

# Size extensive modification of local multireference configuration interaction

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We recently developed a reduced scaling multireference configuration interaction (MRCI) method based on local correlation in the internal (occupied) and external (virtual) orbital spaces. This technique can be used, e.g., to predict bond dissociation energies in large molecules with reasonable accuracy. However, the inherent lack of size extensivity of truncated CI is a disadvantage that in principle worsens as the system size grows. Here we implement an *a priori* size-extensive modification of local MRCI known as the averaged coupled pair functional (ACPF) method. We demonstrate that local MR-ACPF recovers more correlation energy than local MRCI, in keeping with trends observed previously for nonlocal ACPF. We test the size extensivity of local ACPF on noninteracting He atoms and a series of hydrocarbons. Basis set and core correlation effects are explored, as well as bond breaking in a variety of organic molecules. The local MR-ACPF method proves to be a useful tool for investigating large molecules and represents a further improvement in predictive accuracy over local MRCI. © 2004 American Institute of Physics.  
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## I. INTRODUCTION

A primary objective of *ab initio* quantum chemistry is to provide the means to accurately describe the correlated motion of electrons in atoms and molecules. Unlike density functional theory, where the description of electron correlation resides in an unknown functional that has been approximated with varying degrees of success, *ab initio* methods such as configuration interaction (CI), coupled cluster (CC), and Møller–Plesset (MP) perturbation theory provide a hierarchical strategy to include and converge electron correlation up to the exact limit (full CI). However, these methods scale very poorly with system size, making it impossible to study large molecules while simultaneously obtaining accurate values of correlation energies. The MP<sub>x</sub> methods (where *x* is the order of perturbation) are easier to program than the others. Moreover, the MP<sub>x</sub> methods are rigorously size extensive. However, MP2 scales as  $nN^4$ , MP3 and MP4 (confined to single, double, and quadruple substitutions) both contain terms scaling as  $n^2N^4$  and  $n^3N^3$ , while including triple substitutions in MP4 yields  $n^3N^4$  scaling, where *n* is number of orbitals occupied in the reference state and *N* is the number

of basis functions.<sup>1</sup> Single and double excitation CI (SDCI) and the commonly used coupled cluster singles and doubles with perturbative triples [CCSD(T)] method scale similarly poorly, as  $n^2N^4$  and  $n^3N^4$ , respectively,<sup>2</sup> and require iterative solutions, rendering them even more expensive. We see then that the cost of all of these methods increases steeply with the size of the system. Therefore, in order to study large molecules, it is necessary to devise numerical schemes to reduce the scaling of these algorithms.

Most common approaches to reduce the scaling either involve approximations to the two-electron integrals (the pseudospectral<sup>3–12</sup> and the auxiliary basis set<sup>13,14</sup> strategies are particularly noteworthy here) or localization of orbitals so that classes of interactions may be intelligently neglected.<sup>15–22</sup> Saebø and Pulay<sup>1,23,24</sup> pioneered the concept of local correlation for MP<sub>x</sub> ( $x=2–4$ ), where they demonstrated local MP<sub>x</sub> methods could recover more than 99% of the nonlocal MP<sub>x</sub> correlation energy. A number of reduced scaling<sup>7,8,11,12,19–24</sup> MP<sub>x</sub> methods have been developed. A noteworthy work is that of Werner and co-workers, who developed a linear scaling MP2 method based on local correlation.<sup>25–27</sup> Another linear scaling MP2 method was developed by Ayala and Scuseria<sup>28</sup> based on the use of Laplace transforms.<sup>29</sup> Unfortunately, the MP<sub>x</sub> methods have their own limitations, recovering less correlation energy for the same level of excitation compared to CC and CI, as well as having series convergence problems. Moreover, they perform

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poorly for open shell molecules and do not describe covalent bond breaking well due to their single-reference ansatz. Multireference MPx<sup>30,31</sup> algorithms do exist, but often they are not suitable for mapping out potential energy surfaces (e.g., intruder states can lead to singularities at certain points on the surface).

CC methods are employed ubiquitously, offering the advantage of being size extensive. However, as mentioned earlier, the expense of CC methods is significantly greater than the MPx methods at the same excitation rank. Similar to MP2, considerable effort has been devoted to developing local correlation techniques based on CC. The work of Hampel and Werner on local CCSD<sup>32</sup> demonstrated recovery of 98%–99% of the correlation energy, compared to the corresponding nonlocal calculation. Recently Schütz and Werner developed a local CCSD method<sup>33</sup> in which they achieved *linear* scaling by implementing an integral-direct algorithm.<sup>34</sup> Large molecules with up to 1000 basis functions could be treated, while still obtaining results of the same quality as from the nonlocal calculations. Next, Schütz and Werner developed the perturbative triples correction to local CCSD<sup>35</sup> and Schütz went on to construct a *linear* scaling version of local CCSD(T),<sup>36</sup> again based on integral-direct algorithms.<sup>34</sup> This is an impressive achievement. However, the inherent limitations of CC methods (difficulties in treating open-shell molecules or systems requiring multireference wave functions, e.g., transition metals and chemical bond breaking) led us to consider alternatives to CC for development of reduced scaling local correlation methods. We note there exists a significant research effort on multireference CC methods.<sup>37–41</sup> However, multireference CC methods are still challenged when it comes to mapping out potential energy surfaces (PESs).<sup>40–42</sup>

In comparison to CC, CI is conceptually simple and naturally incorporates multireference wave functions. It therefore may be considered the method of choice when near degeneracies occur (e.g., for transition metals, bond breaking events, and resonance phenomena). Local SDCI was first developed by Saebø and Pulay<sup>43</sup> for closed shell molecules. Martinez *et al.* developed pseudospectral approximations of full CI, doubles CI, and multireference singles and doubles CI (MRSDCI)<sup>9,10,12</sup> to reduce the scaling. Reynolds *et al.*<sup>17,18</sup> later incorporated local correlation approximations into pseudospectral SDCI. However, with the exception of the Martinez *et al.* work on pseudospectral MRSDCI, none of the reduced scaling CI methods were developed for multireference wavefunctions.

Recently, Walter *et al.* developed several local MRSDCI methods. Walter and Carter's<sup>15</sup> local correlation in the internal space involves neglect of all excitations from pairs of localized internal orbitals that are far away from each other. This was called the weak pairs (WP) approximation, similar to Saebø and Pulay's classification of strong, weak, and distant pairs in their local MPx method.<sup>23</sup> The pairs are distinguished based on the distance between centroids of orbitals. In Saebø and Pulay's work, strong pairs were included at the full MPx level, weak pairs approximated at a subset of the full level of correlation (e.g., at the MP2 level), while distant pairs were excluded. The work of Walter *et al.* is concerned

with MRCI, where unfortunately no rigorous yet inexpensive subset of MRCI exists with which to approximate the weak pairs. Hence in the work of Walter *et al.*, weak and distant pairs were both neglected. This type of WP approximation was shown to reduce the cost of a typical calculation by 40%, while still recovering 98%–99% of the correlation energy compared to the nonlocal MRCI calculation. Unfortunately, localization in the occupied orbital space quickly loses steam, with the virtual space increasing rapidly with the size of the system. Thus, local correlation in the external space becomes necessary to cut down the cost of the calculation. Local correlation in the virtual space for MRCI was achieved by using Saebø and Pulay's method of obtaining localized virtuals.<sup>24</sup> In the external space, only those external orbitals are included in the CI expansion that are spatially close to the set of correlated internal orbitals. This method is called the truncation of virtuals (TOV) approximation, discussed in a recent paper by Walter *et al.*<sup>16</sup> Here, we will define local CI as the method which incorporates both the WP and TOV approximations. Walter *et al.* showed that this local CI method is an extremely efficient tool to study large systems, while maintaining accurate energies. The major bottlenecks, involving the all- and half-external (*ab|cd*) and (*ij|ab*) integrals, were removed by the TOV approximation, reducing their cost to  $N^3$  from  $\sim N^6$  while recovering 97%–98% of the correlation energy compared to the nonlocal CI calculation.

While MRSDCI is known as the most accurate form of CI that is practical to use (full CI scaling as  $N!$ ), it suffers from a lack of size-extensivity (unlike full CI, which is size extensive). Therefore, the local MRSDCI method also suffers from this same flaw. While local MRSDCI is a good tool for studying large molecules, the lack of size-extensivity means that relative errors in the correlation energy will grow with system size. This makes it difficult to study systems with large number of electrons, e.g., transition metal complexes, polymers, etc. Various *a posteriori* size-extensivity corrections and *a priori* size extensive modifications to CI have been proposed over the years and most can be incorporated easily into existing CI codes.

Among the size-extensivity corrections to CI are those proposed by Davidson,<sup>44,45</sup> Pople *et al.*,<sup>46</sup> Siegbahn,<sup>47,48</sup> Bartlett and Shavitt,<sup>49</sup> and Meissner.<sup>50</sup> Davidson's original proposal<sup>44</sup> is an extremely simple correction to SDCI justified subsequently<sup>51</sup> by perturbation theory. Generally, the others are modifications to or are closely related to Davidson's proposals. Unfortunately, none of these corrections to CI are accurate for large systems. The errors in size-extensivity-corrected SDCI increase linearly<sup>45,46</sup> or even faster<sup>48–50</sup> with the number of subsystems. Moreover, when these corrections are applied to multireference wave functions, the errors in the size-extensivity-corrected MRCI increase with the size of the reference space.<sup>52</sup>

An alternative to *a posteriori* corrections is the coupled pair functional (CPF) method,<sup>53,54</sup> a size extensive approach developed by Ahlrichs and co-workers that modifies *a priori* the CI equations to be solved, leading to a self-consistent size extensive wave function and energy. The original CPF theory was extended in the modified coupled pair functional

(MCPF)<sup>55</sup> method, in order to describe near degeneracies better. Unfortunately, both the CPF and MCPF methods are based on single reference wave functions and do not account for unlinked-cluster terms that arise with multireference wave functions. The unlinked-cluster terms are corrected in the averaged coupled pair functional (ACPF) method developed by Gdanitz and Ahlrichs,<sup>56,57</sup> and it has been applied to conventional nonlocal MRCI.<sup>57</sup>

Here we present an implementation of the ACPF method in order to correct for size-extensivity errors within the local MRSDCI formalism. In Sec. II, we review local MRSDCI theory, size-extensivity issues, and the ACPF method, as well as summarize the implementation of our local ACPF scheme. Computational details are provided in Sec. III, with Sec. IV presenting results. We first provide initial tests of local ACPF theory focusing on recovery of correlation energy as a function of system size, comparing against nonlocal ACPF, non-local CI, and local CI. We then study basis set and core-correlation effects. We then go on to map out a potential energy surface requiring a multireference description and calculate bond dissociation energies of some organic molecules using the local ACPF technique. We conclude in Sec. V by discussing the pros and cons of the local ACPF method and expected future developments.

## II. THEORY

### A. Direct CI and the symmetric group approach

Large scale CI algorithms are based on direct methods where small pieces of the Hamiltonian are computed and then used in an iterative diagonalization<sup>58</sup> procedure in which one forms the product  $\mathbf{Z}$  of the Hamiltonian  $\mathbf{H}$  and the trial CI vector  $\mathbf{C}$ ,<sup>59,60</sup> where

$$\mathbf{Z}_\mu = \sum_\nu \hat{H}_{\mu\nu} \mathbf{C}_\nu. \quad (1)$$

The Hamiltonian is constructed as

$$H_{\mu\nu} = \sum_{ij} A_{ij}^{\mu\nu} (i|\hat{h}|j) + \sum_{ijkl} A_{ijkl}^{\mu\nu} (ij|kl), \quad (2)$$

where  $\mu$  and  $\nu$  are configuration state functions (CSFs),  $i, j, k, l$  are orbitals, and  $A_{ij}^{\mu\nu}$  and  $A_{ijkl}^{\mu\nu}$  are integral coupling coefficients.

These methods were first implemented in terms of the unitary group approach (UGA) in its graphical form (GUGA).<sup>61,62</sup> In these algorithms, both the spin and spatial parts of the wave function are intertwined. Given the strategy adopted in local correlation, where spatial criteria are used to eliminate contributions to the CI vector, this intimate mixture of spin and spatial components adds unnecessary complexity. Here we employ the symmetric group approach (SGA),<sup>63,64</sup> which has the advantage of a natural separation of the spin and spatial parts of the wave function, thereby allowing easy elimination of contributions to the Hamiltonian based on spatial criteria. Efficient graphical SGA algorithms exist<sup>65,66</sup> for computing the coupling coefficients on-the-fly, which reduces disk storage requirements. Lastly, common implementations of the GUGA have had limitations on the number of internal orbitals allowed, making it difficult to study large systems. By contrast, the only practical limitation that must

be imposed in the SGA is the maximum number of open shells allowed in any one CSF. The maximum number of open shells does not depend on the size of the system, but only on the spin multiplicity and the choice of reference space. We have shown that this limitation does not pose any problems for the algorithms used to compute the needed coupling coefficients in typical molecules.<sup>15</sup> Only an exceptional case, such as a highly delocalized  $\pi$  system, is expected to pose difficulties for this approach.

### B. Local multireference configuration interaction

The conventional MRSDCI equations in an orthogonal basis are documented in an article by Saunders and van Lenthe.<sup>67</sup> More detailed derivations can be found in the review article by Duch and Karwowski.<sup>63</sup> Here we only briefly review the methodology of the WP+TOV approximation for local MRSDCI.<sup>16</sup> First, we localize the internal orbitals using the Boys localization procedure.<sup>68</sup> Then, we prune the list of  $N-2$  electron CSFs according to a distance criterion that neglects weak pairs.<sup>15,24</sup> Then we truncate the virtual space into which each  $N-2$  electron configuration is allowed to excite two electrons. We first need to localize these virtuals by forming a set of projected atomic orbitals (PAOs), where the CI equations are written in this new basis. Before the start of the CI calculation in the PAO basis, we determine the set of PAOs (virtuals) associated with each internal orbital pair being correlated (an  $N-2$  electron CSF). This set of PAOs is called a virtual orbital domain. The average virtual domain size is independent of the molecular size; this is the key to the reduced scaling of the method. In the following, orthogonal virtual orbitals obtained as the by-product of a self-consistent field (SCF) procedure are denoted as  $a, b, c$ , and  $d$ , while the PAOs are referred to as  $p, q, r$ , and  $s$ .

The computational savings in the local correlation approximation is achieved by directly forming the Hamiltonian and the resultant vector  $\mathbf{Z}$  in the PAO CSF basis, which is much smaller than the conventional nonlocal CSF basis. However, the iterative diagonalization procedure requires  $\mathbf{Z}$  of Eq. (1) to be in an orthogonal basis in order to update  $\mathbf{C}$ . This orthogonal basis is generated using CSFs that include virtual orbitals obtained through canonical orthogonalization<sup>69</sup> of the PAOs in the domain of the internal ( $N-2$  electron) CSF. We denote these canonically orthogonalized PAOs as  $t, u, v$ , and  $w$ . These orbitals will be orthogonal only if they belong to the domain of the same internal CSF. Although the orthogonalized PAOs in the domain of one internal CSF may not be orthogonal to those in the domain of another internal CSF, the orthogonality of the full CSFs is ensured by the orthogonality of the internal CSFs. Linear dependencies within the PAO domains are removed during the orthogonalization step. Generation of the orthogonalized PAOs and the required transformation matrices is done only once before the start of the CI calculation.

A trial CI vector is then formed in this orthogonal PAO basis in order to start the iterative diagonalization routine. This trial  $\mathbf{C}$  vector is then transformed to the PAO basis as

$$\mathbf{C}_{pq}^\lambda = \sum_{t,u} T_{pt}^\lambda \mathbf{C}_{tu}^\lambda T_{uq}^\lambda, \quad (3)$$

where  $\mathbf{T}$  is the transformation matrix. Then, the resultant vector,  $\mathbf{Z}$ , is obtained in the PAO basis from Eq. (1), where now  $\hat{H}$  is the matrix representation of the Hamiltonian [Eq. (2)] and  $\mathbf{C}$  is the CI vector [Eq. (3)] in the basis of  $N$ -particle CSFs within the PAO basis. The  $\mathbf{Z}$  vector is then transformed to the orthogonal PAO CSF basis as

$$\mathbf{Z}_{tu}^\lambda = \sum_{p,q} T_{tp}^\lambda \mathbf{Z}_{pq}^\lambda T_{qu}^\lambda. \quad (4)$$

The Davidson<sup>71</sup> update is performed within the orthogonal PAO basis and the iterative procedure is repeated using Eqs. (1)–(4).

Although the TOV approximation substantially reduces the cost of the CI calculation, making it possible to perform MRCI calculations on large molecules, the lack of size-extensivity introduces an error that grows with system size. This motivates the next stage of our local correlation development, namely size-extensivity modifications to MRSDCI.

### C. Size-extensivity and the ACPF method

An electronic structure method is called size extensive if the energy increases linearly with the number of electrons. The ACPF method<sup>56</sup> illuminates quite simply the lack of size-extensivity in CI methods and the means to approximately correct the errors. We can decompose the wave function of each subsystem into a sum of its SCF reference wave function, denoted with a subscript 0, and a corresponding orthogonal correlation function denoted with a subscript  $c$ . Then the CI energy functional is given as

$$E_{\text{CI}} = \frac{\langle \Psi_0 + \Psi_c | \hat{H} - E_0 | \Psi_0 + \Psi_c \rangle}{1 + \langle \Psi_c | \Psi_c \rangle}. \quad (5)$$

It can be proven easily that the denominator in Eq. (5) is generally too large, artificially reducing the correlation energy. Gdanitz and Ahlrichs<sup>56</sup> therefore proposed to minimize the following modified CI energy functional:

$$E_{\text{ACPF}} = \frac{\langle \Psi_0 + \Psi_c | \hat{H} - E_0 | \Psi_0 + \Psi_c \rangle}{1 + g \langle \Psi_c | \Psi_c \rangle} \quad (6)$$

which includes a prefactor  $g$  to modulate the effect of the denominator and hopefully confer size-extensivity.

A reasonable value for  $g$  can be determined by considering the CI energy of two-electron subsystems for which SDCI corresponds to full CI.<sup>57,70</sup> For a single two-electron subsystem, the denominator in the ACPF energy functional will be

$$1 + g(2) \langle \Psi_c^1 | \Psi_c^1 \rangle, \quad (7)$$

where  $\Psi_c^1$  is its correlation function. For  $n$  noninteracting two-electron subsystems the denominator will take the form

$$1 + g(2n) \langle \Psi_c^n | \Psi_c^n \rangle = 1 + ng(2n) \langle \Psi_c^1 | \Psi_c^1 \rangle, \quad (8)$$

where  $\Psi_c^n$  is the correlation function for  $n$  noninteracting subsystems. For a single subsystem, SDCI is exact and  $g(2)$  will therefore be equal to 1. In order to achieve size-extensivity, the denominator in the ACPF energy functional should not change going from a single subsystem to  $n$  subsystems. Otherwise, the ACPF energy of  $n$  noninteracting

subsystems would not equal  $n$  times the energy of a single subsystem. Thus, it should also be true that  $ng(2n)$  is equal to 1. This requirement can be simultaneously satisfied for both a single two-electron subsystem and  $n$  noninteracting two-electron subsystems by choosing  $g$  to be equal to  $2/N$  where  $N$  is the total number of correlated electrons.

Although we motivated the single reference (SR) ACPF method by considering noninteracting two-electron systems, this does not imply that when the ACPF method is applied to interacting pairs of electrons that it will neglect the coupling between electron pairs.<sup>57</sup> Since SDCI includes this coupling, then ACPF will as well.

The ACPF method can also be used with multiconfigurational reference wave functions. This is accomplished by partitioning the CI wave function into mutually orthogonal components and applying a different  $g$  factor for each component. The partitioning employed by Gdanitz and Ahlrichs<sup>56,57</sup> involves dividing the wave function into five parts. The first part includes the reference CSFs only. The second part includes CSFs having excitations only within the active space (i.e., excitations from one active orbital to another active orbital), and the third part involves configurations in which inactive (doubly occupied in all references) orbitals are replaced by active orbitals (i.e., excitations from inactive orbitals to active orbitals). The fourth and fifth components involve the usual single and double replacements of any occupied orbitals in the CSF references with virtuals. For the first two components, the  $g$  value is taken to be equal to 1. The choice of  $g=1$  for the reference follows naturally from our preceding discussion, since the reference CSFs are part of  $\Psi_0$  of Eq. (6). The choice of  $g=1$  for the second component relies on the assumption that the reference space is close to some complete active space (CAS) and that extensivity corrections therefore are not needed for these terms. For this reason, ACPF methods can be sensitive to the choice of the reference space. If the reference space is far from some CAS, the  $g$  value for this component of the CI wave function may require alteration. For the remaining classes of terms,  $g$  is usually taken to be equal to  $2/N$ . The ACPF method using the above-mentioned  $g$  values is called multi-reference ACPF (MR ACPF).

The choice of  $2/N$  as the  $g$  factor for the double excitations is well motivated by our previous discussion. However, for single excitations, there is no obvious reason that this is the most appropriate choice. Recently, Gdanitz proposed an ACPF method<sup>57</sup> in which the  $g$  values for the single excitations are “damped” according to

$$g = \frac{4}{N} \left[ 1 - \frac{1}{2(N-1)} \right]. \quad (9)$$

This damping is introduced with the aim of reducing the overestimation of the contribution of the single excitations due to the inherent double counting of such excitations.<sup>57</sup> The ACPF method which uses the modified  $g$  values is called the MR ACPF-2 method.

Upon introducing the partitioning of the correlation function, the ACPF functional becomes

$$E_{\text{ACPF}} = \frac{\langle \Psi_0 + \Psi_c | \hat{H} - E_0 | \Psi_0 + \Psi_c \rangle}{1 + \sum g_i \langle \Psi_i | \Psi_i \rangle}, \quad (10)$$

where the  $\Psi_i$  and  $g_i$  are the different partitions of the correlation function,  $\Psi_c$ , and their associated  $g$  values, respectively, and where

$$\langle \Psi_0 | \Psi_c \rangle = 0 \quad (11)$$

and

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle. \quad (12)$$

Variational optimization of the ACPF functional with respect to the various components of  $\Psi_c$  leads to the following equation for  $\Psi_c$ :

$$\begin{aligned} \sigma &= (1 - |\Psi_0\rangle\langle\Psi_0|) \left[ \hat{H} - E_0 - E_{\text{ACPF}} \sum_i g_i \hat{P}_i \right] |\Psi_0 + \Psi_c\rangle \\ &= 0, \end{aligned} \quad (13)$$

where the operator  $\hat{P}_i$  projects out the  $i$ th component of the correlation function from the total  $\Psi_c$  and has no effect on  $\Psi_0$ . Similar to the MRSDCI method, the important ingredient in the iterative algorithms for solving Eq. (13) is the  $\sigma$  (residual) vector. This is used to construct an improved solution,  $\Psi'_c$ , given by

$$|\Psi'_c\rangle = |\Psi_c\rangle - \left( H_0 - E_0 - E_{\text{ACPF}} \sum_i g_i \hat{P}_i \right)^{-1} \sigma, \quad (14)$$

where  $H_0$  are the diagonal elements of the Hamiltonian, which are used as preconditioners.<sup>58</sup> The ACPF correlation energy ( $E_{\text{ACPF}}$ ) is computed iteratively in Eqs. (13) and (14) using the Jacobi method.<sup>56</sup> Incorporating the ACPF method into traditional MRSDCI algorithms is straightforward, since construction of the residual and trial vectors resembles very closely the traditional MRSDCI method.

#### D. Local ACPF

We refer to the incorporation of the ACPF scheme into local MRCI as local ACPF. In our original local MRCI code, we use Davidson's iterative diagonalization procedure.<sup>71</sup> In local ACPF, we replace this diagonalization with the ACPF iterative solver given in Eqs. (13) and (14). The algorithm for performing the local ACPF is as follows: We first obtain the reference wave function [from some SCF (Hartree-Fock (HF), generalized valence bond (GVB), complete active space SCF (CASSCF), etc., calculation)] and compute the reference energy  $E_0$  before the start of the ACPF calculation. The trial correlation energy ( $E_{\text{ACPF}}$ ) and the trial vector  $\psi_c$  are initialized to 0. We compute the residual vector as given in Eq. (13) and we use this residual vector to compute a new trial vector as shown in Eq. (14). This new trial vector is used to compute a new  $E_{\text{ACPF}}$  via Eq. (10) and this ACPF correlation energy is then used to generate a new residual vector in Eq. (13) and the procedure is repeated until convergence. The savings from the local correlation approximation here is achieved by constructing  $\hat{H}|\Psi_c\rangle$  in the PAO basis and then backtransforming this  $\mathbf{Z}$  vector to the orthog-

onal PAO basis using Eq. (4). Then the construction of the residual and trial vectors are carried out in the orthogonal PAO basis.

### III. CALCULATIONAL DETAILS

The JAGUAR version 4.1 quantum chemistry package<sup>72</sup> from Schrödinger, Inc., was used to solve for HF or GVB-perfect pairing (GVB-PP) orbitals used as the one-particle basis in the subsequent CI or ACPF calculation. The Pople-style<sup>73</sup> and Dunning correlation-consistent<sup>74</sup> 1-particle Gaussian basis sets were used. All molecular geometries were optimized at the GVB-PP level of theory. For single reference CI or ACPF, either a closed shell HF or a restricted open-shell HF (ROHF) reference wave function was employed. For multireference CI or ACPF, we used either GVB-PP<sup>75</sup> or the GVB with restricted configuration interaction (GVB-RCI)<sup>76</sup> reference wave functions.

The GVB-PP wave function uses two spatial configurations for each correlated pair of electrons: the first places the electron pair in a bonding orbital and the second places the electron pair in an antibonding orbital. The one-electron GVB orbitals in each pair are nonorthogonal, but the natural orbitals formed from them are orthogonal. GVB-RCI consists of allowing, in addition to GVB-PP double excitations within each correlated pair of natural orbitals, the corresponding single excitations within each pair of orbitals. The GVB-PP and GVB-RCI calculations are denoted as ( $n/2n$ ), where  $n$  is the number of electron pairs and  $2n$  is the number of orbitals used to describe these pairs of electrons. GVB-PP wave functions have a total of  $2^n$  spatial configurations, while GVB-RCI has a maximum of  $3^n$  spatial configurations (some may be disallowed by symmetry). GVB-RCI is a particularly useful reference wave function for the computation of bond dissociation energies (BDEs) involving multiple bonds, as it allows bonds to dissociate properly to ground state fragments.<sup>77</sup>

The HERMIT package by Helgaker *et al.*<sup>78</sup> was used to compute all the one-electron and two-electron integrals in the atomic orbital (AO) basis. In the current version of our code, depending on the type of CI calculation, the AO integrals are transformed to the molecular orbital (MO) or to the PAO basis and then the various classes of transformed integrals used in the CI calculation are written to disk.

In order to perform the local MRCI and local ACPF calculations, we must localize the orbitals and set parameters to specify our truncation procedures. The MOs are localized using the Boys algorithm<sup>68</sup> in JAGUAR. The GVB active orbitals are localized naturally as a by-product of the GVB orbital optimization.<sup>75,76</sup> As discussed previously, truncation parameters are established for the WP and TOV approximations. The specific definitions are given in Refs. 3 and 16. For the internal orbitals, the scaling parameter  $\alpha$  was 1.2 and 0.8 for the WP and TOV approximations, respectively. The default sphere radius was 0.8 bohr and the occupation threshold was 0.8 for both the WP and TOV approximations. For the PAOs,  $\alpha$  was 0.4, the default radius was 0.4 bohr, and the occupation threshold was 0.8. As explained previously,<sup>16</sup> for the purpose of studying bond breaking, we use a cylinder with hemispherical ends that expands along with the bond to

determine the weak pairs and virtual orbital domains for the active orbitals used to describe the bond cleavage. This is necessary due to the delocalized nature of the bonding natural orbitals as the bond is cleaved. This process leads to PESs that are comparable in smoothness to the nonlocal CI surfaces. For active orbitals, the cylinder radius was taken to be 2.0 and 0.5 in the WP and TOV approximations, respectively.

All reported BDEs are 298 K binding enthalpies. For the nonlocal and local SDCI and ACPF calculations, these 298 K binding enthalpies were calculated in the following manner. We first compute the Born–Oppenheimer binding energies from the CI or ACPF energy difference between the “supermolecule” (fragments at their equilibrium geometries separated by 50 a.u.) and the bound molecule at its equilibrium geometry. We then add zero-point vibrational energies and 298 K heat capacity corrections. Zero-point energies are computed using HF or ROHF harmonic vibrational frequencies. Unless otherwise noted, the experimental values of BDEs are obtained from tables of BDEs and heats of formation in the CRC Handbook of Chemistry and Physics.<sup>79</sup>

For the carbon–carbon double bond in tetrafluoroethylene, an additional complication arises in the calculation of the BDE. The supermolecule diabatically dissociates carbon–carbon double bonds to triplet fragments, whereas in this case the actual ground state fragments are singlets ( $^1A_1$  CF<sub>2</sub>). Therefore, the diabatic  $D_e$  (for tetrafluoroethylene) must be reduced by the splitting between the triplet and singlet states of the fragment molecules. The triplet state is treated using a SDCI or ACPF calculation based on a ROHF reference configuration and the singlet state is treated using an MRSDCI, MR ACPF, or MR ACPF-2 calculation based on a GVB-RCI (1/2) reference state. This choice of reference wave functions yields two active orbitals in the treatments of both the triplet and singlet states, leading to a more balanced description of the electron correlation in both states.<sup>80</sup> For example, correlating both core and valence electrons, this procedure leads to triplet–singlet energy splittings for each CF<sub>2</sub> fragment of 53.1/51.4 kcal/mol for nonlocal/local MRSDCI, 54.7/52.3 kcal/mol for nonlocal/local MR ACPF, and 54.4/52.4 kcal/mol for nonlocal/local MR ACPF-2 within 6-31G\*\* basis sets. The adiabatic  $D_e$  is obtained by subtracting twice the triplet–singlet energy splitting of the CF<sub>2</sub> fragment from the diabatic  $D_e$ . The 298 K BDE is then obtained by adding zero-point vibrational energy and enthalpy corrections for C<sub>2</sub>F<sub>4</sub> and CF<sub>2</sub> ( $^1A_1$ ) to this adiabatic  $D_e$ .

A similar problem arises for carbon–carbon triple bonds. The supermolecule approach diabatically dissociates a carbon–carbon triple bond to quartet fragments, whereas the actual ground state fragments are usually doublets. Therefore, the diabatic  $D_e$  [e.g., in (CH<sub>3</sub>)<sub>3</sub>CC≡CCH<sub>3</sub>] will be reduced by the splitting between the quartet and doublet states of the fragment molecules. For each fragment, the quartet state is treated using a SDCI or ACPF calculation based on a ROHF reference configuration and the doublet state is treated using an MRSDCI, MR ACPF, or MR ACPF-2 calculation based on a GVB-RCI(1/2) reference state. This choice of reference wave functions yields three active orbitals in the treatments of both the doublet and quar-

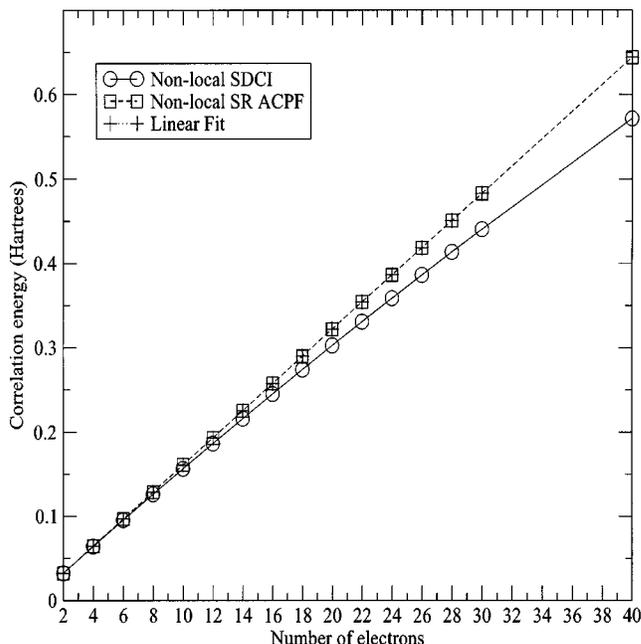


FIG. 1. Correlation energy recovered using nonlocal SDCI and nonlocal SR ACPF for a linear chain of noninteracting He atoms. The linear fit is to the nonlocal SR ACPF data.

ter states. The quartet–doublet energy splitting for the (CH<sub>3</sub>)<sub>3</sub>CC fragment is 21.8 kcal/mol for local MRSDCI and 23.1 kcal/mol for local MR ACPF-2, whereas for the CCH<sub>3</sub> fragment it is 21.8 kcal/mol for local MRSDCI and 22.3 kcal/mol for local MR ACPF-2. The sum of these quartet–doublet energy splittings is 43.6 kcal/mol for local MRSDCI and 45.4 kcal/mol for local MR ACPF-2 within the 6-31G\*\* basis set. The adiabatic  $D_e$  is then computed by subtracting this total quartet–doublet energy splitting from the diabatic  $D_e$  and the 298 K BDE is obtained as discussed before.

## IV. RESULTS AND DISCUSSION

### A. Noninteracting He atoms

The ACPF modification to MRSDCI was first tested by performing nonlocal CI and SR ACPF calculations on a linear chain of noninteracting He atoms, where we varied the number of He atoms along the chain. Each He atom was separated from its neighboring He atom by a distance of 50 a.u. Figure 1 shows that SR ACPF nicely recovers the correlation energy not recovered by SDCI. The correlation energy recovery by SR ACPF is shown to be completely linear in system size, demonstrating that SR ACPF exhibits rigorous size-extensivity.

The difference in correlation energy between SDCI and SR ACPF increases with the number of electrons. For two noninteracting He atoms, the difference in correlation energy between the SR ACPF and SDCI is 0.3 kcal/mol, while for 20 noninteracting He atoms, the correlation energy recovered by SDCI and SR ACPF is 358.5 and 404.2 kcal/mol, respectively, a difference of 45.7 kcal/mol. Hence SR ACPF recovers 12.75% more correlation energy compared to SDCI in the latter case. A similar test was performed using our local version of SR ACPF, yielding (as it should) the same results

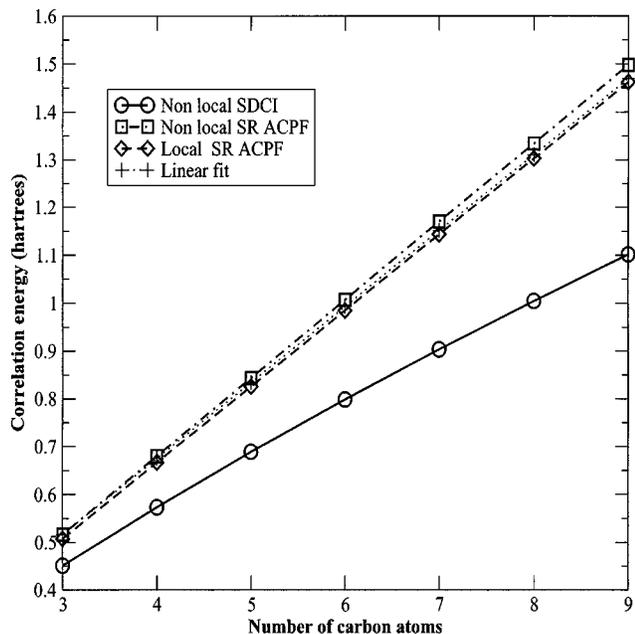


FIG. 2. Correlation energy recovered using nonlocal SDCI, nonlocal and local SR ACPF methods for series of straight chain hydrocarbons. The linear fit is to the nonlocal SR ACPF data.

as that of nonlocal SR ACPF. These were simply preliminary tests to ensure that our ACPF implementation performs similarly to trends seen earlier.<sup>56,57</sup>

## B. Straight chain alkanes

To check the effectiveness of local ACPF in recovering the correlation energy *vis-à-vis* standard nonlocal ACPF, we carried out a series of calculations correlating all core and valence electrons on straight chain hydrocarbons. Figure 2 shows the nonlocal SDCI, as well as nonlocal and local SR ACPF correlation energies for propane through nonane at their equilibrium geometries. Again, the difference between nonlocal SR ACPF and nonlocal SDCI correlation energies increases with system size. A linear fit shows that the ACPF approach exhibits size-extensivity even for interacting systems. For the case of nonane ( $C_9H_{20}$ ), the difference in correlation energies between nonlocal SDCI and nonlocal SR ACPF is  $\sim 248$  kcal/mol! This illustrates starkly the importance of including size-extensivity corrections for large molecules. Figure 2 also shows that the local SR ACPF approximation recovers the majority of the correlation energy yielded by the nonlocal ACPF method. For example, the percentage of correlation energy recovered by local SR ACPF relative to nonlocal SR ACPF is  $\sim 98.4\%$  for  $C_3H_8$  and  $\sim 97.5\%$  for  $C_9H_{20}$ . Thus, the amount of correlation energy recovered by local SR ACPF decreases slightly with system size. This is likely due to the (deliberate) neglect of long-range correlation effects in local CI.

The fact that local SR ACPF does not deviate from linearity with respect to correlation energy recovery as a function of number of carbon atoms suggests that local SR ACPF exhibits good size-extensivity. Moreover, the cost savings is substantial with the local version: the total number of CSFs for nonane used in the nonlocal SR ACPF case is 26.8 mil-

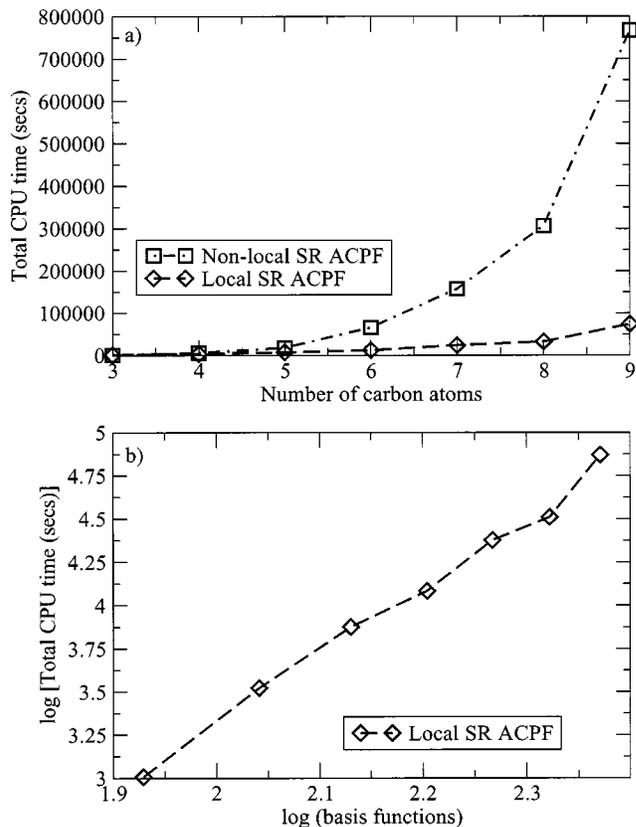


FIG. 3. (a) Performance of local SR ACPF vs nonlocal SR ACPF. (b) Scaling of local SR ACPF.

lion, while local SR ACPF uses only 0.64 million. In terms of CPU time for nonane, the nonlocal SR ACPF takes 48 372 s/iteration while local SR ACPF takes only 3530 s/iteration (all calculations were performed on Compaq DEC ES40 machines): more than an order of magnitude speedup. The overall performance of local SR ACPF versus nonlocal SR ACPF is shown in Fig. 3(a). We find that local SR ACPF takes two to three iterations more than nonlocal SR ACPF to converge (with 11 being the typical number of iterations required), but since the local ACPF takes far less time per iteration, substantial computational time is still saved. The extra number of iterations is not due to the ACPF approach, but to the inherent convergence characteristics of the local CI method.<sup>16</sup> Figure 3(b) provides a plot whose slope reveals the scaling of local SR ACPF to be  $\sim N^4$  for this system size regime.

## C. Basis set effects

Next we investigated how predictions of BDEs via the local and nonlocal versions of MRSDCI and MR ACPF are affected by basis set quality. Here we focused on the C=C BDE in ethylene, since it is well known experimentally. Table I provides these results, where all electrons were correlated. The 6-31G basis set gives the lowest BDE for all methods. The 6-31G\*\* basis set increases the BDE by 9.7 kcal/mol for local MRSDCI and 11.7 kcal/mol for local MR ACPF-2, compared to the BDEs obtained using the 6-31G basis set. Polarization functions are clearly very important for obtaining an accurate description of the molecule and

TABLE I. Basis set dependence of 298 K BDEs (kcal/mol) for  $\text{H}_2\text{C}=\text{CH}_2$ , calculated via nonlocal and local versions of MRSDCI and MR ACPF-2.<sup>a</sup>

Basis set	MRSDCI		MR ACPF-2	
	Nonlocal	Local	Nonlocal	Local
6-31G	151.3	150.9	151.2	150.7
6-31G**	163.2	161.6	167.3	162.4
aug-6-31G** <sup>b</sup>	169.1	167.5	171.0	169.1
6-31G** <sup>++</sup>	162.0	160.3	163.1	161.1
6-311G	151.8	150.5	151.8	150.5
6-311G**	161.4	159.6	162.5	160.4
6-311G** <sup>++</sup>	161.8	160.0	162.9	162.4
cc-pVDZ	161.0	159.0	161.9	159.6
cc-pVTZ(-f)	163.4	161.1	164.4	161.9
aug-cc-pVTZ(-f)	163.4	160.9	164.4	161.7
cc-pVTZ	170.1	166.8	171.5	168.1
Experiment	171 ± 1.0			

<sup>a</sup>GVB-RCI(2/4) reference wave function; all core and valence electrons correlated.

<sup>b</sup>One *f* function on each carbon atom; one *d* function on each hydrogen atom.

recovery of extra correlation energy. Note also that the local MR ACPF-2 gives a higher BDE than local MRSDCI, due to the size-extensivity conferred by local ACPF. Addition of diffuse functions to the 6-31G\*\* basis set slightly lowers the BDE for all methods. Of course for neutral  $\text{C}_2\text{H}_4$ , diffuse functions are not expected to be necessary and we indeed see that they make little difference to the BDEs. The BDEs computed using the 6-311G basis set for both the local MRSDCI and the local MR ACPF-2 resemble quite closely those from the 6-31G basis set. Thus, a triply split valence basis is not necessary for neutral organic molecules. Using a 6-311G\*\* basis, we find BDEs about 9.1 kcal/mol higher for local MRSDCI and 9.9 kcal/mol higher for local MR ACPF-2 compared to the 6-311G basis set. We see that, as in the 6-31G case, adding polarization functions has a dramatic effect. And again, addition of diffuse functions to the 6-311G\*\* basis set results in a very marginal increase in the BDE using local MRSDCI, though it yields a 2.0 kcal/mol increase in the BDE using local MR ACPF-2 for reasons that are unclear. The BDEs obtained from the augmented 6-31G\*\* basis set are 6 kcal/mol higher for nonlocal and local MRSDCI and local MR ACPF-2 and 4 kcal/mol higher for nonlocal MR ACPF-2 than those obtained using the 6-31G\*\* basis set. Inclusion of *f* functions on heavy atoms

and *d* functions on hydrogen are clearly crucial, lowering the total energy in the equilibrium geometry more than in the supermolecule, and yielding larger BDEs in excellent agreement with experiments.

We also investigated how Dunning's cc-pVDZ, cc-pVTZ(-*f*), cc-pVTZ, and augmented cc-pVTZ(-*f*) correlation-consistent basis sets affect the BDEs. Overall, these basis sets gave roughly similar trends to the Pople bases: small improvements are seen going from cc-pVDZ to cc-pVTZ and no improvement is provided by augmentation with diffuse functions. Again, similar to augmented 6-31G\*\*, the cc-pVTZ yielded higher BDEs for all methods, where the inclusion of  $l_{\text{max}}+2$  polarization functions is again seen to be crucial for obtaining  $\sim 1$  kcal/mol accuracy in BDEs.

In similar fashion, we also estimated basis set effects on BDEs for prototypical single C–C and triple  $\text{C}\equiv\text{C}$  bonds in  $\text{H}_3\text{C}-\text{CH}_3$  and  $\text{HC}\equiv\text{CH}$ , as shown in Table II. We will use all of these findings to estimate the error due to finite basis sets for BDEs in large molecules.

#### D. Core correlation effects

We also investigated how omitting core electron correlation affects BDEs calculated with local and nonlocal MRSDCI and ACPF methods (Table III). Inclusion of core correlation increased the BDEs in all cases. Generally, this effect is fairly small for all methods,  $\sim 1$  kcal/mol or less. For several cases, nonlocal MRSDCI and nonlocal ACPF were sensitive to omission of the core orbitals, showing differences of  $\sim 3$  kcal/mol. Generally, invocation of the local correlation approximation for either MRSDCI or ACPF reduced the importance of including core correlation. This is because the WP approximation neglects all weakly correlated pairs, and the tightly held core electrons are spatially far apart from other core electrons on another atom, so these pairs will be eliminated anyway in both local methods. The small differences seen are due to the core-valence correlation on the same atom that will be included in the local methods. Given that the core correlation effects within the local MRSDCI and local MR ACPF are so small ( $<1$  kcal/mol), we conclude that it is generally unnecessary to include such effects in large molecules.

TABLE II. Basis set dependence of 298 K BDEs (kcal/mol) for  $\text{H}_3\text{C}-\text{CH}_3$  and  $\text{HC}\equiv\text{CH}$  calculated via nonlocal and local versions of MRSDCI and MR ACPF-2.<sup>a</sup>

Molecule/Ref. Wave function	Basis set	MRSDCI		MR ACPF-2		Experiment
		Nonlocal	Local	Nonlocal	Local	
$\text{H}_3\text{C}-\text{CH}_3$ /RCI(1/2)	6-31G**	86.9	85.0	88.2	85.8	87.9 ± 0.5 <sup>b</sup>
	aug-6-31G** <sup>d</sup>	89.5	86.3	91.4	87.5	
$\text{HC}\equiv\text{CH}$ /RCI(3/6)	6-31G**	221.1	220.6	217.6	219.5	230.6 ± 0.7 <sup>c</sup>
	aug-6-31G** <sup>d</sup>	229.2	227.2	228.1	226.4	

<sup>a</sup>All core and valence electrons correlated.

<sup>b</sup>Reference 79.

<sup>c</sup>Reference 89.

<sup>d</sup>One *f* function on each carbon atom; one *d* function on each hydrogen atom.

TABLE III. BDEs (kcal/mol) at 298 K for some organic molecules examining core correlation effects within a 6-31G\*\* basis set. For the last two molecules, only the valence electrons were correlated. Best estimates are extrapolations of 6-31G\*\* BDEs to aug-6-31G\*\* values.

Molecule/Ref. wave function Core-valence correction <sup>b</sup> Basis set extrapolation <sup>c</sup>	Nonlocal/local MRSDCI	Nonlocal/local MR ACPF	Nonlocal/local MR ACPF-2	Experiment
C <sub>2</sub> H <sub>5</sub> -OCH <sub>3</sub> /RCI(1/2)/	76.7/76.1 79.8/76.9 <sup>a</sup>	81.0/77.6 81.1/77.8 <sup>a</sup>	81.1/77.8 81.5/78.2 <sup>a</sup>	85±1.0 <sup>c</sup>
$\Delta E_{\text{core-val}}$ <sup>b</sup>	3.1/0.8	0.1/0.2	0.4/0.4	
Best estimate <sup>c</sup>	82.4/78.2 <sup>a</sup>	...	84.7/79.9 <sup>a</sup>	
H <sub>2</sub> N-C(CH <sub>3</sub> ) <sub>3</sub> /RCI(1/2)/	79.7/76.1 80.4/76.3 <sup>a</sup>	82.4/77.1 83.0/77.4 <sup>a</sup>	82.6/77.1 83.2/77.5 <sup>a</sup>	85.7±0.5 <sup>c</sup>
$\Delta E_{\text{core-val}}$ <sup>b</sup>	0.7/0.2	0.6/0.3	0.6/0.4	
Best estimate <sup>c</sup>	83.0/77.6 <sup>a</sup>	...	86.4/79.2 <sup>a</sup>	
H <sub>2</sub> C=CH <sub>2</sub> /RCI(2/4)/	162.7/161.2 163.2/161.6 <sup>a</sup>	163.7/161.9 164.3/162.4 <sup>a</sup>	163.7/162.0 167.3/162.4 <sup>a</sup>	171±1.0 <sup>c</sup>
$\Delta E_{\text{core-val}}$ <sup>b</sup>	0.5/0.4	0.6/0.5	3.6/0.4	
Best estimate <sup>c</sup>	169.1/167.5 <sup>a</sup>	...	171.0/169.1 <sup>a</sup>	
F <sub>2</sub> C=CF <sub>2</sub> /RCI(2/4)/	65.7/67.7 67.0/68.5 <sup>a</sup>	62.2/65.9 63.2/67.0 <sup>a</sup>	63.0/66.2 64.3/67.0 <sup>a</sup>	53.4±0.7 <sup>f</sup> 69.0±2.7 <sup>g</sup>
$\Delta E_{\text{core-val}}$ <sup>b</sup>	1.3/0.8	1.0/1.1	1.3/0.8	76.3±3.0 <sup>h</sup>
Best estimate <sup>c</sup>	72.9/74.4 <sup>a</sup>	...	68.0/73.7 <sup>a</sup>	
CH <sub>3</sub> CH=CHCH <sub>3</sub> /RCI(2/4)/	160.4/160.0 163.0/160.7 <sup>a</sup>	...	171.5/162.1 173.0/162.5 <sup>a</sup>	...
$\Delta E_{\text{core-val}}$ <sup>b</sup>	2.6/0.7	...	1.5/0.4	
Best estimate <sup>c</sup>	168.9/166.6 <sup>a</sup>	...	176.7/169.2 <sup>a</sup>	
C <sub>2</sub> H <sub>5</sub> CH=CHC <sub>2</sub> H <sub>5</sub> /RCI(2/4)/	-160.9 -161.2 <sup>a</sup>	...	-164.1 -164.5 <sup>a</sup>	...
$\Delta E_{\text{core-val}}$ <sup>b</sup>	-0.3	...	-0.4	
Best estimate <sup>c</sup>	-167.1 <sup>a</sup>	...	-171.2 <sup>a</sup>	
Corrected for local truncation <sup>d</sup>	169.4	...	178.7	
PhCH=CH <sub>2</sub> /RCI(2/4)/	-177.2	...	-180.4	...
Best estimate <sup>c</sup>	-183.1	...	-187.1	
Corrected for local truncation <sup>d</sup>	185.4	...	194.6	
(CH <sub>3</sub> ) <sub>3</sub> CC≡CCH <sub>3</sub> /RCI(3/6)/	-208.2	...	-203.6	...
Best estimate <sup>c</sup>	-214.8	...	-210.5	
Corrected for local truncation <sup>d</sup>	216.8	...	212.2	

<sup>a</sup>Includes correlation of both core and valence electrons.

<sup>b</sup> $\Delta E_{\text{core-val}}$ =BDE (all electrons correlated)—BDE (valence only correlated).

<sup>c</sup>Using values from Tables I and II, aug-6-31G\*\* BDEs were estimated, except for C<sub>2</sub>H<sub>4</sub>, where they were calculated explicitly (see Table I).

<sup>d</sup>The local truncation errors found for CH<sub>3</sub>CH=CHCH<sub>3</sub> and HC≡CH are used to get better estimates of these BDEs.

<sup>e</sup>Reference 79.

<sup>f</sup>Reference 83.

<sup>g</sup>Reference 84.

<sup>h</sup>Reference 85.

### E. Potential energy surface in 3-hexene

In earlier work, we demonstrated that local MRSDCI produced smooth potential energy surfaces for bond breaking.<sup>16</sup> Here, we examine if the same is true for local ACPF. Figure 4 displays the potential energy surface for breaking the C=C double bond in trans-3-hexene, calculated using nonlocal and local MRSDCI, as well as the local MR ACPF-2 method. At the equilibrium geometry, the lowest energy (highest BDE) is obtained using the local MR ACPF-2 approach, as shown in the inset in Fig. 4. All three approaches give rise to smooth potential energy surfaces, suggesting they all may be used with confidence to study a variety of bond breaking processes. Use of a spherocylinder that expands in length with the breaking bond to determine the orbital domains (described in Sec. III) is critical to obtaining smooth potential energy surfaces for bond breaking.

This represents a qualitative improvement over earlier attempts to break bonds with local correlation employing orbital domains, which showed discontinuities along the bond-breaking path.<sup>81</sup>

### F. BDEs of some organic molecules

Table III also provides comparisons of local MRSDCI and local MR ACPF/MR ACPF-2 estimations of some single, double, and triple BDEs at 298 K. The nonlocal MR ACPF/MR ACPF-2 method recovers up to ~8 kcal/mol more correlation energy than nonlocal MRSDCI, bringing nonlocal ACPF BDEs closer to the experimental values. Indeed, the extended basis set extrapolations for the “best estimate” BDEs show excellent agreement between nonlocal MR ACPF-2 and experiment. These “best estimates” are obtained using the  $\Delta$ BDEs in Tables I and II, comparing

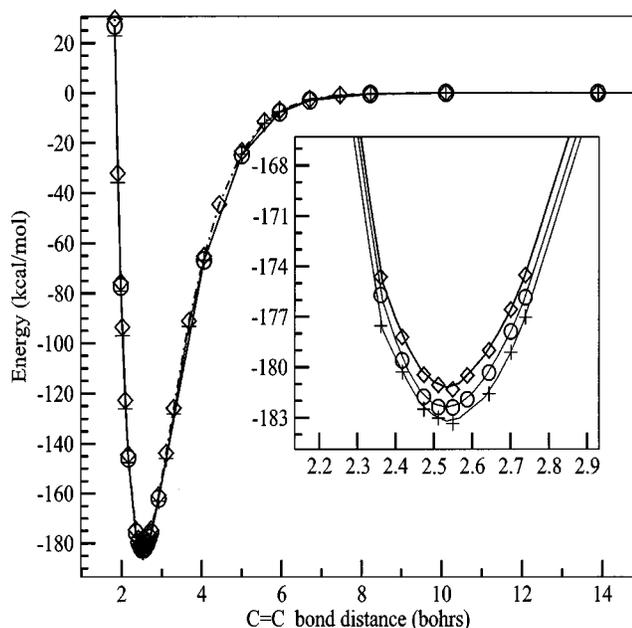


FIG. 4. Potential energy surface for 3-hexene using nonlocal MRSDCI (○), local MRSDCI (◇), and local MR ACPF-2 (+).

6-31G\*\* and aug-6-31G\*\* basis sets. On the other hand, use of the local correlation approximation degrades the BDEs by up to  $\sim 8$  kcal/mol. This truncation error can be used to further correct the BDEs calculated with local ACPF for large molecules, as shown toward the bottom of Table III. For both local and nonlocal cases, the BDEs from MR ACPF and MR ACPF-2 are very similar to (though generally higher than) MRSDCI. Overall, MR ACPF-2 appears to be slightly better than MR ACPF, so for the largest molecules examined, we only used MR ACPF-2 to compare with MRSDCI.

Tetrafluoroethylene ( $C_2F_4$ ) has one of the weakest  $C=C$  double bonds known, due to final state electronic relaxation effects that are extremely large.<sup>77,82</sup> Experimental estimates<sup>83–85</sup> of the  $C=C$  bond energy in  $C_2F_4$  range from 53 to 67 kcal/mol. Local MRSDCI/MR ACPF/MR ACPF-2 yielded higher  $F_2C=CF_2$  BDEs than the corresponding nonlocal methods. This can be traced to differences in the estimates of the  $CF_2$  triplet–singlet energy splitting ( $\Delta E_{ST}$ ), which is used to calculate the adiabatic bond energy (see Sec. III). Local MRSDCI predicts  $\Delta E_{ST}(CF_2) = 51.5$  kcal/mol, whereas nonlocal MRSDCI yields  $\Delta E_{ST}(CF_2) = 53.1$  kcal/mol. Similarly, local MR ACPF-2 predicts  $\Delta E_{ST}(CF_2) = 52.5$  kcal/mol, whereas nonlocal MR ACPF-2 produces  $\Delta E_{ST}(CF_2) = 54.6$  kcal/mol. The larger  $\Delta E_{ST}$  in the nonlocal calculations lowers the adiabatic BDE reported here. We consider the basis set extrapolated BDE of 68.0 kcal/mol from nonlocal MR ACPF-2 to be our best estimate at this level of basis set, which is very close to the middle experimental value<sup>84</sup> and also agrees well with the earlier correlation consistent CI (CCCI) result of  $64.5 \pm 2.5$  kcal/mol by Carter and Goddard.<sup>82</sup>

The strength of this local ACPF approach is that it can be used to estimate BDEs of large molecules for which little experimental data exist and where conventional correlation methods are impractical to employ. For example, due to their

prohibitive computational costs, nonlocal calculations for 3-hexene, styrene, and  $(CH_3)_3CC\equiv CCH_3$  could not be performed, while their local counterparts were entirely manageable. The BDEs of double bonds like 2-butene, 3-hexene, and styrene show a consistent increase in the BDEs going to local ACPF from local MRSDCI, suggesting an improved recovery of correlation. The case of  $(CH_3)_3CC\equiv CCH_3$  exhibits behavior similar to  $F_2C=CF_2$ , where the BDE for the  $C\equiv C$  triple bond using local MR ACPF-2 is lower than the local MRSDCI prediction. The reason is the same: here also the adiabatic bond energy is affected by the electronic energy differences of the dissociated fragments. The quartet–doublet energy difference obtained from local MR ACPF-2 is higher than that obtained by local MRSDCI, which lowers the binding energy. The last half of Table III serve as predictions of some large molecule thermochemistry, where we have estimated corrections for basis set and correlation truncation.

## V. CONCLUDING REMARKS

We have implemented an *a priori* size extensive modification to local MRSDCI via the MR-ACPF method. We obtain improved descriptions of electron correlation in large molecules. First, we demonstrated correlation energy recovery is linear in system size within this local ACPF approach. Then, the effectiveness of local ACPF was tested by its application to straight chain alkanes, mapping a potential energy surface, calculating single and multiple BDEs of sample organic molecules, and predicting large molecule thermochemistry. The method exhibits dramatic speedups over nonlocal ACPF and improved accuracy over local MRSDCI. In almost all cases, local ACPF performs better than the corresponding local MRSDCI approach, recovering extra correlation energy and yielding BDEs closer to experiment.

As is well known, the choice of basis employed for calculations is very crucial in the determination of BDEs. Here we have shown that polarization through *f* functions on heavy atoms and *d* functions on hydrogen atoms in the basis set are required to obtain chemical accuracy in BDEs ( $\leq 1$  kcal/mol error), while diffuse and triple zeta valence functions do not play a significant role in the calculation of BDEs of neutral organic molecules. Also, while inclusion of core electron correlation improves BDEs calculated with nonlocal methods, the error in computing BDEs by omitting core correlation is less than 1.0 kcal/mol for both local MRSDCI and local MR ACPF methods, since many of these terms are already eliminated by WP truncation.

The BDEs obtained using local ACPF can be as much as  $\sim 8$  kcal/mol lower than their nonlocal ACPF counterparts. Part of this truncation error is already evident in the local MRSDCI predictions, but the error roughly doubles upon going to the local ACPF scheme. Systematically, local ACPF does yield higher BDEs than local MRSDCI, but truncation error should be taken into account when attempting to make predictions of large molecule thermochemistry.

The local ACPF method clearly still could benefit from further improvement, due to the neglect of long-range correlation effects by the WP approximation. In principle, one would like to treat these weak pairs by an inexpensive ap-

proximation to MRSDCI. For example, some sort of perturbational estimation of long-range correlation effects may be made. Dunietz and Friesner proposed a local version of multiconfigurational perturbation theory based on GVB-style wave functions,<sup>86</sup> based upon the multireference GVB-type perturbation method of Murphy and Messmer.<sup>87</sup> Another alternative is to use the Epstein–Nesbet perturbation theory employed by Reinhardt and Malrieu,<sup>88</sup> due to its low computational cost and its proven success using localized orbitals to accurately compute correlation energies for large molecules. It might be feasible to incorporate certain aspects of these methodologies into our local ACPF method to treat long-range correlation.

Walter *et al.*<sup>3,15</sup> reviewed the advantages of the symmetric group graphical approach<sup>63</sup> to CI, which forms the foundation for the method presented here. The principal advantage of this approach is that the integral coupling coefficients can be computed rapidly on-the-fly from a set of matrices representing elementary permutations of the electrons. The cost of computing these elementary matrices depends only on the spin multiplicity and the reference wave function used, not the size of the system. Thus, the local ACPF method discussed here is particularly well suited to the study of large systems. Unfortunately, one major bottleneck not yet addressed by us is the calculation and transformation of the two-electron integrals from the AO to the PAO basis. Currently, this is the only remaining computational limit to the treatment of extremely large molecules with our theory. As was shown by Schütz, Lindh, and Werner,<sup>33,35</sup> integral direct techniques are particularly well suited for use with local correlation methods and can yield algorithms that scale linearly with the size of the system. The use of integral direct techniques is the only remaining barrier to the development of linear scaling local MRSDCI and ACPF methods and work in this direction is ongoing in our group.

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