

ARTICLES

Local correlation in the virtual space in multireference singles and doubles configuration interaction

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We describe a multireference configuration interaction method that takes advantage of local correlation methods in both the internal (originally occupied) and external (originally unoccupied or virtual) orbital spaces. In the internal space, implementation of local correlation is trivial and involves neglecting configurations having simultaneous excitations out of widely separated orbitals. In the external space, the method involves restricting the space of allowed correlating orbitals to those localized near the hole orbitals. Of course, this necessitates the use of localized virtual orbitals which in turn requires one to sacrifice the orthogonality of the virtual space. This complicates the formalism substantially, and we discuss the necessary changes to the traditional expressions in detail. The scaling of the method with system size, basis set size, and the average number of allowed virtual orbitals is explored. An examination of systems having up to 8 heavy atoms reveals that the computational costs of the method scales somewhere between the third and fourth power of the size of the system. Furthermore, this reduced scaling method is capable of recovering greater than 97% of the correlation energy. Additionally, we demonstrate that the method can produce smooth potential energy surfaces and recover bond dissociation energies in organic molecules at a fraction of the cost (\geq tenfold less expensive) while retaining accuracy. We go on to use this new reduced scaling approach to predict bond energies in several large organic molecules for which no experimental data are available. © 2003 American Institute of Physics.

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I. INTRODUCTION

It is well known that the cost of *ab initio* quantum chemistry calculations scale very poorly with the size of the system. Accordingly, a great deal of research has been devoted to the development of reduced scaling quantum chemistry methods. Some of the oldest efforts towards reducing the cost of these calculations have been based on local correlation¹ techniques in which one exploits the rapid decay of the Coulomb potential between pairs of electrons. These methods have a long history of success: there have been numerous implementations of highly accurate local Møller–Plesset (MP) perturbation theories^{2–14} and local coupled cluster (CC) theories.^{15–20} The recent work of Schütz and Werner^{17,18} is particularly noteworthy as they have achieved a linear scaling CC method by combining local correlation techniques with integral direct methods.

Compared to CC and MP perturbation theory, there has been much less work devoted to the development of local configuration interaction (CI) techniques. Early on, Saebø and Pulay published a few papers^{21,22} on local CI based on a single closed shell reference, but work in this area was not continued. Certainly, the principle reason most work on local correlation has focused on CC and MP perturbation theory rather than CI is because CI is not rigorously size extensive. However, CI has the important advantage of being straightforwardly used with multiconfigurational reference states.

Although much research has been devoted to extending CC and MP for use with multiconfigurational references, a completely general and computationally practical multireference CC or MP theory is still not available. As a result, CI is still the *ab initio* correlation method of choice for studying systems where near degeneracies occur such as in transition metals or partially cleaved bonds.

Most of the recent work on reduced scaling CI has focused on the development of methods that use local correlation in the internal space and pseudospectral (PS) methods²³ to treat the most costly parts of the external space. Reynolds *et al.* developed local pseudospectral single reference CI methods,^{24,25} and more recently Walter *et al.* have explored analytic and PS versions of local weak pairs multireference singles and doubles CI (MRSDCI).^{26,27} Although the savings obtained in the PS CI methods of Reynolds *et al.* and Walter *et al.* were substantial, PS methods are not easily combined with methods that take advantage of local correlation methods involving truncation of the virtual space. There are many practical reasons why this is the case, but the main reason is that the use of a limited number of virtual orbitals would necessitate the use of extremely small, well-localized numerical quadrature grids in order to realize any computational savings. This would surely limit or destroy the accuracy of the pseudospectral method. Unfortunately, this limitation is rather severe, as the use of PS techniques by

themselves (i.e., without the use of local correlation) can at best lead to a method that scales cubically with the size of the system. As has been shown by Schütz and Werner,¹⁷ methods based on truncation of the virtuals can be made to scale linearly with the size of the system and are therefore more promising than PS techniques.

In this article, we present a local MRSDCI method that extends our previous work^{26,27} by including local correlation in the virtual space for a general multireference wave function. Similar to the work of Saebø and Pulay,^{1-4,22} we do this by excluding terms from our CI expansion involving excitations to virtual orbitals localized far from the hole orbitals. Of course, this scheme requires localized virtual orbitals, and for this purpose we use projected atomic orbitals (PAOs). These orbitals are quite commonly used in local correlation techniques^{2-4,17,18,20,22,24} and are generated by projecting out the internal space from individual atomic orbitals (AOs). Unfortunately, these orbitals have the disadvantage of not being orthogonal to one another and this complicates the usual MRSDCI equations substantially. We discuss here all of the necessary changes to the usual equations and how these are incorporated into our MRSDCI program. We then go on to examine the scaling and performance of the resulting local MRSDCI method with increasing system size and basis set size. Finally, we apply the local MRSDCI method to study a few simple potential energy surfaces and compute some bond dissociation energies (BDEs) in organic molecules. In the discussion of these applications, special emphasis is placed on the use of the local correlation method with multiconfigurational references and the ability of this method to yield smooth potential energy surfaces to describe bond cleavage.

II. THEORY

A. Local correlation approximation

The basic theory behind the local correlation approximation is exceedingly simple and is based upon the rapid decay of the Coulomb potential between pairs of electrons. In the internal space, the local correlation approximation simply involves the neglect or approximation of excitations out of internal orbitals that are widely separated. The simple logic here is that the motion of electrons in widely separated orbitals is only weakly correlated and therefore does not make a substantial contribution to the correlation energy. These weakly-correlated orbitals are referred to as weak-pairs (WP) and we will therefore refer to this approximation as the WP approximation.¹ In our previous work^{26,27} using the WP approximation, the WPs were simply neglected. Certainly, it would have been desirable to approximate the WPs using perturbation theory, as is commonly done in local CC methods. However, it is not straightforward to combine perturbation theory with CI in a consistent manner. This is especially true when a multiconfigurational reference wavefunction is used, as is the case here. Nevertheless, WP methods based on neglecting the WPs can lead to CI methods that recover greater than 99% of the correlation energy using less than 50% of the computational effort.^{26,27} Furthermore, the WP approximation is quite easy to implement. Unfortunately, all

possible excitations to the virtual orbital space are retained for the CSFs which survive the WP approximation. As a result, the WP approximation does not effect the overall scaling of the cost of treating the virtual space, which is by far the most expensive part of a MRSDCI calculation. The details of our implementation of the WP approximation in the MRSDCI method are given elsewhere²⁶ and are not discussed further here.

In the external space, the local correlation approximation is also conceptually simple. The most important excitations for describing the correlation of electrons in a given occupied orbital are those to virtual orbitals localized near that orbital. Such a set of virtual orbitals will be referred to as the “domain” of that orbital and this term shall be used throughout this article to refer to the set of virtual orbitals associated with a given entity. Thus, in order to most efficiently describe electron correlation one should keep *only* excitations to virtual orbitals within the domain of a given internal orbital and neglect or approximate all others. Obviously, the average number of virtual orbitals per domain, \bar{N}_v , will not increase with the size of the system. Rather, this quantity will depend mainly on the size of the basis set. The usual basis sets used in quantum chemistry lead to virtual orbital spaces which are much larger than internal spaces. The savings that can be had through this truncation of the virtuals (TOV) approximation are therefore far more substantial than those available from the WP approximation. Furthermore, the magnitude of the savings from the TOV approximation can be easily estimated by substituting the total number of virtual orbitals, N_v , with \bar{N}_v in all determinations of the cost of conventional nonlocal MRSDCI.

Obviously, the TOV scheme relies on the use of both localized occupied and virtual orbitals. Here, the internal orbitals that are not in the active space are localized using the Boys algorithm,²⁸ which preserves their orthogonality. The active orbitals used in this study are localized naturally as a byproduct of their optimization, by using a generalized valence bond (GVB) SCF wave function.²⁹ If a GVB wave function had not been used, all orbitals could still be localized by means of a Boys transformation. As mentioned previously, localized virtuals are obtained through the use of PAOs. The set of allowed correlating PAOs for a given internal configuration state function (CSF; the product of a spatial orbital configuration and a spin eigenfunction properly antisymmetrized) is determined in a manner similar to the method used for determining the weak pairs in our previous work.²⁶ Briefly, the internal “hole” orbitals that are replaced by virtual orbitals must be enumerated for each $N-1$ or $N-2$ electron internal CSF. Spheres are then associated with these hole orbitals and all the PAOs as follows: First, a list of atoms that contribute most to a given orbital is obtained. The center of the sphere is then determined as an electronic-density-weighted average of the coordinates of the atoms that contribute most to the orbital. The radius of the sphere is then taken to be equal to the maximum separation of any two atoms in the group of atoms contributing most to the orbital multiplied by a scaling factor α . The set of correlating orbitals for a given $N-1$ or $N-2$ electron internal

CSF is taken to be the set of PAOs whose spheres overlap with hole orbitals of the internal CSF.

In our weak-pairs work, we found that values for α of slightly greater than 1.0 lead to CI expansions that contained roughly 50% of the CSFs contained in the nonlocal CI expansions and recovered about 99% of the correlation energy for double- ζ basis sets. Here, the situation is complicated since spheres need to be determined for both the internal and virtual orbital spaces, and it is not obvious whether or not the parameters used in the WP approximation are appropriate in the TOV approximation. Furthermore, it is not immediately obvious whether the parameters used in the TOV approximation should be the same for both the internal and virtual orbital spaces. Unfortunately, we find that optimal CI expansions (i.e., CI expansions giving the highest fraction of the correlation energy with the fewest CSFs) are obtained when different scaling factors are used for the WP and TOV approximations and when different scaling factors are used for the internal and virtual orbital spaces in the application of the TOV approximation. The scaling factor used for the internal orbitals in the TOV approximation is taken to be one-half to two-thirds as large as the scaling factor used in the WP approximation. Similarly, the scaling factor for the PAOs is taken to be smaller than the scaling factor used in the WP approximation. Here, we use either 0.4 or 0.5 for the PAOs. An additional complication arises for active orbitals that are used to describe bond cleavage, as they can become delocalized over two infinitely separated fragments. To treat this situation, we place a cylinder with hemispherical ends around each active orbital. The endpoints of the cylinder are determined by finding the two atoms contributing most to the given active orbital, and the cylinder radius is determined by a chosen input parameter. Again, we find that different cylinder radii should be used in the WP and TOV approximations. For the WP approximation, the cylinder radius is taken to be about 2.0 bohrs and for the TOV approximation it is taken to be about 0.5 bohrs. Using these parameters, we arrive at CI expansions which have average domain sizes of about 50 PAOs and are capable of recovering close to 98% of the correlation energy with standard double- ζ basis sets.

For multiconfigurational references, one could envision cases where ambiguity arises in the determination of hole orbitals for a given internal CSF. However, by far the most common use of a multiconfigurational wave function is to treat chemical phenomena that are well localized (i.e., a bond cleavage or a near degeneracy at a given site). If this is the case, then ambiguities in the determination of the hole orbitals are permissible as all of the active orbitals will be localized in the same region of space and will require more or less the same set of correlating PAOs. Nevertheless, it should be noted that in cases where the active space is delocalized, the method presented here may not perform quite as well.

B. Treatment of a nonorthogonal virtual space: Overview

As we have pointed out, the PAOs are localized but not orthogonal to one another. Furthermore, for every AO one can generate a single PAO and the resulting set of PAOs span *only* the virtual space and not the full space spanned by the

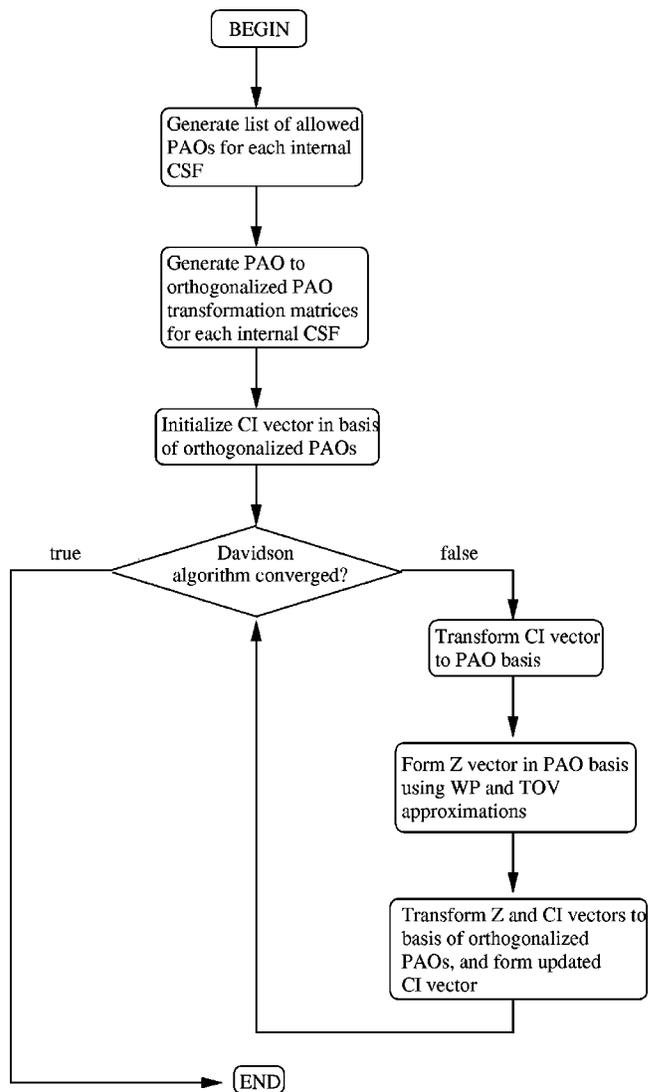


FIG. 1. Flow chart summarizing the steps in a WP+TOV MRSDCI calculation.

AO basis. Thus, there are linear dependencies in the PAO basis. In this section we give an overview of the general strategy used to take these facts into account.

Figure 1 summarizes the steps required to carry out a MRSDCI calculation making use of the WP and TOV approximations. The diagonalization of the CI Hamiltonian using iterative techniques requires successive formation of the product of the Hamiltonian with a trial vector of CI expansion coefficients.³⁰ This vector of expansion coefficients is referred to as the CI vector and will be denoted as \mathbf{C} . The vector resulting from the multiplication is referred to as the Z vector and will be denoted as \mathbf{Z} . This Z vector is used to form a residual vector from which an update to the CI vector, $\delta\mathbf{C}$, is formed,

$$\delta C_i = \frac{E C_i - Z_i}{\hat{H}_{ii} - E}. \quad (1)$$

Here, E is the current approximation to the total energy eigenvalue and \hat{H} is the matrix representation of the Hamil-

tonian in the basis of N -particle CSFs. The index i is used to index the CSFs in the CI expansion and the quantity Z_i is defined as

$$Z_i = \sum_j \hat{H}_{ij} C_j, \quad (2)$$

where the index j is also used to index the CSFs in the CI expansion. Formation of the Z vector constitutes almost all of the computational effort required for diagonalization of the CI Hamiltonian. Very similar to the local CCSD method of Hampel and Werner,²⁰ two bases are used in our local MRSDCI method. The formation of the Z vector takes place in the nonorthogonal, yet local, single-particle PAO basis and this is where the local correlation approximation is included in the MRSDCI. However, it is technically far simpler to carry out the diagonalization in an orthogonal CSF (i.e., N -particle) basis so that one may solve a usual eigenvalue problem rather than a generalized eigenvalue problem. The resulting Z vector is therefore transformed back to an orthogonal CSF basis once it has been formed.

An orthogonal CSF basis can be generated by using CSFs that include virtual orbitals obtained through canonical orthogonalization³¹ of the PAOs in the domain of the internal portion of the CSF. This process involves transforming the PAOs according to a matrix \mathbf{T} that is obtained as the product of the matrix \mathbf{U} and $\mathbf{s}^{-(1/2)}$. The matrix \mathbf{U} consists of the eigenvectors of the overlap matrix of PAOs in the domain of the internal portion of the CSF. The diagonal matrix $\mathbf{s}^{-(1/2)}$ contains the inverse of the square roots of the eigenvalues of the overlap matrix of PAOs in the domain of the internal portion of the 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. The linear dependencies within the PAO domains may be removed during the orthogonalization phase. It should be noted that the generation of the orthogonalized PAOs and the required transformation matrices is done only once at the beginning of the program.

One additional inconvenience arises when carrying out the diagonalization in the orthogonal basis: forming $\delta\mathbf{C}$ requires the diagonal elements of the Hamiltonian for use as preconditioners [see Eq. (1)].³⁰ Of course, these diagonal elements need to be computed in the orthogonal basis. Since the virtual orbital space is different for every internal hole orbital or pair of internal hole orbitals, a different integral transformation will be required for each of them. This situation appears at first to be quite complicated and computationally expensive. However, a number of factors simplify the problem: First, only a small subclass of integrals in the orthogonal basis are needed in order to compute the diagonal elements of the Hamiltonian. More specifically, only the $(t|uu)$, $(tu|tu)$, and $(t|u)$ integrals are required, where t and u are canonically orthogonalized PAOs. Second, the integral transform does not need to be done for the weak pairs, since the WP approximation neglects excitations out of pairs of widely separated orbitals. Third, the transform can be done starting with integrals in the PAO basis. As a result, the transformations only scale as \tilde{N}_v^5 rather than the fourth power

of the number of basis functions, N , times \tilde{N}_v . Finally, substantial savings can be had by taking advantage of the fact that approximate preconditioners are sufficient for the diagonalization. Here, we exploit this fact by only considering transformation coefficients above a certain threshold and that threshold is taken to be 0.01.

C. Z vector in the PAO basis

The final remaining issue is the calculation of the Z vector in the PAO basis, and we now examine this in detail for the case of the most computationally demanding classes of two electron integrals, which couple doubly excited CSFs to one another. It should be noted that the CI equations in the PAO basis have been implemented for *all* classes of integrals and not just the computationally demanding classes discussed in detail here. The integrals which are less computationally demanding and involve single excitations can be rewritten in the nonorthogonal basis following exactly the same procedure as described below. All of the MRSDCI equations in the orthogonal basis are documented in the article by Saunders and van Lenthe.³² More detailed derivations can be found in the review article of Duch.³³ In the following discussion, virtual orbitals obtained as the by-product of a SCF procedure shall be denoted as a, b, c , and d . These orbitals are all orthogonal to one another. Canonically orthogonalized PAOs shall be referred to as t, u, v , and w . These orbitals will only be orthogonal if they belong to the domain of the same internal CSF. The PAOs themselves shall be referred to as p, q, r , and s .

The integrals involving purely external orbitals couple doubly excited CSFs that include different pairs of virtual orbitals. Consequently, they are the most computationally demanding, their treatment scaling as N_v^4 . In a fully orthogonal virtual orbital basis, the equation for treating the $(ab|cd)$ integrals is

$$Z_{ab}^\lambda = \sum_{c,d} (ac|bd) C_{cd}^\lambda, \quad (3)$$

where λ indexes the internal $N-2$ electron CSF. This equation will of course hold in any basis where all of the virtual orbitals associated with the internal CSF λ are orthogonal to one another. Thus, in a virtual orbital basis where the internal CSF λ is restricted to the set of orthogonalized PAOs in the domain of λ , we can write

$$Z_{tu}^\lambda = \sum_{v,w} (tv|uw) C_{vw}^\lambda, \quad (4)$$

which has exactly the same structure as Eq. (3). The difference between Eqs. (3) and (4) is that in Eq. (4) the sums over v and w run over only the number of virtuals in the domain of λ . This number is always much smaller than the total number of virtuals obtained as the by-product of a SCF procedure, and this is where the savings arise in the TOV approximation. If the canonically orthogonalized PAOs are related to the PAOs in the domain of the internal CSF λ according to the following expression:

$$t = \sum_p T_{ip}^\lambda p, \quad (5)$$

then, in order to maintain invariance of the total wave function upon transforming between bases, the elements of the CI vector must transform as

$$C_{iu}^\lambda = \sum_{p,q} \tilde{T}_{pt}^\lambda \tilde{T}_{qu}^\lambda C_{pq}^\lambda, \quad (6)$$

where $\tilde{\mathbf{T}}^\lambda \mathbf{T}^\lambda = \mathbf{1}$. Inserting Eqs. (5) and (6) into Eq. (3) we arrive at the following expression for the Z vector:

$$Z_{iu}^\lambda = \sum_{p,q} T_{ip}^\lambda T_{uq}^\lambda Z_{pq}^\lambda, \quad (7)$$

where

$$Z_{pq}^\lambda = \sum_{r,s} (pr|qs) C_{rs}^\lambda. \quad (8)$$

A few comments should be made regarding Eqs. (7) and (8). First, note that similar notation is used for the Z vector in both an orthogonal basis and in the PAO basis. Only the subscripts are used to distinguish whether or not we are referring to the Z vector in a basis of orthogonalized PAOs or the PAO basis itself. This is done to reflect the fact that we have only one Z vector which must be written in two different bases. Second, note that the transforms associated with indices appearing simultaneously in the integral and CI vector cancel. This is a direct result of the fact that elements of the CI vector and the individual orbitals transform opposite to one another [see Eqs. (5) and (6)]. This cancellation of transforms will also occur when an index of the CI vector is contracted with an index of the analytic overlap matrix, and examples of this kind of cancellation will be discussed below. For the all-external integrals, this leads to equations for the Z vector in the PAO basis that are identical in structure to those in the orthogonal basis.

The situation is complicated for the class of integrals involving two internal orbitals (denoted as i, j, k , and l) and two virtual orbitals, that, like the $(ab|cd)$, couple pairs of doubly excited CSFs. However, unlike the $(ab|cd)$, these integrals couple doubly excited CSFs having one virtual orbital in common. For medium-sized molecules having about five heavy atoms, the treatment of these integrals can consume more than 60% of the total CPU time in a MRSDCI calculation. We shall discuss in detail the treatment of the $(ia|jc)$ class of “exchange” integrals. The “Coulomb” type $(ij|ac)$ integrals are treated using expressions that have exactly the same structure as those for the $(ia|jc)$ integrals. In subsequent sections of the paper, these two classes of integrals shall be collectively referred to as the $(ij|ab)$ class of integrals. In the usual virtual orbital basis, where all virtual orbitals for all internal CSFs are orthogonal, the equation for treating the $(ia|jc)$ integrals is

$$Z_{ab}^\lambda = \sum_{\mu,c} BK^{\lambda\mu}(ia|jc) C_{cb}^\mu, \quad (9)$$

where μ indexes an internal CSF and the $BK^{\lambda\mu}$ is a constant that depends only on the internal occupation pattern and spin

coupling. Here, we are working in a basis where the virtual orbitals in different domains are not necessarily orthogonal. In this case, the $(ia|jc)$ equation takes the form

$$Z_{iu}^\lambda = \sum_{\mu,v,w} BK^{\lambda\mu}(it|jv) S_{uw} C_{uv}^\mu. \quad (10)$$

In Eq. (10), the orbitals t and u are associated with the internal CSF λ , the orbitals v and w are associated with the internal CSF μ , and S_{uw} is the overlap of virtual orbitals u and w . Inserting Eqs. (5) and (6) into Eq. (10) we arrive at the following expression:

$$Z_{rs}^\lambda = \sum_{\mu,p,q} BK^{\lambda\mu}(ir|jp) S_{sq} C_{pq}^\mu. \quad (11)$$

Here, the quantity S_{sq} is the overlap of the PAOs s and q and is related to S_{uw} via the following expression:

$$S_{uw} = \sum_{s,q} T_{us}^\lambda T_{wq}^\mu S_{sq}. \quad (12)$$

Note that different transformation matrices are required for the virtual orbitals u and w since they are part of the domain of different internal CSFs. Note also that the subscripting convention used to denote the Z vector is used for the analytic overlap matrix as well. The transformation of the Z_{rs}^λ back to the Z_{iu}^λ is given by Eq. (7). Unlike Eq. (8), Eq. (11) includes an extra contraction with the PAO overlap matrix. In general, an extra contraction with the PAO overlap matrix will arise in the equations in the PAO basis whenever an index of the C vector is left uncontracted with an integral index in the equations in a fully orthogonal basis. Fortunately, the cost of these additional floating point operations is easily outweighed by the benefits of the TOV approximation, as we will show below.

The final class of integrals we consider are the all-internal integrals, which couple doubly excited CSFs differing by two internal orbitals. In a basis where all virtual orbitals are orthogonal, the equation for treating these integrals is very simple,

$$Z_{ab}^\lambda = \sum_{\mu} A_{ijkl}^{\lambda\mu}(ij|kl) C_{ab}^\mu, \quad (13)$$

where $A_{ijkl}^{\lambda\mu}$ is a constant depending on the internal occupation pattern and spin coupling. Following a procedure analogous to the one followed for the $(ab|cd)$ and $(ij|ab)$, we arrive at the following expression for treating the all-internal integrals in the PAO basis:

$$Z_{rs}^\lambda = \sum_{\mu,p,q} A_{ijkl}^{\lambda\mu}(ij|kl) S_{rp} C_{pq}^\mu S_{qs}. \quad (14)$$

In the PAO basis, two additional contractions with the overlap matrix are required to treat the $(ij|kl)$ integrals. This is expected, as the indices a and b in Eq. (13) are uncontracted with the indices of the integral. Unfortunately, these extra contractions increase the formal scaling of treating the $(ij|kl)$ from N_v^2 in the fully orthogonal basis to \tilde{N}_v^4 in the PAO basis. As a result, the cost of treating the $(ij|kl)$ in the PAO basis with TOV is comparable to the cost of treating the $(ij|kl)$ in an orthogonal basis without truncation. Fortu-

nately, the CPU time required to treat the $(ij|kl)$ is not overwhelming and does not grow rapidly with the size of the system. The latter is a result of two facts: First, the WP approximation restricts the pairs of orbitals i and k and j and l to be localized near one another. Additionally, the integral $(ij|kl)$ will decay exponentially as the distance between the pairs of orbitals i and j and k and l increase. Prescreening on these integrals is therefore done in order to eliminate entire evaluations of Eq. (14) which will not contribute significantly to the CI vector. Second, the TOV approximation restricts the contraction over the virtual space so that the sums over p and q run only from 1 to \tilde{N}_v . As we have pointed out, \tilde{N}_v is typically much smaller than N_v and it does not increase with the size of the system for a given basis set.

One might suggest that the troublesome $(ij|kl)$ integrals could simply be handled nonlocally, using an expression similar to Eq. (13), and that all other integrals be handled using the TOV approximation. However, this approach is not compatible with the TOV approximation. Recall that the PAOs in the domains of each internal CSF are canonically orthogonalized. This orthogonalization does not guarantee that the PAOs in the domains of two different internal CSFs are orthogonal to one another, and this will introduce overlap matrix elements into the equations. An expression similar in structure to Eq. (13) could only be used if it were possible to simultaneously orthogonalize the PAOs in the domain of a given internal CSF to each other and the orthogonalized PAOs in the domains of all other internal CSFs. However, this is not possible, and one must therefore include the overlap matrix in the treatment of the $(ij|kl)$.

III. CALCULATIONAL DETAILS

The JAGUAR quantum chemistry package³⁴ was used to compute all SCF reference wave functions. For studies on bond cleavage, a multiconfigurational SCF reference wave function is required. Here we use generalized valence bond perfect pairing (GVB-PP) (Ref. 29) or GVB restricted configuration interaction (GVB-RCI) references³⁵ based on orbitals obtained in GVB-PP calculations. These wave functions provide the simplest possible proper zeroth order description of bond cleavage. The GVB-PP wave function uses two orbitals to describe a pair of electrons participating in a bond cleavage. One orbital is bonding in nature and is doubly occupied in one reference configuration. The other orbital is antibonding in nature and is doubly occupied in the other reference configuration. The nature of the GVB-RCI wave functions go one step further and also include a reference configuration in which the bonding and antibonding GVB orbitals are each singly occupied. It should be noted that the orbitals are not further optimized in the presence of this additional configuration. Such configurations are necessary to describe the cleavage of multiple bonds into open shell fragments. The method presented here is not restricted to use with GVB-style multiconfigurational references, and more complicated multiconfigurational references can be used just as easily.

Unless noted otherwise, all calculations were performed with the Pople-style 6-31G** basis set.³⁶ All analytic one

and two electron integrals in the AO basis were computed using the HERMIT integral package³⁷ of Helgaker *et al.* All calculations were performed on Compaq DEC ES40 machines. Unless noted otherwise, the parameters used in the local CI calculations^{26,27} are as follows. For the internal orbitals, the parameter α was 0.8 and 1.2 for the TOV and WP approximations, respectively. The default radius was 0.8 bohr, and the occupation threshold was 0.8 for both the WP and TOV approximations. For the PAOs, parameters are required only for the TOV approximation. The parameter α was 0.4, the default radius was 0.4 bohr, and the occupation threshold was 0.8. For active orbitals, the cylinder radius was taken to be 2.0 and 0.5 bohrs in the WP and TOV approximations, respectively.

All bond dissociation energies (BDEs) reported here are given as 298 K binding enthalpies. The procedure used to convert our CI D_e s to 298 K binding enthalpies is described in detail elsewhere.²⁷ Briefly, zero point energies and enthalpy corrections are calculated using JAGUAR for the molecule in question in both its equilibrium geometry and a geometry where the bond is fully cleaved. All geometries were optimized at the GVB-PP level of theory. For studies on bond breaking, the geometry was allowed to relax as the bond was cleaved. The difference between the zero point energies and enthalpies at the two geometries is computed and added to the CI D_e to obtain the 298 K binding enthalpy.

There are a number of sources of error in our BDE calculations that we do not take into account. The two most important errors are the usual scaling problems associated with truncated CI (a comprehensive discussion of these issues can be found in the review article on coupled cluster theory by Crawford and Schaefer³⁸) and basis set incompleteness. As is well known, truncated CI is not size-consistent or size-extensive. Size consistency is accounted for in large part by taking a "supermolecule" approach in our BDE calculations (i.e., the separated fragments are calculated together and not individually). However, we make no correction for size extensivity in our calculations. A number of size extensivity corrections for MRSDCI have been proposed.³⁹ Although trivial to compute, none of these corrections are theoretically well justified and we therefore have chosen not to use them. Furthermore, the error associated with size extensivity is usually a few percent of the correlation energy and will hopefully largely cancel upon computing a BDE. The final serious source of error is basis set incompleteness. This will have the effect of slightly lowering our BDEs because of an underestimation of correlation effects in the fully bound molecule. Unlike size extensivity, basis set incompleteness is not unique to truncated CI and is in fact a problem in all quantum chemistry methods. The problem is only mentioned here as it is a principal reason our theoretically determined BDEs do not agree perfectly with experimentally determined BDEs. However, the goal of this work is not to obtain the most accurate thermochemistry. Rather, we attempt here to develop a reduced scaling MRSDCI method that agrees to within some tolerance with the nonlocal MRSDCI method. Comparison with experimental thermochemistry is only done here to get a rough idea of the accuracy of the method with moderate basis sets.

TABLE I. Percentage of WP SDCI correlation energy in *n*-butane recovered using the WP+TOV approximations as a function of the average size of the virtual space, \bar{N}_v . The percentage of the nonlocal correlation energy recovered by the combined WP+TOV method is denoted as % E_{corr} . The column labeled α denotes the radius multiplier for the PAOs.

α	6-31G		6-31G**		6-311G		6-311G**	
	\bar{N}_v	% E_{corr}						
0.4	24.3	97.5	38.7	97.7	33.8	94.6	49.3	96.2
0.56	25.2	97.6	41.7	97.9	35.6	94.7	52.3	96.4
0.64	27.4	97.7	47.1	98.1	38.4	95.0	58.6	96.8
0.76	28.6	97.8	48.2	98.1	39.3	95.0	59.6	96.8
0.88	31.3	98.0	49.3	98.2	43.9	95.3	61.2	96.8
1.08	33.0	98.2	56.1	98.5	46.3	95.5	70.8	97.1
1.3	35.2	98.9	58.8	98.8	48.5	95.6	74.2	97.2
1.6	39.2	99.1	65.5	98.9	53.3	95.6	81.3	97.4
2.0	44.1	99.3	75.5	99.1	61.8	96.8	94.4	97.8
Full basis	56	99.4 ^a	110	99.3 ^a	82	97.2 ^a	136	98.0 ^a

^aPercentage of the nonlocal correlation energy recovered when the WP approximation is used by itself.

Experimental thermochemistry was taken from the work of Blanksby and Ellison⁴⁰ and Berkowitz *et al.*⁴¹ For carbon–carbon double and triple bonds in large systems, there is unfortunately no experimental thermochemistry available. We therefore estimate the experimental values for these BDEs using the following method. For carbon–carbon double bonds, the theoretical D_0 in ethylene is first computed. The difference between this D_0 and the experimental D_0 , 171 ± 1 kcal/mol,⁴¹ is computed as an estimate of the error made in our theoretical method. This error is then added to our theoretically determined BDEs to arrive at an estimate of the experimental BDE. When a 6-31G** basis set is used, this leads to a correction of 9.5 kcal/mol for carbon–carbon double bonds. For carbon–carbon triple bonds, an analogous approach based on the acetylene molecule (carbon–carbon $D_0 = 229 \pm 1$ kcal/mol) is used. However, an additional correction must also be applied to account for the supermolecule description of the separated fragments. Namely, the supermolecule diabatically dissociates a carbon–carbon triple bond to quartet fragments, whereas the actual ground state fragments are doublets. Therefore, the diabatic D_e (for acetylene, this is predicted by MRSDCI to be 252.2 kcal/mol) must be reduced by the splitting between the quartet and doublet states of the fragment molecules. The quartet state is treated using a SDCI calculation based on a ROHF reference configuration and the doublet state is treated using a MRSDCI calculation based on a GVB-RCI reference state. This choice of reference wave functions yields three active orbitals in the treatments of both the doublet and quartet states, and therefore leads to a more balanced description of the electron correlation in both states.⁴² This procedure leads to a quartet–doublet (T_e) splitting of 10.9 kcal/mol compared to the experimental value of 16.3 kcal/mol.⁴³ Subtracting twice T_e for the diabatic D_e yields an adiabatic D_e of 230.4 kcal/mol. Upon correction for zero point energy [for acetylene, 18.8 kcal/mol; for CH ($^2\Pi$), 4.1 kcal/mol], this yields a MRSDCI D_0 of 220.0 kcal/mol for acetylene. Overall, this produces a correction to D_0 of 9.0 kcal/mol for carbon–carbon triple bonds when a 6-31G** basis set is used in the supermolecule MRSDCI approach.

IV. RESULTS AND DISCUSSION

A. Performance of the method as a function of domain size and basis set

Table I lists the percentage of the SDCI correlation energy recovered as a function of the average number of virtuals per internal CSF in SDCI calculations employing the WP and TOV approximations on the *n*-butane molecule. For the 6-31G and 6-31G** basis sets, the WP approximation alone recovers 99.4% and 99.3% of the correlation energy, respectively. These percentages are therefore upper limits for the fraction of correlation energy that can be recovered by the combination of the WP and TOV approximations. For the 6-31G and 6-31G** basis sets, there are 56 and 110 basis functions, respectively. Thus, according to Table I, using domain sizes that are roughly one-third of the maximum domain sizes, the combination of the WP and TOV approximations are capable of recovering almost 98% of the correlation energy when double- ζ basis sets are used. For most applications, this level of precision will be sufficient. As the size of the domain is increased to about half of its maximum value, the percentage of the correlation energy increases by an additional half a percent. Beyond this point, the percentage of the correlation energy continues to increase slowly, but the savings that can be had from the TOV approximation decrease rapidly.

Compared to the double- ζ basis sets, the triple- ζ basis sets recover a smaller fraction of the correlation energy when the WP approximation is used by itself: the 6-311G (82 basis functions) and 6-311G** (136 basis functions) basis sets recover 97.2% and 98.0% of the correlation energy, respectively. This result is in line with those observed previously by Walter *et al.*²⁷ and is likely due to the WP approximation neglecting long range correlation effects that the more extended basis set is capable of recovering. Clearly, this will limit the effectiveness of the combined WP and TOV method. Nevertheless, the performance of the TOV approximation does not seem to be significantly impacted on going from double- ζ to triple- ζ basis sets. This is indicated by the similarity in the percentage of the WP correlation energy

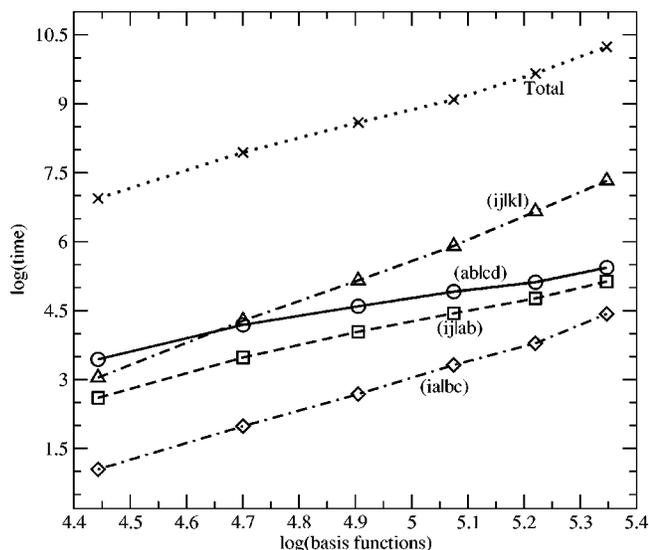


FIG. 2. Natural log of CPU time for treating various classes of integrals within the WP+TOV approximations to SDCI vs natural log of number of basis functions. The calculations were carried out on the system n -propane through n -octane. The slopes of the lines are 3.7 for the total, 4.7 for the $(ij|kl)$, 2.2 for the $(ab|cd)$, 2.8 for the $(ij|ab)$, and 3.7 for the $(ia|bc)$.

recovered by the combined WP and TOV methods when either double- ζ or triple- ζ basis sets are used. For example, when α is chosen to be 0.88, the combined WP and TOV method recovers 98.9% and 98.8% of the WP correlation energy when the 6-31G** and 6-311G** basis sets are used, respectively.

One point regarding the performance of the triple- ζ basis sets that is not apparent in Table I is that slower convergence of the diagonalization algorithm is observed when triple- ζ basis sets are used. Typically, twice as many iterations are required to converge calculations using triple- ζ basis sets as are required using double- ζ basis sets. However, the savings per iteration obtained with the combined WP and TOV method are so substantial that the additional iterations required represent only a minor inconvenience. Furthermore, faster convergence can very likely be achieved through a more appropriate choice of an orthogonal virtual orbital basis. Previous work^{20,24} in this area has made use of an orthogonal basis consisting of eigenfunctions of the Fock operator formed in the basis of the PAOs in the domain of each internal CSF. Unfortunately, this approach is not easily generalized to the case where one has a multiconfigurational reference, as there are usually different Fock operators for the different classes of orbitals. Nevertheless, it is possible that adopting this approach for the class of doubly occupied orbitals will speed convergence.

B. Scaling of the method with system size

Figure 3 shows the CPU times required to treat selected classes of integrals in both nonlocal and local SDCI calculations on the alkanes n -propane through n -octane. Data for the combined WP+TOV method is also plotted on a log-log scale in Fig. 2, from which the scalings of the method with the number of basis functions can be derived. It should be noted that these scalings are appropriate only for systems

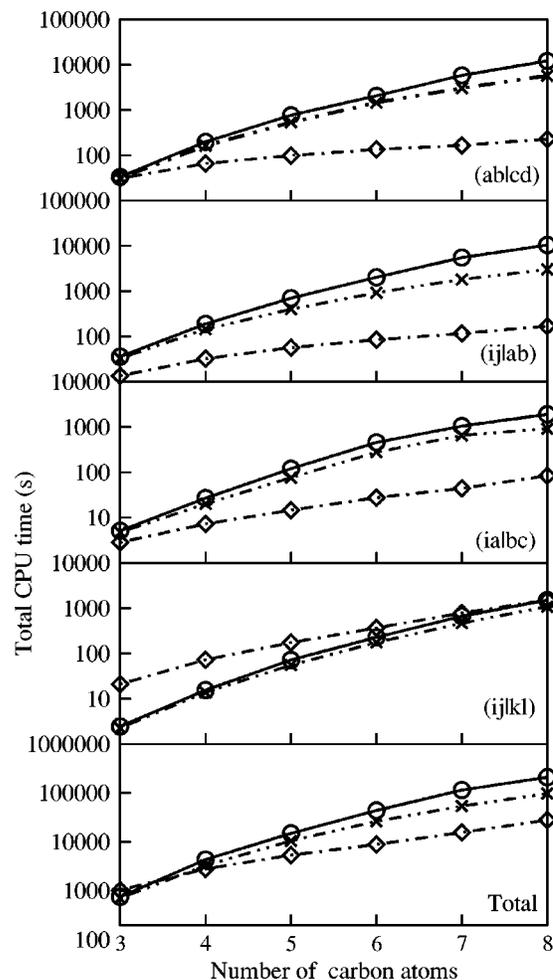


FIG. 3. Cost of treating various classes of integrals in the WP and WP+TOV methods as a function of the size of the system. Solid lines with circles, nonlocal SDCI; dashed line with crosses, WP approximation; alternating dots and dashes with diamonds, WP+TOV approximation. The 6-31G** basis set (Ref. 36) was used for all calculations.

similar in size to those examined here. It is quite likely that a study of significantly larger systems will yield asymptotic scalings lower than those presented here. Unfortunately, limitations in our ability to handle the transformation of the two electron integrals prevents us from doing such studies at this time.

As we have noted, the $(ab|cd)$, due to its N_v^4 scaling, ultimately becomes the dominant computational requirement in SDCI calculations as the size of the system increases. Clearly, the TOV approximation goes a long way towards eliminating the rapid increase in the cost of treating the $(ab|cd)$ integrals as the size of the system increases. For the SDCI calculations involving both WP and TOV, the cost of treating the $(ab|cd)$ increased from 31 s to only 230 s on going from propane to octane. This corresponds to slightly greater than quadratic scaling with the number of basis functions. By comparison, in the analytic SDCI the cost of treating the $(ab|cd)$ went from 34 to 12203 s on going from propane to octane. Compared to the TOV, the WP approximation reduces the cost of treating the $(ab|cd)$ by only a small amount. This is expected as the treatment of the

$(ab|cd)$ involves no contractions over internal indices [Eq. (3)].

The second panel of Fig. 3 shows the combined cost of treating the $(ia|jb)$ and $(ij|ab)$ integrals, collectively referred to as the $(ij|ab)$. Although the treatment of the $(ij|ab)$ scales formally as N_v^3 and the treatment of the $(ab|cd)$ scales formally as N_v^4 , the cost of treating the $(ij|ab)$ can often exceed the cost of treating the $(ab|cd)$. This is a result of the very complicated internal space contributions that arise in the treatment of the $(ij|ab)$. Since the contributions of both the internal and external spaces are important for the $(ij|ab)$, both the WP and TOV approximations can be expected to have a significant effect on the cost of treating the $(ij|ab)$. As indicated in Fig. 3, this is indeed the case. In octane, for example, the TOV approximation reduced the cost of treating the $(ij|ab)$ from 10511 to 492 s. The addition of the WP approximation reduced this cost further by more than a factor of 2. Similar savings were seen for the other systems listed in Fig. 3. Overall, the cost of treating the $(ij|ab)$ integrals in the WP+TOV method was observed to scale slightly less than N^3 .

The $(ia|bc)$ integrals couple singly excited CSFs to doubly excited CSFs. The equations for treating the $(ia|bc)$ integrals in a purely orthogonal basis are

$$Z_a^\lambda = \sum_{bc} B_i^{\lambda\mu}(ib|bc) C_{bc}^\mu, \quad (15)$$

$$Z_{bc}^\mu = \sum_a B_i^{\lambda\mu}(ib|ac) C_a^\lambda. \quad (16)$$

Similar to the $(ij|ab)$, the treatment of the $(ia|bc)$ scales formally as N_v^3 . However, the internal space contribution is much simpler compared to the $(ij|ab)$. As a result, the relative savings from the TOV seen for the $(ia|bc)$ are very similar to those seen for the $(ij|ab)$. However, similar to the $(ab|cd)$, the additional savings from the WP are nearly insignificant. Overall, the cost of treating the $(ia|bc)$ was observed to scale slightly less than N^4 .

The most substantial penalty from using a nonorthogonal virtual orbital basis is incurred in the treatment of the $(ij|kl)$ integrals where two additional contractions with the PAO overlap matrix are required. As a result of this, the cost of treating the $(ij|kl)$ integrals can actually be significantly more expensive when the TOV approximation is used than when the calculation is done without TOV in a fully orthogonal basis. Indeed, the cost of treating the $(ij|kl)$ scales almost as N^5 , which is the poorest scaling of all classes of integrals. Fortunately, the WP approximation has the largest effect for the $(ij|kl)$ integrals and this reduces the cost of treating the $(ij|kl)$ with TOV down to approximately the cost of treating the $(ij|kl)$ in an orthogonal basis without the TOV approximation. Certainly, it is discouraging that local correlation does not ultimately reduce the cost of treating the $(ij|kl)$. However, the $(ij|kl)$ integrals do not present a significant computational bottleneck in nonlocal SDCI. Furthermore, as we have noted earlier, in calculations that make use of the TOV approximation the treatment of the $(ij|kl)$ is not expected to grow rapidly with the size of the system.

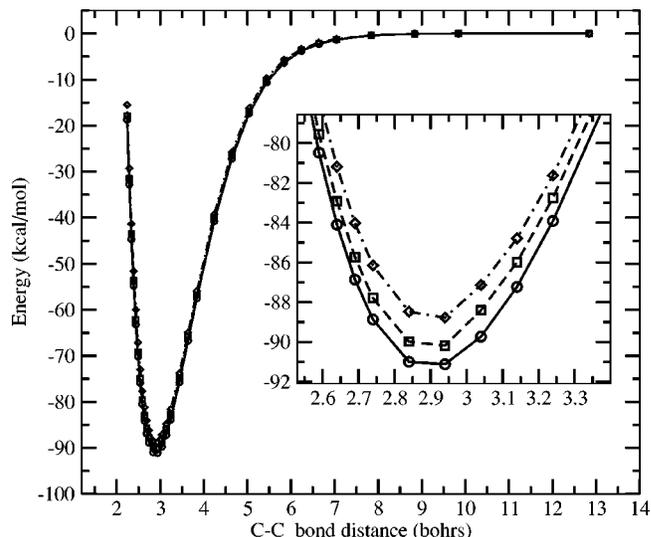


FIG. 4. PES for cleavage of the central C–C bond in *n*-butane. Solid lines with circles, nonlocal MRSDCI; dashed line with squares, WP approximation; alternating dots and dashes with diamonds, WP+TOV approximation. The inset shows the region immediately surrounding the equilibrium geometry.

C. Use of local correlation for the calculation of potential energy surfaces

Figure 4 shows the potential energy surface (PES) for cleavage of the central carbon–carbon bond in *n*-butane. Here, a GVB-RCI (1/2) reference wave function is used to describe the cleavage (i.e., two active orbitals are used to describe the electrons participating in the bond). Clearly, both the WP and WP+TOV surfaces are comparable in smoothness to the nonlocal surfaces. Indeed, the surfaces are almost superimposable. This smoothness is a direct result of using a cylinder that expands with the bond to determine the weak-pairs and virtual orbital domain for the active orbitals. The D_e s obtained using the three methods differ slightly, as is evident in the inset in Fig. 4. The nonlocal D_e is the largest of the three, the WP D_e is roughly 1 kcal/mol smaller, and the WP+TOV D_e decreases by yet an additional 1 kcal/mol. The decrease in the BDEs is very likely attributable to the neglect of long range correlation effects, and can be explained as follows. As the degree of local correlation approximation that is used becomes more severe, the long range correlation effects are progressively neglected. These effects are more prevalent for the molecule in its equilibrium geometry since for the separated supermolecule much of the long range correlation vanishes completely. Thus, the local correlation approximation raises the energy of the molecule in its equilibrium configuration more than it does for the separated supermolecule leading to a corresponding decrease in the D_e .

Figure 5 shows the potential energy surface for cleavage of the central carbon–carbon double bond in *trans*-3-hexene. For these calculations, a GVB-PP (2/4) reference wave function was used. Although this reference wave function does not have the flexibility required to rigorously describe cleavage of the double bond, it still provides a useful test of the performance of the local MRSDCI relative to the nonlocal

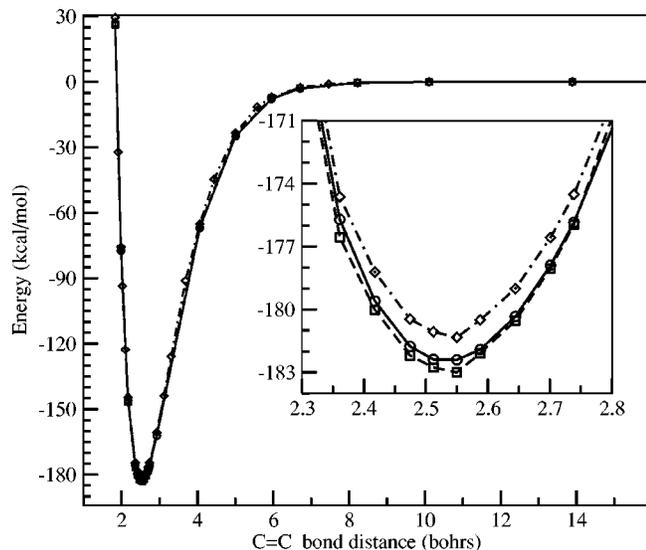


FIG. 5. PES for the cleavage of the central C=C double bond in *trans*-3-hexene. Solid lines with circles, nonlocal MRSDCI; dashed line with squares, WP approximation; alternating dots and dashes with diamonds, WP+TOV approximation. The inset shows the region immediately surrounding the equilibrium geometry.

MRSDCI. With some small differences, the results are similar to those observed for the *n*-butane case. Compared to the *n*-butane results, the WP approximation appears to perform slightly better in *trans*-3-hexene. The WP D_e is in fact about 1 kcal/mol lower than the nonlocal D_e as a consequence of the fact that the WP approximation recovers a slightly larger fraction of the correlation energy for the molecule in its equilibrium geometry than for the separated supermolecule. However, when the TOV approximation is introduced, the resulting D_e falls below the nonlocal D_e by about 1 kcal/mol. This result indicates that the neglect of long range correlation is more severe in the use of the TOV approximation than the WP approximation. Additional BDE calculations support this hypothesis (discussed below).

In terms of computational effort, the cost of carrying out a nonlocal CI calculation on *n*-butane is not particularly taxing. However, the same is not true for *trans*-3-hexene. One of the CI calculations for the nonlocal curve in Fig. 5 includes over 18 million CSFs and requires over 14 000 s of CPU time per iteration. On the other hand, for the WP+TOV curve, each CI calculation includes only about 1 million CSFs and requires only 1300 s of CPU time per iteration. Clearly, the use of the WP+TOV approximations will enable one to inexpensively map out PESs in large molecules with a reasonable degree of precision.

Figure 6 shows the potential energy surfaces computed using various CI techniques for rotation of the central C-C bond in *n*-butane, keeping all other geometrical parameters fixed at their equilibrium values. The small barrier in the surface corresponds to the terminal methyl groups being eclipsed with hydrogen atoms and the large barrier corresponds to the terminal methyl groups being eclipsed with each other. Unlike for the systems described in Figs. 4 and 5, a cylinder cannot be used to approximate the orbitals that change most dramatically or that are affected by the geo-

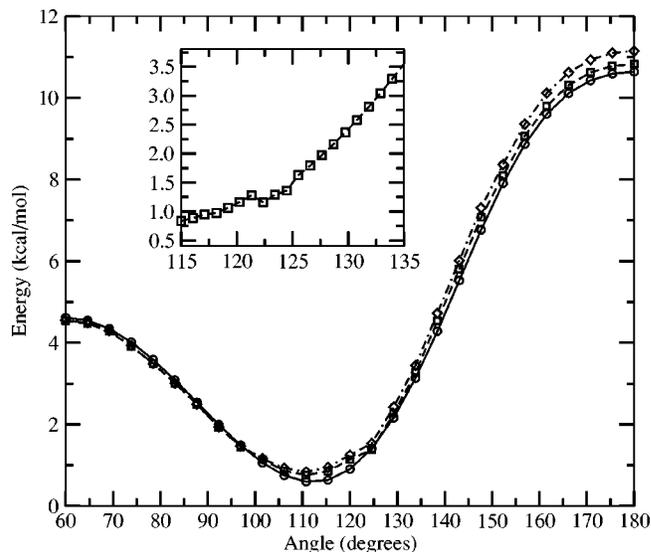


FIG. 6. PES for the rotation of the central C-C bond in butane. Solid lines with circles, nonlocal SDCI; dashed line with squares, WP approximation; alternating dots and dashes with diamonds, WP+TOV approximation. The inset shows the region immediately surrounding the discontinuity in the surface near 120° for the WP approximation.

metrical changes. As a result, there is a small discontinuity in the WP PES near 120°. Although this discontinuity is only 0.1 kcal/mol in magnitude and likely to be insignificant for most purposes, it nevertheless indicates that care should be taken when the local SDCI method is used to study non-bonded interactions. In particular, problems may arise when one tries to compute gradients at points in the potential energy surface where this discontinuity occurs. However, it should be noted that the potential energy surface for this interaction is quite smooth in the region immediately surrounding the equilibrium point, where one is most likely to compute a gradient. As has been shown by Werner *et al.*,^{44,45} it is possible to fix the virtual orbital domains at these points and compute analytical gradients based on local wave functions that differ only negligibly from those computed using nonlocal wave functions. Thus, it is likely that the local correlation approximation ultimately will not present practical difficulties in the computation of gradients.

D. Use of local correlation to calculate bond dissociation energies

Table II lists the theoretically determined BDEs in a series of hydrocarbons and the CPU time required to treat various classes of integrals for a single iteration of the corresponding MRSDCI calculation. There are a number of important points apparent in Table II. First, as was observed in our PES calculations, the introduction of the local correlation approximation has the effect of decreasing the BDEs relative to the nonlocal CI calculations. This is likely due to the total neglect of long range correlation.

Compared to the experimental BDEs, the nonlocal theoretical BDEs are lower by an average of 2.8 kcal/mol. This result is quite typical and has been observed previously.²⁷ Unfortunately, the neglect of long range correlation in the local correlation approximation will almost always have the

TABLE II. Nonlocal and local BDEs at 298 K and CPU times for a series of hydrocarbons. The 6-31G** basis set (Ref. 36) was used for all calculations unless noted otherwise. The acronym NA stands for "not available."

System and reference wave function	Method	CPU times per iteration (s)				Total	BDE (kcal/mol)	
		(<i>ij ab</i>)	(<i>ab cd</i>)	(<i>ij kl</i>)	(<i>ai jk</i>)		This work	Expt.
CH ₃ CH ₂ -OCH ₃ RCI(1/2)	nonlocal	334	289	29	21	796	79.5	
	WP	185	196	21	13	494	78.3	85 ± 1
	WP+TOV	53	96	96	28	361	76.9	
H ₂ N-C(CH ₃) ₃ RCI(1/2)	nonlocal	1576	1375	115	89	3651	80.0	
	WP	661	820	79	41	1891	78.1	85.7 ± 0.5
	WP+TOV	127	202	397	75	900	76.1	
NC-CH(CH ₃) ₂ RCI(1/2)	nonlocal	689	537	59	41	1533	122.5	
	WP	257	313	39	19	744	120.8	120.9 ± 0.5
	WP+TOV	86	150	191	46	600	119.7	
CH ₃ CH ₂ CH ₂ -CH ₂ CH ₂ CH ₃ ^a RCI(1/2)	nonlocal	25030	21979	1002	849	59258	85.9	
	WP	15819	13267	499	574	35145	85.7	88.0 ± 1
	WP+TOV	6598	890	2305	360	5087	84.0	
CH ₃ CH ₂ CH=CHCH ₂ CH ₃ RCI(2/4)	WP	8598	7434	502	611	21929	162.6	
	WP+TOV	955	842	2707	770	6730	161.1	NA
	Estimated	NA	NA	NA	NA	NA	172.1 ± 1.0 ^b	
PhCH=CH ₂ ^c RCI(2/4)	WP+TOV	2826	2271	8245	2212	19848	177.2	NA
	Estimated	NA	NA	NA	NA	NA	186.7 ± 1.0 ^b	
(CH ₃) ₃ CC≡CCH ₃ ^d RCI(3/6)	WP+TOV	15915	8031	51382	17616	120458	208.2	NA
	Estimated	NA	NA	NA	NA	NA	217 ± 1.0 ^e	

^aA 6-311G** basis set (Ref. 50) was used here. The parameter α for the WP approximation was 1.7 and the default radius was 0.8. For the TOV approximation the parameter α and default radius were 0.5. For the active orbitals, the cylinder radius was 2.25 and 0.5 bohrs for the WP and TOV approximations, respectively.

^bBest estimate of experimental BDE obtained as described in text (see Computational Details) using a correction of 9.5 kcal/mol.

^cPh denotes the aromatic C₆H₅ group.

^dCylinder radius for active orbitals taken to be 0.5 and 0.75 bohrs for the TOV and WP approximations, respectively. All other parameters as described in the text.

^eBest estimate of experimental BDE obtained as described in text (see Computational Details) using a correction of 9.0 kcal/mol.

effect of further lowering the BDEs, as we have discussed previously. This underscores the need for some approximate treatment of long range correlation in the local correlation approximation.

For the most part, the CPU times listed in Table II are in line with the results shown in Fig. 3 that were obtained using HF reference wave functions. However, when a multiconfigurational reference is used, the internal space becomes significantly enlarged. As a result, the treatment of the (*ij|kl*) integrals becomes more costly than the nonlocal calculations when the WP and TOV approximations are used in combination with a multiconfigurational reference wave function. For example, in the case of a CH₃CH₂CH₂-CH₂CH₂CH₃ calculation using an RCI (1/2) reference wave function (two active orbitals, three reference configurations) the treatment of the (*ij|kl*) increases from 1002 to 2305 s on going from nonlocal MRSDCI to the fully local MRSDCI. The example of a calculation on the (CH₃)₃CC≡CCH₃ molecule using a GVB-RCI (3/6) reference (6 active orbitals, 27 reference configurations) provides another illustration of the high cost of treating the (*ij|kl*) when a multiconfigurational reference is used. In this case, it takes over 14 h to treat the (*ij|kl*). However, a nonlocal calculation on this molecule would involve over 307 million CSFs and would therefore be out of the question on a single processor. Thus, in spite of the in-

crease in the cost of treating the (*ij|kl*), substantial savings are still obtained through the use of the WP and TOV approximations. These savings are derived principally from the reduction in the cost of treating the (*ij|ab*) and (*ab|cd*) integrals that are the usual bottleneck in nonlocal MRSDCI calculations. For the case of CH₃CH₂CH₂-CH₂CH₂CH₃, the cost of treating the (*ij|kl*) and (*ab|cd*) decrease by about 4- and 25-fold, respectively. It should be noted that these decreases will also easily compensate for any extra iterations of the diagonalization algorithm, which we observe to be required when more extended basis sets are used.

Last, this now allows us to make predictions of BDEs for large molecules where experimental data does not exist. For example, it is interesting to observe that the predicted C=C BDE in styrene is nearly 15 kcal/mol higher than that in *trans*-3-hexene. This is likely due to the resonance stabilization present in styrene. Second, we predict that the C≡C BDE in (CH₃)₃CC≡CCH₃ is significantly lower (by 13.5 kcal/mol) than that in acetylene. This is due primarily to the much larger quartet-doublet splitting in (CH₃)₃CC and CH₃C (local MRSDCI T_e = 21.9 kcal/mol for both molecules) than in CH. This increased splitting is due to steric repulsion from the methyl and *t*-butyl groups which destabilizes occupation of the carbon *p* orbitals and therefore destabilizes the quartet state.

V. CONCLUSIONS AND FUTURE OUTLOOK

Here we have presented a method of using local correlation in both the internal and external spaces in MRSDCI. The use of the WP approximation, which only affects the size of the internal space, reduces the cost of a typical MRSDCI calculation on a system with four or more heavy atoms by about 50%. For larger molecules, one can expect this percentage to increase slightly. However, no further gains can be made through the use of the WP approximation as it does not affect the treatment of the virtual space. The TOV approximation, on the other hand, accomplishes exactly this task and therefore leads to much more significant savings. The cost of treating the $(ab|cd)$ integrals, the bottleneck in CI calculations on large molecules, can be reduced over 15-fold through the use of the TOV approximation for medium sized molecules. Furthermore, the savings obtained from this method will increase with the size of the system, since the TOV approximation leads to average domain sizes that are roughly independent of system size for a given basis set. We find that the treatment of the all-internal integrals becomes more expensive when the WP and TOV approximations are used as a result of two extra contractions with the PAO overlap matrix that are required when working in a nonorthogonal virtual orbital basis. The treatment of these $(ij|kl)$ integrals in fact become the bottleneck in the use of the TOV approximation. Nevertheless, the combination of the WP and TOV approximation leads to a local MRSDCI method that is overall about tenfold faster than the nonlocal MRSDCI method for the systems studied here. For larger systems, we can expect the savings to be even more substantial as the savings from both the WP and TOV approximations will increase.

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. Unfortunately, the neglect of long range correlation in the method presented here leads to D_e s that are up to 4 kcal/mol lower than those determined by the nonlocal method. Furthermore, care should be taken when the local correlation method is used to study surfaces involving predominantly nonbonded interactions as it can lead to small discontinuities. In the case of the rotation of the central bond in *n*-butane, a discontinuity of roughly 0.1 kcal/mol was observed.

Clearly, the first priority in improving the method presented here is to implement some method of estimating long range correlation effects. This may come in the form of approximately treating the terms in the CI equations most important for describing long range correlation effects. Alternatively, some sort of perturbational estimation of long range correlation effects may be made. Recently, Dunietz and Friesner have proposed a local version of multiconfigurational perturbation theory based on GVB style wave functions,⁴⁶ which is based upon the multireference perturbation method of Murphy and Messmer.⁴⁷ It might be fea-

sible to incorporate certain aspects of this methodology into our local MRSDCI method to treat long range correlation.

As we have pointed out, MRSDCI is not size consistent nor size extensive. In the work presented here, size consistency errors have been largely avoided by taking a supermolecule approach in the computation of BDEs. However, in some cases this approach is not suitable. For example, in describing the cleavage of certain multiple bonds, multiconfigurational wave functions might dissociate diabatically to excited state fragments. Under these circumstances, a size extensive method is preferable, so that the energies of dissociated ground state fragments can be computed separately. The MR-ACPF method⁴⁸ is a very attractive modification of the CI method that is approximately size extensive. Work is currently underway to implement a local MR-ACPF method.⁴⁹

In our previous work, we^{26,27} commented on the advantages of the symmetric group graphical approach³³ to CI, upon which the method presented here is based. The principal advantage of this approach that the integral coupling coefficients (denoted in this work as $BK^{\lambda\mu}$ and $A_{ijkl}^{\lambda\mu}$) 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 wavefunction used, not the size of the system. Thus, the MRSDCI program discussed here is particularly well suited to the study of large systems. Unfortunately, one major bottleneck not addressed in our work 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 systems. As has been shown by Schütz and Werner,^{17,18} 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 a linear scaling MRSDCI or MRACPF method and work in this direction is ongoing in our group. It is quite likely that such a linear scaling and size extensive MRACPF technique will be a valuable tool for the examination of extremely large systems that require a multiconfigurational reference, an arena where local CC methods currently are not applicable.

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¹S. Saebø and P. Pulay, *Annu. Rev. Phys. Chem.* **44**, 213 (1993).

²P. Pulay and S. Saebø, *Theor. Chim. Acta* **69**, 357 (1986).

³S. Saebø and P. Pulay, *J. Chem. Phys.* **86**, 914 (1987).

⁴S. Saebø and P. Pulay, *J. Chem. Phys.* **88**, 1884 (1988).

⁵R. B. Murphy, M. D. Beachy, R. A. Friesner, and M. N. Ringnalda, *J. Chem. Phys.* **103**, 1481 (1995).

⁶R. B. Murphy, W. T. Pollard, and R. A. Friesner, *J. Chem. Phys.* **106**, 5073 (1997).

- ⁷M. D. Beachy, D. Chasman, R. A. Friesner, and R. B. Murphy, *J. Comput. Chem.* **19**, 1030 (1998).
- ⁸M. S. Lee, P. E. Maslen, and M. Head-Gordon, *J. Chem. Phys.* **112**, 3592 (2000).
- ⁹P. E. Maslen and M. Head-Gordon, *Chem. Phys. Lett.* **283**, 102 (1998).
- ¹⁰P. E. Maslen and M. Head-Gordon, *J. Chem. Phys.* **109**, 7093 (1998).
- ¹¹G. Hetzer, P. Pulay, and H.-J. Werner, *Chem. Phys. Lett.* **290**, 143 (1998).
- ¹²M. Schütz, G. Hetzer, and H.-J. Werner, *J. Chem. Phys.* **111**, 5691 (1999).
- ¹³G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, *J. Chem. Phys.* **113**, 9443 (2000).
- ¹⁴P. Y. Ayala and G. E. Scuseria, *J. Chem. Phys.* **110**, 3660 (1999).
- ¹⁵P. Constans, P. Y. Ayala, and G. E. Scuseria, *J. Chem. Phys.* **113**, 10451 (2000).
- ¹⁶G. E. Scuseria and P. Y. Ayala, *J. Chem. Phys.* **111**, 8330 (1999).
- ¹⁷M. Schütz and H.-J. Werner, *J. Chem. Phys.* **114**, 661 (2001).
- ¹⁸M. Schütz and H.-J. Werner, *Chem. Phys. Lett.* **318**, 370 (2000).
- ¹⁹P. E. Maslen, M. S. Lee, and M. Head-Gordon, *Chem. Phys. Lett.* **319**, 205 (2000).
- ²⁰C. Hampel and H.-J. Werner, *J. Chem. Phys.* **104**, 6286 (1996).
- ²¹P. Pulay, *Chem. Phys. Lett.* **100**, 151 (1983).
- ²²S. Saebø and P. Pulay, *Chem. Phys. Lett.* **113**, 13 (1985).
- ²³R. A. Friesner, *Annu. Rev. Phys. Chem.* **42**, 341 (1991).
- ²⁴G. Reynolds and E. A. Carter, *Chem. Phys. Lett.* **265**, 660 (1997).
- ²⁵G. Reynolds, T. J. Martinez, and E. A. Carter, *J. Chem. Phys.* **105**, 6455 (1996).
- ²⁶D. Walter and E. A. Carter, *Chem. Phys. Lett.* **346**, 177 (2001).
- ²⁷D. Walter, A. B. Szilva, K. Niedfeldt, and E. A. Carter, *J. Chem. Phys.* **117**, 1982 (2002).
- ²⁸S. F. Boys, *Quantum Theory of Atoms, Molecules, and the Solid State* (Academic, New York, 1966), p. 263.
- ²⁹F. W. Bobrowicz and W. A. Goddard III, *Methods of Electronic Structure Theory* (Plenum, New York, 1977), p. 79.
- ³⁰E. R. Davidson, *Comput. Phys. Commun.* **53**, 49 (1989).
- ³¹A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989).
- ³²V. R. Saunders and J. H. van Lenthe, *Mol. Phys.* **48**, 923 (1983).
- ³³W. Duch and J. Karwowski, *Comput. Phys. Rep.* **2**, 93 (1985).
- ³⁴JAGUAR 4.1, Schrödinger, Inc., Portland, Oregon, 2000.
- ³⁵R. B. Murphy, R. A. Friesner, and W. A. Goddard III, *J. Chem. Phys.* **101**, 2986 (1994).
- ³⁶W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
- ³⁷HERMIT integral program, T. U. Helgaker, 1984 (unpublished).
- ³⁸T. D. Crawford and H. F. Schaefer III, "An introduction to coupled cluster theory for computational chemists," in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (Wiley, New York, 2000), p. 33.
- ³⁹W. Duch and G. H. F. Diercksen, *J. Chem. Phys.* **101**, 3018 (1994).
- ⁴⁰S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.* (to be published).
- ⁴¹J. Berkowitz, G. B. Ellison, and D. Gutman, *J. Phys. Chem.* **98**, 2744 (1994).
- ⁴²E. A. Carter and W. A. Goddard III, *J. Chem. Phys.* **88**, 1752 (1988).
- ⁴³K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules*, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg, Maryland, 2001).
- ⁴⁴A. E. Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, *J. Chem. Phys.* **108**, 5185 (1998).
- ⁴⁵R. Guntram, A. E. Azhary, F. Eckert, U. Schumann, and H.-J. Werner, *Spectrochim. Acta, Part A* **55**, 647 (1999).
- ⁴⁶B. D. Dunietz and R. A. Friesner, *J. Chem. Phys.* **115**, 11052 (2001).
- ⁴⁷R. B. Murphy and R. P. Messmer, *J. Chem. Phys.* **97**, 4170 (1992).
- ⁴⁸R. J. Gdanitz, *Int. J. Quantum Chem.* **85**, 281 (2001).
- ⁴⁹A. Venkatnathan, A. Szilva, R. J. Gdanitz, and E. A. Carter (unpublished results, 2002).
- ⁵⁰R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).