-1}$ for hole transfer, in accord with the present MSDFT value and previous computational studies.^{55,58,59}

In summary, we presented MSDFT to estimate the effective transfer integral associated with electron and hole transfer reactions. In this approach, a molecular system is partitioned into fragmental blocks according to the Lewis structure as in valence bond theory for the reactant (initial) and product (final) charge-localized diabatic states. The effective electronic coupling, or transfer integral, between the initial and final states for an electron (hole) transfer process is determined using the transition density from the corresponding BLKS determinants. For a series of simple diatomic models as well as molecular systems, we found that the computed transfer integrals are consistent with results from early studies and in agreement with another diabatization method based on Boys localization in resonance energy and excitation energies of $(\text{He}_4)^+$. The present MSDFT method has about the same computational cost for each diagonal and off-diagonal matrix element as that of standard KS-DFT, making it applicable to large systems, but it builds the effective diabatic states

based on BLKS orbitals. The present density-constraining procedure is very different from that used in CDFT in that the density is constrained in orbital space in MSDFT, whereas it is partitioned within specific spatial regions in CDFT. As shown by Mavros and Van Voorhis²⁹ and others,⁶⁰ the latter can have significant charge transfer contamination between donor and acceptor groups. As a result, the computed effective electronic coupling using these spatially constrained diabatic states shows arbitrary dependence (increases or decreases nonexponentially as well as exponential attenuation) with donor–acceptor distance for different systems. Furthermore, the results can be highly dependent on the amount of Hartree–Fock exchange included in a density functional. On the other hand, there is no abnormal behavior in MSDFT. At short interfragment proximity within the van der Waals radius, the exponential dependence is no longer fully observed because of the coupled contributions of exchange and correlation interactions. In this case, the off-diagonal matrix elements from MSDFT are still valid, representing resonance delocalization interactions.^{31,52}

We note in closing that we begin by constructing the effective diabatic states for electron and hole transfer reactions. Then, we employ either configuration interaction involving the individual VDC or the procedure of MCSCF to optimize both orbital and configuration coefficients to yield the energies of the adiabatic ground and excited states. This is in contrast to most other approaches for constructing diabatic states, which typically start from a delocalized calculation of the adiabatic states.^{21,24} The latter procedure includes effects of orthogonalization tails, an issue recently investigated by Subotnik and co-workers, whereas in MSDFT,²² the diabatic states are generally nonorthogonal. For systems involving more than two noncollinear charge-localized states, we have described an approach to reduce multistate valence bond configurations into two diabatic states.²⁵ The latter can be particularly useful in chemical reactions as well as processes involving coupled electron and proton transfer.³¹

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Schematic illustration of the potential energy surfaces for the initial reactant (H_{11} , blue) and final product (H_{22} , green) diabatic states and the adiabatic ground (ϵ_g) and excited (ϵ_e) states (both in red) associated with an ET reaction (or hole transfer in the reverse direction). The transfer integral, or effective electronic coupling, V_{12} , is defined as half of the splitting between the ground and excited adiabatic states. For the reactant diabatic state, the electron donor ($\text{CH}_2=\text{CH}_2$) and acceptor ($\text{CH}_2=\text{CH}_2^+$) fragments are partitioned into two blocks, in yellow and purple, respectively, and BLKS orbitals are obtained as linear combinations of the basis functions within each block only. For the product diabatic states, the identities for the donor and acceptor are reversed, and they are shown in the same coloring scheme. The determinant functions for the diabatic states, Ψ_1 and Ψ_2 , are constructed using the BLKS orbitals, from which constrained electron densities are determined. At a fixed interfragment distance, R , the reaction coordinate z is the difference between the donor and acceptor C–C bond lengths, which corresponds to the inner-sphere reorganization coordinate. The example shown has a computed effective electronic coupling of about 310 cm^{-1} at $R = 5\text{ Å}$ using PBE0/cc-pVTZ.

Figure 2. Transfer integral in eV as a function of Fe–Fe distance for a hexaaqua-iron(II)/hexaaqua-iron(III) self-exchange ET reaction computed using 0 (black), 25 (red), and 100% (blue) Hartree–Fock exchange mixed with the PBE functional. In the hybrid density functional theory calculations, PBE0 is used to determine the diabatic state energies.

Figure 3.

Computed transfer integral in eV as a function of internuclear distance for the Ne/Ne⁺ (black) and Zn/Zn⁺ (red) self-exchange ET reactions. The effective electronic coupling (i.e., transfer integral) is defined as half of the energy splitting between the adiabatic ground and excited states corresponding to eq 4 in the text (solid), whereas the approximate value is obtained as the energy difference between the adiabatic ground state and diabatic state at the crossing point (eq 5, dashed curves). Calculations are performed using PBE0/6-31+G(d) with 100% Hartree–Fock exchange in the off-diagonal matrix element, whereas the TZV basis is used for metallic atoms.

Figure 4.

Computed transfer integral (eV) using MSDFT as a function of interfragment distance for self-exchange ET reactions. The effective electronic coupling (i.e., transfer integral) is defined as half of the energy splitting between the adiabatic ground and excited states corresponding to eq 4 in the text. PBE/6-31+G(d) was used except for metal atoms, for which the TZV basis was used.

Figure 5.

Computed transfer integral (eV) using MSDFT as a function of interfragment distance for self-exchange ET reactions. The effective electronic coupling (i.e., transfer integral) is defined as half of the energy splitting between the adiabatic ground and excited states corresponding to eq 4 in the text. PBE0/6-31G+(d) was used to determine the diagonal matrix elements except metal atoms, for which the TZV basis was adopted. For the off-diagonal matrix elements, 100% Hartree–Fock exchange was included.

Figure 6.
Exponential attenuation of the computed transfer integral (eV) with donor-acceptor distance R for the AuS-(CH=CH) $_n$ HAu system using MSDFT with PBE0/SBKJC.

Table 1

Computed Excitation Energies, Resonance Energy (RE) between the Adiabatic Ground State and the Charge Localized Diabatic Configuration, and Effective Electronic Coupling for the Adjacent Localized Cationic States (1–2) and for the Diagonally Localized Pairs (1–3)^a

method	excited states			V_{12}		
	S_1/S_2	S_3	RE	1–2	1–3	
Boys-diabat, CASSCF(7,8)/6-31G(d)	1.15	2.46	1.19	0.615	0.040	
MSDFT/6-31G(d)	1.16	2.47	1.14	0.614	0.012	
MSDFT/6-31+G(d)	1.17	2.53	1.14	0.624	0.032	

^a All energies are given in eV.