

Benchmark calculations using the individually selecting configuration interaction method

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Further progress is reported on the implementation of the configuration-selecting multi-reference configuration interaction method for massively parallel architectures with distributed memory which allows calculations with Hilbert spaces in excess of 10^{11} configurations, 2×10^7 of which can now be included in the variational subspace. This code makes it possible to elucidate the importance of the correlated treatment of triple and quadruple excitations into the (3s3p) shell of the oxygen molecule, to account quantitatively for its electron affinity. Also included are extensive calculations to elucidate the reaction pathways of members of the acetylene family.

1. Introduction

In the development of quantum chemical methods for complex molecules, a consensus has emerged that two important effects must be taken into account in a balanced and accurate fashion in order to arrive at quantitatively correct results. First, dynamic correlations, i.e. the mutual influence two electrons exercise on each other when they pass at a close distance, must be accounted for. Second, one must be able to accommodate the multi-reference nature of the electronic states in many complex molecules. This effect is particularly significant when one wants to describe an entire potential energy surface, where bond breaking or bond rearrangements can occur. An adequate treatment of multi-reference effects is mandatory for the quantitative treatment of electronically excited states.

For many years the multi-reference configuration interaction method (MRCI) has been one of the benchmark tools for accurate calculations of the electronic structure of atoms and molecules [1-3]. Ever since the development of the direct CI algorithm [1], which obviates the explicit storage of the CI matrix, highly efficient implementations [4] have been used for a wide variety of molecules. The generic lack of extensivity of the MRCI method has been at least partially addressed with a number of *a posteriori* [5, 6] corrections and through direct modification of the CI energy functional [7-11].

Due to the high computational cost, however, applications of the MRCI method remain constrained to

relatively small systems. For this reason the configuration-selecting version of the MRCI-method (MRD-CI), introduced by Buenker and Peyerimhoff [12-14], has arguably become one of its most widely used versions. In this variant only the most important configurations of the interacting space of a given set of primary configurations are chosen for the variational wavefunction, while the energy contributions of the remaining configurations are estimated on the basis of second-order Rayleigh-Schrödinger perturbation theory [15, 16]. A configuration is selected for the variational wavefunction if its perturbative energy contribution or coefficient is above a given threshold X and the total energy (the sum of the variational and the perturbative contributions) is extrapolated to the limit $X \rightarrow 0$. While this extrapolation is known to fail in isolated instances, it gives remarkably good resolution of relative energies across the potential energy surface (PES) in the overwhelming majority of applications. Since the variationally treated subspace of the problem consists of only a fraction of the overall Hilbert space, the determination of eigenstates in the truncated space requires far less computational effort. Indeed, for typical applications the overwhelming majority of the computational effort is concentrated in the expansion loop, where the energy contribution of candidate configurations is computed.

Even within this approximation, the cost of MRCI calculations remains rather high. The development of efficient configuration-selecting CI codes [16-21] is inherently complicated by the sparseness and the lack of structure of the selected state-vector. In order to further extend the applicability of the method, it is

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thus desirable to employ the most powerful computational architectures available for such calculations. Here we report on the progress of the massively parallel implementation of the MRD-CI method for distributed memory architecture. In our implementation the difficulty in the construction of the subset of nonzero matrix elements is overcome by the use of a residue-based representation of the matrix elements that was developed originally for the distributed memory implementation of MR-SDCI [22]. This approach allows us to evaluate the matrix elements efficiently both in the expansion loop and during the variational improvement of the coefficients of the selected vectors.

In this report we briefly document the recent improvements in the massively parallel MRD-CI implementation that permit the treatment of larger Hilbert spaces, i.e. the correlation of a larger number of electrons in larger basis sets. We then use this method to elucidate the applicability and limitations of various formulations of MRD-CI in applications to two very sensitive chemical problems: the ring-closure reaction of enediynes and the electronic structure of benzofuroxanes.

2. Technical improvements

As reported previously, matrix elements between two configurations are computed using a residue tree such that each matrix element between two determinants (or configuration state functions $|4\rangle$ and $|4\rangle$) is associated with the subset of orbitals that occur in both the target and the source determinant. This unique subset of orbitals is called the 'transition residue' mediating the matrix element, and serves as a sorting criterion to facilitate the matrix element evaluation on distributed memory architectures. For a given many-body state, we consider a tree of all possible transition residues, as illustrated in figure 1. For each such residue we build a list of residue entries, composed of the orbital pairs (or orbital for a single-particle residue) that combine with the residue to yield a selected configuration and a pointer to that configuration. While the number of transition residues is comparatively small, the overall number of residue entries grows rapidly (as $N_{\text{selected}} n_e$) with the number of configurations N_{selected} and the number of electrons n_e .

Once the residue tree is available the evaluation of the matrix elements is very efficient, but its size limits the number of configurations in the variational subspace. In order to increase the size of the variational subspace we have removed all transition residues containing two external orbitals from the residue tree. Matrix elements mediated by such transition residues can be computed by gathering all the elements of the coefficient vector that contain a particular external pair on a single node of the machine. We have then implemented a scheme

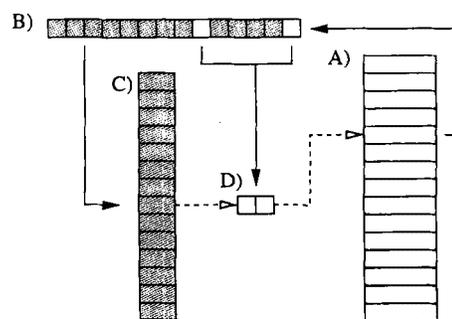


Figure 1. Schematic representation of the two-particle residue tree. For each element of the configuration list (A) all possible two-particle residues are constructed. In the configuration illustrated in (B) each box represents one occupied orbital: the shaded region corresponds to the residue and the two white boxes to the orbital pair. The $(n_e - 2)$ -electron residue configuration is looked up in the residue tree (C), where an element (D) is added that encodes the orbitals that were removed, with information regarding the permutation required and the index of the original configuration in the configuration list. Solid arrows in the figure indicate logical relationships, and dashed arrows indicate pointers incorporated in the data structure. The residue list, along with all elements, must be rebuilt once after each expansion loop. The effort to do so is proportional to the product of n_e and the number of configurations. The number of matrix elements encoded in a single element of the residue tree is proportional to the square of the number of entries of type (D).

that efficiently evaluates the orbital difference map of the internal part of two such configurations to determine if any matrix element between the two configurations exists. In a MR-SDCI calculation the value of this matrix element is obtained readily from the table of all integrals with only internal indices that can be replicated on all nodes. Implementing this change reduces the size of the residue tree significantly, and lets us increase the size of the variational subspace by a factor of almost ten, to about 40 million configurations. The state vectors for the Davidson iterations may be split across the nodes, such that only two copies of the total state vector are required on each node for the evaluation of the matrix elements.

Once the residue tree has been constructed, its 'heads', i.e. the information regarding the transition residue itself, can be discarded. During the matrix evaluation, only the orbital lists are required. The space freed by eliminating the information pertaining to the content of the individual residues can be reused to address those orbital lists that contain a particular orbital pair. Once a set of integrals in the physicist's notation $(i_1 i_2 | i_3 i_4) = \int dx_1 dx_2 x_i(x_1) x_i(x_2) r_{12} X_3(x_1) x_4(x_2)$ with a given orbital pair, e.g. $i_1 i_2$, is served to the node, this information can be used to identify all orbital lists that generate nonzero matrix elements for this integral list.

Using this information, an integral driven matrix element evaluation scheme can be implemented, during which all integral lists $(i_1 i_2 | \dots |)$ are distributed across the nodes and rotated in a cyclic fashion until every integral list has visited every node. Since MPI permits very fast cyclic data exchange and no search operations are required to identify nonzero matrix elements for a given set of integrals, this mechanism allows for the efficient integral driven evaluation of all matrix elements not mediated by double external transition residues.

3. Benchmark calculations

3.1. Oxygen

Previous work has established that the accurate calculation of the electron affinity of O_2 remains a formidable challenge even for present day quantum chemical techniques. At the level of a CAS-SCF description the adiabatic electron affinity of the oxygen molecule is predicted with the wrong sign even in the basis set limit. A careful study [23] concluded that strong differential dynamic correlation effects are most probably entirely responsible for the source of this discrepancy. In MRCI-SD calculations the correct sign for the electron affinity can barely be reached using augmented quadruple-zeta quality basis sets. A semiquantitative agreement between experiment and theory was reached when the multi-reference generalization of the Davidson correction [6] was applied to estimate the effect of higher excitations.

O_2 is therefore one of the simplest molecules that challenges one of the central paradigms of modern quantum chemical correlation methods that rest on the assumption that the explicit treatment of single and double excitations of a chemically motivated reference set is sufficient to account quantitatively for dynamic correlation effects. This observation, as well as the desire to explicitly test approximations for extensivity corrections to MR-SDCI [7-10] motivated the development of the present code. Since the CAS + SDTQ Hilbert space of O_2 in an aug-cc-pVDZ basis has dimension 32×10^9 , this problem cannot be treated with any of the presently available MR-SDCI or MRD-CI implementations, but provides a suitable challenge for our parallel implementation.

Figure 2 demonstrates that the energies of both the neutral molecule and the anion converge smoothly with the threshold to their respective MRCI values. Treating single and double excitations alone (table 1) in calculations using up to cc-pV5Z basis sets we find in agreement with earlier results that the electron affinity of O_2 saturates at approximately -0.03 eV at the basis set limit for full valence (2s2p) CAS-MRD-CI calculations. Thus the experimental electron affinity of 0.42 eV (corrected for vibrational and other non-electronic effects) cannot

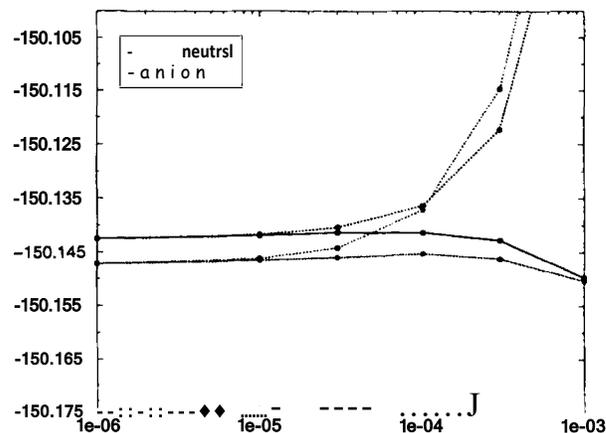


Figure 2 Convergence of the (2s2p) CAS MRD-CI energy of the oxygen molecule and its anion in an augmented cc-pVQZ basis set in BW-MRPT approximate natural orbitals as a function of the coefficient threshold.

Table 1. Adiabatic electron affinity (in mH) of the oxygen molecule in MRD-CI in approximate BW-MRPT natural orbitals in a (2s2p) active space, i.e. the space of the natural orbital dominated by atomic 2s and 2p functions, and with correlated triple and quadruple excitations into the (3s3p) space, respectively. Inclusion of correlated triples and quadruples into the (4s4p) has no significant impact on the results. We report results without and with Davidson corrections (in mH).

Basis	Mode	EA	EA (Dav)
aug-cc-pVTZ	(SD)	-3.6	156
aug-cc-pVQZ	(SD)	-3.4	158
aug-cc-p5QZ	(SD)	-3.2	157
aug-cc-pVTZ	(SD) + (3s3p)TQ	9.0	126
aug-cc-pVQZ	(SD) + (3s3p)TQ	9.7	133
aug-cc-pV5Z	(SD) + (3s3p)TQ	103	
aug-cc-pVTZ	(SD) + (3s3p 4s4p)TQ	9.7	109

be reproduced at this level of calculation. We have incorporated a special mode into our program that allows the selective treatment of triple and quadruple excitations into the (3s3p) space and correlations therefore. Table 1 demonstrates that the inclusion of these terms accounts qualitatively, and for large basis sets quantitatively, for the remaining difference in the experimental result. It appears that the correlation of excitations into the (3s3p) Rydberg orbitals have an important stabilizing effect on the oxygen anion. Preliminary calculations on B_0 [24] and NO [25] demonstrate similarly important effects for the electron affinities of these molecules.

3.2. Eneidyne

Eneidyne have been investigated for some time because of their propensity to undergo a cyclization

Table 2 Electronic differences between the energies of enediyne (en), dihydro-p-benzene (pb) and its forward transition state (ts) in cc-pVDZ and cc-pVTZ basis sets in B3LYP optimized geometries. Absolute energies are reported in au and relative energies (A) in kcal mol⁻¹. The values at c = 0 are extrapolated from various thresholds.

	e = 5 x 10 ⁻⁵			e = 2 x 10 ⁻⁵			e = 0		
	MRCI	A	A+Dav	MRCI	A	A+Dav	MRCI	A	A+Dav
	cc-pVDZ								
en	- 230.086 830			-230.085 833			-230.085 825		
ts	- 230.036 549	31.6	293	-230.034981	31.9	298	-230.034208	32.4	305
pb	- 230.074 551	7.7	69	- 230.073 750	7.7	69	-230.073 618	7.7	6.8
	cc-pVTZ								
en	- 230.256 606			-230.248 273			-230.244050		
ts	-230.211104	28.6	283	- 230.203 850	27.8	37.1	-230.198 587	28.5	28.0
pb	- 230.243 537	82	112	- 230.237 112	7.0	106	- 230.234 362	61	8.1

reaction to para-dihydrobenzene derivatives that are capable of lysing cellular DNA and hence cause cell death [26]. This property, if selectively activated in diseased or cancerous cells, offers the possibility of applications in cell-specific drugs against such diseases. The ultimate goal is to design a compound that in cancerous cells will spontaneously undergo cyclization under physiological conditions and thus kill the cell. In order to predict the effectiveness of specific compounds it is important to understand the electronic structure of educt and product of the cyclization reaction as well as the height of its barrier. However, the quantum chemical description of the cyclization reaction proves difficult and interesting because of the strong change in the electronic structure of the molecule during the reaction.

We have therefore undertaken a set of MRD-CI benchmark calculations into the Bergman cyclization of the simplest member of the enediyne family. As figure 3 illustrates, the reaction is strongly endothermic at the Hartree-Fock level of theory (results produced with our code), in contrast to experimental evidence. This indicates that dynamic correlation is very important for the description of this reaction. CCSD calculations [27, 28] significantly reduce deviation from experiment (black bars in the figure), but fail to account quantitatively for the ring-closure energy. Only CCSD(T) calculations, which account partially for triple excitations and thus non-dynamic correlation effects, yield quantitative agreement between experiment and theory. These observations indicate that a balanced treatment of both dynamic and non-dynamic correlation effects is required to account quantitatively for the reaction energetics of these compounds.

Our own calculations were motivated by two observations. An earlier MRCI [29] study failed to reach even qualitative agreement with the experiment, presumably because the basis set employed (DZ only) was too small

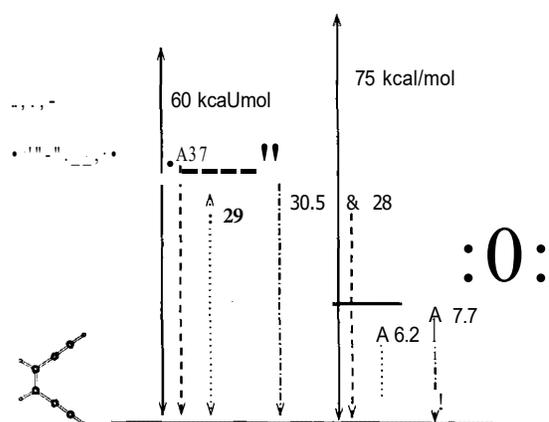


Figure 3 Schematic representation of the energetics (electronic contribution only) of the cyclization reaction of enediyne to para-dihydrobenzene in a cc-pVDZ basis set computed by a variety of methods (SCF, --; CCSD, ---; CCSD (T), ···; and MRD-CI, - · - · -). For details see the discussion in the main text. All energies are in kcal mol⁻¹ relative to the educt.

to account for the dynamic correlation effects. These are strongest in the educt, and hence MCSCF leads to stabilization of the product with respect to the educt. Second, no calculations employing larger basis sets than DZP have been reported in the literature so far. Considering the N⁷ scaling of the computational cost of CCSD(T), the application of this method poses significant challenges both for larger basis sets and compounds larger than the model considered here. Thus our goal was (i) to establish that MRD-CI as a quantitative benchmark method for the model compound at the cc-pVDZ level, and (ii) to explore larger basis sets with this method to ensure that the agreement obtained at that level of theory is not fortuitous.

As summarized in table 3 we have been successful in establishing that MRD-CI reproduces the CCSD(T) results in the cc-pVDZ basis set. The transition state

Table 3 Electronic differences between the energies of ethyne, p-dihydrobenzene and its forward transition state calculated with various methods in cc-pVDZ and cc-pVTZ basis sets in B3LYP optimized geometries. Relative energies are reported in kcal mol⁻¹. The experimental values are taken from [30] and are corrected to the energies of OK according to [31].

Method	Basis	Transition state	Dihydrobenzene
MRD-CI	aug-cc-pVDZ	32.4	7.7
MRD-CI+Dav	aug-cc-pVDZ	30.5	6.8
CCSD	aug-cc-pVDZ	37.0	28.0
CCSD(T)	aug-cc-pVDZ	29.0	6.2
MRD-CI	aug-cc-pVDZ	28.5	6.1
MRD-CI+Dav	aug-cc-pVDZ	28.0	7.7
Experimental		30.1 ± 0.5	7.8 ± 1.0

(using the CCSD geometry) is predicted to be 15 kcal mol⁻¹ higher than by CCSD(T): the product lies 6.8 kcal mol⁻¹ above the educt when the multi-reference Davidson correction is applied in the MRD-CI calculation. This is comparable with the values of the CCSD(T) calculation.

We have performed configuration selecting MRCI calculations on product, educt and transition state in OFT (B3LYP) optimized geometries [28] using cc-pVDZ and cc-pVTZ basis sets. As indicated in table 3 no significant differences in the relative energies of product and educt appear between the double- and triple-zeta quality basis sets. Taking the difference in zero-point vibrational energy into account, the triple-zeta results are in quantitative agreement with the best available experimental data [30, 31].

4. Conclusion

Accurate benchmark methods for the treatment of dynamic correlation effects, such as MRCI, have made a significant impact on the development of quantum chemistry. Since their computational effort rises rapidly (as n) with the number of electrons, only the use of the most powerful computational architectures ensures their continued relevance to the field. Because massively parallel architectures with distributed memory will yield the highest computational throughput in the foreseeable future, it is worthwhile to pursue the use of these machines for quantum chemical benchmark calculations. The development of our scalable implementation of one of the most popular variants of the MRCI method family on such architectures is one important step in this direction. The present implementation allows the treatment of Hilbert spaces, and systems that are larger than those that can be treated on traditional

architectures, while significantly reducing the turnaround time for more moderate applications. With the ability to routinely treat Hilbert space exceeding 10^{12} determinants (10^7 in the variational subspace) many questions that require a delicate balance of dynamic and non-dynamic correlation effects, e.g. in transition meta! chemistry, become amenable to the MRCI method.

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