Decomposition of the Electronic Energy in Terms of Density, Density Coherence, and the Connected Part of the Two-Body Reduced Density Matrix

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ABSTRACT: We analyzed static and dynamic electron correlation by decomposing the total electronic energy of calculations by restricted Hartree-Fock theory, complete active space selfconsistent field (CASSCF) theory, and multireference configuration interaction (MRCI). We used three different schemes to break down the relative energy contributions to the potential energy curves for the dissociation of H₂, F₂, and N₂. The first decomposition scheme involves the classical and nonclassical components of the energy. The second and third recognize the part of the energy that is not expressible in terms of the one-body reduced density matrix (1-RDM); this is called the connected energy. The unconnected component is further decomposed into a part calculable from the density and the part calculable from the density coherence. The first decomposition scheme shows that the sum of the one-electron energy and the classical twoelectron energy contains a negligible portion of the static correlation. This quantity has a relatively small variance between the three levels, especially for CASSCF and MRCI. This provides an explanation of why multiconfiguration pair-density functional theory and multiconfiguration density-coherence functional theory are able to improve the CASSCF energy. The latter two decompositions show that the connected energy contains a significant portion of static correlation. The energy representable by either the density or the density coherence is significantly different at the three levels. Mixing the density and density coherence between different methods may lead to systematic error in the bond dissociation energy and the equilibrium bond distance, indicating that the density energy component and the density coherence energy component both include a significant amount of both static and dynamic correlation. These wave function decompositions can be useful for developing new functionals for density functional theory, density-coherence functional theory, density matrix functional theory, and pair-density functional theory and for guiding expectations for these theories.

1. Introduction

The electronic energy of a molecule is the most common target of quantum chemical calculations. In order to understand trends in electronic energies and to devise more accurate computational schemes, one often considers partitions of the energy in various ways—sometimes called energy decomposition schemes. For example, one may decompose the energy into the Hartree–Fock (HF) energy and the remainder, which is usually defined as the correlation energy¹

(although a more fundamental definition of correlation energy² that does not depend on the HF approximation may be preferable). One may further partition the HF energy to separate a charge transfer component,³ or one may divide the correlation energy into static and dynamic correlation,⁴ where static correlation arises from nearly degenerate configurations. We agree with the generalization that "there are few systems for which one can distinguish unambiguously between these two types of correlations."⁵ Nevertheless, it is useful to further divide static correlation into subtypes.⁶

One may alternatively divide the energy into the internal energy of configuration interaction within a valence active space and the external energy involving configurations outside this space.⁷ Some energy decompositions are straightforward and others involve less well-defined divisions, such as separating dispersion-like components⁸ or a distortion energy component.⁹ We can learn something from all of these partitions.

The present article presents new kinds of energy decomposition with the hope that they can help inform future work on density functional theories,¹⁰ density matrix theories,¹¹ density matrix functional theories,^{12,13} and density-coherence theory.¹⁴ Improving our understanding of the extent to which static and dynamic correlation can be described in terms of the one-body and two-body reduced density matrices and the connected and unconnected parts of the latter is the primary motivation for the present study.

It is well known that the total electronic energy can be calculated using¹⁵

$$E^{\text{tot}} = E^{\text{nuc}} + \sum_{PQ} h_{PQ} D_{PQ} + \frac{1}{2} \sum_{PQRS} g_{PQRS} d_{PQRS}$$
(1)

where subscripts *P*, *Q*, *R*, and *S* denote atomic spin-orbitals, D_{PQ} is the one-body reduced density matrix (1-RDM), d_{PQRS} is the two-body reduced density matrix (2-RDM), h_{PQ} and g_{PQRS} are one- and two-electron integrals, and E^{nuc} is the nuclear repulsion energy (which, as usual, is included in the "electronic energy"). Here we use the same subscript convention as ref 16 for the 2-RDM and two-electron integrals. According to eq 1, the total energy depends on both the 1-RDM and the 2-RDM. While this is true, the HF total energy can be described by the 1-RDM and does not require the 2-RDM. Furthermore, a portion of the 2-RDM can be calculated from the 1-RDM; 2,17,18,19,20 in particular¹⁷

$$d_{PQRS} = D_{PQ}D_{RS} - D_{PS}D_{QR} + \Delta_{PQRS}$$
⁽²⁾

where Δ_{PQRS} is the connected part of the 2-RDM (also called the residual part, the irreducible part, the non-factorizable part, or the cumulant). It will be convenient to have shorthand names for the portion of the electronic energy that can be calculated knowing only the 1-RDM and the portion requiring the 2-RDM; we therefore call these portions the unconnected energy and the connected energy, respectively. (The connected and unconnected energy have previously appeared in the literature as a redefinition of the correlation energy,²¹ but that is not the widely used definition of correlation energy.) By combining eqs 1 and 2, we can derive the unconnected energy as

$$E^{\text{unc}} = E^{\text{nuc}} + \sum_{PQ} h_{PQ} D_{PQ} + \frac{1}{2} \sum_{PQRS} g_{PQRS} D_{PQ} D_{RS} - \frac{1}{2} \sum_{PQRS} g_{PQRS} D_{PS} D_{QR}$$
(3)

For singlets, one can also write the unconnected energy in terms of spatial orbitals (labeled p, q, r, and s) and the spinless density matrix:

$$E^{\text{unc}} = E^{\text{nuc}} + \sum_{pq} h_{pq} D_{pq} + \frac{1}{2} \sum_{pqrs} g_{pqrs} D_{pq} D_{rs} - \frac{1}{4} \sum_{pqrs} g_{pqrs} D_{ps} D_{qr}$$
(4)

The connected energy is then given by

$$E^{\rm con} = E^{\rm tot} - E^{\rm unc} \tag{5}$$

Given these expressions for E^{unc} and E^{con} , the question arises of their relative magnitudes for various situations and their relationship to static and dynamic correlation. In this article, we will break down the total energy into multiple components, then recombine these components using components from different methods in order to trace the source of the static and dynamic correlation energies. For this analysis, we found it informative to further divide E^{unc} and then recombine the energy components based on three schemes. These schemes are explained in section 2. We introduced a set of notations to analyze the combinations more easily in section 3. Section 4 includes computational details. In section 5, we analyzed the recombined potential energy curves for dissociation of prototype diatomic molecules, in particular H₂, F₂, and N₂, and we discussed the sources of the components of the correlation energies. Section 6 contains concluding remarks.

2. Energy Decomposition Schemes

In this article, we only consider singlet spin states. We consider three decompositions. In two of the decompositions we divide the total electronic energy into two components; we label these schemes as the classical–nonclassical (CN) decomposition and unconnected–connected (UC) decomposition. The third decomposition has three components; we label this scheme as the density–coherence–connected (DCC) decomposition.

Classical–Nonclassical (CN) Decomposition. The CN decomposition divides the total electronic energy into classical energy and nonclassical energy. The classical energy is defined as:

$$E^{\rm cl} = E^{\rm nuc} + \sum_{PQ} h_{PQ} D_{PQ} + \frac{1}{2} \sum_{pqrs} g_{pqrs} D_{pq} D_{rs}$$
(6)

where the last term is the classical approximation to the electron-electron interaction. The nonclassical energy is defined as:

$$E^{\text{noncl}} = -\frac{1}{4} \sum_{pqrs} g_{pqrs} D_{ps} D_{qr} + E^{\text{con}}$$
(7)

where the first term on the right-hand side is the nonclassical part of the unconnected electronelectron interaction.

The separation of the energy into classical and nonclassical components is important because it is the separation used in Kohn–Sham density functional theory (KS-DFT), in multiconfiguration pair-density functional theory (MC-PDFT), and in multiconfiguration density-coherence theory (MC-DCFT). These theories all calculate the classical portion of the energy from a reference wave function and the nonclassical portion from a functional, which is an exchange-correlation functional in KS-DFT, an on-top functional in MC-PDFT, and a density-coherence functional in MC-DCFT. Therefore, these functionals may all be considered to be functionals for the nonclassical energy, and it is interesting to separate the effects of changing the level of wave function calculations into its separated effects on the classical energy and the nonclassical energy. It is worth noting that MC-PDFT and MC-DCFT are not iterative methods; the classical portion of the MC-PDFT and MC-DCFT energy is identical to the classical part of the energy evaluated directly from the reference wave function. The CN decomposition on the multiconfigurational reference wave function reveals amount of classical energy that is used in MC-PDFT or MC-DCFT.

Unconnected–Connected (UC) Decomposition. The UC decomposition divides the total electronic energy into two parts: the unconnected energy and the connected energy. These components are defined in eqs 4 and 5.

Density–Coherence–Connected (DCC) Decomposition. For the DCC decomposition, we divide the matrix elements in the unconnected energy into two sets: diagonal elements and off-diagonal elements. The diagonal elements are densities (also called populations), and the off-diagonal elements are density coherences.^{22,23} The first component of the DCC decomposition is the unconnected energy calculable knowing only the densities; we label this with a superscript "d" to denotes density:

$$E^{d} = E^{nuc} + \sum_{p} h_{pp} D_{pp} + \frac{1}{2} \sum_{pq} g_{ppqq} D_{pp} D_{qq} - \frac{1}{4} \sum_{pq} g_{pqqp} D_{pp} D_{qq}$$
(8)

The second component is the part of the unconnected energy calculable from the density coherences; we use superscript "dc" to denote density coherence:

$$E^{dc} = E^{unc} - E^d \tag{9}$$

The third component is the connected energy E^{con} .

Many discussions of exchange and correlation are written in terms of the exchange hole,²⁴ which may be calculated from the density and the density coherence.²⁵ The density coherence is a more fundamental property than the exchange hole, and studying the density coherence directly may provide a more direct connection to the many-electron wave function. The density coherence is also used as an ingredient in some nonclassical energy functionals, in particular hybrid exchange functionals,¹⁰ rung-3.5 functionals,²⁶ and density coherence functionals.¹⁴ Therefore it is interesting to separate out the contribution of the density coherence to the wave function energy.

3. Energy Decomposition Analysis

The primary goal of this work is to gain a better understanding of what level of theory is required for treating each component of the energy in the new decomposition schemes. To proceed toward this goal, we calculated the various components using three different wave function theories. In particular, we considered three kinds of calculations:

- restricted Hartree–Fock (RHF)
- complete active space self-consistent field (CASSCF)
- multireference configuration interaction (MRCI)

For example, in one implementation of the UC decomposition, we take unconnected energy from an RHF calculation, and the connected energy from an MRCI calculation. For another example,

in one implementation of the DCC decomposition, we take E^{d} from an RHF calculation, E^{dc} from a CASSCF calculation, and E^{con} from an MRCI calculation.

To label these kinds of combinations concisely, we use the letter H to represent RHF calculations, C to represent CASSCF calculations, and M to represent MRCI calculations. A combination is represented by two or three letters; the *n*th letter represents the *n*th component of the energy decomposition. For example, the UC decomposition example mentioned above is denoted as HM, and the DCC example mentioned above is denoted as HCM. A pure MRCI calculation can therefore be denoted as MM or MMM.

4. Computational Details

We performed RHF, CASSCF, and MRCI calculations in a locally modified version of *OpenMolcas*,²⁷ in which we modified the source code to export the nuclear repulsion energy, the one- and two-electron integrals, and the one-body density matrix in the atomic orbital basis. These quantities were loaded into a *Python* script to calculate the different energy components. The cc-pVTZ basis set²⁸ was used for all calculations.

The RHF method approximates the wave function by a single Slater determinant.

For the CASSCF calculations on H_2 and F_2 , we used an active space of 2 electrons in 2 orbitals. For N_2 , we used an active space of 6 electrons in 6 orbitals.

The MRCI calculations include all single and double excitations from the CASSCF reference function. We did not use the frozen-core approximation or internal contraction for MRCI calculations.

To construct the potential energy curves, we performed a scan by varying the bond distances from 0.50 Å to 5.00 Å with a 0.05 Å increment.

5. Results and Discussion

In this paper, we present the full results for H_2 , N_2 , and F_2 for the UC and CN decompositions and selected results for the DCC decomposition. The remaining results for the DCC scheme can be found in the Supporting Information (SI). Figures and tables with the prefix S are in the SI. We present the absolute energies of each term of the decomposition schemes in the SI.

Note that MRCI (denoted MM or MMM as explained above) is the most accurate method in this study because it is either equivalent (for H₂) or closest (for F₂ and N₂) to full configuration interaction (FCI). The CASSCF wave function includes internal correlation,⁷ which consists of static correlation plus a portion of dynamic correlation. HF has only the correlation due to antisymmetrization. If we are comparing MC-PDFT with its reference wave function (e.g., CASSCF), then the improvement is mostly because the on-top pair density functional recovers most of the dynamic correlation. If we are comparing MC-PDFT with single-reference methods (e.g., RHF), then both the classical and nonclassical energy could be the source of improvement because MC-PDFT can recover both the static and dynamic correlation.

In the discussions below, we will use the MRCI dissociation curves as the benchmark. All discussions of errors refer to the error relative to the MRCI dissociation curves.

5.1. RHF, CASSCF, and MRCI

Before we analyze various energy combination components in the decompositions, we first look at the pure RHF, CASSCF, and MRCI potential energy curves of H_2 . Note that these curves are the HH, CC, and MM curves in the notation explained above. The potential energy curves are given in Figure 1, where we present them in the left panel as absolute energies and in the right panel as energies relative to the energy at equilibrium.

Figure 1(a) shows that the absolute electronic energy is lowered with an increasing number of configurations. Although the H₂ ground state is considered to have no static correlation energy at the equilibrium geometry (because there is no near-degeneracy), the energy is lowered significantly for CASSCF; this shows that although CASSCF is intended to recover static correlation, it inevitably recovers a fraction of dynamic correlation. In other words, the internal correlation energy includes a significant amount of dynamic correlation energy. At longer bond distances, CASSCF and MRCI both dissociate to the correct theoretical dissociation limit (-27.2eV), while RHF has a significant error. This shows that both CASSCF and MRCI completely recover the correlation energy of H₂ at the dissociation limit. Since H₂ has no dynamic correlation at the dissociation limit, this shows that the error in the RHF potential curve caused by neglect of static correlation is much larger than that due to neglect of dynamic correlation. When we look at the bond dissociation energies (Figure 1(b)), we can see that adding internal correlation error to RHF lowers the bond dissociation energy, but adding external correlation energy to CASSCF increases the bond dissociation energy.



Figure 1. Dissociation curves of MRCI (MMM), CASSCF (CCC), and RHF (HHH) for H₂. (a) Absolute electronic energies. (b) Using the energy at the equilibrium bond distance as the zero of energy.

5.2. The CN Decomposition

Here we analyze the energy components in the classical–nonclassical decomposition. Because the total energies generated by recombining different calculations are not variational, we study the potential energy curves using the lowest energy of the potential energy curve as the zero of energy, which is the choice made in Figure 1(b). Therefore, all discussion of energies in the rest of the discussion refers to relative energies.

The dissociation curves of the CN decomposition of the three molecules are shown in Figures 2–4. Nearly all dissociation curves predict an accurate equilibrium bond distance and give accurate energies near the equilibrium bond distance. In general, the dissociation curves have increasing accuracy as we move from the top left panel to the bottom right panel of each figure. From the first columns of each figure, one can find that HH, CH, and MH have a much larger error at the dissociation limit than the other combinations; the dissociation energies are significantly overestimated. The HC and HM dissociation curves have smaller errors than the three combinations mentioned above, but both curves may have an unphysical shape. The remaining four combinations, which are the ones that do not contain any HF energy component, have significantly lower overall error than the five combinations discussed first. This is consistent with CASSCF recovering the static correlation error that is present in RHF. Since the large overestimation of the dissociation energy of RHF mainly results from the large static correlation error, one concludes that the classical energy contains at most a small portion of the static correlation.

When MC-PDFT and MC-DCFT use a CASSCF reference, the classical energy from CASSCF is the first component of their total energy, where the nonclassical energy is approximated by an on-top density functional or a density coherence functional. This treatment is similar to the CM combination. In Figures 2–4, one sees that the CM dissociation curves are in good agreement with the CC dissociation curves for all three molecules. We conclude that the high accuracy usually achieved with MC-PDFT is understandable in terms of the high accuracy of the CM combination. Therefore, using a functional to accurately approximate the nonclassical energy contribution is a reasonable approach to obtaining accurate post-CASSCF energy.



Figure 2. Dissociation curves of H_2 using the CN decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.



Figure 3. Dissociation curves of F_2 using the CN decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.



Figure 4. Dissociation curves of N_2 using the CN decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.

5.3. The UC Decomposition

The dissociation curves of the UC decomposition of the three molecules are shown in Figures 5–7. Most dissociation curves in UC decomposition, although having qualitatively accurate shapes, are quantitatively less accurate than the CN decomposition curves near the equilibrium bond distance. The accuracy of the dissociation curves has a similar trend to what we saw for the CN decomposition; the dissociation curves at the bottom right have higher accuracy than the ones on the top left, and the curves in the first column and the first row have significantly lower accuracy. This shows that connected energies make large contributions to the shapes of the potential curves. By comparing the combinations with and without HF energy component as we did in CN decomposition, we conclude that most of the static correlation error within the nonclassical component comes from the connected part. Since the connected part is zero for RHF (at all distances for all molecules), a significant portion of the MRCI energy cannot

be represented by the 1-RDM, indicating that the static correlation is mostly recovered in the connected 2-RDM of MRCI rather than the 1-RDM.

Figures 5 and 7 show that the potential energy curves near the equilibrium bond distance are very accurate for H₂ and N₂. (The HC decomposition of N₂ might appear from these figures to be an exception, but if one plots the potential curve using the equilibrium geometry as the zero of energy, one sees that the HC and MM curves have very good agreement at this region.) However, Fig. 6 shows that there is a noticeable error in the potential energy curves near the equilibrium bond distance for F₂. This may be attributed to the weak covalent binding of the F₂ molecule, which has been discussed by Schipper et al. in terms of exchange repulsion of the doubly occupied orbitals on the two centers;²⁹ consequently, RHF has a relatively large dynamic correlation error near the equilibrium bond distance for F₂. The curves presented here indicate that a major portion of the dynamic correlation of F₂ is in the unconnected energy term and that it is necessary to go to the MRCI level to get this right.



Figure 5. Dissociation curves of H_2 using the UC decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.



Figure 6. Dissociation curves of F_2 using the UC decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.



Figure 7. Dissociation curves of N_2 using the UC decomposition. The unlabeled curves in light blue are the MRCI (MM) curves. Note that plots in the first column have different scales for the vertical axis.

5.4. The DCC Decomposition

The dissociation curves of the DCC decomposition are presented in Figures 8–13 and S1–S3. Although there are 27 combinations of RHF, CASSCF, and MRCI in the DCC decomposition, we only present the 21 combinations involving no more than two methods. In other words, we omit the 6 combinations where all three methods are involved. Because the trends related to the connected energy have already been discussed in terms of the UC decomposition, we will mainly discuss the trends related to E^{d} and E^{dc} in this section. For each molecule, we present the dissociation curves in three figures, where each figure contains two panels. The figures are grouped by methods, and the panels are grouped by the source of E^{con} . This results in each panel containing four curves, of which two curves are also present in the UC decomposition, while the other two curves are not. We will call the former curves the UC curves,

and the latter will be called the non-UC curves. One of the two UC curves in each panel will be one of HHH, CCC, or MMM. We call the UC curve that is not one of HHH, CCC, or MMM the nontrivial UC curve.

We first discuss the shapes of the dissociation curves. In nearly all the DCC dissociation curves that we present, the nontrivial UC curve lies between the two non-UC curves. For example, in Figure 8(a), MMH (the nontrivial UC curve) is located between HMH and MHH (the two non-UC curves). One notable exception to this trend is the DCC decomposition of H₂ for CASSCF and MRCI as shown in Figure 10, where all curves are very close to each other. This shows that there is a systematic overestimation or underestimation of E^d and E^{dc} between two different methods, except for CASSCF and MRCI for H₂. Such systematic error is very large between RHF and CASSCF, as well as between RHF and MRCI, while a significantly smaller yet not negligible difference is present between CASSCF and MRCI. This implies that static correlation error might be a major contribution to the error of both E^d and E^{dc} . This also shows that the density coherence is significantly different between RHF and CASSCF, and this is consistent with our previous study of the density coherence in the coordinate representation.³⁰ We conclude that higher-level calculations do not improve the results only by improving the connected energy; they also must improve the unconnected energy.

The magnitude of the systematic overestimation or underestimation of E^{d} and E^{dc} shows a maximum at a bond distance slightly larger than the equilibrium bond distance. This often leads to an unphysical local maximum, local minimum, or point of inflection near the internuclear distance of 2 Å for the non-UC curves. Such an unphysical shape suggests that the connected energy contains a portion of a correction of the dynamic correlation that must be treated consistently to eliminate the systematic error. Moreover, for RHF, the error caused by E^{dc} is larger than the one caused by E^{d} . For example, in Figures 8(a), the energy difference between CHH and CCH at around 2 Å is much larger than the difference between HCH and CCH. This shows that the density coherence has a larger impact on the total energy than the density when static correlation is involved.

We then discuss the equilibrium bond distance of the DCC decomposition. As we discussed with regard to the UC decomposition, the UC curves for H₂ and N₂ predict relatively accurate equilibrium bond distances. However, in the case where RHF energies are involved, the accurate equilibrium bond distances for H₂ and N₂ lie between the one predicted by the two non-UC curves in each panel. In other words, one of the non-UC curves underestimates the equilibrium bond distance while the other non-UC curve overestimates the equilibrium bond distance. This shows that the systematic error in E^d and E^{dc} may affect the equilibrium bond distance. However, the equilibrium bond distances of F₂ do not show such a consistent trend. This again shows that E^d and E^{dc} needs to be calculated consistently with each other.

We conclude the discussion of the trends in the DCC and UC decompositions by noting that the connected energy mainly accounts for the static correlation; mixing connected energies from different methods often results in a dissociation curve that has a physical shape near the equilibrium bond distance. The E^{d} and E^{dc} component contain both static correlation and dynamic correlation; mixing E^{d} and E^{dc} from different methods not only results in error near the equilibrium bond distance, but also results in large error in the dissociation energy.



Figure 8. Dissociation curves of H₂ using the DCC decomposition for RHF and MRCI. (a) combinations with E^{con} from RHF. (b) combinations with E^{con} from MRCI.



Figure 9. Dissociation curves of H_2 using the DCC decomposition for RHF and CASSCF. (a) combinations with E^{con} from RHF. (b) combinations with E^{con} from CASSCF.



Figure 10. Dissociation curves of H₂ using the DCC decomposition for CASSCF and MRCI. (a) combinations with E^{con} from CASSCF. (b) combinations with E^{con} from MRCI.



Figure 11. Dissociation curves of F_2 using the DCC decomposition for RHF and MRCI. (a) combinations with E^{con} from RHF. (b) combinations with E^{con} from MRCI.



Figure 12. Dissociation curves of F_2 using the DCC decomposition for RHF and CASSCF. (a) combinations with E^{con} from RHF. (b) combinations with E^{con} from CASSCF.



Figure 13. Dissociation curves of F_2 using the DCC decomposition for CASSCF and MRCI. (a) combinations with E^{con} from CASSCF. (b) combinations with E^{con} from MRCI.

6. Concluding Remarks

Davidson stated, "The first-order correction to the Hartree-Fock wave function makes firstorder changes in the electron-pair distribution function but only second-order changes in the electron density and the energy. Hence the pair distribution function is the natural place to look when developing a qualitative interpretation of electron correlation effects."³¹ In the present work we have looked there. In particular, we decomposed the potential energy curves of H_2 , F_2 , and N₂ into components defined by three new energy decomposition schemes. Our discussion is entirely in terms of the relative energies of points along the potential energy curve. The decomposition schemes are named the classical-nonclassical (CN) decomposition, the unconnected–connected (UC) decomposition, and the density–coherence–connected (DCC) decomposition. The schemes studied here have the advantage that they are less ambiguous than the division into static and dynamic correlation^{4,5,6} because they are well defined in terms of reduced density matrices for any wave function. By combining the components evaluated with different levels of configuration interaction, we obtained a variety of potential energy curves. The levels chosen were RHF, CASSCF, and MRCI. The resulting composite potential energy curves allow us to understand the expression of static and dynamic correlation energy in terms of well-defined components of the energy.

From the three decomposition schemes, we draw several practical conclusions:

- (i) Negligible static correlation is included in the sum of the effective one-electron energy and the classical two-electron energy.
- (ii) The high accuracy usually achieved in previous work with multiconfiguration pair-density functional theory is understandable in terms of the high accuracy achievable by combining a CASSCF calculation of the classical energy and an MRCI calculation of the nonclassical energy.
- (iii) Connected components of the energies make large contributions to the shapes of the potential curves.
- (iv) Most of the static correlation error within the nonclassical energy component comes from the connected part. Since the connected part is zero for RHF (at all distances for all molecules), a significant portion of the MRCI energy cannot be represented by the 1-RDM, indicating that the static correlation is mostly recovered in the connected two-body reduced density matrix of MRCI rather than the 1-RDM.
- (v) A major portion of the dynamic correlation of F_2 is in the connected energy term, and it is necessary to go to the MRCI level to get this right.
- (vi) Higher-level calculations do not improve the results only by improving the connected energy; they also must improve the unconnected energy.
- (vii) Mixing connected energies from different methods results in a dissociation curve that has a physical shape near the equilibrium bond distance.
- (viii) The energy components attributable to the density and the density coherence contain both static correlation and dynamic correlation; mixing the density component from one correlated level of theory with the density coherence component from another not only results in error near the equilibrium bond distance, but also results in large error in the dissociation energy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/

 $\label{eq:post} Dissociation \ curves \ of \ the \ DCC \ decomposition \ for \ N_2, \ absolute \ energies, \ and \ sample \ input \ files. \ (PDF)$

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was supported in part by the National Science Foundation under grant no.

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