

# Linear scaling multireference singles and doubles configuration interaction

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A linear scaling multireference singles and doubles configuration interaction (MRSDCI) method has been developed. By using localized bases to span the occupied and virtual subspace, local truncation schemes can be applied in tandem with integral screening to reduce the various bottlenecks in a MRSDCI calculation. Among these, the evaluation of electron repulsion integrals and their subsequent transformation, together with the diagonalization of the large CI Hamiltonian matrix, correspond to the most computationally intensive steps in a MRSDCI calculation. We show that linear scaling is possible within each step. The scaling of the method with system size is explored with a system of linear alkane chains and we proceed to demonstrate this method can produce smooth potential energy surfaces via calculating the dissociation of trans-6-dodecene ( $C_{12}H_{24}$ ) along the central C=C bond. © 2008 American Institute of Physics. [DOI: 10.1063/1.2937443]

## I. INTRODUCTION

*Ab initio* electron correlation methods, among them Møller–Plesset (MP) perturbation theory, coupled cluster (CC), and configuration interaction (CI) can reproduce highly accurate molecular energies and properties. However, these methods are notorious for their poor algorithmic scaling with system size. For example, the commonly used coupled cluster method with inclusion of all singles, doubles, and perturbative triples excitation [CCSD(T)] conventionally scales as  $O(N^7)$  and is only computationally tractable for small chemical systems. For extended systems to be amenable to computational studies, reduced scaling electronic structure methods which incorporate electron correlation treatment are needed.

Local correlation techniques, such as those introduced by Saebø and Pulay,<sup>1–6</sup> can reduce the steep scaling associated with the aforementioned methods, by exploiting the short range dynamic electron correlation ( $r^{-6}$  dependence). Apart from neglecting correlation effects between spatially distant electrons, such methods mostly involve restricting the allowed correlating orbitals for an occupied orbital according to some predefined spatial criteria. More recently, Head-Gordon and co-workers introduced the triatomics in molecules (TRIM) and diatomics in molecules (DIM) schemes.<sup>7,8</sup> At the level of double substitutions, the former requires at least a single excitation from an occupied to a correlating virtual orbital localized on the same atom while the latter enforces two such excitations in order for the configuration state function (CSF) to be retained in the many-body wavefunction.

After introducing local correlation approximations,

evaluation of the electron repulsion integrals (ERIs) and their subsequent transformation to the MO basis scale formally as  $O(N^4)$  and  $O(N^5)$ , respectively, which then will dominate the overall computation. Various methods have been devised to either speed up the processing of ERIs or to avoid the calculation of numerically insignificant quantities altogether via prescreening techniques. For instance, pseudospectral methods as pioneered by Friesner,<sup>9</sup> and subsequently exploited in  $MP_n$  and CI by Martinez *et al.*,<sup>10–15</sup> were used to reduce the bottlenecks associated with the evaluation of ERIs. Murphy *et al.*<sup>16</sup> and Reynolds *et al.*,<sup>17,18</sup> respectively, developed MP2 and CI methods that combined local correlation with pseudospectral techniques for compounded computational savings. More recent approaches to expedite integral evaluation include the application of Cholesky decomposition to the two-electron integrals supermatrix<sup>19–25</sup> and density fitting procedures (also known as resolution of identity).<sup>26–32</sup>

Indeed, reduced scaling algorithms with the above features have been adapted into some of the most common single reference based electron correlation methods [e.g., density fitting MP2 (DF-MP2) and local MP2/CCSD (LMP2/LCCSD)].<sup>33–40</sup> Schütz *et al.* presented the first linear scaling MP and CC algorithm based on localization of the occupied and virtual subspace combined with integral-direct techniques.<sup>41–43</sup> The low cost of their method allows them to accurately examine systems with up to 300 electrons and 1000 basis functions on a single workstation. More recently, Flocke and Bartlett presented a divide-and-conquer implementation of coupled cluster singles and doubles (CCSD), based on the naturally localized hybrid orbitals proposed by Laidig *et al.*,<sup>44</sup> that leads to a linear scaling algorithm.<sup>45</sup>

Although these linear scaling algorithms are very impressive, to date they are based on a single reference model.

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The lack of a general linear scaling, multireference MP or CC method is unfortunate, since multiconfigurational reference states are required to accurately describe cases where near degeneracies exist, such as diradicals, transition metal complexes, and bond dissociation processes. Nevertheless, work is ongoing to extend MP and CC theory for use with multiconfigurational reference states.<sup>46–70</sup> For example, Piecuch and co-workers<sup>71,72</sup> are developing extensions to the noniterative completely renormalized (CR) CC scheme for analysis of bond breaking and vertical excitation energies. Their current method includes multireference MP corrections to CC for a better description of the wavefunction along reaction coordinates. However, the underlying CR-CC formulation retains a scaling of  $O(N^7)$  for the CR-CCSD(T) variant.

By comparison, the CI formalism is easily adapted to incorporate multiconfigurational reference states. Although reduced scaling algorithms have also been developed for CI,<sup>1,2,13,17,18,43,73–75</sup> the lack of size extensivity in truncated CI can severely limit its accuracy in large systems. To this end, Ahlrichs and co-workers developed a size extensive modification of multi-reference singles and doubles CI (MRSDCI) known as the averaged coupled pair functional (ACPF) theory.<sup>76–78</sup> Venkanathan *et al.* later developed a local MRSDCI algorithm with the ACPF correction incorporated, which scales between  $O(N^3)$  and  $O(N^4)$ .<sup>79</sup> The ACPF size extensivity modification to the reduced scaling local MRSDCI algorithm retained size extensivity upon local correlation truncation.

The aim of the present work is to reduce our cubic-to-quartic scaling MRSDCI algorithm<sup>75</sup> to linear scaling by eliminating the last remaining bottlenecks. This is accomplished via integral screening that is carried out during each of the computationally intensive steps of the CI calculation: (i) evaluation of ERIs, (ii) transformation of ERIs to their localized bases, (iii) Hamiltonian-CI ( $\sigma$ ) vector product formation. As a result, each of these steps can be made to scale linearly with system size. We investigate the scaling and accuracy of the method with system size using a series of linear alkane chains. Finally, we employ the method to calculate the potential energy surface (PES) for the dissociation of trans-6-dodecene ( $C_{12}H_{24}$ ) along the central C=C bond, in order to determine if this linear scaling version of MRSDCI retains smooth PESs and accuracy.

## II. THEORY

A detailed discussion of the MRSDCI formulation in an orthogonal basis can be found in the review by Saunders and van Lenthe,<sup>80</sup> while the underlying principles behind our local implementation of the MRSDCI method can be found elsewhere.<sup>75</sup> Here, we focus on the remaining bottlenecks in our previous algorithm.

In brief, to exploit the short ranged nature of electron correlation, localized orbitals are used to span the occupied and the virtual subspaces. Localized orbitals in the occupied subspace can be obtained by a unitary transformation of canonical Hartree-Fock (HF) orbitals, e.g., using the Boys localization procedure.<sup>81</sup> Projected atomic orbitals (PAOs) gen-

erated by projecting the atomic orbital basis functions into the virtual subspace are used as correlating orbitals.<sup>1</sup> The PAOs have the important properties of being inherently localized and orthogonal to the occupied subspace even though they are not orthogonal to one another. As a result, two local truncation schemes, namely, weak pairs (WP) and truncation of virtuals (TOV),<sup>1–6</sup> can be applied to reduce computation cost. The TOV approximation restricts the number of PAOs into which an electron pair can be excited from orbitals ( $ij$ ) to those PAOs which are spatially close to orbitals  $i$  and  $j$ . Consequently, the number of correlating PAOs for any given hole orbital pair ( $ij$ ) eventually will be independent of system size for some preset spatial criterion. The WP approximation takes into account that spatially distant pairs of electrons are only very weakly correlated and therefore their contribution to the electron correlation energy may be neglected, leading to a linearly increasing number of correlated electron pairs in the asymptotic limit.

### A. Evaluation of electron repulsion integrals (ERIs)

As a prerequisite to a CI algorithm that scales linearly, the number of computed ERIs,

$$(\mu\nu|\rho\sigma) = \int \int \chi_\mu(1)\chi_\nu(1)r_{12}^{-1}\chi_\rho(2)\chi_\sigma(2)dr_1dr_2, \quad (1)$$

should scale linearly as well. In conventional CI methods, all ERIs are calculated, transformed, and held in peripheral storage. For large molecules, the required disk space requirement frequently exceeds available capacity. Even though Eq. (1) suggests that the total number of ERIs has a formal scaling of  $O(N^4)$ , the differential overlap within each pair of basis functions ( $\chi_\mu, \chi_\nu$ ) decays exponentially, leading to a linearly increasing number of ( $\chi_\mu, \chi_\nu$ ) pairs in the asymptotic limit. Unfortunately, the long range coupling of the Coulomb operator,  $1/r$ , leads to an overall asymptotic scaling of  $O(N^2)$  in the total number of ERIs. To this end, there are established methods to avoid the calculation of numerically small integrals by performing integral prescreening of two-electron integrals at the shell level. For example, Häser and Ahlrichs used the Cauchy-Schwarz inequality to obtain a rigorous upper bound for the ERIs in shell batches.<sup>82</sup> More recently, Ochsenfeld and co-workers developed the multipole-based integral estimate (MBIE) method, which was shown to be much more effective at leaving out numerically small ERIs.<sup>83,84</sup>

In this work, we follow the approach of Schütz *et al.*<sup>42,43</sup> by using test densities as a second criterion in addition to the Cauchy-Schwarz upper bound, to achieve linear scaling. The prescreening of the integrals to be evaluated is performed at the shell level according to a test quantity,  $\text{Thr}_{\text{AO}}$ , defined as

$$\text{Max}(D_{\nu\sigma}^{\text{max}}, D_{\mu\rho}^{\text{max}})|(\mu\nu|\mu\nu)|^{1/2}|(\rho\sigma|\rho\sigma)|^{1/2} \leq \text{Thr}_{\text{AO}}, \quad (2)$$

$$D_{\nu\sigma}^{\text{max}} = \text{Max}_{ij \in P}(L_{\sigma i}L_{\nu j}). \quad (3)$$

This test density  $D_{\nu\sigma}^{\text{max}}$  represents the maximum product of localized molecular orbital (LMO) transformation coefficients  $\{L_{\sigma i}\}$  required to transform atomic orbitals  $\sigma$  and  $\nu$  to

the LMO basis. In addition, the domain  $P$  is limited by the weak pairs approximation to orbitals  $i$  and  $j$  which are in close proximity and as such the test densities will be sparse when a localized basis is used. Whenever the estimate in Eq. (2) falls below  $\text{Thr}_{\text{AO}}$ , the integral will not be computed. By performing integral prescreening prior to the actual computation of the ERIs, the number of the evaluated ERIs can be made to scale linearly. This is a necessary first step towards a

linear scaling algorithm but it is not sufficient. The subsequent transformation of the integrals to the localized bases also must be made linear scaling, as we discuss next.

## B. Transformation of ERIs to localized bases

The transformation of ERIs into the molecular orbital basis is commonly divided into four separate quarter-transformation steps (denoted by  $Q1$ ,  $Q2$ ,  $Q3$ , and  $Q4$ ).

$$(ij|ab) = \left[ \sum_{\sigma} P_{\sigma b} \left[ \sum_{\rho} P_{\rho a} \left[ \sum_{\nu} L_{ij} \left[ \sum_{\mu} L_{\mu i} (\mu\nu|\rho\sigma) \right] \right] \right] \right]_{Q1} \right]_{Q2} \right]_{Q3} \right]_{Q4}.$$

A straightforward implementation of the transformation involving four consecutive loops over each index scales approximately as  $O(N^5)$ , but this steep scaling can be surmounted if rigorous screening procedures are carried out at each step of the transformation process. Following the work of Schütz *et al.*,<sup>42,43</sup> we first exploit the fact that the number of significant LMO coefficients is already independent of system size due to the localized nature of the atomic orbitals. For example, in the first transformation step denoted as  $Q1$ , the following operation is carried out:

$$(i\nu|\rho\sigma) = \sum_{\mu} L_{\mu i} (\mu\nu|\rho\sigma), \quad (4)$$

where  $L_{\mu i}$  transforms the AO index  $\mu$  to the LMO index  $i$ . Thus, an effective screening test quantity,  $\text{Thr}_{Q1}$ , for this transformation step would be

$$D_{\mu\nu}^{i,\max} |(\mu\nu|\mu\nu)|^{1/2} |(\rho\sigma|\rho\sigma)|^{1/2} \leq \text{Thr}_{Q1}, \quad (5)$$

$$D_{\mu\nu}^{i,\max} = L_{\nu j}^{\max} L_{\mu i} \{ij \in P\}, \quad (6)$$

where  $L_{ij}^{\max}$  represents the maximum LMO coefficient that will be used in the subsequent  $Q2$  transformation step, for some LMO  $j$  which lies in the domain of  $i$  in a local truncation scheme. If the product of the Cauchy–Schwarz estimate and the test density  $D_{\mu\nu}^{i,\max}$  falls below the preset threshold, then we do not need to compute and store that partially transformed integral. In addition, these test densities are necessarily sparse due to the localized nature of the orbitals. Analogous screening methods are used in the subsequent  $Q2$ ,  $Q3$ , and  $Q4$  transformation steps to generate a very much reduced list of MO integrals. We note that our method of integral screening matches up precisely with the method used by Schütz and Werner<sup>43</sup> in their linear scaling local coupled cluster singles and doubles (LCCSD) theory.

## C. $\sigma$ vector formation

The matrix formulation of the direct CI method requires large matrix diagonalizations to solve the eigenvalue problem  $\mathbf{HC}=\mathbf{EC}$ .<sup>85</sup> Standard methods for diagonalizing symmetric  $N \times N$  matrices typically scale as  $O(N^3)$  and are unsuitable since the storage and computational time

requirements would be untenable even for chemical systems of moderate size, typically involving millions of configuration state functions. Instead, the Davidson diagonalization algorithm<sup>86</sup> is routinely used for this purpose, whereby the CI vector  $\mathbf{C}$  that contains the CI expansion coefficients is iteratively updated starting from some initial guess via

$$\delta C_i = \frac{EC_i - Z_i}{H_{ii} - E}. \quad (7)$$

Constructing the  $\sigma$  vector  $\mathbf{Z}$ , which is the product of the Hamiltonian matrix  $\mathbf{H}$  and the CI vector  $\mathbf{C}$ , is by far the most computationally intensive step in a MRSDCI calculation. In practice, the  $\sigma$  vector is computed piecewise by matrix multiplication between portions of the Hamiltonian matrix and the corresponding portion of the CI vector.

$$Z_i = \sum_j H_{ij} C_j. \quad (8)$$

By applying the WP and TOV approximations, the cost to construct the  $\sigma$  vector is massively reduced by shrinking the size of  $\mathbf{H}$  and  $\mathbf{C}$ . To illustrate, consider computing the components of the  $\sigma$  vector involving the  $(ab|cd)$  class of electron integrals where indices  $a$ ,  $b$ ,  $c$ , and  $d$  refer to external (virtual or initially unoccupied) orbitals,

$$Z_{ac}^{\lambda} = \sum_{bd} (ab|cd) C_{bd}^{\lambda}. \quad (9)$$

Here,  $\lambda$  indexes the internal (initially occupied)  $N-2$  electron CSFs while  $C_{bd}^{\lambda}$  is the corresponding portion of the CI vector. In a nonlocal MRSDCI setting, the computation of  $Z_{ac}^{\lambda}$  involving the  $(ab|cd)$  integrals scales quartically with the number of external orbitals,  $N_v$ , and quadratically with the number of internal orbitals,  $N_i$  (since there are approximately  $N_i^2$  internal  $N-2$  configurations). The WP approximation reduces the total  $Z_{ac}^{\lambda}$  required by eliminating all  $\lambda$  with hole orbital pairs  $(ij)$  that are weak pairs.

$$Z_{ac}^{\lambda,\text{WP}} = \sum_{b,d} (ab|cd) C_{bd}^{\lambda} \{ij \in P\}. \quad (10)$$

As such, the scaling in the computation of  $Z_{ac}^{\lambda}$  is then reduced formally from  $N_i^2 N_v^4$  to  $AN_i N_v^4$ , where  $A$  represents the

asymptotic domain size of the internal space configurations. The TOV approximation then can be used to reduce the cost associated with external orbitals by selecting a best set of correlating orbitals for a given internal orbital. The physical rationale here is that the most effective correlating orbitals are those that are spatially close to the internal orbitals involved in the excitation. Hence, this necessitates the use of PAOs to span the virtual space, which are inherently localized. Under the TOV approximation, excitations from the internal orbitals  $i$  and  $j$ , to PAOs  $p$ ,  $q$ ,  $r$ , and  $s$  are neglected if these PAOs are not spatially close to  $i$  and  $j$ .

The new calculation of  $\mathbf{Z}$  in the PAO basis is as follows:<sup>75</sup>

$$Z_{pq}^{\lambda, \text{WP, TOV}} = \sum_{r,s} (pr|qs) C_{rs}^{\lambda} \{p, q, r, s \in [ij]_p\}. \quad (11)$$

Imposition of the TOV approximation restricts the sum over  $r$  and  $s$  to only the PAOs in the virtual domain of the internal configuration,  $\lambda$ . Since the untruncated virtual space tends to be quite large, the TOV approximation leads to substantial savings. With the inclusion of TOV, the formal scaling is now reduced from  $AN_i N_v^4$  to  $AA'N_i$ , where  $A'$  is the asymptotic domain size of the correlating orbitals. On the whole, the formal scaling now reduces to a linear fashion by eliminating the  $N_v^4$  dependence via the TOV approximation (by reducing to a constant virtual domain size asymptotically) and by reducing the dependence on the internal orbitals from  $N_i^2$  to  $N_i$  via the WP approximation.

Next we consider the construction of the  $\sigma$  vector  $\mathbf{Z}$  involving the class of integrals with four internal indices ( $ij|kl$ ) in the PAO basis<sup>75</sup>

$$Z_{rs}^{\lambda} = \sum_{\mu, p, q} A_{ijkl}^{\lambda\mu} (ij|kl) S_{rp} C_{pq}^{\mu} S_{qs}. \quad (12)$$

$\lambda$  and  $\mu$  index the internal  $N-2$  electron CSFs and  $A_{ijkl}^{\lambda\mu}$  is a constant that depends on the internal occupation pattern and spin coupling. This sum arises from the coupling of doubly excited CSFs that differ from each other by two internal orbitals. Since the virtual domain of each internal CSF is different and in general is nonorthogonal to other virtual domains, extra contractions with overlap matrices,  $S_{rp}$  and  $S_{qs}$ , are necessary, which add to the computational overhead. Nevertheless, like the case before, the WP and TOV approximation will ensure that the virtual domain of each internal CSF will reach a constant value while the total number of internal CSFs will increase linearly. Hence, this does not detract from the linear scaling potential of this method. In our work, we also introduce additional screening so that electron integrals which fall below a preset threshold value will not be used to construct the  $\sigma$  vector.

The  $\sigma$  vector construction is done using integrals in the nonorthogonal PAO basis, but the actual diagonalization of the CI Hamiltonian matrix must be performed in an orthogonal basis to avoid solving a generalized eigenvalue problem. A temporary orthogonal basis can be obtained by canonical orthogonalization of the PAOs in the domain of each internal CSF. Even though CSFs with different internal configurations will have different virtual domains which are nonorthogonal, the mutual orthogonality of the CSFs is maintained

due to the internal orbitals which are orthogonal. The virtual domain for each internal CSF is different and, as such, a separate transformation matrix is required for each internal CSF. Accordingly, each portion of the  $\sigma$  vector constructed initially using integrals in the nonorthogonal PAO basis is transformed to their respective temporary orthogonal PAO bases.<sup>75</sup> From a logistical standpoint, forming the Hamiltonian matrix elements (i.e., the ERIs) involving external indices in the nonorthogonal PAO basis is advantageous, since it obviates the need to otherwise transform the integrals into the many temporary orthogonal bases at the onset.

Unfortunately, constructing the Davidson preconditioner requires the diagonal matrix elements of the CI Hamiltonian matrix ( $H_{ii}-E$ ) to be formed in an orthogonal basis [Eq. (7)]. Since integrals containing external indices are in their nonorthogonal PAO basis, the necessary transformation is

$$(tt|uu) = \sum_{p,q \in \{i,j\}} (pp|qq) T_{ip} T_{ip} T_{uq} T_{uq}, \quad (13)$$

where  $t, u$  refers to external indices in the orthogonal PAO basis while  $T_{ip}, T_{uq}$  are the transformation matrices. Even though this cumbersome procedure is alleviated by the fact that the diagonal elements constitutes only a relatively small subset of integrals corresponding to Coulomb and exchange types such as  $(pp|pp)$ ,  $(pp|qq)$ , and  $(pq|pq)$ , it will become increasingly expensive as the system size increases, since separate transformation matrices have to be generated by orthogonalization of the virtual orbitals for each of the millions of CSFs in addition to the actual transformation in Eq. (13).

To cut down on the computational expense required to form the preconditioner, an alternative scheme is considered here. In the first step, the entire set of PAOs is canonically orthogonalized after removing their linear dependencies. The diagonal integrals are then transformed into this new orthogonal basis. Subsequently, the diagonal integrals are sorted into Coulomb and exchange types and the average of each class is computed. Accordingly, during the construction of the preconditioner, whenever diagonal integrals involving external indices of each type are required, they are replaced with one of the relevant averaged integrals. The overhead of this process is negligible compared to the original implementation of strictly forming the preconditioner in the temporary orthogonal PAO bases and the savings will be discussed in the results section.

### III. CALCULATION DETAILS

We have implemented the above formalism as a plug-in to the MOLCAS quantum chemistry package.<sup>87</sup> For local SDCl calculations on the linear alkane chains, localized internal orbitals are generated using the Boys' method.<sup>81</sup> Pipek–Mezey localized internal orbitals are used for the study on the dissociation of trans-6-dodecene ( $C_{12}H_{24}$ ) along the central C=C bond, since the method is known to preserve the separation of  $\sigma$  and  $\pi$  bonds.<sup>88</sup> The virtual subspace is spanned by PAOs in all cases. Additionally, "spheres" and "cylinders" are separately generated in association with each of the internal and external orbitals. These are used to demarcate virtual domains (correlating external

orbitals) for each internal electron pair ( $ij$ ) and to determine if they are spatially far enough away to be considered as weak pairs and thus neglected. The generation of these “spheres” and “cylinders” has been described earlier.<sup>75</sup>

The processing of ERIs is done in an integral-direct fashion (generating the AO ERIs only as needed) during the first transformation step,  $Q1$ . Prescreening of the ERIs is performed at the shell level. The partially transformed integrals for each step after  $Q1$  are stored on disk before retrieval in the subsequent  $Q2$ ,  $Q3$ , and  $Q4$  steps. Once a subsequent step is completed, the partially transformed integrals from the earlier step are discarded; ultimately, only the final transformed integrals are stored on disk. For prescreening of the ERIs, we set  $\text{Thr}_{\text{AO}}=10^{-8}$  while for each of the subsequent transformation steps,  $Q1$ ,  $Q2$ ,  $Q3$ , and  $Q4$ , we find that  $\text{Thr}_{Q1-4}=10^{-9}$  is enough to retain accuracy of the final energies at the  $\mu\text{H}$  level. During the formation of the  $\sigma$  vector, integrals which fall below  $10^{-9}$  are also discarded.

To test whether the various approximations we impose to achieve linear scaling affect the smoothness of potential energy surfaces, we examine the dissociation of the central C=C bond in trans-6-dodecene. In these calculations, the reference wavefunctions for the MRSDCI runs were generated from CASSCF calculations using a 6-31G\*\* basis set. The active space consists of the  $\sigma$ ,  $\sigma^*$ ,  $\pi$ , and  $\pi^*$  orbitals. The bond dissociation energy (BDE) was calculated at 0 K without zero point corrections, since we are only interested here in comparing the exact MRSDCI curve to curves involving truncation and screening.

## IV. RESULTS AND DISCUSSION

### A. Scaling of total CSFs with system size

The WP and TOV approximations applied to MRSDCI have been analyzed previously for efficiency and accuracy.<sup>74,75</sup> Here, we examine the effects of introducing additional integral screening on the local MRSDCI procedure in each of the rate limiting steps. The scaling is explored by examining a system of straight chain alkanes ( $\text{C}_n\text{H}_{2n+2}$ ) with a 6-31G\*\* basis set. Although alkanes have a somewhat simple electronic structure, their simplicity also leads to a clean analysis of the scaling of the method. We recognize that linear alkanes represent a best case for linear scaling due to their quasi-one-dimensional structure. However, the only difference expected for more 3D-like structure is that the onset of linear scaling will be at a larger number of atoms.

The length of the CI vector and the size of the Hamiltonian matrix depend on the total number of CSFs. Even in a normal implementation of the first order interaction space (FOIS) where a maximum of double substitutions is allowed from any given reference configuration, the total number of CSFs grows quickly with the size of the basis set. In our local truncation schemes with the WP and TOV approximations, the latter controls the number of excited configurations generated from an ( $ij$ ) pair while the number of correlated electron pairs, ( $ij$ ), is limited to only those which are spatially close due to the WP approximation. As such, the total

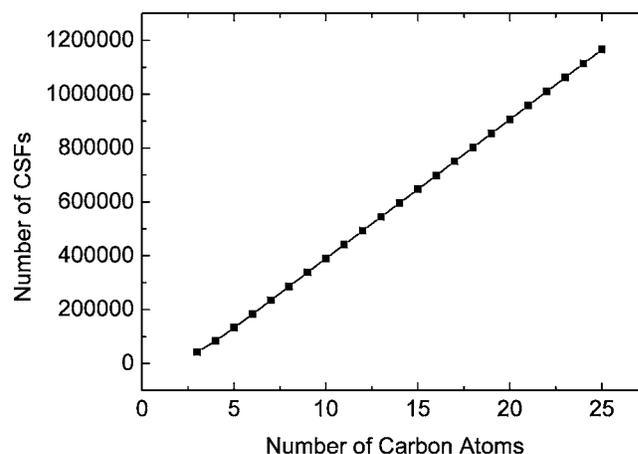


FIG. 1. Number of CSFs included for the series of alkanes,  $\text{C}_n\text{H}_{2n+2}$  using a 6-31G\*\* basis set. Applying the WP/TOV approximation leads to a linear increase in the number of CSFs with system size.

number of excited configurations generated from a reference configuration can be made to scale linearly with system size. The trend is summarized in Fig. 1.

### B. Accuracy of local MRSDCI with integral screening

Previously, we reported that using 6-31G or 6-31G\*\* basis sets, the WP approximation alone recovers approximately 99% of the correlation energy relative to nonlocal MRSDCI.<sup>74,75</sup> When the TOV approximation is used in conjunction with WP, about 98% of the correlation energy is recovered together with large savings in computational overhead.<sup>75</sup> Here, adding integral prescreening to WP +TOV leads to further reduction in CPU time while retaining accuracy. For comparison, the linear aliphatic alkane chains  $\text{C}_n\text{H}_{2n+2}$  ( $n=3-14$ ) are studied using both the 6-31G and 6-31G\*\* basis set with results summarized in Tables I and II. It is evident that introduction of integral prescreening reproduces the total energies to within  $\mu\text{H}$  for both basis sets and for all molecules considered. The percentage of correlation

TABLE I. SDCI total energies for the alkane series  $\text{C}_n\text{H}_{2n+2}$  ( $n=3-14$ ) using a 6-31G basis set.

Molecule	SDCI	LSDCI <sup>a</sup>	LSDCI-IS <sup>b</sup>	% correl. $E^c$
$\text{C}_3\text{H}_8$	-118.507 039 7	-118.504 671 2	-118.504 671 2	99.2
$\text{C}_4\text{H}_{10}$	-157.607 192 6	-157.603 071 3	-157.603 071 3	98.9
$\text{C}_5\text{H}_{12}$	-196.703 235 5	-196.697 193 9	-196.697 194 2	98.7
$\text{C}_6\text{H}_{14}$	-235.795 784 1	-235.788 015 7	-135.788 016 0	98.5
$\text{C}_7\text{H}_{16}$	-274.885 273 4	-274.875 863 7	-274.875 864 5	98.4
$\text{C}_8\text{H}_{18}$	-313.972 066 9	-313.961 086 1	-313.961 086 3	98.3
$\text{C}_9\text{H}_{20}$	-353.056 461 6	-353.044 014 6	-353.044 015 0	98.3
$\text{C}_{10}\text{H}_{22}$	-392.138 700 6	-392.124 821 3	-392.124 822 5	98.3
$\text{C}_{11}\text{H}_{24}$	-431.218 993 1	-431.203 795 5	-431.203 795 7	98.2
$\text{C}_{12}\text{H}_{26}$	-470.297 503 5	-470.281 013 0	-470.281 014 0	98.2
$\text{C}_{13}\text{H}_{28}$	-509.374 387 9	-509.356 691 5	-509.356 692 2	98.2
$\text{C}_{14}\text{H}_{30}$	-548.449 777 9	-548.430 876 7	-548.430 877 7	98.2

<sup>a</sup>Local SDCI with WP/TOV approximation.

<sup>b</sup>Local SDCI with WP/TOV augmented with integral screening using threshold given in the text.

<sup>c</sup>The percentage correlation energy recovered (% correl.  $E$ ) is the same for LSDCI and LSDCI-IS, since their total energies agree to within  $\mu\text{H}$ .

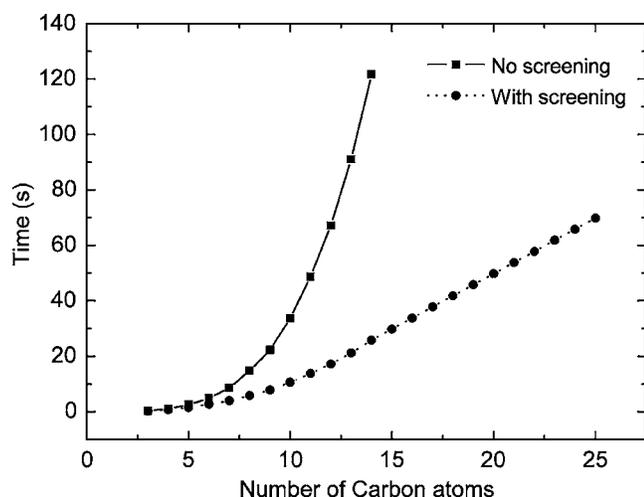
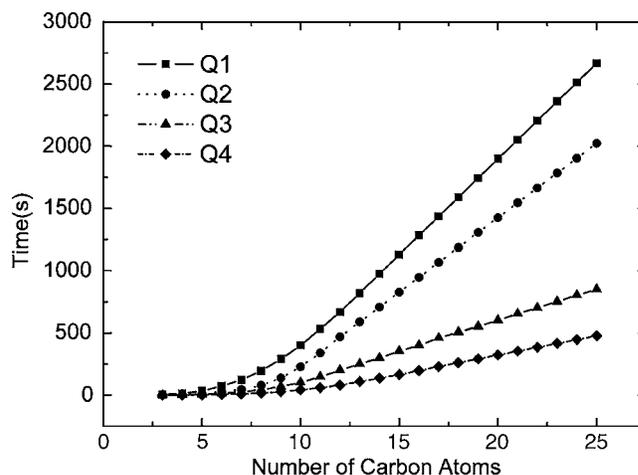
TABLE II. SDCI total energies for the alkane series  $C_nH_{2n+2}$  ( $n=3-10$ ) using a 6-31G\*\* basis set.

Molecule	SDCI	ISDCI <sup>a</sup>	LSDCI-IS <sup>b</sup>	% correl. $E^c$
C <sub>3</sub> H <sub>8</sub>	-118.726 898 7	-118.723 643 4	-118.723 643 4	99.3
C <sub>4</sub> H <sub>10</sub>	-157.886 830 8	-157.881 548 9	-157.881 548 9	99.1
C <sub>5</sub> H <sub>12</sub>	-197.040 055 1	-197.032 883 2	-197.032 883 0	99.0
C <sub>6</sub> H <sub>14</sub>	-236.187 661 3	-236.178 740 9	-236.178 740 5	98.9
C <sub>7</sub> H <sub>16</sub>	-275.330 436 7	-275.319 903 6	-275.319 900 0	98.8
C <sub>8</sub> H <sub>18</sub>	-314.469 005 1	-314.456 974 8	-314.456 974 1	98.8
C <sub>9</sub> H <sub>20</sub>	-353.603 861 3	-353.590 420 9	-353.590 420 0	98.8
C <sub>10</sub> H <sub>22</sub>	-392.735 411 0	-392.720 647 9	-392.720 647 0	98.8

<sup>a</sup>Local SDCI with WP/TOV approximation.<sup>b</sup>Local SDCI with WP/TOV augmented with integral screening using threshold given in the text.<sup>c</sup>The percentage correlation energy recovered (% correl.  $E$ ) for both LSDCI and LSDCI-IS.

energy recovered over this range of molecular sizes is 99.2–98.2; this is determined entirely by the WP+TOV approximation.

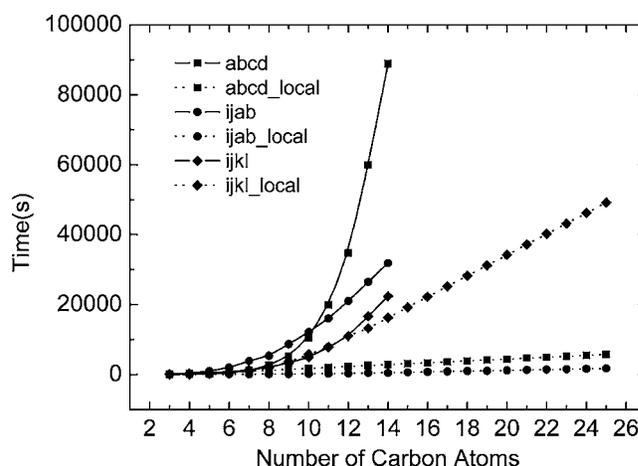
In earlier work, we reported that inclusion of diffuse functions in Pople-type basis sets can be problematic (accuracy degrades) in local MRSDCI due to their long range character, which are not optimal for local correlation methods.<sup>73,79</sup> In the present context, our nonlocal, non-screened (exact) MRSDCI code cannot handle molecules larger than C<sub>7</sub>H<sub>16</sub> when a 6-31+G\*\* basis set is used. For this size of molecule, the corresponding local, screened MRSDCI recovers 97.9% of the correlation energy of non-local, non-screened MRSDCI, which is only slightly worse than the range of correlation energy recovery given above for smaller basis sets. This suggests that diffuse functions can be used in local, screened MRSDCI, with the caveat that the accuracy does decline slightly. The accuracy might improve when such diffuse functions are contracted with more compact components, such as in the ANO-RCC basis sets, but these basis sets are too large to use in MRSDCI on any reasonably sized molecules; so that we cannot test this hypothesis at present.

FIG. 2. CPU time (seconds) expended for the evaluation of 6-31G\*\* basis electron repulsion integrals (ERIs) with increasing hydrocarbon chain length. When integral prescreening is applied,  $\text{Thr}_{\text{AO}}$  is set to  $10^{-8}$ .FIG. 3. Scaling of each quarter-transformation step,  $Q_1$ ,  $Q_2$ ,  $Q_3$ , and  $Q_4$ . The threshold for each transformation,  $\text{Thr}_{Q_{1-4}}$ , is set to  $10^{-9}$ .

### C. Scaling of the method with system size

Figures 2 and 3 and 4 summarize the scaling pattern for the three bottlenecks in our MRSDCI algorithm: (i) evaluation of the ERIs, (ii) transformation of the ERIs to the localized basis, and (iii) construction of the  $\sigma$  vector for diagonalizing the CI Hamiltonian matrix. Each of the above steps must scale linearly for an overall linear scaling code.

In the evaluation of ERIs, we apply the screening parameter,  $\text{Thr}_{\text{AO}}$ , to a test set of linear hydrocarbon chains (C<sub>3</sub>H<sub>8</sub>–C<sub>25</sub>H<sub>52</sub>) using a 6-31G\*\* basis set. Figure 2 shows that the CPU time expended in ERI evaluation when  $\text{Thr}_{\text{AO}}$  is set to  $10^{-8}$ . When the timings in Fig. 2 are examined along with the data in Table II, we see that the precision of the local correlation energy is preserved to the  $\mu\text{H}$  level, while dramatically reducing the integral computation time. The overhead associated with calculating the Cauchy–Schwarz upper bounds and test densities is negligible compared with the total time taken for the computation of the ERIs, even for the largest hydrocarbon considered. For instance, in the case of the largest hydrocarbon considered, C<sub>25</sub>H<sub>52</sub>, computing the test densities amounts to less than 0.1% of the total computation time.

FIG. 4. Scaling of the  $\sigma$  vector formation for three classes of integrals,  $(ij|kl)$ ,  $(ij|ab)$ , and  $(ab|cd)$ , with and without local truncation and integral prescreening.

With the prescreening of ERIs in place, the onset of linear scaling occurs around  $C_{11}H_{24}$ . This can be altered by changing the screening parameter,  $\text{Thr}_{\text{AO}}$ . However, we find that this chosen threshold is sufficient to maintain  $\mu\text{H}$  accuracy in the final total energies.

The scaling for each transformation steps  $Q_1$ ,  $Q_2$ ,  $Q_3$ , and  $Q_4$  is summarized in Fig. 3. Here the onset of linear scaling also occurs around  $C_{11}H_{24}$  when  $\text{Thr}_{Q_{1-4}}$  were each set to  $10^{-9}$ . The final transformed integrals are written to disk before they are retrieved at a later stage to form the CI matrix elements in an “on-the-fly” fashion. Using the very much truncated list of transformed integrals reduces the demand on secondary storage and also speeds up the  $\sigma$  vector formation, which now involves far fewer matrix multiplications. Taken together, this allows us to perform MRSDCI calculations on much larger molecules than has been possible before.

The time required for the formation of the  $\sigma$  vector  $\mathbf{Z}$  dominates the calculation even in a local truncation setting. For illustration, the scaling behavior for constructing the portions of the  $\sigma$  vector that involve three different classes of integrals,  $(ij|kl)$ ,  $(ij|ab)$ , and  $(ab|cd)$ , are shown in Fig. 4. The comparison is between a nonlocal MRSDCI calculation and a local MRSDCI one with additional integral prescreening. The most expensive step in a nonlocal MRSDCI calculation are the matrix multiplications of the  $(ab|cd)$  integrals with the CI vector  $\mathbf{C}$ . This is drastically reduced in local MRSDCI augmented with integral screening primarily because of the TOV approximation. In contrast to nonlocal MRSDCI, forming the portions of the  $\sigma$  vector that involve the  $(ij|kl)$  integrals dominates the cost of a local calculation due to the extra matrix multiplications involving the overlap matrix, but the process scales linearly when integral screening is incorporated into the local MRSDCI implementation.

### D. Convergence in Davidson's diagonalization

Regarding the formation of the preconditioner ( $H_{ii}-E$ ) prior to diagonalization of the CI matrix, use of the approximate preconditioner outlined earlier works very well to reduce the total computation time without sacrificing numerical accuracy. For example, building the approximate preconditioner for  $C_{25}H_{52}$  takes only 2.3% of the time taken to assemble the exact preconditioner in the original temporary orthogonal PAO basis (Fig. 5).

Importantly, the approximate nature of this approach does not affect the final results as long as the scheme converges, even though it may affect the rate of convergence. Since the  $\sigma$  vector construction during each iteration is typically the most computationally demanding aspect of a CI calculation, savings derived from a quickly assembled preconditioner will be negated by increases in the overall number of iterations. In our work, the approximated preconditioner works as well as the original implementation for most molecules and, at its worst, lengthen the calculation by only one iteration (Table III).

So far, we have shown that the major bottlenecks in our implementation can be reduced to scale linearly and thus the overall computation effort will also display this trend. The total CPU time taken for SDCI calculations on the linear

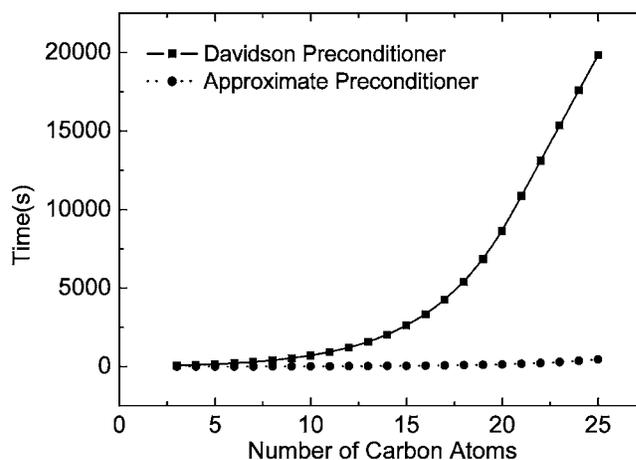


FIG. 5. Time taken to construct the preconditioner for Davidson diagonalization of the CI Hamiltonian matrix.

alkane chains  $C_nH_{2n+2}$  ( $n=3-25$ ) is shown in Fig. 6. This includes all the bottlenecks previously mentioned along with the evaluation of test densities which are used for integral screening and the setting up of orbital domains used in local truncations. In addition, the total CPU time is the duration for each system to complete nine iterations of Davidson's diagonalization. The onset of linear scaling again occurs around  $C_{11}H_{24}$  which is similar to Figs. 2-4.

### E. Local MRSDCI applied to bond dissociation of trans-6-dodecene

We previously showed that the WP/TOV approximation generates potential energy curves that are smooth along the reaction coordinate, provided the orbital domains are kept constant along the reaction coordinate.<sup>75</sup> Here, we examine the bond dissociation curve for trans-6-dodecene,  $C_{12}H_{24}$ , along the central  $C=C$  bond using a 6-31G\*\* basis set to test whether this remains true upon addition of integral screening. As displayed in Fig. 7, the BDE calculated using non-local MRSDCI is 710 kJ/mol whereas our local MRSDCI with or without integral screening leads to a consistent value of 707 kJ/mol, demonstrating the high accuracy retained in our linear scaling MRSDCI algorithm. Electron correlation effects are more important at the equilibrium geometry of 1.36 Å than when the two separated fragments of trans-6-dodecene are far away and the neglect of long range correlation effects may account for the slightly lower BDE in the local method.

The dissociation curves from our local calculations remain visually smooth. Apart from properly describing the bond dissociation process, a smooth PES free from local/spurious minima and/or discontinuities facilitates the evaluation of energy gradients. In local correlation methods, the virtual domain for a hole orbital is dependent on the molecular structure, which changes along the reaction coordinate of the PES, potentially leading to discontinuities. In our implementation, the active space is linked using a “cylinder” of growing length that ensures the same set of correlating orbitals are used throughout for the evaluation of the PES.<sup>75</sup> As a result, the cross section of the PES for the homolytic dissociation of trans-6-dodecene remains smooth.

TABLE III. Number of Iterations required to converged the CI calculation to  $10^{-7}$  H.

Molecule	Iterations <sup>a</sup>	Iterations <sup>b</sup>	Molecule	Iterations <sup>a</sup>	Iterations <sup>b</sup>
C <sub>3</sub> H <sub>8</sub>	7	7	C <sub>15</sub> H <sub>32</sub>	10	10
C <sub>4</sub> H <sub>10</sub>	7	7	C <sub>16</sub> H <sub>34</sub>	10	10
C <sub>5</sub> H <sub>12</sub>	8	8	C <sub>17</sub> H <sub>36</sub>	10	10
C <sub>6</sub> H <sub>14</sub>	8	8	C <sub>18</sub> H <sub>38</sub>	11	11
C <sub>7</sub> H <sub>16</sub>	8	8	C <sub>19</sub> H <sub>40</sub>	11	11
C <sub>8</sub> H <sub>18</sub>	9	9	C <sub>20</sub> H <sub>42</sub>	11	12
C <sub>9</sub> H <sub>20</sub>	9	10	C <sub>21</sub> H <sub>44</sub>	11	11
C <sub>10</sub> H <sub>22</sub>	9	9	C <sub>22</sub> H <sub>46</sub>	11	11
C <sub>11</sub> H <sub>24</sub>	9	9	C <sub>23</sub> H <sub>48</sub>	11	11
C <sub>12</sub> H <sub>26</sub>	9	9	C <sub>24</sub> H <sub>50</sub>	11	11
C <sub>13</sub> H <sub>28</sub>	9	9	C <sub>25</sub> H <sub>52</sub>	11	11
C <sub>14</sub> H <sub>30</sub>	9	9			

<sup>a</sup>Exact Davidson preconditioner.<sup>b</sup>Approximate preconditioner.

## V. CONCLUSIONS

We have developed a linear scaling local correlation implementation of MRSDCI. The rate limiting steps in our previous local MRSDCI approach were (i) evaluation of ERIs, (ii) transformation of the ERIs to the localized bases, and (iii) diagonalization of the CI Hamiltonian matrix. By using local correlation truncations in tandem with integral screening for all three bottlenecks above, the overall computational overhead is drastically reduced. We benchmarked our method for the series of linear alkanes  $C_nH_{2n+2}$  and showed that local MRSDCI with integral screening leads to linear scaling behavior for the three rate limiting steps while retaining chemical accuracy at the  $\mu$ H level.

In the diagonalization of the CI Hamiltonian matrix, the construction of the Davidson preconditioner requires the diagonal elements ( $H_{ii}$ ) to be formed in an orthogonal basis. Its rigorous construction involves repeated orthogonalization of the external orbitals in the domain of each internal CSFs followed by transformation of the diagonal elements to the new orthogonal basis. This gets increasingly computationally intensive as the system size increases beyond approximately

ten heavy atoms. As such, we introduced an approximate preconditioner that can be quickly assembled and demonstrated that calculations converge as efficiently as with the original preconditioner.

We have also demonstrated for the case of C=C bond dissociation in trans-6-dodecene that our local implementation of MRSDCI with integral screening generates a visually smooth PES that is free from spurious minima and discontinuities. At the same time, we obtain results nearly identical (within 3 kJ/mol) to non-local MRSDCI calculations.

As a final remark, the lack of size extensivity in truncated CI methods such as MRSDCI limits their accuracy when applied to large molecules. To this end, we previously implemented<sup>79</sup> an MR-ACPF size extensive modification to the local MRSDCI framework. Our local MRACPF method recovers more of the correlation energy than LMRSDCI and yields BDEs that are in closer agreement with experimental values. Work is underway to extend our linear scaling LMRSDCI work to incorporate the MR-ACPF correction.

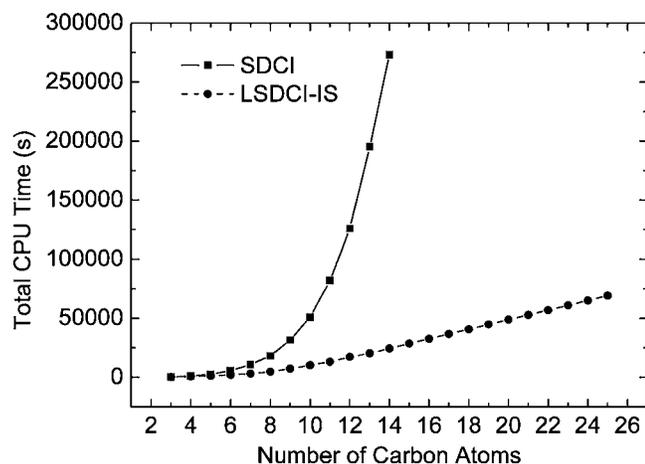


FIG. 6. Total CPU time for SDCI and LSDCI-IS (LSDCI augmented with integral screening) calculations of  $C_nH_{2n+2}$  ( $n=3-25$ ) using a 6-31G\*\* basis set. Nine iterations of Davidson's diagonalization were used for each system.

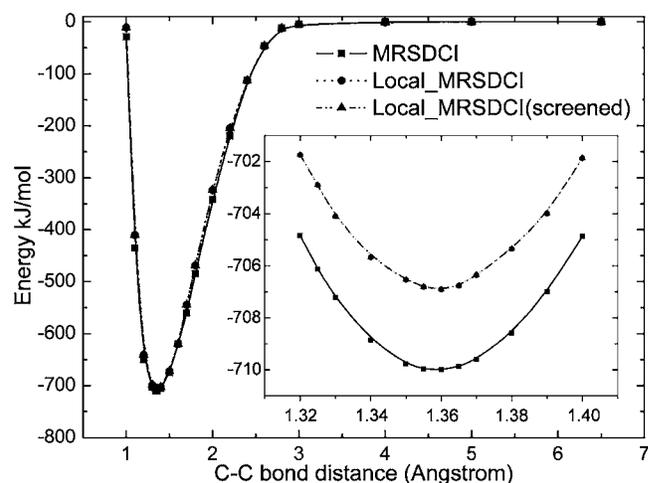


FIG. 7. PES along the reaction coordinate for bond cleavage along the C=C bond in trans-6-dodecene. Inset shows an expanded view of the curves minima.

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