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THEORETICAL RESEARCH PROGRAM TO STUDY CHEMICAL REACTIONS IN AOTV BOW SHOCK TUBES

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Two main areas of code development have been undertaken. The first is the implementation of CASSCF and SCF analytical first derivatives on the CRAY X-MP. Codes for performing geometry optimization using the analytical gradients have also been installed and interfaced to the integral program and the wave function generation programs. As a result it is possible to obtain equilibrium geometries and saddle points with little input from the user beyond an initial guess, and with greatly increased efficiency relative to methods based on computing grids of energy values.

The second major area of code development has been the installation of the complete set of electronic structure codes on the CRAY 2, an activity carried out in collaboration with Dr C. W. Bauschlicher jr. Particular effort was required to make the CASSCF and multireference CI programs operational, as a result of numerous compiler bugs and the incomplete version of FORTRAN offered. The gradient program was much less troublesome. In addition, a new scheme for performing Hartree-Fock calculations with the integral list in memory has been implemented on the CRAY 2. This has been used for calculations with 300 basis functions locally and with basis sets of double this size in Minneapolis. Finally, a proposed method for extending the direct SCF approach to permit beyond-Hartree-Fock calculations has been written up for publication.

In the area of application calculations the main effort has been devoted to performing full CI calculations using the CRAY 2 and using these results to benchmark other methods. The main observation of this work has been the generally excellent agreement between multireference CI results and the full CI. The attached preprints describe some of the systems studied, other work is presently being written up for publication. In addition, calculations on the recombination of H with OH have been commenced, with particular emphasis at this stage on the choice of active space for CASSCF and multireference CI wave functions.

APPENDIX 1

N86-30374

Special note to printer on MS "Integral Processing in beyond-Hartree-Fock calculations, by Peter R. Taylor"

The three "figures" should be typeset by the printer, as they appear. In particular, the indentation structure should be preserved exactly, as this is designed to illustrate computer program loops. The typefaces used should be somewhat smaller than those used for the text.

Integral processing in beyond-Hartree-Fock calculations

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Abstract

The increasing rate at which improvements in processing capacity outstrip improvements in input/output performance of large computers has led to recent attempts to bypass generation of a disk-based integral file. The "direct" SCF method of Almlöf and co-workers represents a very successful implementation of this approach. The present work is concerned with the extension of this general approach to CI and MCSCF calculations. After a discussion of the particular types of MO integrals for which — at least for most current generation machines — disk-based storage seems unavoidable, it is shown how all the necessary integrals can be obtained as matrix elements of Coulomb and exchange operators that can be calculated using a direct approach. Computational implementations of such a scheme are discussed.

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I. Introduction

One of the most interesting recent developments in computational quantum chemistry is the "direct SCF" approach of Almlöf, Faegri and Korsell (AFK) [1]. Recognizing that in some circumstances it may not be feasible to generate a disk file of two-electron integrals (or supermatrix elements) to be used repeatedly in subsequent SCF iterations, AFK suggested that the two-electron integrals be recalculated in each SCF iteration. That is, the Fock matrix contributions from each batch of integrals are computed and then each batch is discarded. There are two distinct sets of circumstances where this strategy should prove advantageous. Where computations are performed using an "in-house" minicomputer it will often be the case that the available disk storage is inadequate for large basis sets (150 – 200 CGTOs, say), or that the performance of the input/output (IO) system is too low for the integral file to be processed in an acceptable real time. Alternatively, where computations are being done on a supercomputer (or even a large conventional mainframe computer), the available disk system capacity and/or performance may not be adequate for the size of basis set (300 or more CGTOs) for which the integral generation time would be acceptable. (Even the arrival of large primary memories, such as the 268 million words available on the CRAY 2, does not provide a complete solution to the problem of storing the integrals). The direct SCF method has proved its worth in both sets of circumstances: basis sets of over 300 CGTOs having been handled on NORD 500 and VAX 11/780 minicomputers and over 500 CGTOs on an IBM 3033 [1]. Of course, AFK's implementation of the direct SCF method incorporates a number of factors designed to improve overall performance. The full symmetry of the nuclear framework is used to minimize the number of distinct two-electron integrals which *might* have to be calculated, while density matrix pre-screening techniques are used to avoid calculation of integrals which contribute negligibly to the Fock matrix [1,2].

While it is very desirable to have a method of this type, there are, of course, many chemical problems for which correlation effects play an important role. Consequently, it seems appropriate to explore schemes whereby a similar general approach — that is, recalculating integrals when they are required — could be taken for CI and MCSCF methods. This work presents an approach in which it is assumed that some integrals are required so frequently that it would be inefficient to recompute them repeatedly, while other integrals can be recomputed as required. Clearly, there is an operational difference between this approach and the philosophy behind direct SCF, as in the latter it is assumed that all integrals are in the same class as far as frequency of use is concerned.*

II. MO Integrals in Direct MR-CI(SD).

The various types of MO integrals appearing in single and double excitation direct CI calculations have been discussed in detail by Siegbahn [3], Ahlrichs [4] and Saunders and van Lenthe [5]. These treatments cover not only the cases of one or several reference configurations, but also the case where the reference configuration is "internally contracted" [4,6-8]. It is clear from these treatments that it is desirable to have the integrals $[ij|kl]$, $[ij|ka]$, $[ij|ab]$ and $[ia|jb]$ (where $i, j\dots$ denote MOs occupied in at least one reference configuration, and $a, b\dots$ the remaining MOs; charge density notation has been used for the integrals) available in the MO basis: these integrals contribute to many different terms in different ways. If *Coulomb operator matrices* $\mathbf{J}^{ij}$ and *exchange operator matrices* $\mathbf{K}^{ij\pm}$ are defined via the matrix elements

$$(p|J^{ij}|q) = [ij|pq] \tag{1}$$

$$(p|K^{ij+}|q) = [ip|jq] + [iq|jp] \tag{2}$$

$$(p|K^{ij-}|q) = [ip|jq] - [iq|jp] \tag{3}$$

for $p, q\dots$ arbitrary MOs, the above required integrals are all included in $\mathbf{J}^{ij}$, $\mathbf{K}^{ij+}$ and $\mathbf{K}^{ij-}$, $i \geq j$.

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* A note on terminology may be appropriate here. The expression "direct CI" has an accepted and widely understood meaning: it refers to a CI calculation in which the Hamiltonian matrix is never computed explicitly and stored. It is not unreasonable to use the term "direct SCF" for an SCF calculations in which the AO integral list is not stored. The expression "direct MCSCF" is closer in meaning to direct CI: the Hessian is not computed explicitly. It is difficult to combine these meanings to cover the sort of method proposed in this work, and while this author has previously used the term "direct direct CI" this is both ugly and confusing. No convenient alternative readily presents itself, however.

The remaining possible integral types, $[ia|bc]$ and $[ab|cd]$, are not required in the MO basis for direct CI calculations [4,5]. Their contribution to the residual vector $\sigma = \mathbf{H}\mathbf{c}$ can be written in terms of AO integrals for a suitable renormalization of $\mathbf{c}$ [4,5,8]. This approach is discussed further in section V below.

It appears, therefore, that if a direct CI scheme is used for optimization of an MR-CI(SD) wave function, the integrals which must be computed (and stored) in the MO basis are just the $\mathbf{J}^{ij}$ and $\mathbf{K}^{ij\pm}$ for *correlated* MOs $i \geq j$. It should be noted that while the term "CI" has been used here, all of the above remarks apply also to methods based on the coupled-pair many-electron theory of Cizek [9]. This includes both coupled-cluster methods and approximate CEPA-type schemes [10-13].

III. MO integrals in MCSCF calculations.

The question of which integral types need to be transformed into the MO basis has been investigated in some detail by Almlöf and Taylor [2]. Their conclusion is that it is generally necessary to have matrix elements of $\mathbf{J}^{tu}$ and $\mathbf{K}^{tu\pm}$ in the MO basis: here t and u denote partially occupied (*active*) MOs in the MCSCF wave function. The availability of operators $\mathbf{J}^{ij}$, $\mathbf{K}^{ij\pm}$, $\mathbf{J}^{it}$ and $\mathbf{K}^{it\pm}$ (here $i, j...$ denote doubly occupied (*inactive*) MOs) in the MO basis allows a very simple formulation of the MCSCF orbital optimization problem (see e.g. refs 14 and 15), but in a "direct" MCSCF formulation [14] it is always possible to rewrite the contributions of these operators in terms of the AO integrals [2,16]. Elements of $\mathbf{J}^{tu}$ and $\mathbf{K}^{tu\pm}$ are needed for the CI step (or, in a full second-order treatment, the CI sub-block of the Hessian and the CI gradient term) and for some CI-orbital rotation coupling terms, and most of these contributions are awkward to reformulate in terms of AO integrals. In this way, each cycle of the MCSCF optimization requires construction of $\mathbf{J}^{tu}$ and $\mathbf{K}^{tu\pm}$ once, followed by contraction of a supermatrix with quantities similar to density matrices. This contraction must be performed in every micro-iteration through the MCSCF linear equation system if a full second-order optimization is performed — for first-order schemes [15,17,18] intermediate Fock-type operator matrices can be constructed with one such contraction step and then re-used within the given cycle. Full details are given in ref 18.

For a second-order MCSCF scheme with the minimum number of integrals stored on disk, therefore, it will be necessary to recompute the AO integrals in every micro-iteration of every cycle. In individual cases it may be preferable to construct $\mathbf{J}^{ij}$, $\mathbf{K}^{ij\pm}$, $\mathbf{J}^{it}$ and $\mathbf{K}^{it\pm}$ once in each cycle, and then to process all the integrals in the MO basis: this would depend on the balance between the transformation labour to obtain these operators (and how many there are) and the integral evaluation time. For large extended systems it may be that sparseness in the integral list combined with pre-screening of density matrices might make the completely direct MCSCF approach favourable. Dynamic adjustment of the number of micro-iterations used in a given cycle (solving the linear equations less accurately when far from overall convergence) will also improve performance. In any event, for the purposes of the present discussion it is clear that the problem of generating MO integrals for use in an MCSCF calculation is equivalent to that of a CI calculation: J and $K^{\pm}$ operators over certain occupied MOs must be available.

IV. Construction of operator matrices.

Where the AO integral list is available, and disk capacity or performance is adequate, the most efficient route to the required $\mathbf{J}$ and $\mathbf{K}^{\pm}$ matrices is via a limited four-index transformation [4,5] (see also ref 19 and refs therein), performed as the four quarter-transformations

$$[i\nu|\lambda\sigma] = \sum_{\mu} [\mu\nu|\lambda\sigma] C_{\mu i} \tag{4a}$$

$$[ij|\lambda\sigma] = \sum_{\nu} [i\nu|\lambda\sigma] C_{\nu j} \tag{4b}$$

$$[ij|p\sigma] = \sum_{\lambda} [ij|\lambda\sigma] C_{\lambda p} \tag{4c}$$

$$[ij|pq] = \sum_{\sigma} [ij|p\sigma] C_{\sigma q} \tag{4d}$$

for the element J^{ij}_{pq}. Here μ, ν, λ and σ denote AOs and $\mathbf{C}$ is the matrix of MO coefficients. The most time-consuming of the four steps is ($4a$), which behaves as nN^4 operations for n active or correlated MOs and N AOs; ($4b - d$) behave as n^2N^3. Similar behaviour is obtained for calculation of $K^{ij\pm}_{pq}$ provided that the AO integrals are sorted differently before the transformation.

A less efficient (in terms of floating-point operations) procedure essentially involves combining the first two quarter-transformations into a single step, generating, say,

$$(\mu|J^{ij}|\nu) = \sum_{\lambda}\sum_{\sigma}[\mu\nu|\lambda\sigma]C_{\lambda i}C_{\sigma j} \tag{5}$$

and then transforming μ and ν to the MO basis. Defining "density matrices" $\mathbf{D}^{ij}$ via

$$D^{ij}_{\mu\nu} = C_{\mu i}C_{\nu j} \tag{6}$$

allows (5) to be viewed as contraction of integrals with a density matrix, analogous to Fock matrix construction in an SCF calculation. (5) behaves as n^2N^4, that is, some n times worse than (4). However, a scalar implementation of (5) requires no sorting of the AO integrals, and there is no need to expand the integral list beyond the normal canonical indexing $\mu \geq \nu$, $\lambda \geq \sigma$ and $(\mu\nu) \geq (\lambda\sigma)$.

Consider now an approach in which AO integrals are computed, used in some transformation process and then discarded, without being written to disk and reread. If the n^2N^4 process defined by (5) is used, it will be possible to hold simultaneously $2L/N(N+1)$ operator arrays $\mathbf{J}$ or $\mathbf{K}^{\pm}$ in L words of memory. As there are some $\frac{3}{2}n^2$ operators *in toto* to be constructed, it will be necessary to generate the integrals $3n^2N^2/4L$ times. For 200 AOs, 20 correlated or active MOs and 4 million words of memory some 3 passes would be required, however, a 50% increase in n or N results in a factor of 2 increase in the number of passes, as would a 50% reduction in the memory available. The n^2 and N^2 scaling in the number of passes is clearly a considerable disadvantage of the n^2N^4 approach.

On the other hand, by defining a "test density" as

$$D^{test}_{\lambda\sigma} = \max_{[ij]}|C_{\lambda i}C_{\sigma j}|, \tag{7}$$

where the notation $[ij]$ denotes all MO pairs whose operators are being processed in the current pass, an effective pre-screening technique can be implemented to decide whether a particular $[\mu\nu|\lambda\sigma]$ need be calculated. (This process is readily extended to the case of calculating AO integrals in shells, as discussed below and in refs 1 and 2). Clearly, as n or N increases, the number of operators generated in each pass decreases. It may be expected that, in turn, the sparsity of $\mathbf{D}^{test}$ will increase (certainly $\mathbf{D}^{test}$ cannot become less sparse) which will decrease the number of AO integrals to be calculated in each pass. This phenomenon will tend to offset the effect of the n^2 and N^2 scaling discussed above, and will play an important role when localized MOs are used.

Completion of the transformation of the $\mathbf{J}^{ij}$, etc, is also simple in the case of the n^2N^4 approach. Each operator matrix, once constructed in the AO basis, can be transformed to the MO basis and then written to disk directly. No additional sorting is required and the final operator matrices are in exactly the form required for "matrix-formulated" direct CI [4,5,20]. Typical loop structures for constructing various operators are discussed in section VI below.

In an implementation of the nN^4 scheme different procedures must be followed for the J and K cases. For J operators, it is necessary to compute blocks of integrals $[\mu\nu|\lambda\sigma]$, for all $\mu \geq \nu$ and for as many $\lambda\sigma(\lambda \geq \sigma)$ pairs as will fit in L words of memory. It is then possible to carry out the first two quarter-transformations $(4a, b)$ for *all* ij $(i \geq j)$ pairs. The resultant $[ij|\lambda\sigma]$ must then be written to disk, so that once all of the $[ij|\lambda\sigma]$ are available they can be re-sorted to AO $\mathbf{J}$ matrices for the final half-transformation. Note that in the AO integral generation it is not possible to restrict consideration to the case $(\mu\nu) \geq (\lambda\sigma)$ (the normal canonical ordering): effectively, the integrals must be computed twice. For $K^{\pm}$ integral blocks $[\mu\nu|\lambda\sigma]$, with all $\mu\lambda$ and for as many $\nu\sigma(\nu \geq \sigma)$ as can be held in memory, are transformed to $[i\nu|j\sigma] \pm [i\sigma|j\nu]$ for all $i \geq j$. Again, these half-transformed integrals must be re-sorted for the final transformation. Clearly, this latter ordering of $[\mu\nu|\lambda\sigma]$ is different from the J case and the n^2N^4 scheme. Indeed, it not only differs from the conventional ordering used in integral programs, but it also involves some redundant recomputation of integrals because of the need to have all $\mu\lambda$ pairs, not just $\mu \geq \lambda$. Essentially, the AO integrals must be computed four times. There are thus not only disk and IO overheads associated with the nN^4 scheme, but also additional CPU costs occasioned by recomputation of integrals. It will depend on the individual case whether these additional overheads offset the much more favourable floating-point behaviour of the transformation step relative to the n^2N^4 scheme. It should be noted that the disk space (and IO required) behave as n^2N^2, which is usually very much less than the N^4 requirements for the initial sorting of a disk-based integral list for a conventional transformation. A disadvantage of the suggested implementation of the nN^4 procedure is that it is not possible to make as much use of pre-screening as in the n^2N^4 case. This is because the first half-transformation is used to produce $[ij|\lambda\sigma]$ for all ij from $[\mu\nu|\lambda\sigma]$ for all $\mu\nu$: the effective "test density" analogous to (6) would involve all ij pairs and would thus be as dense as the worst possible case for the n^2N^4 scheme. It is quite conceivable that in some cases, such as large extended organic systems, the n^2N^4 approach with its effective pre-screening would be the method of choice, while for relatively compact systems of heavier atoms, such as polynuclear transition metal complexes, the nN^4 approach would be preferable.

V. External Exchange Operators.

As was noted above, it has been pointed out by several authors [4,5,8] that the direct CI contribution of the MO integrals $[ab|ci]$ and $[ab|cd]$ can be evaluated in the AO basis using the operator matrices $\mathbf{K}^P$ with elements

$$K^P_{ab} = (a|K^P|b) = \sum_{\mu}\sum_{\nu}(\mu|K^P|\nu)C_{\mu a}C_{\nu b}, \tag{8}$$

where

$$(\mu|K^P|\nu) = \sum_{\lambda}\sum_{\sigma}[\mu\lambda|\nu\sigma]V^P_{\lambda\sigma}, \tag{9}$$

with

$$V^P_{\lambda\sigma} = \sum_{p}\sum_{q}\tilde{c}^{pq}_P C_{\lambda p}C_{\sigma q} \tag{10}$$

The "CI coefficient" array $\tilde{c}$ is obtained as follows. For doubly-excited CSFs which differ only in virtual MO occupation (i.e. all have the same virtual MO spin-coupling and the same $(N_e - 2)$-electron occupied MO part P (for N_e electrons correlated)) the various CI coefficients c^{ab}_P are collected into the array $\mathbf{c}_P$ which is then renormalized to give $\bar{c}_P$ according to refs [4,5]. We then have

$$\tilde{c}^{pq}_P = \bar{c}^{pq}_P + \sum_{Q}\delta_{ip}\delta_{dq}c^a_Q B^{PQ}_{iabd} \tag{11}$$

where B^{PQ}_{iabd} is a two-electron coupling coefficient and c^a_Q is the CI coefficient of a singly-excited CSF.

Clearly, the construction of $\mathbf{K}^P$ in the AO basis using $(8-11)$ parallels the construction of the $\mathbf{K}^{ij}$ operators via the n^2N^4 scheme outlined above in section IV. Indeed, by explicitly recognizing that the two virtual MOs can be either singlet or triplet coupled it is possible to proceed via $\mathbf{K}^{P\pm}$ operators obtained from sums and differences of integrals as in eqns (2) and (3). Pre-screening via a test density matrix can be used to reduce the number of AO integrals which must be calculated, offsetting in part the n^2N^4 dependence of the K^P generation. However, the external exchange operator construction must be performed in each CI iteration, which (when the time taken to re-evaluate the integrals is included) is likely to lead to its dominating the timing for calculations with large basis sets.

It is also possible to consider an alternative scheme for computing the contribution from the external exchange operators which shares features with the nN^4 scheme for $\mathbf{J}^{ij}$ and $\mathbf{K}^{ij\pm}$. It is possible to form arrays $\mathbf{K}^{cd}$ according to

$$K_{\mu\nu}^{cd} = \sum_{\lambda}\sum_{\sigma}[\mu\lambda|\nu\sigma]C_{\lambda c}C_{\sigma d} \tag{12}$$

and then, without any intermediate IO, to combine these half-transformed integrals with CI-coefficients as

$$K_{\mu\nu}^{P} = \sum_{c}\sum_{d} K_{\mu\nu}^{cd} c_{P}^{cd}. \tag{13}$$

The $K_{\mu\nu}^{P}$ would be written out to disk for re-sorting. The strategy would be to hold all $\lambda\sigma$ values in memory (in (12)) for as many $\mu\nu$ values as possible. The floating-point behaviour of (12) (assuming that in practice it would be performed as two successive quarter-transformations) is $(N-n)N^4$, while that of (13) is essentially $n^2(N-n)^2N^2$. Of course, the same recomputation of integrals is required for (12) as for the nN^4 approach to construction of $\mathbf{K}^{ij\pm}$ matrices discussed in the previous section.

For the case of the "externally contracted" CI method of Siegbahn [7], integrals such as $[ac|bd]$ are used not simply to form K_{ab}^{P} but rather to form Δ_P where

$$\Delta_P = \sum_{a}\sum_{b} K_{ab}^{P} c_{P}^{ab} \tag{14}$$

Here c_P^{ab} is a CI coefficient in a wave function obtained in the lowest order of perturbation theory. Δ_P need be constructed only once during the contracted CI calculation, and thus there is a very considerable advantage over the normal CI methods, since these require recalculation of the external exchange contribution in each iteration.

VI. Treatment of symmetry

The direct SCF implementation of AFK benefits enormously from the exploitation of symmetry. This is used to reduce the number of distinct integrals which must be computed, and to reduce the dimensions of the various matrices which must be processed. It is well known that the incorporation of symmetry considerably improves the efficiency of conventional 4-index transformation and CI programs, and it is certainly desirable to extend these improvements to the present approach to beyond-Hartree-Fock methods. This is not difficult, although there are several points worthy of note.

First, the operators J^{ij} and $K^{ij\pm}$ will not always transform according to the totally symmetric irreducible representation of the molecular point group, G. Thus

$$RJ^{ij}R^{\dagger} = \sum_{\Lambda} D^{\alpha}_{K\Lambda}(R)^{*} J^{ij}, \tag{15}$$

where $R \in G$, and $D^{\alpha}_{K\Lambda}(R)^{*}$ is an element of a representation matrix for α, which may not be an irreducible representation. By choosing appropriate combinations of ij and their partner MOs in degenerate irreducible representations, it is possible to restrict attention to the case of α irreducible. In (15), therefore, J^{ij} would represent a combination of J operators which transform according to row K of irreducible representation α. In an SCF calculation, the Fock and density matrices transform according to the case of α being the totally symmetric irreducible representation, and for this case a straightforward scheme for using a list of symmetry-distinct AO integrals to construct "skeleton" matrices which are later symmetrized to give the full result has been derived by Dupuis and King [21], based on earlier work by Dacre [22] and Elder [23]. The present author has extended the Dupuis and King scheme to the case of non-totally symmetric operators [24]. The only difficulty that arises in this extension is the need for full representation matrices (not merely characters) in the symmetrization of the skeleton matrices. These can be calculated from the characters of the group and a chain of subgroups by an ingenious method due to Hurley [25].

It is thus possible to use the technique of ref 24 to generate integrals over MOs from a list of symmetry-distinct AO integrals. Use of the n^2N^4 scheme (5) for the transformation step leads to very similar processing as in the SCF case, as for (5) there is no need to order the integrals. Fig 1 shows the loop structure of an integral routine designed to implement this scheme. The loop structure is greatly simplified: most codes would feature double loops over centres and then shells on those centres. Loops over shell components have not been shown explicitly. In the figures, the *stabilizer* [24] of a shell or centre is that subgroup of G under which the centre is invariant. Distinct integrals are generated in terms of double coset representatives for various pairs of stabilizers: for full details the reader is referred to Davidson [26]. As far as the overall loop structure of Fig 1 is concerned there is essentially no change from the SCF case, for which the statements in the innermost loop would simply add or subtract appropriate Fock matrix contributions.

It is also possible to handle symmetry in J operator construction by the nN^4 scheme (4) straightforwardly and a possible loop structure is given in Fig 2. However, complications ensue for the $K^{\pm}$ operators. This is because integral evaluation schemes are based on charge densities (products of basis functions) and determining the symmetry-distinct AO integral list is also based on charge densities. Such an approach naturally works for J operators, since what is required is a list of $[\mu\nu|\lambda\sigma]$ with $\mu\nu$ fixed and all $\lambda\sigma$, and this is simply all charge densities $\lambda\sigma$ for the single charge density $\mu\nu$. Symmetry-distinct integrals are obtained from $[\mu R\nu|T(\lambda S\sigma)]$, where R, S and T are operators from the point group: the range of operators giving distinct integrals is determined by the symmetry transformation properties of the points on which the AOs are centred. Again, it is simple to work in terms of unique charge distributions $\mu R\nu$ and $\lambda S\sigma$ and their transforms, and to form all $T(\lambda S\sigma)$ for a fixed $\mu R\nu$. For $K^{\pm}$ operators, however, what is needed from the list $[\mu R\nu|T(\lambda S\sigma)]$ are terms with $\mu T\lambda$ fixed and all possible $R\nu TS\sigma$. Not only is this clearly not charge distribution based, but the range of T operators giving distinct integrals cannot be determined until $\mu, \nu, \lambda, \sigma, R$ and S are known. This complicates the loop structure of the integral program, and, since it is usually desirable to compute information about charge distributions in the outermost possible loop, it will be necessary either to compute this information in inner loops or to compute information about all possible charge distributions in the outer loops, performing redundant work since some of these distributions will turn out to be non-unique. A nN^4 scheme loop structure for $K^{\pm}$ operators, incorporating symmetry, is given in Fig 3, and the problems associated with $K^{\pm}$ operators can be clearly seen by comparing Fig 3 with Fig 2.

VII. Computational considerations

The need for repeated calculation of AO integrals, particularly in implementations of the n^2N^4 transformation procedure (5), suggests that a primary goal must be an efficient integral evaluations scheme. This problem has received considerable attention in the last fifteen years [27-29], and a number of very efficient schemes have been devised. A key feature of these schemes is the use of shells of basis functions, a shell being defined by a set of contracted Gaussian functions of the same L value, located on the same centre, with the same exponents and contraction coefficients but differing in their angular behaviour. Integrals over four such shells — a "shell block" of integrals — share many common factors, and avoiding redundant recomputation of these factors results in a substantial increase in efficiency. Such use of shells rather than individual basis functions is implicit in the loop structures of Figs 1 - 3. The use of shells requires a modification of the pre-screening procedure: clearly, as long as one integral in a shell block is required it will be necessary to compute the entire block. It is therefore convenient to define test densities (7) for shells rather than basis functions. Thus

$$D_{MN}^{test} = \max_{[ij]} |C_{\mu i} C_{\nu j}|, \mu \in M, \nu \in N \tag{16}$$

for shells M and N.

Most AO integral evaluation schemes are rather readily vectorized [30]. Integral evaluation is also a task which is suited to parallel architectures [30]. For the rest of this section, therefore, we shall assume that the problem of efficient integral evaluation has been solved and concentrate on the processing of the AO integrals once they are available.

The nN^4 transformation (4) is vectorizable in terms of successive matrix multiplications in which the innermost loop is of order N. For vector processors such as the CRAY machines, multiplication of matrices of this order leads to performance close to the theoretical maximum. For computers that require greater vector lengths to achieve maximum performance it is possible to write (4) as a set of "vector = vector + scalar*vector" (SAXPY [31]) operations of length n^2 to N^2 or even n^2N to N^3 [2]. It is also possible to perform the first half-transformation ($4a, b$) efficiently on a parallel architecture, by generating and processing subsets of integrals (such as $[\mu\nu|\lambda\sigma]$, $\forall\ \lambda \geq \sigma$ and fixed $\mu \geq \nu$) on each processor. However, the reordering and subsequent processing of the half-transformed integrals will require considerable data movement between processors; and the overall efficiency will depend critically on the speed of inter-processor communication [32]. For machines with a large common memory or solid-state disk this will obviously be much less of a problem than for polytope architectures, such as hypercubes, with relatively slow data paths between nodes.

The n^2N^4 scheme (5) is straightforward to vectorize (in terms of SAXPYs) on the number of operator matrices which can be held in memory simultaneously. The maximum possible value is $\frac{3}{2}n^2$, when all J, K^+ and K^- operators can be processed in one pass. For large basis sets the memory requirements would usually be prohibitive, and a subrange of operators would be processed in each pass. This may lead to vector lengths too short for efficient processing. This scheme is very easy to adapt to parallel architectures: each processor simply generates a subset of the J^{ij}, etc. although this requires each processor to generate all the AO integrals if inter-processor communication is to be avoided. Of course, for multi-processor architectures with common memory, such as the CRAY X-MP or CRAY 2 the latter problem does not arise.

It is clear that similar reasoning can be applied to the external exchange contribution discussed in section V. Indeed, some additional steps which arise in this case, such as (10) and (13), are also readily vectorized. It therefore seems that processing of integrals along the lines described here can be made very efficient on most current generation computing machinery.

Finally, it may be useful to give an example of the data storage and recalculation requirements in a large CI calculation using the schemes suggested here. We consider a calculation on the molecule $Fe(CO)_5$, similar to the largest calculations reported by Lüthi and co-workers [33], but using a larger basis. Assuming that an [$8s6p4d1f$] basis is used for Fe and a [$4s2p1d$] basis for C and O, there will be 233 AOs (using spherical harmonics) and 39 occupied MOs at the Hartree-Fock level. If only the Fe $3d$ and $4s$ and ligand σ lone pair electrons are correlated there will be 9 MOs correlated, if the ligand π electrons are included there will be 19. We assume that 4 million words of central memory are available. For 9 MOs correlated there will be 126 J^{ij} and $K^{ij\pm}$ operators, and using the n^2N^4 scheme all could be computed in a single pass over the integrals, using (5). If density matrices (6) are formed in advance, the storage for operator matrices is halved and two passes over the integrals would be required. The final operator matrices would require less than one million words of disk space, assuming that C_{2v} symmetry is used. Use of the full D_{3h} symmetry would reduce this even further. If the nN^4 scheme (4) is used, one pass each for J and K operators would be required: this would be equivalent to recomputing the integrals about six times. Re-sorting of the half- transformed operators could be done in memory. For 19 MOs correlated the number of passes for the nN^4 scheme would not change, however, the n^2N^4 scheme would require about six passes over the integrals using (5), or nine using (5) and (6). In either case some 4 million words of disk space would be needed for the final operators. For the n^2N^4 case these calculations would all vectorize with a vector length greater than 60, which would be very efficient on machines such as the CRAY 1 or CRAY X-MP.

In each iteration of the direct CI it is most efficient to generate the contribution from the external exchange operators first. For 9 MOs correlated there are 81 external exchange operators to be computed, these could be generated in two passes using (9). For 19 MOs there are 361 operators, these would require five passes. Using (12) one pass only would be required for either 9 or 19 MOs correlated, but again this is equivalent to computing the integrals four times. The completed exchange operators can be used as the first contributions to the vector σ, which would be of length about 350 000 words for 9 MOs correlated, assuming C_{2v} symmetry, or 3 000 000 for 19 MOs correlated. In the latter case it would be necessary to process the CI coefficients from disk if all of σ is to be held in memory. Calculations on this scale would hardly be possible using a "conventional" disk-based transformation and direct CI approach.

It is clear that the overall labour in such a calculation, while substantial, is not unreasonably large for a modern supercomputer, or even a large mainframe. It is also clear that if the only consideration is to minimize the number of times the AO integrals are recomputed there is little to choose between the nN^4 and n^2N^4 transformation schemes, at least for calculations of this size.

VII. Conclusions

The present work is an attempt to outline some novel prospects for large basis set electronic structure calculations that include electron correlation. In general, the various approaches suggested are well suited to modern computer architectures and share the overall philosophy of avoiding or minimizing the disk-based storage and retrieval of integrals. Only certain MO integrals need be stored: no storage of AO integrals is required and the method is thus a natural generalization of the direct SCF method of Almlöf and co-workers.

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Fig 1. Loop structure for n^2N^4 operator matrix generation

```
Loop on subranges of $ij$ such that all matrices fit in memory
  Loop on shells $M$, stabilizer is $\mathcal{M}$
    Loop on shells $N$ ($\leq M$), stabilizer is $\mathcal{N}$
      Define $\mathbf{R}$ as generators for double cosets $\mathcal{M}G\mathcal{N}$ $\forall\ G \in \mathcal{G}$
      Loop on elements $R$ of $\mathbf{R}$ generating shells $RN$
        Define $\mathcal{U}$ as stabilizer of $M.RN$
        Loop on shells $\Lambda$ ($\leq M$), stabilizer is $\mathcal{L}$
          Loop on shells $\Sigma$ ($\leq \Lambda$, unless $\Lambda = M$, when $\Sigma \leq N$), stabilizer is $\mathcal{S}$
            Define $\mathbf{S}$ as generators for $\mathcal{L}G\mathcal{S}$ $\forall\ G \in \mathcal{G}$
            Loop on elements $S$ of $\mathbf{S}$ generating shells $S\Sigma$
              Define $\mathcal{V}$ as stabilizer of $\Lambda.S\Sigma$
              Define $\mathbf{T}$ as generators for $\mathcal{U}G\mathcal{V}$ $\forall\ G \in \mathcal{G}$
              Loop on elements $T$ of $\mathbf{T}$ generating $T(\Lambda S\Sigma)$
                Compute $[\mu R\nu|T(\lambda S\sigma)]$ $\forall\ \mu \in M$, etc
                Accumulate contributions into $J^{ij}_{\mu\ R\nu}$, $J^{ij}_{T\lambda\ TS\sigma}$
                  $K^{ij}_{R\nu\ TS\sigma}$ or whichever skeleton operator
                  matrices are being generated in this pass
              End loop on $T$
            End loop on $S$
          End loop on $\Sigma$
        End loop on $\Lambda$
      End loop on $R$
    End loop on $N$
  End loop on $M$
  Symmetrize operator matrices, complete transformation
    and write operators from this subrange to disk
End loop on subranges of $ij$
```

Fig 2. Loop structure for nN^4 J operator matrix generation

```
Loop on shells $M$, stabilizer is $\mathcal{M}$
  Loop on shells $N$ $(\leq M)$, stabilizer is $\mathcal{N}$
    Define $\mathbf{R}$ as generators for double cosets $\mathcal{M}G\mathcal{N}$ $\forall$ $G \in \mathcal{G}$
    Loop on elements $R$ of $\mathbf{R}$, generating shells $RN$
      Define $\mathcal{U}$ as stabilizer of $M.RN$
      Loop on shells $\Lambda$, stabilizer is $\mathcal{L}$
        Loop on shells $\Sigma$ $(\leq \Lambda)$, stabilizer is $\mathcal{S}$
          Define $\mathbf{S}$ as generators for $\mathcal{L}G\mathcal{S}$ $\forall$ $G \in \mathcal{G}$
          Loop on elements $S$ of $\mathbf{S}$, generating shells $S\Sigma$
            Define $\mathcal{V}$ as stabilizer of $\Lambda.S\Sigma$
            Define $\mathbf{T}$ as generators for $\mathcal{U}G\mathcal{V}$ $\forall$ $G \in \mathcal{G}$
            Loop on elements $T$ of $\mathbf{T}$, generating $T(\Lambda\ S\Sigma)$
              Compute $[\mu R\nu|T(\lambda S\sigma)]$ $\forall$ $\mu \in M$, etc
                stored in memory, indexed by $\mu, \nu, \Lambda, \lambda, \Sigma, \sigma, S$ and $T$
            End loop on $T$
          End loop on $S$
        End loop on $\Sigma$
      End loop on $\Lambda$
      Form skeleton $J^{ij}_{\mu\ R\nu}$ for each $ij, i \geq j$ and $\mu \in M, \nu \in N$
        symmetrize and write to disk
    End loop on $R$
  End loop on $N$
End loop on $M$
(Read back, re-sort and transform — loop structure not given)
```

Fig 3. Loop structure for nN^4 K operator matrix generation

```
Loop on shells $M$, stabilizer is $\mathcal{M}$
  Loop on shells $N$ $(\leq M)$, stabilizer is $\mathcal{N}$
    Define $\mathbf{H}$ such that $H\mathcal{N}$ $\forall$ $H \in \mathbf{H}$, are distinct left cosets of $\mathcal{N}$
    Loop on elements $H$ of $\mathbf{H}$, generating shells $HN$
      Loop on shells $\Lambda$, stabilizer is $\mathcal{L}$
        Define $\mathbf{R}$ as generators for double cosets $\mathcal{M}G\mathcal{L}$ $\forall$ $G \in \mathcal{G}$
        Loop on shells $\Sigma$, stabilizer is $\mathcal{S}$
          Define $\mathbf{S}$ as generators for $\mathcal{N}G\mathcal{S}$ $\forall$ $G \in \mathcal{G}$
          Loop on elements $R$ of $\mathbf{R}$, generating shells $R\Lambda$
            Define $\mathcal{U}$ as stabilizer of $M.R\Lambda$
            Loop on elements $S$ of $\mathbf{S}$ generating shells $S\Sigma$
              Define $\mathcal{V}$ as stabilizer of $N.S\Sigma$
              Define $\mathbf{T}$ as generators for $\mathcal{U}G\mathcal{V}$ $\forall$ $G \in \mathcal{G}$
              If $H \in \mathbf{T}$ then
                Compute $[\mu R\lambda|H(\nu S\sigma)]$ $\forall$ $\mu \in M$, etc
                  stored in memory, indexed by $\mu, \nu, \Lambda, \lambda, \Sigma, \sigma, R, S$ and $H$
              Endif
            End loop on $S$
          End loop on $R$
        End loop on $\Sigma$
      End loop on $\Lambda$
      Form skeleton $K^{ij}_{\mu H\nu}$for each $ij, i \geq j$ and $\mu \in M, \nu \in N$
        symmetrize and write to disk
    End loop on $H$
  End loop on $N$
End loop on $M$
(Read back, re-sort and transform — loop structure not given)
```

APPENDIX 2

N86-30375

Benchmark full configuration-interaction calculations on H_2O, F and F^-

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Abstract

Full configuration-interaction calculations are reported, and compared to other methods, for H_2O at its equilibrium geometry and at two geometries with the H-O bonds stretched. Since the percentage of the SCF reference in the FCI wave function decreases greatly with the bond elongation, the accuracy of techniques based on a single reference do not compare well with the FCI results. However, the results from a CASSCF/MRCI treatment are in good agreement with the FCI. Correlation effects in F compared to Ne are far more similar than for F^- compared to Ne, despite F^- and Ne being isoelectronic. Since the importance of higher than double excitations is more important for F^- than F, a very high percentage of the correlation must be obtained to accurately compute the electron affinity. In a CASSCF/MRCI treatment the higher than quadruple excitations contribute 0.02 eV to the EA, even for modest basis sets.

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I. Introduction

We have recently compared several different computational procedures to full configuration-interaction (FCI) calculations for Ne atom [1], O atom and its negative ion O^- [2], HF and NH_2 [3]. Unlike previous FCI calculations [4-5] and subsequent tests of methods [6-8], double zeta plus polarization (DZP) or larger basis sets were used. Our recent calculations were made possible by recent theoretical [9-10] and technological advances [11]. The benchmark calculations [1-3] showed that the quality of such approximations as the Davidson correction [12] or the coupled-pair functional (CPF) method [13] varied with the basis set and with the weight of the SCF reference in the CI expansion. While the dependence of the accuracy of such approximations on the weight of the SCF reference is not unexpected, the dependence upon the basis set was a surprise. For example, in Ne atom the Davidson correction underestimates the importance of quadruples for basis sets without polarization functions, but overestimates their importance by 20% for a basis set with two sets of polarization functions. The CPF approach shows the opposite effect, improving as the basis set is expanded.

Normally, it is not the absolute accuracy of the methods, but the relative accuracy across a potential surface, that is more important. The HF and NH_2 calculations show that for large geometrical distortions, the SCF reference becomes sufficiently poor that the above approximations are in general unreliable. Multi-reference singles and doubles CI (MRSDCI) calculations based upon a complete active space SCF (CASSCF) [14] wave function give potentials that far better parallel the FCI results. The inclusion of the multi-reference analog of the Davidson correction is found to either improve or leave unchanged the accuracy of the CASSCF/MRCI treatment. While the calculations on HF and NH_2 lead to considerable optimism as to the accuracy of the CASSCF/MRCI approach, calculations on the electron affinity (EA) of O atom show that even this method has its limitations; a very large CASSCF/MRCI treatment (308 reference configuration state functions (CSF's) in D_{2h}) is not able to account for all of the differential higher excitation contributions to the EA.

The previous results have led us to consider H_2O, F and F^-. H_2O has one more electron than NH_2, thus we are able to see if the accuracy of the different approximations depends upon the number of electrons. The decomposition of the correlation by excitation level shows F to be more similar to Ne, while F^- is different from either F or Ne. It is this different character of the correlation which leads to the problems associated with computing the EA.

II. Method of calculation

The O basis set is the Dunning [15] [4s2p] contraction of the Huzinaga [16] (9s5p) primitive set augmented with a d polarization function with an exponent of 1.2. The H basis set is the [2s] contraction of the (4s) primitive set scaled by 1.2 [15] and augmented with a set of p (α=0.8) polarization functions. For the F and F^- calculations the (9s5p) primitive set is contracted to either [4s2p] following Dunning [15], or to [5s3p] by freeing the outermost primitive in the contraction. To adequately describe F^-, the diffuse p set optimized by Dunning and Hay [17] is added, yielding a final valence basis sets of the form (9s6p)/[4s3p] and (9s6p)/[5s4p]. Since the bases sets are given to a different number of significant figures in references 15 and 17, to avoid confusion we tabulate the basis sets in Table I. A 3d polarization function is optimized at the FCI level for F^-. The optimal value was found to be 1.60, the same as that found by Ahlrichs et al. [18] in the optimization for HF at the independent electron pair approximation (IEPA). Therefore, when two d functions are added, the exponents are taken from Ahlrichs [18], α=4.5 and 1.3. In all calculations the 3s components of the 3d orbitals are deleted.

For H_2O we consider the equilibrium geometry (r_e), as defined in Table II, and two configurations where the H-O-H angle is unchanged and the O-H bonds are stretched to $1.5*r_e$ and $2*r_e$. At these three geometries we consider several different levels of treatment. Many correlation treatments are based on a single reference, and for these the SCF orbitals are used. In order to reduce the dimension of the FCI expansion, the 1s electrons are not correlated in any of the calculations. The first level of correlation includes single and double excitations from the SCF reference (SDCI). We use both the Davidson correction [12] (denoted +Q) and the CPF [13] (an essentially size-consistent reformulation of SDCI) to estimate the importance of higher excitations. The importance of higher excitations is also treated via a multi-reference SDCI calculation. These MRCI calculations are based upon a CASSCF optimization of the orbitals and include all of the CSF's in the CASSCF as references. Two different CASSCF calculations are performed. The first correlates the two O-H bonds; the four bonding electrons are distributed within the two active a_1 and two active b_2 orbitals. Although this CASSCF gives proper dissociation, the MRCI calculation shows important configurations (coefficient greater than 0.05 in the MRCI wave function) not included in the reference space. These additional CSF's involve excitations out of the b_1 lone pair of oxygen. To account for this additional important correlation effect, the two b_1 electrons and two b_1 orbitals are added to the CASSCF active space. The MRCI(BIG) calculation based upon the CASSCF(BIG) orbitals does not show any additional important CSF's. The importance of the additional CSF's associated with the b_1 lone pair decreases as the bond length is increased. As the H atoms donate charge to the oxygen, this additional correlation reflects some O^- character near r_e which vanishes as H_2O dissociates. The MRCI(BIG) calculations contain only 31096 CSF's, as compared to the FCI calculations which contain 6 740 280 CSF's, expanded into 28 233 466 determinants and 113 million intermediate states [9,10] in the Knowles and Handy FCI procedure.

The calculations for F and F^- proceed along the same lines as for H_2O. The 1s electrons are not correlated in any of the calculations. The CASSCF wave functions have the 2p electrons and the 2p and 2p′ orbitals as active. In addition to the calculations performed for H_2O, two additional single-reference procedures are used. The first includes all single, double and triple excitations (SDT), while the second includes in addition the quadruple excitations (SDTQ). For the largest basis set, the SDTQ calculation leads to a CI expansion of 110679 CSF's, which is at about the limit of our conventional CI program. This is far larger than the 19996 CSF's in the MRCI expansion, but far smaller than the 6 574 356 CSF's (27 944 852 determinants and 224 million intermediate states) in the FCI wave function.

III. Results and discussion

The total energies of the H_2O calculations are summarized in Table II, while the correlation contributions are decomposed in Table III. The correlation energy, relative to SCF, varies rapidly with R(O-H), increasing by a factor of 1.71 between r_e

and $2*r_e$. The single and doubles correlation energy shows a much smaller change, increasing by a factor of only 1.45. Thus the error in the SDCI calculation is quite large. (The difference between the FCI potential and those at other levels is illustrated by shifting the potential curves to bring them into agreement with the FCI potential at r_e, see Table IV). The smaller increase in the correlation energy with r for the SDCI relative to the FCI shows the differential importance of the higher than double excitations with increasing r. The Davidson correction applied to the SDCI and the CPF method both show the correct trend of increasing rapidly with distance. However, the Davidson correction is too small everywhere, with the error increasing with increasing r. The CPF estimate is also too small at r_e, but becomes too large at $2*r_e$. Thus, at each point, the CPF has about the same error as the Davidson correction, but since the error changes sign, the error in the CPF between $1.5*r_e$ and $2*r_e$ is larger.

The CASSCF treatments, when compared to the SCF, show an even larger change in correlation energy with R(O-H) than does the FCI. This is to be expected, since the CASSCF correctly dissociates to ground state atoms while the SCF does not. Since there is more correlation in the molecule than in the atoms, when compared to the FCI, the CASSCF's show a difference with the FCI with R(O-H) which in the opposite direction from the SCF. However, the shape of the potential in the CASSCF calculations is in better agreement with the FCI than either the SCF or SDCI calculations. The inclusion of more extensive correlation reduces the error further, but the differential correlation effect is much smaller than that at other levels (for example E(MRCI)-E(CASSCF) changes by only a factor 1.26, which reduces to 1.12 with the larger CASSCF reference). The inclusion of the multi-reference analog of the Davidson correction leads to an energy lower than that at the FCI level. This overshoot for the MRCI+Q calculations was also found for NH_2 [3]. The inclusion of this correction reduces the error in the calculation, but the error is actually reduced further for the smaller reference space. Thus the increase in the number of references improves the MRCI results, but the MRCI+Q results do not show the same monotonic improvements with the number of references; this is also true for NH_2 [3]. However, the errors in either of the MRCI+Q calculations are acceptable, and much smaller than the single reference based approaches.

The ratio of the total correlation energy for the $^1A_1$ state of H_2O to the $^2B_1$ state of NH_2 decreases from 1.27 at r_e to 1.17 at $2*r_e$. This is to be expected considering that H_2O has one more electron than NH_2. However, in spite of the increase in the total correlation energy, the accuracy of the MRCI and MRCI+Q potentials is very similar for H_2O and NH_2, that is, errors of no more than 1.2 kcal/mole in the potentials relative to r_e; in fact H_2O has a slightly smaller relative error. Thus the accuracy of the MRCI approach does not appear to depend on the number of electrons correlated for systems of this size.

The correlation contributions for F and F^- are decomposed in Table V, and the results for the EA is summarized in Table VI. The previous Ne atom results are also summarized in Table V for comparison. The total correlation energy of F^- is 1.09 times larger than for Ne, even though they have the same number of electrons. For comparison F has only 83% of the correlation energy of Ne. The difference in correlation energy between Ne and F^- arises from the increased (by about a factor of two) importance of the triple (measured as E(SDT)-E(SD)), quadruple, and higher than quadruple excitations. This is quite different from F, for which the higher than double excitations contribution is 85% of that for Ne, that is, the relative importance of the single and doubles and the higher excitations is about the same for F and Ne. The greater importance of the higher excitations for F^- than F makes the determination of the EA, which depends on obtaining all the differential correlation energy, a difficult task, as compared, say to a potential curve where only relative accuracy is needed. The importance of higher than double excitations is illustrated in Table VI: for the smallest basis set used ([4s3p1d]) the SCF EA is in error by 2 eV, which is reduced by 1.37 eV with the inclusion of SD correlation, but the FCI EA is still larger by 0.21 eV. Higher excitations comprise about 13% of the correlation contribution to the EA. If the basis set is improved to [5s4p2d], the contribution of the higher than double excitation increases to 15% of the total correlation. If the Davidson correction or CPF approach is used to account for the higher excitations the EA is improved over the SDCI, but is still not equal to the FCI result. These corrections underestimate the importance of higher excitations for both systems. It is well known [19] that the most important correlation effect for F and F^- is the 2p to 2p′ excitation. When this is included in the CASSCF calculation, the EA is considerably improved over the SCF result, giving about 80% of the difference between SCF and SDCI. Using this CASSCF reference leads to a MRCI EA which is better than either the CPF or SDCI+Q treatments, and in good agreement with the FCI, being only 0.02eV smaller. If the estimate of higher excitations is included, an energy lower than the FCI result is obtained for both F and F^-. However, this correction may overestimate the higher excitations in an equivalent manner for both systems, since the results at this level are equal to those at the FCI level.

At the FCI level, the 2s correlation was found to contribute significantly to the EA of oxygen [2]. In Table VI, we also report the EA when only the 2p electrons are correlated. While correlating only the 2p electrons increases the SDCI EA by 0.13 to 0.18 eV relative to correlating both the 2s and 2p electrons, at the FCI level the EA is increased by only 0.08 to 0.12 eV. The negative contribution to the EA of the 2s-2s and 2s-2p correlation decreases with the inclusion of higher excitations. For O/O^-, with a very large basis set the 2s contribution actually increases the EA, but only when higher excitations are included. This is understandable in light of the factor of two larger contribution from higher excitations in the negative ions.

IV. Conclusions

The MRCI potentials (and MRCI with the multi-reference analog of the Davidson correction) are found to be in excellent agreement with FCI calculations. The error in the H_2O calculations are very similar to that found for NH_2, even though the total correlation energy of H_2O is about 1.2 times larger. The contribution of higher than double and of higher than quadruple excitations is found to be a factor of two larger for F^- than Ne, whereas the single and doubles correlation energy differs by only 10%. For F, the single and doubles, and higher than doubles, are the same percentage of the correlation as in Ne. Since the distribution of the correlation energy by excitation level is different between F and F^-, all of the correlation must be computed to account for the difference in order to obtain accurate EA.

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Table I. The valence basis sets.

O (9s5p)/[4s2p]

s		p	
exponent	coefficient	exponent	coefficient
7817.0	0.002031	35.18	0.019580
1176.0	0.015436	7.904	0.124200
273.2	0.073771	2.305	0.394714
81.17	0.247606	0.7171	0.627375
27.18	0.611832	0.2137	1.000000
3.414	0.241205		
9.532	1.000000		
0.9398	1.000000		
0.2846	1.000000		

H (4s)/[2s]

exponent	coefficient
19.2384	0.032828
2.89872	0.231204
0.653472	0.817226
0.177552	1.000000

F (9s5p)/[4s2p]

exponent	coefficient	exponent	coefficient
9994.79	0.002017	44.3555	0.020868
1506.03	0.015295	10.0820	0.130092
350.269	0.073110	2.9959	0.396219
104.053	0.246420	0.9383	0.620368
34.8432	0.612593	0.2733	1.000000
4.3688	0.242489		
12.2164	1.000000		
1.2078	1.000000		
0.3634	1.000000		

Table II. Total energies (a.u.) for the H_2O calculations.

Calculation		geometry[a]	
	r_e	$1.5*r_e$	$2*r_e$
SCF	-76.040542	-75.800494	-75.582286
SDCI	-76.243772	-76.040984	-75.876606
FCI	-76.256624	-76.071405	-75.952269
CPF	-76.252504	-76.064365	-75.956222
SDCI+Q	-76.254549	-76.067003	-75.942257
CAS	-76.094713	-75.924781	-75.823721
MRCI	-76.251643	-76.066885	-75.948557
MRCI+Q	-76.257983	-76.072741	-75.952973
CAS(BIG)	-76.129876	-75.953141	-75.839916
MRCI(BIG)	-76.254108	-76.069363	-75.950517
MRCI(BIG)+Q	-76.257805	-76.072943	-75.953731

[a] The O is located at (0,0,0) and the H nuclear coordinates are: r_e (±1.494187, 0, 1.156923), $1.5*r_e$ (±2.241281, 0, 1.735385), and $2*r_e$ (±2.988374, 0, 2.313846).

Table III. A decomposition of the correlation contributions for water, in a.u.

Calculation		geometry	
	r_e	$1.5*r_e$	$2*r_e$
E(SDCI)-E(SCF)	0.203230	0.240490	0.294320
E(FCI)-E(SCF)	0.216082	0.270911	0.369983
E(FCI)-E(SDCI)	0.012852	0.030421	0.075663
E(CPF)-E(SDCI)	0.008732	0.023381	0.079616
E(SDCI+Q)-E(SDCI)	0.010777	0.026019	0.065651
E(CAS)-E(SCF)	0.054171	0.124287	0.241435
E(MRCI)-E(CAS)	0.156930	0.142104	0.124836
E(MRCI)-E(SDCI)	0.007871	0.025901	0.071951
E(FCI)-E(MRCI)	0.004981	0.004520	0.003712
E(MRCI+Q)-E(MRCI)	0.006340	0.005856	0.004416
E(FCI)-E(MRCI+Q)	-0.001359	-0.001336	-0.000704
E(CAS(BIG))-E(SCF)	0.089334	0.152647	0.257630
E(MRCI(BIG))-E(CAS(BIG))	0.124232	0.116222	0.110601
E(MRCI(BIG))-E(SDCI)	0.010336	0.028379	0.073911
E(FCI)-E(MRCI(BIG))	0.002516	0.002042	0.001752
E(MRCI(BIG)+Q)-E(MRCI(BIG))	0.003697	0.003580	0.003214
E(FCI)-E(MRCI(BIG)+Q)	-0.001181	-0.001538	-0.001462

Table IV. A comparison of the potential curves for water, in a.u. All curves are shifted in energy to bring the energies at r_e into agreement with that at the full CI level. The difference energy between r_e and the other geometries is compared to the FCI potential.

Calculation	$1.5*r_e$-r_e	$2*r_e$-r_e
SCF	-0.05482900	-0.15390100
SDCI	-0.01756900	-0.06281100
CPF	-0.00292000	0.00807300
SDCI+Q	-0.00232700	-0.00793700
CAS	0.01528700	0.03336300
MRCI	0.00046100	0.00126900
MRCI+Q	-0.00002300	-0.00065500
CAS(BIG)	0.00848400	0.01439500
MRCI(BIG)	0.00047400	0.00076400
MRCI(BIG)+Q	0.00035700	0.00028100

Table V. A comparison of the correlation contributions, in a.u, for F^-, F and Ne.

		F^- ion		
Basis	[4s3p]	[4s3p1d]	[4s3p2d]	[5s4p2d]
E(SCF)	-99.442848	-99.442848	-99.442848	-99.443696
E(SD)-E(SCF)	0.132219	0.197820	0.220160	0.245405
E(SDT)-E(SD)	0.001913	0.003241	0.004297	0.006369
E(SDTQ)-E(SDT)	0.006558	0.008848	0.009707	0.010480
E(FCI)-E(SDTQ)	0.000486	0.000584	0.000664	0.000740
E(FCI)-E(SD)	0.008957	0.012673	0.014668	0.017589
E(SD+Q)-E(SD)	0.006106	0.009711		0.012071
E(CPF)-E(SD)	0.005043	0.008155		0.010077
E(CASSCF)-E(SCF)				0.107265
E(MRCI)-E(CASSCF)				0.152776
E(MRCI)-E(SD)				0.014636
E(MRCI+Q)-E(SD)				0.018473
		F atom		
Basis		[4s3p1d]	[4s3p2d]	[5s4p2d]
E(SCF)		-99.394273	-99.394273	-99.394684
E(SD)-E(SCF)		0.147416	0.165916	0.192421
E(FCI)-E(SD)		0.004931	0.006294	0.007772
E(CPF)-E(SD)				0.004741
E(SD+Q)-E(SD)				0.006344
E(FCI)-E(SCF)		0.152347	0.172210	0.200193
E(CASSCF)-E(SCF)				0.061620
E(MRCI)-E(SD)				0.005684
E(MRCI+Q)-E(SD)				0.008689
		Ne atom[a]		
Basis				[5s3p2d]
E(SD)-E(SCF)				0.235733
E(SDT)-E(SD)				0.003258
E(SDTQ)-E(SDT)				0.005670
E(FCI)-E(SD)				0.009131
E(FCI)-E(SDTQ)				0.000203
E(CPF)-E(SD)				0.005276
E(SD+Q)-E(SD)				0.006823

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[a] Results are taken from Reference 1.

Table VI. A comparison of the computed EA[a] for F, in eV.

		2s and 2p correlated	
Basis	[4s3p1d]	[4s3p2d]	[5s4p2d]
SCF	1.32	1.32	1.33
SDCI	2.69	2.79	2.78
FCI	2.90	3.03	3.04
DVD			2.93
CPF			2.92
CAS			2.58
MRCI			3.02
MRCI+Q			3.04
		2p correlated	
Basis	[4s3p1d]	[4s3p2d]	[5s4p2d]
SDCI	2.82	2.97	2.95
FCI	2.98	3.15	3.16

[a] For comparison the experimental value is 3.399 eV, see Reference 20.

APPENDIX 3

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Benchmark full configuration-interaction calculations on HF and NH_2

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Abstract

Full configuration-interaction (FCI) calculations are performed at selected geometries for the $^1\Sigma^+$ state of HF and the $^2B_1$ and $^2A_1$ states of NH_2 using both DZ and DZP gaussian basis sets. Higher excitations become more important when the bonds are stretched and the SCF reference becomes a poorer zeroth-order description of the wave function. The CASSCF-MRCI procedure gives excellent agreement with the FCI potentials, especially when corrected with a multi-reference analog of the Davidson correction.

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I. Introduction

Recent improvements in methods for full configuration-interaction (FCI) calculations [1-2] combined with the extensive memory (>256 million words) and excellent vector capabilites of the CRAY 2, permit FCI calculation with larger basis sets than used in previous benchmark calculations [3-4]. Recently, we presented FCI calculations for the ^1S state of Ne atom [5] to assess the reliability of methods such as the Davidson correction [6] and the coupled pair functional (CPF) [7] for estimating the energy contribution of higher excitations. An important observation was that the accuracy of both the Davidson correction and the CPF approximation depended on basis set quality. For example, the CPF accounted for only 40% of the quadruples contribution for a DZ basis set, but 60% of the quadruples contribution for a DZP basis set. However, the total contribution of higher excitations was relatively small in Ne, which is well described by an SCF reference. To investigate further the accuracy of approximate methods of including higher excitations, we consider herein the $^1\Sigma^+$ state of the isoelectronic HF molecule and the $^2B_1$ and $^2A_1$ states of NH_2 using both DZ and DZP gaussian basis sets. To investigate structures where the SCF is not a good zeroth-order description we consider geometries away from equilibrium.

II. Methods

For the nitrogen and fluorine atoms we used the Dunning 4s2p contraction [8] of the Huzinaga 9s5p primitive basis sets [9]. For hydrogen we used the 2s contraction [8] of the Huzinaga 4s primitive set scaled by a factor of 1.2. When polarization functions are included, the exponents are: F(3d=1.6), N(3d=0.9), and H(2p=0.8). The 3s component of the 3d functions is deleted in all calculations.

For HF the geometries considered are r_e (1.733 bohr), 1.5 times r_e (2.5995 bohr), and twice r_e (3.466 bohr). For NH_2 we consider r_e, 1.5 times r_e and twice r_e, as well as a fourth point with the H-H bond distance at the H_2 equilibrium value and the N-H distance at about twice the r_e for NH_2. The NH_2 molecule is placed in the xz plane, with the N at the origin. The coordinates actually used for NH_2 are given explicitly in Table I.

In this study we have used both an SCF and a complete-active-space self-consistent field (CASSCF) wave function [10] as the zeroth-order reference. The SCF reference is used for the single-reference singles plus doubles configuration-interaction calculation, SDCI, SDCI + triples (SDT), SDT + quadruples (SDTQ), the coupled pair functional (CPF) wave function and the Chong-Langhoff modification [11] of CPF (MCPF). The SCF reference is also used for the FCI calculations, which are found to be invariant to the orbital basis to within a few microhartrees. The slight differences arise because the two core electrons on nitrogen and fluorine are not correlated in any calculations since this restriction dramatically reduces the length of the FCI expansion. For the $^1\Sigma^+$ state of HF the SCF reference configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$, and for the $^2B_1$ state of NH_2 it is $1a_1^2 2a_1^2 3a_1^2 1b_1^1 1b_2^2$ at all geometries. For the $^2A_1$ state of NH_2 the three geometries stretching the two N-H bonds correspond to the $3a_1 \rightarrow 1b_1$ excitation relative to the $^2B_1$ configuration whereas the fourth point denoted N···H-H corresponds to the $1b_1 \rightarrow 4a_1$ excitation.

The multi-reference CI calculations (MRCI) are based on CASSCF wave functions. For HF, the hydrogen 1s and fluorine 2pσ orbitals and electrons are active. The MRCI calculations consist of single and doubles from the two non-vanishing configurations in the CASSCF wave function. For both states of NH_2, the nitrogen 2s and 2p orbitals and electrons are active, as well as the two hydrogen 1s orbitals and electrons. The first set of MRCI calculations using these CASSCF optimized orbitals include all references arising from all distributions of the nitrogen 2p and hydrogen 1s electrons among the active orbitals; hence the 2s electrons are correlated, but the 2s orbital is doubly occupied in all reference configurations. In the second set of MRCI calculations, denoted MRCI(BIG), all configurations in the CASSCF are included as references. For the SDCI wave functions we also include the Davidson estimate for unlinked quadruple excitations, denoted +Q. For the MRCI calculations we use a multi-reference analogue of this correction, namely $\Delta E_{SD}\,(1-\sum_R C_R^2)$, where Δ_{SD} is the difference between the energy of the reference CSF's and the MRCI, and the C_R are the coefficients of the reference configurations in the MRCI wave function.

III. Results and discussion.

The total energies at the SCF and FCI level are summarized in Table I for both HF and NH_2. The molecular geometries used for the $^2B_1$ and $^2A_1$ states of NH_2 are given explicitly as well.

In Table II we have summarized the CI results for HF using both the DZ and DZP basis sets at three geometries (r_e,1.5*r_e,2*r_e). It is interesting that although the SDCI-SCF energy difference is considerably larger for the DZP basis, this difference increases more slowly with increasing R than for the DZ basis. The ratio of this difference at 2*r_e compared to r_e is 1.21 with the DZP basis and 1.47 with the DZ basis. Hence, the addition of the polarization function substantially improves the description of the distortions taking place as the bond is broken, and less of this effect shows up as electronic correlation. For the DZP basis the energy contribution of the triples, quadruples and higher than quadruple excitations all increase at about the same rate as the bond is broken (by about a factor of three between 2*r_e and r_e). The energy contribution of quadruple excitations at 2*r_e using the DZP basis is about 0.5 eV, which is about 40 times greater than the combined contribution of quintuple through octuple excitations.

The results in Table II show that the three configuration CASSCF calculation followed by all single and double excitations from the two configurations (σ^2 and $\sigma*^2$) that have non-vanishing coefficients in the CASSCF, provide a much more uniform description of the potential. Also, the multi-reference quadruples correction is much more uniform as a function of bond distance.

The next three rows for each basis set in Table II give a measure of the reliability of CPF methods and the Davidson correction for estimating the energy contribution of higher excitations. Note that at r_e these corrections all underestimate the quadruples correction, but as the bond length is increased the corrections become a substantial overestimate. In fact the SDCI+Q energies at 2*r_e are well below the FCI energies. Note also that this overcorrection of SDCI+Q is much less severe for the DZP basis than the DZ basis.

Since it is a rather stringent requirement of any method to reproduce the FCI total energies, a better criterion for judging a method is how well the resulting potentials parallel the FCI potential. In Table III we report for HF the energy difference between r_e and 1.5*r_e and 2*r_e at different levels of theory. That is, all potentials are normalized at r_e so that the energy differences in Table III reflect directly deviations with the FCI potential. The SCF description becomes quite poor as the bond is stretched, although somewhat less so for the DZP basis. The CASSCF description is better, but overcorrects because it overestimates the contribution of the dissociative configuration. The SDCI is a substantial improvement over SCF, but still retains some of the bias of the SCF. The SDCI results are improved by the Davidson correction, especially for the DZP basis, but overestimates the effect of higher excitations. The coupled pair methods are generally more reliable than SDCI+Q, and the MCPF results for the DZP basis are in particularly good agreement with the FCI results. Note that the results at the SDT level are still inadequate since the energy contribution of quadruple excitations is both large and rapidly increasing as the bond is broken. At the SDTQ level the error at $2*r_e$ in the DZP basis is less than 0.02 eV. However, the SDTQ configuration expansions are quite lengthy (48,963 CSFs for the DZP basis), and hence do not represent an optimal approach of including higher excitations. This is illustrated by the results of the much smaller MRCI expansions (1015 CSFs), which are of comparable quality. Most impressive, however, are the MRCI+Q results which agree with the FCI potential to well within chemical accuracy in every case. The comparison of the MRCI and MRCI+Q results in Table III provide strong support for the validity of the multi-reference analog of the Davidson correction.

In addition to the dissociation of HF, where one chemical bond is being broken, we consider for the $^2B_1$ and $^2A_1$ states of NH_2 the simultaneous extension of both N-H bonds. The energy difference between the FCI and various levels of theory using both the DZ and DZP gaussian basis sets are summarized for the $^2B_1$ and $^2A_1$ states in Tables IV and V, respectively. Four geometries are considered – equilibrium, both bonds stretched to 1.5 and 2.0 times r_e, and an N···H-H structure with the H-H bond length that of the ground state of H_2 and the N-H bond at about $2*r_e$. Explicit coordinates are given in Table I. As for the HF molecule, the SCF reference becomes an increasingly poorer zeroth-order description of the system as the bond length is increased, particularly for the $^2B_1$ ground state. Although the SDCI accounts for a substantial portion of this difference, the difference with the FCI and hence the contribution of higher excitations increases rapidly as the bonds are stretched. In contrast, the difference between the FCI and CASSCF is more constant and actually decreases slightly with increasing r; hence the errors in the MRCI treatment are generally less at $2*r_e$ than at r_e. In general, the differences with the FCI are further reduced when the multi-reference quadruples correction is added, although in every case MRCI+Q is below the FCI energy. The coupled pair functional methods and the SDCI+Q, which are based on the SCF reference, have larger differences with the FCI, and these differences increase as the SCF reference becomes a poorer representation of the wave function. These approximate methods for incorporating higher excitations are substantially closer to the FCI energies than are the SDCI energies. Generally they give energies that lie above the FCI for the r_e and $1.5*r_e$ geometries, but often overshoot (particularly CPF) the energy at $2*r_e$. The MCPF method, which uses somewhat more complex but more realistic renormalization denominators, tends to overshoot less and thus has a larger domain of applicability.

The theoretical potentials at various levels of theory are compared to the FCI potentials for the $^2B_1$ and $^2A_1$ states in Tables VI and VII, respectively. These results again illustrate how poor the SCF potential becomes as r increases. The CASSCF overestimates the importance of the dissociative configurations and errs in the opposite direction, although it is better than the SDCI potential, which retains much of the bias of the SCF. However, the Davidson correction helps substantially and the SDCI+Q potential is approaching chemical accuracy. The MRCI potentials are substantially better. Again, the multi-reference Davidson correction generally gives further improvements in the potentials.

The energy between the minimum in the $^2B_1$ and $^2A_1$ potentials of NH_2 (T_e) is given with respect to the FCI result at each level of correlation treatment for the DZ and DZP basis sets in Table VIII. Since the SCF reference provides nearly equivalent descriptions of both states, the differences with the FCI results are not very large. Apart from the SCF and CASSCF results, the T_e are within 0.05 eV of the FCI result. Interestingly the multi-reference Davidson correction actually makes the agreement worse, although the errors are in every case small.

IV. Conclusions

The CASSCF MRCI calculations are in excellent agreement with the FCI calculations, especially after including a correction for quadruple excitations. This is not surprising considering that the CASSCF potential parallels the FCI potential better than does the SDCI potential. The inclusion of an estimate of higher excitations, either by the Davidson correction or by CPF works reasonably well, except for NH_2 at $2*r_e$, where the SCF reference is much poorer. The MCPF method gives an improved description of the $2*r_e$ point, but does not significantly alter the results at the other points, where the SCF is a better reference.

The accuracy of the different approximations are found to vary somewhat with the quality of the basis set used. These results should supply a better test of methods than the previous FCI calculations, most of which were restricted to a DZ basis set.

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Table I. Total energies (a.u.) for the full CI(SCF) calculations.

	DZ	DZP	geometry[a]
r_e	-100.147204(-100.021973)	-100.250969(-100.047087)	1.733
$1.5*r_e$	-100.079441(-99.924625)	-100.160393(-99.933229)	2.5995
$2*r_e$	-100.008676(-99.815206)	-100.081108(-99.817572)	3.466
		NH_2 $^2B_1$	
	DZ	DZP	geometry[b](x,z)
r_e	-55.646028(-55.543825)	-55.742620(-55.573008)	1.5186,1.1993
$1.5*r_e$	-55.534809(-55.373780)	-55.605209(-55.387413)	2.2779,1.79895
$2*r_e$	-55.449427(-55.185112)	-55.505524(-55.188719)	3.0372,2.3986
$N+H_2$	-55.472746(-55.383141)	-55.544560(-55.388944)	0.7006,3.8062
		NH_2 $^2A_1$	
	DZ	DZP	geo(x,z)
r_e	-55.603404(-55.505424)	-55.688762(-55.523192)	1.7972,0.5840
$1.5*r_e$	-55.449846(-55.311550)	-55.517614(-55.32145)	2.6958,0.8760
$2*r_e$	-55.355766(-55.155112)	-55.415133(-55.157046)	3.5944,1.1680
$N+H_2$	-55.462119(-55.364954)	-55.536081(-55.370425)	0.7006,3.8062

[a] The H-F bond length in bohr.

[b] The x,z corridinates, where the molecule is placed in the xz plane with the N at 0,0,0, and the H atoms at x,0,z, and -x,0,z.

Table II. Energy differences (au) between different levels of correlation treatment for the $^1\Sigma^+$ state of HF.

A. DZ BASIS	r_e	$1.5*r_e$	$2*r_e$
SDCI-SCF	-0.11951300	-0.14499600	-0.17531200
SDT-SDCI	-0.00106500	-0.00189500	-0.00491100
SDTQ-SDT	-0.00444400	-0.00756900	-0.01261700
FCI-SDTQ	-0.00020900	-0.00035600	-0.00063000
MRCI-CASSCF	-0.09672100	-0.09518000	-0.08502900
MRCI+Q-MRCI	-0.00251900	-0.00273100	-0.00228300
CPF-SDCI	-0.00302000	-0.00637900	-0.01430100
SDCI+Q-SDCI	-0.00391000	-0.00914200	-0.02510300
MCPF-SCCI	-0.00320500	-0.00712900	-0.01713700
B. DZP BASIS			
SDCI-SCF	-0.19450300	-0.21229400	-0.23596100
SDT-SDCI	-0.00236800	-0.00375300	-0.00842200
SDTQ-SDT	-0.00672900	-0.01062300	-0.01823500
FCI-SDTQ	-0.00028200	-0.00049400	-0.00091800
MRCI-CASSCF	-0.17409400	-0.16719100	-0.15418300
MRCI+Q-MRCI	-0.00607600	-0.00615600	-0.00528000
CPF-SDCI	-0.00613000	-0.01063900	-0.02227100
SDCI+Q-SDCI	-0.00778300	-0.01345900	-0.02886600
MCPF-SDCI	-0.00640100	-0.01139400	-0.02466700

Table III. Energy differences (au) between the FCI and different levels of correlation treatment for the $^1\Sigma^+$ state of HF.

Method	$1.5*r_e-r_e$	$2*r_e-r_e$
	DZ Basis	
SCF	0.029585	0.068239
SDCI	0.004102	0.012440
SDCI+Q	-0.001130	-0.008753
CPF	0.000743	0.001159
MCPF	0.000178	-0.001492
SDT	0.003272	0.008594
SDTQ	0.000147	0.000421
CASSCF	-0.001289	-0.011865
MRCI	0.000252	-0.000173
MRCI+Q	0.000040	0.000063
	DZP basis set	
SCF	0.023282	0.059654
SDCI	0.005491	0.018196
SDCI+Q	-0.000185	-0.002887
CPF	0.000982	0.002055
MCPF	0.000498	-0.000070
SDT	0.004106	0.012142
SDTQ	0.000212	0.000636
CASSCF	-0.006811	-0.020667
MRCI	0.000092	-0.000756
MRCI+Q	0.000012	0.000040

Table IV. Energy differences (au) between the FCI and other levels of correlation treatment for the ${}^2B_1$ state of NH_2.[a]

DZ Basis

Method	r_e	$1.5*r_e$	$2*r_e$	$N\cdots H_2$
SCF	0.102203	0.161029	0.264315	0.08960518
SDCI	0.004609	0.016439	0.055109	0.00621524
MCPF	0.001403	0.002836	0.009711	0.00032756
CPF′[b]	0.001489	0.002595	-0.005823	0.00082237
CPF	0.001460	0.001868	-0.023677	0.00078711
SDCI+Q	0.000447	-0.000890	-0.004487	0.00075817
CASSCF	0.051976	0.045721	0.039039	0.04644218
MRCI	0.001172	0.000714	0.000542	0.00114810
MRCI(BIG)	0.001116	0.000644	0.000509	0.00098085
MRCI+Q	-0.000154	-0.000492	-0.000264	-0.00029528
MRCI(BIG)+Q	-0.000055	-0.000355	-0.000219	-0.00007293
		DZP Basis		
SCF	0.169612	0.217796	0.316805	0.15561649
SDCI	0.009003	0.023472	0.069157	0.01329291
MCPF	0.002365	0.004967	0.015670	0.00200373
CPF′[b]	0.002509	0.004707	0.003116	0.00178015
CPF	0.002480	0.004190	-0.009212	0.00169289
SDCI+Q	0.000572	0.001584	0.009026	0.00244093
CASSCF	0.121869	0.107084	0.094456	0.11400831
MRCI	0.003446	0.002279	0.001501	0.00337559
MRCI(BIG)	0.003202	0.001940	0.001338	0.00292420
MRCI+Q	-0.001271	-0.002047	-0.001735	-0.00162566
MRCI(BIG)+Q	-0.001239	-0.001980	-0.001741	-0.00146699

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[a] Negative entry indicates the energy is lower than the FCI.

[b] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table V. Energy differences (au) between the FCI and other levels of correlation treatment for the $^2A_1$ state of NH_2.[a]

DZ Basis

Method	r_e	$1.5*r_e$	$2*r_e$	$N\cdots H_2$
SCF	0.097980	0.138296	0.200654	0.09716511
SDCI	0.004336	0.012032	0.032600	0.01312506
MCPF	0.001456	0.003365	-0.000088	0.00118610
CPF'[b]	0.001532	0.003347	-0.018390	0.00297603
CPF	0.001519	0.003375	-0.014174	0.00289667
SDCI+Q	0.000616	0.000893	-0.004761	0.00542632
CASSCF	0.058332	0.058208	0.043838	0.04449573
MRCI	0.001251	0.001572	0.000811	0.00090852
MRCI(BIG)	0.001009	0.001114	0.000735	0.00087816
MRCI+Q	-0.001631	-0.002968	-0.000326	-0.00005773
MRCI(BIG)+Q	-0.000516	-0.000610	-0.000238	-0.00007346
		DZP Basis		
SCF	0.165570	0.196167	0.258087	0.16565612
SDCI	0.008482	0.018097	0.048673	0.02229559
MCPF	0.002290	0.004900	0.005865	0.00550461
CPF'[b]	0.002431	0.004970	-0.015832	0.00424528
CPF	0.002413	0.005022	-0.016182	0.00412679
SDCI+Q	0.000618	0.002403	0.006886	0.00922251
CASSCF	0.127696	0.118050	0.102355	0.11461881
MRCI	0.003929	0.003935	0.002267	0.00316584
MRCI(BIG)	0.003228	0.002836	0.001803	0.00278544
MRCI+Q	-0.003106	-0.005010	-0.001670	-0.00117540
MRCI(BIG)+Q	-0.001809	-0.002219	-0.001918	-0.00157857

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[a] Negative entry indicates the energy is lower than the FCI.

[b] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table VI. Energy differences (au) between the FCI and different levels of correlation treatment for the $^2B_1$ state of NH_2.

DZ Basis

Method	$1.5*r_e$-r_e	$2*r_e$-r_e	$N\cdots H_2$-r_e
SCF	0.05882552	0.16211179	-0.01259813
SDCI	0.01183033	0.05050009	0.00160673
MCPF	0.00143290	0.00830835	-0.00107530
CPF'[a]	0.00110573	-0.00731251	-0.00066686
CPF	0.00040776	-0.02513683	-0.00067285
SDCI+Q	-0.00133646	-0.00493371	0.00031155
CASSCF	-0.00625527	-0.01293716	-0.00553361
MRCI	-0.00045866	-0.00062996	-0.00002432
MRCI(BIG)	-0.00047153	-0.00060722	-0.00013494
MRCI+Q	-0.00033712	-0.00010991	-0.00014079
MRCI(BIG)+Q	-0.00029993	-0.00016385	-0.00001821
	DZP Basis		
SCF	0.04818368	0.14719287	-0.01399544
SDCI	0.01446939	0.06015405	0.00428998
MCPF	0.00260180	0.01330525	-0.00036150
CPF'[a]	0.00219774	0.00060737	-0.00072896
CPF	0.00171006	-0.01169217	-0.00078678
SDCI+Q	0.00101197	0.00845456	0.00186908
CASSCF	-0.01478520	-0.02741322	-0.00786048
MRCI	-0.00116640	-0.00194520	-0.00007021
MRCI(BIG)	-0.00126231	-0.00186384	-0.00027800
MRCI+Q	-0.00077575	-0.00046378	-0.00035453
MRCI(BIG)+Q	-0.00074106	-0.00050181	-0.00022757

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[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table VII. Energy differences (au) between the FCI and different levels of correlation treatment for the $^2A_1$ state of NH_2.

DZ Basis

Method	$1.5*r_e-r_e$	$2*r_e-r_e$	$N\cdots H_2-r_e$
SCF	0.04031524	0.10267371	-0.00081533
SDCI	0.00769570	0.02826419	0.00878918
MCPF	0.00190896	-0.00154370	-0.00026974
CPF′[a]	0.00181481	-0.01992232	0.00144354
CPF	0.00185597	-0.01569280	0.00137788
SDCI+Q	0.00027680	-0.00537750	0.00480983
CASSCF	-0.00012341	-0.01449361	-0.01383588
MRCI	0.00032109	-0.00043952	-0.00034228
MRCI(BIG)	0.00010478	-0.00027385	-0.00013077
MRCI+Q	-0.00133786	0.00130498	0.00157288
MRCI(BIG)+Q	-0.00009474	0.00027806	0.00044224
DZP Basis			
SCF	0.03059766	0.09251729	0.00008646
SDCI	0.00961563	0.04019126	0.01381379
MCPF	0.00261021	0.00357473	0.00321466
CPF′[a]	0.00253934	-0.01826289	0.00181431
CPF	0.00260866	-0.01859546	0.00171334
SDCI+Q	0.00178540	0.00626841	0.00860488
CASSCF	-0.00964579	-0.02534059	-0.01307699
MRCI	0.00000590	-0.00166202	-0.00076318
MRCI(BIG)	-0.00039130	-0.00142503	-0.00044209
MRCI+Q	-0.00190407	0.00143620	0.00193059
MRCI(BIG)+Q	-0.00041014	-0.00010893	0.00023031

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[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

Table VIII. T_e's relative to the full CI.

Method	DZ	DZP
SCF	-0.004223	-0.004042
SDCI	-0.000273	-0.000521
MCPF	0.000053	-0.000075
CPF'[a]	0.000043	-0.000078
CPF	0.000059	-0.000066
SDCI+Q	0.000170	0.000046
CASSCF	0.006356	0.005827
MRCI	0.000078	0.000483
MRCI(BIG)	-0.000107	0.000025
MRCI+Q	-0.001476	-0.001835
MRCI(BIG)+Q	-0.000461	-0.000569
FCI[b]	0.042624	0.053858

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[a] The Chong-Langhoff implemention of CPF [11], which for open shell systems differs from that of Ahlrichs et al. [7].

[b] Full CI T_e.

APPENDIX 4

N86 - 30377

On the Electron Affinity of the oxygen atom

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Abstract

The electron affinity of oxygen is computed to be 1.287 eV, using 2p electron full CI wave functions expanded in a 6s5p3d2f Slater-type orbital basis. The best CASSCF-MRCI result including only 2p correlation is 1.263 eV. However, inclusion of 2s intrashell and 2s2p intershell correlation increases the computed EA to 1.290 at the CASSCF-MRCI level. At the full CI basis set limit, the 2s contribution to the electron affinity is estimated to be as large as 0.1 eV. This study clearly establishes the synergistic effect between the higher excitations and basis set completeness on the electron affinity when the 2s electrons are correlated.

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I. Introduction

The calculation of the electron affinity (EA) of the oxygen atom has proved to be a challenging task [1-5]. A noteworthy study of atomic correlation and its effects on calculated electron affinities is the work of Sasaki and Yoshimine [1] (SY). Using extremely large Slater basis sets, they were able to estimate the SDCI basis limit for the electron affinity of oxygen as 1.041 eV, which is substantially less than the experimental value [6] of 1.462 eV. This work indicated that earlier pair-correlation calculations [7-10] obtained electron affinities in fortuitously good agreement with experiment owing to a cancellation between atomic basis set incompleteness and the excess energy from neglected pair-pair interaction energies. By including selected triple and quadruple excitations, SY obtained an electron affinity of 1.17 eV including only L shell correlation. SY also showed that correlation of the 1s electrons makes a very small contribution to the EA.

The study of Botch and Dunning [2] (BD), demonstrates that the differential higher excitation contribution to the EA is more efficiently accounted for by an MCSCF multi-reference CI procedure, MRCI, than by using selected triple and quadruple excitations from an SCF reference. Their MCSCF calculation was restricted to double excitations out of the 2p into 2p′ correlating orbitals, and yielded an EA of 0.46 eV, about 1 eV improvement over the Hartree-Fock limit of -0.54 eV. When all single and double excitations from this MCSCF reference were included, they obtained an electron affinity of 1.09 eV. This value is less than that of SY owing to the much smaller basis set employed, but indicates a considerably larger contribution from higher excitations. The most important correlation contribution was observed to arise from 2p→2p′ excitations.

The first systematic study of the EA of oxygen correlating only the 2p electrons was given by Bauschlicher [3]. Using a large (6s6p3d2f) Slater-type orbital (STO) basis that is within about 0.05 eV of the SDCI basis set limit value, a CASSCF calculation with the 2p and 2p′ orbitals in the active space was performed. This CASSCF yields an EA of 0.59 eV which is similar to the EA from the MCSCF calculation of Botch and Dunning [2]. More extensive correlation was included via a second-order CI including only the 2p electrons. The second-order CI yields an

EA of 1.26 eV, which is larger than that of SY, but still in error by 0.2 eV. When the MCSCF and MRCI reference spaces were expanded to include the 3d shell, the EA increased to only 1.28 eV.

Recently, Feller and Davidson [4] (FD) calculated the EA of O using an MCSCF-MRCI approach. Unlike Bauschlicher [3], FD explicitly included the 2s in both the MCSCF and multi-reference CI calculations. The gaussian type orbital (GTO) basis used by FD is within 0.02 eV of the SY SDCI limit EA. The results of FD parallel those of Bauschlicher, and their best EA is 1.29 eV, or 1.32 eV if an estimate of higher excitations is made. This work suggests that 2s does not have a differential correlation contribution to the EA, and therefore either the differential contribution of higher excitations to the EA converges very slowly with basis set, or else none of the MCSCF-MRCI studies to date have properly accounted for this 2s contribution. This latter possibility seems unlikely considering the stability of the EA to further improvements in the treatment, e.g. including the 3d shell in the active space. However, Raghavachari [5] finds with a comparable basis set that a coupled cluster doubles (CCD) calculation with a correction for single and triple excitations yields an EA of 1.41 or 1.36 eV, depending upon the approximation used for the single and triple excitations.

It has recently become possible to perform very large full CI calculations which can be analyzed to separate the effect of higher excitations from basis set incompleteness. This is a result of: (i) Siegbahn's realization [11] that the full CI procedure can be vectorized in terms of matrix multiplies, (ii) Knowles and Handy's suggestion [12] that the Siegbahn approach be changed to determinants from configuration state functions, thus eliminating the IO bottleneck associated with the formula file, and (iii) the delivery of the CRAY 2 which allows very large CI expansions because of its extremely large memory.

In this work we report full CI calculations of the EA of O atom, and compare these results to those obtained using an MCSCF-MRCI approach. One of the goals of the present study is to decompose the remaining error in the EA into effects of basis set incompleteness, higher excitations not accounted for by the CASSCF-MRCI treatment, and to contributions from correlating the 2s electrons. In addition, we report on our initial attempts to compute the EA using Green's function Monte

Carlo methods [13]. This approach seems particularly relevant to the EA affinity problem since it is potentially capable of accounting for all of the electronic correlation energy. However, technical problems make such calculations difficult at present for systems with this many electrons.

Section II contains a brief description of the methods and basis sets employed in this study. Section III contains an analysis of the full CI and CASSCF-MRCI calculations. Section IV contains a description of the Monte Carlo calculations. The conclusions are given in Section V .

II. Methods

In our theoretical calculations we employ a 6s5p valence Slater-type orbital set obtained by combining six s functions optimized for O, and five p functions optimized for O^- [14]. The total SCF energy of the 6s5p basis is only 0.0001 Hartree above the numerical Hartree Fock (NHF) energy; this can be compared to, for example, an uncontracted 12s7p GTO basis set [15] which has an error six times larger. However, both O and O^- are affected similarly by basis set limitations, so the EA is at the HF limit.

To the 6s5p valence basis we construct a small basis by adding one 3d function with an exponent of 2.66 and a larger 3d2f polarization set with exponents of 4.0, 2.8284 and 2.0 for the three 3d functions and exponents of 4.06 and 2.87 for the two 4f functions. The exponents were optimized by Bauschlicher [3], under an even-tempered constraint, by minimizing the mean of the O and O^- energies at the SDCI level, with only the 2p electrons correlated. However, the optimal exponents are not significantly different for O and O^- and hence little bias is expected for the larger polarization set.

Several zeroth-order references are used. The simplest is the SCF, in which symmetry and equivalence restrictions are imposed. For the MCSCF reference spaces, we use the CASSCF approach. In the smaller CASSCF only the 2p electrons are active, and are distributed in the 2p and 2p′ orbitals; this CASSCF wave function is denoted CASSCF(2p). Since the question of the correlation effect of the O 2s is of interest, a second CASSCF wave function is also used, CASSCF(2s2p), which includes the 2s as active and adds a 2s′ correlating orbital.

In order to analyze the various correlation effects, more extensive correlation is added to the zeroth-order references in several ways. To separate the contribution to the EA from the 2s and 2p electrons, only the 2p electrons are correlated in some calculations, denoted CI(2p), while in others both the 2s and 2p are correlated, denoted CI(2s2p). For the SCF reference, only single reference SDCI calculations, or full CI calculations, FCI, are performed; the calculations are denoted CI(SCF,2s2p), for a single reference CI calculation (using SCF orbitals) which correlated the 2s and 2p electrons, or FCI(2p) for a full CI calculation which correlates only the 2p electrons. For the single reference CI calculations, we use the Davidson correction [16] (denoted +Q) to estimate the importance of quadruple excitations. For the CASSCF optimized orbitals, all calculations consist of single and double excitations from all of the configurations in the CASSCF calculation. For these calculations the notation indicates the origin of the orbitals and which electrons are correlated. Thus CI(CASSCF(2p),2s2p) denotes a calculation using orbitals optimized in a CASSCF(2p) calculation, and which includes single and double excitations out of the 2s and 2p orbitals in all configurations in the CASSCF(2p) wave function, while CI(CASSCF(2p),2p) involves the same orbitals and same references, but the 2s electrons are not correlated.

III. Results and discussion

The improvement of the electron affinity with enhancements of the polarization basis at the CI(SCF,2p) level is shown in Table I. These results using the 6s6p valence basis [3] are essentially unchanged if the valence basis is replaced by the 6s5p set used this study. The three d functions contribute a substantial 0.338 eV at this level, whereas the two f functions contribute 0.055 eV. For the 6s6p3d2f STO basis, the CI(SCF,2s2p) EA is 0.993eV (0.991 eV, for the 6s5p3d2f STO basis). This is about 0.05 eV less than the Sasaki and Yoshimine [1] CI(SCF,2s2p) EA of 1.041 eV, which should be near the basis set limit at this level. Feller and Davidson find a very similar CI(SCF,2s2p) EA using a 4d2f GTO basis. They also add a single g function, which is not optimized; this increases the CI(SCF,2s2p) EA by 0.037 eV, but increases the CI(CASSCF(2s2p),2s2p) EA by only 0.019 eV. The optimization

[3] of the d and f polarization function shows that the O energy is more sensitive to the choice of exponents than is O^-. Thus any error in the choice of the polarization function exponents tends to lead to too large an EA. Therefore we conclude that the 0.037 eV g function contribution is too large, and that 0.02 eV is probably a better estimate, with the saturation of the d and f spaces being of about the same importance.

The EA at various levels of correlation treatment using the 6s5p1d and 6s5p3d2f STO bases are summarized in Table II. Consider first the 6s5p1d basis set results where we have been able to perform the FCI(2s2p) calculation. The difference of 0.13 eV between the CI(SCF,2p) and CI(SCF,2s2p) electron affinities suggests a substantial reduction from 2s correlation. However, the reduction from including 2s correlation is only 0.085 eV if a correction is added for quadruple excitations. At the full CI level this reduction is only 0.027 eV. Clearly the importance of including the 2s changes markedly with increasing excitation level.

Since certain classes of higher excitation can be included efficiently using the MCSCF-MRCI approach, we next considered calculations from a CASSCF reference. When only 2p correlation is included, the CI(CASSCF(2p),2p) EA is only 0.011 eV less than the FCI value. If the 2s correlation is included for this choice of reference space, CI(CASSCF(2p),2s2p), the EA of 1.025eV is 0.034 eV less than the FCI value. If the same orbitals are used, but the CI reference space is increased to include all distributions of the 2s and 2p electrons in the 2s, 2p and 2p′ orbitals, the EA is increased by only 0.003 eV. Thus to improve the computed EA, more orbitals must be included in the CASSCF orbital space and CI reference space. While the inclusion of the 2s electrons and the 2s′ orbital in the CASSCF improves the CASSCF(2s2p) EA by 0.157 eV, relative to the CASSCF(2p) EA, the CI(CASSCF(2s2p),2s2p) EA is only 0.011 eV larger than the CI(CASSCF(2p),2s2p) EA, and is thus still in error by 0.023 eV.

The importance of higher excitations is considerably enhanced for the larger 6s5p3d2f basis. Including 2s correlation in the SCF reference SDCI decreases the EA by only 0.073 eV, and by only 0.017 eV when the Davidson correction for unlinked quadruples is added. The same coupling of basis set effects and the importance of higher excitations is illustrated by the difference between the CI(SCF,2p) and the

FCI(2p) electron affinities, which is 0.223 eV for the 6s5p3d2f STO basis and 0.183 eV for the 6s5p1d STO basis. The difference between the CI(CASSCF(2p),2p) and FCI(2p) EA also increases with the basis set improvement, being 0.024 eV for the larger basis compared to 0.011 eV for the 1d basis set. The difficulty of fully accounting for the effect of higher excitations is much more pronounced when the 2s electrons are correlated. For example, Feller and Davidson using a comparable basis obtain essentially the same CI(SCF,2s2p) EA, but their selected-reference MRCI calculation, based on CASSCF(2s2p) orbitals and correlating 2s and 2p, obtains 1.229 eV, compared to our CI(CASSCF(2s2p),2s2p) result of 1.290 eV. Thus the FD selection of references compared to our use of all CASSCF configurations as CI references has a substantial effect, even for a coefficient selection threshold of 0.01. Note that the CI(CASSCF(2s2p),2s2p) calculation for O^- in the 6s5p3d2f basis consists of all single and double excitations from 588 CSF's yielding a total 545,952 CSF's in D_{2h} symmetry. The motivation for reference selection is clearly evident, but leads to ambiguities for further improvements in the CASSCF treatment. For example, inclusion of the 3d orbital in the CASSCF treatment makes some selection of the CI references mandatory to keep the computations tractable. The relatively small affect of this extension is difficult to assess considering the effect of reducing the CI reference space.

The positive contribution of the 2s correlation at the CASSCF-MRCI level using the 6s5p3d2f basis is consistent with the trends observed at the CI(SCF) and CI(SCF)+Q levels as the basis set is improved. The contribution of the 2s correlation increases but is more difficult to account for as the basis set size is increased. At present, we are unable to perform the FCI(2s2p) calculations for the 6s5p3d2f basis set, since this involves an expansion consisting of 488 million determinants and about 4 billion intermediate states. However, the FCI(2s2p) EA can be estimated assuming that the difference CI(CASSCF(2p),2s2p)-FCI(2s2p) or CI(CASSCF(2s2p),2s2p)-FCI(2s2p) increases at the same rate as the difference CI(CASSCF(2p),2p)-FCI(2p) with basis set improvements. From the CI(CASSCF(2p),2s2p) calculation, we estimate the EA to be 1.35 eV, and from the CI(CASSCF(2s2p),2s2p) calculations we estimate 1.34 eV. These are probably underestimates, because the importance of higher excitations increases faster for the FCI(2s2p) wave function than for FCI(2p) wave function. Thus, the FCI(2s2p) EA in the 6s5p3d2f could easily be as large as 1.36 eV. The remaining error of 0.1 eV can be rationalized in terms of the synergistic effect of basis set incompleteness and the contribution of higher excitations. That is, a basis set incompleteness error of 0.05 eV at the SDCI level becomes twice as large at the FCI(2s2p) level. These arguments also imply a relatively large positive differential contribution of the 2s correlation at the FCI level of 0.07 eV in the 6s5p3d2f basis, and quite possibly 0.1 eV in a complete one-particle basis.

Our theoretical results are reasonably consistent with a recent study of the EA of oxygen using Moller-Plesset perturbation theory by Raghavachari [5]. In particular, the value of 1.36 eV obtained by performing coupled-cluster calculations including all double substitutions, augmented by an estimate of the contributions of single and triple substitutions from the CCD wave function, CCD+ST(CCD), is in good agreement with our FCI(2s2p) result. When the ST contribution is estimated from fourth-order Moller Plesset theory, CCD+ST(MP4), the value of 1.41 eV is probably too large. It would, however, be of considerable interest to see a more exact comparison of CCD calculations and the full CI results. This would resolve whether the excitations neglected in CCD make only a small contribution or whether the good agreement results from a cancellation of errors.

IV. Green's Function Monte Carlo

Although our full CI calculations give insight into what the computational requirements are for computing an electron affinity of oxygen with chemical accuracy, we presently cannot perform these calculations. Since the EA and the differential correlation energy (of 2.0 eV), are not expected to converge more rapidly than the total valence correlation energy, a calculation accounting for over 95% of the valence correlation energy is required to produce an EA to within 0.1 eV. Therefore, methods such as released node Green's function Monte Carlo [13], that can in principle account for all of the correlation energy, would seem to be especially appropriate for this problem.

Using a vectorized implementation of Green's function Monte Carlo on the Cyber-205, we describe here our initial attempts to compute the EA of oxygen in collaboration with David Ceperley. The trial wavefunction used to guide the random walk consisted of a Slater determinant times a pair correlation function (Slater-Jastrow). The trial function only affects the statistical error of the energy, and not its limiting value. The atomic orbitals were determined from an SCF calculation using a 4s3p STO basis set. The EA computed at the fixed node level is 1.137±0.063 eV. The nodal release procedure [17] employed, however, did not converge. The calculation was still far from convergence (especially for oxygen) after 42 generations [13,17]. It is impractical to continue the calculation further as the expectation values would become increasingly noisy and the total number of walks grows geometrically. This indicates that either a substantially better trial function is required, that is, the nodes need to be more accurately positioned by the trial function so that the relaxation to the correct nodes occurs more quickly, or that a more efficient nodal release procedure is required. We conclude that it is presently not feasible to compute an accurate EA for a system as heavy as oxygen using released node Green's function Monte Carlo. We present this problem as a challenge to future developments of the method.

Recently Barnett, Reynolds and Lester [18] reported a calculation of the EA of fluorine using fixed-node Monte Carlo. They obtained over 90% of the correlation for both the neutral and the anion, and an electron affinity of 3.45±0.11 eV in excellent agreement with experiment. A single determinant, constructed with a double-zeta basis set, multiplied by electron-electron and electron-nuclear Jastrow functions were used as importance functions. These results contradict our experience with oxygen and the concept that methods which obtain 90% of the total correlation energy, such as CASSCF-MRCI, should yield 90% of the differential correlation contribution to the EA, which should lead to an error of about 0.2 eV for the EA of both O and F. Perhaps their trial function fortuitously places the nodes better for F^-, or some bias is introduced by the extrapolation to a zero time step.

V. Conclusions.

The CASSCF-MRCI and full CI calculations reported here show that higher excitations become more important as the one-particle basis set is improved. At high levels of correlation treatment, correlation of the 2s electrons makes a positive contribution to the electron affinity of oxygen. In fact, we estimate that at the full CI basis set limit the 2s contribution could be as large as 0.1 eV. Reduction of the CASSCF reference space from which the MRCI is carried out is found to significantly affect the electron affinity, even for a selection threshold of 0.01 on the coefficients. Our attempts to compute a quantitative electron affinity for oxygen using both fixed-node and released-node Monte Carlo was not very successful. It is hoped that future developments in the released node procedure will significantly improve the applicability of Monte Carlo methods to systems as heavy as oxygen.

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Table I. The computed EA as a function of the addition of polarization functions, for the CI(SCF,2p) level, in eV, taken from Reference 3.

Basis	EA
6s6p	0.676
1d	0.912
2d	0.996
3d	1.014
3d1f	1.047
3d2f	1.069
NHF	-0.54
EXP	1.462[a]

[a] Reference 6.

Table II. Summary of computed EA's, in eV.

Calculation	EA
valence basis	
NHF	-0.54
SCF 6s5p	-0.54
6s5p1d	
CI(SCF,2p)	0.903
CI(SCF,2p)+Q	1.042
CI(CASSCF(2p),2p)	1.075
FCI(2p)	1.086
CI(SCF,2s2p)	0.771
CI(SCF,2s2p)+Q	0.956
CI(CASSCF(2p),2s2p)	1.025[a]
CI(CASSCF(2s2p),2s2p)	1.036
FCI(2s2p)	1.059
6s5p3d2f	
CI(SCF,2p)	1.064
CI(SCF,2p)+Q	1.217
CI(CASSCF(2p),2p)	1.263[b]
FCI(2p)	1.287
CI(SCF,2s2p)	0.991
CI(SCF,2s2p)+Q	1.200
CI(CASSCF(2p),2s2p)	1.277
CI(CASSCF(2s2p),2s2p)	1.290
EXP	1.462[c]

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[a] If the CI calculations are modified to include single and double excitations from all possible distributions of the 2s and 2p electrons among the 2s, 2p and 2p′ orbitals the EA is increased to 1.028eV.

[b] If the MCSCF and MRCI are expanded to include the 3d orbital as active, the EA is increased by 0.017eV.

[c] Reference 6.

APPENDIX 5

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A FULL CI TREATMENT OF Ne ATOM – A BENCHMARK CALCULATION PERFORMED ON THE NAS CRAY 2

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Full CI calculations are performed for Ne atom using Gaussian basis sets of up to triple-zeta plus double polarization quality. The total valence correlation energy through double, triple, quadruple and octuple excitations is compared for eight different basis sets. These results are expected to be an important benchmark for calibrating methods for estimating the importance of higher excitations.

1. Introduction

In a configuration-interaction (CI) calculation, the electronic correlation energy is obtained through a double basis set expansion [1]. The one-particle molecular orbitals are first expanded in an atomic basis set, and the *n*-particle basis set is then expanded in determinants (or a spin and space symmetry adapted linear combination of determinants, namely configuration state functions, CSFs). Although one can obtain the one-particle basis limit for uncorrelated self-consistent-field, SCF, wavefunctions, it is impossible to reach the basis set limit for full configuration-interaction, FCI, wavefunctions. Presently, the most common approach for including electron correlation is to include all single and double (or perturbation theory selected) excitations from a zeroth-order space consisting of the most important configurations (see refs. [1,2], and references therein). For such wavefunctions, it is now possible to use very large one-particle basis sets. Thus, the calculations are limited in accuracy primarily by the truncation of higher excitations from the *n*-particle space. Various methods have been proposed to estimate the importance of higher excitations both on the energy and on properties [3–5].

The factorial increase in the number of CSFs with excitation level has limited CI calculations which account explicitly for higher than double excitations to small one-particle basis sets. Of particular significance are the FCI calculations of Handy and co-workers [6,7]. These calculations have been useful in calibrating the effect of higher excitations, but the small atomic basis sets employed have resulted in rather small total correlation energies. However, with the advent of super computers such as the CRAY 2, with is combination of large memory and vectorized matrix multiply capabilities, it is possible by exploiting recent developments in the FCI methodology to consider FCI

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calculations in larger basis sets. The first such development was Siegbahn's realization [8] that the FCI could be vectorized in terms of matrix multiplies if the two-electron coupling coefficients are expanded as products of one-electron matrix elements. Further, Knowles and Handy showed [9] that of the FCI wavefunction is expanded in determinants instead of CSFs, matrix elements can be easily constructed as needed (with increased memory requirements), thereby avoiding a formula tape and greatly decreasing the input/output (I/O) operations. This formulation of the FCI problem is ideal for the CRAY 2 which has extensive memory and a matrix multiply performance in excess of the CRAY XMP. Thus by using an implementation of the Knowles and Handy full CI procedure on the Numerical Aerodynamic Simulation (NAS) Project CRAY 2, we have performed benchmark FCI calculations on the Ne atom using Gaussian basis sets of up to triple-zeta plus double polarization quality correlating the eight valence electrons. The resulting correlation energy is more than twice that of double-zeta basis sets used in previous full CI calibration calculations. For comparison we have performed conventional CI calculations incorporating up through quadruple excitations to assess the relative importance of different excitation levels.

2. Methods

Three valence basis sets are used in this work. The first two use the Huzinaga (9s5p) primitive set [10], contracted to [4s2p] and [5s3p] following Dunning [11]. The third basis is a [6s4p] contraction of van Duijneveldt's (11s7p) primitive basis set [12]. Since these calculations are intended for calibration, the basis sets are given explicitly in table 1. To these valence basis sets, one and two sets of d functions are

Table 1
The GTO basis sets [a]

Function	s	p
9s5p/4s2p [b]		
1	12100.0000(0.001200)	56.4500(0.020875)
2	1821.0000(0.009092)	12.9200(0.130032)
3	432.8000(0.041305)	3.8650(0.395679)
4	132.5000(0.137867)	1.2030(0.621450)
5	43.7700(0.362433)	0.3444(1.000000)
6	5.1270(0.130035)	
7	14.9100(1.000000)	
8	1.4910(1.000000)	
9	0.4468(1.000000)	
11s6p/6s4p		
1	47479.00000(0.000219)	155.15100(0.003157)
2	7066.93000(0.001708)	36.45440(0.023920)
3	1603.00000(0.008936)	11.42280(0.098494)
4	450.72400(0.036608)	4.11803(0.251086)
5	146.13900(0.118542)	1.55464(1.000000)
6	52.42280(0.285128)	0.57919(1.000000)
7	20.26510(1.000000)	0.20612(1.000000)
8	8.14482(1.000000)	
9	2.41510(1.000000)	
10	0.92900(1.000000)	
11	0.33687(1.000000)	

[a] The total SCF energies are [4s2p] = −128.522354, [5s3p] = −128.524013, and [6s4p] = −128.543823 hartree.

[b] The 5s3p contraction is obtained by uncontracting s primitive number 6 and p primitive number 4.

added. The exponents for the d functions are taken from Ahlrichs et al. [13]; for the one d basis we used $\alpha = 2.15$, and for the 2d basis we used $\alpha = 4.5$ and 1.3. The 3s component of the d functions is deleted in all calculations.

The orbitals are optimized at the SCF level for the ^1S state of Ne atom in D_{2h} symmetry. The 1s orbital is frozen in all correlated wavefunctions. To estimate the importance of different excitation levels, conventional CI calculations are performed on the Cyber-205 that include all CSFs through doubles (SD), through triples (SDT) and through quadruples (SDTQ). Recently, Ahlrichs and co-workers [5] have proposed the coupled pair functional (CPF) method to account for the importance of higher excitations, and have reported [14,15] impressive results for selected molecules containing first-row atoms. Hence, we also include for comparison the CPF results as well as the results of the frequently used Davidson correction [3] for unlinked quadruple excitations.

We compute the importance of a given excitation level from the difference between it and the next lower level. For example, the importance of triples is computed as the difference between CI(SDT) and CI(SD). We do not decompose the difference between the CI(SDTQ) and the CI(FCI), thus the quintuple through octuple excitations are combined.

3. Results and discussion

The breakdown of the correlation contribution by excitation level is summarized for the eight Gaussian basis sets in table 2. Since the HF reference is a good zeroth-order description of the ground state of Ne atom, the correlation energy is dominated by the double excitations, which account for over 96% of the correlation energy. The contribution from the triple excitations is significant varying from 45% to 60% of the quadruples contribution. The fractional contribution from five-fold and higher excitations is very small and tends to decrease with increasing basis set quality. For example, the contribution of higher than double excitations (3.7–3.8% of the total correlation energy) is nearly identical for the [4s2p] and [5s3p2d] basis set, but the percent contribution from five-fold and higher excitations for the larger basis (0.08%) is only about half that of the [4s2p] basis.

The correlation energies obtained at various excitation levels are summarized for the Gaussian basis sets in table 3. This table again illustrates how close is the energy through quadruples to the full CI energy. Table 3 also compares the quadruples contribution to the correlation energy obtained using the coupled pair functional (CPF) approach and the Davidson correction for unlinked quadruple excitations. The CPF approach accounts for only about 40% of the contribution from higher than double excitations for the [4s2p] basis set. This underestimation arises in part from the fact that the CPF approach does not account for the sizable contribution from triple excitations and also does not account fully for the quadruple excitations. In contrast, the Davidson correction is larger, accounting for about 90% of the

Table 2
Comparison of percent correlation energy contribution by excitation level

Basis	[4s2p]	[5s3p]	[6s4p]	[4s2p1d]
singles + doubles	96.22	96.25	96.07	96.68
triples	1.36	1.31	1.41	1.05
quadruples	2.25	2.34	2.41	2.15
quintuples–octuples	0.17	0.10	0.10	0.11
	[5s3p1d]	[6s4p1d]	[4s2p2d]	[5s3p2d]
singles + doubles	96.60	96.41	96.46	96.27
triples	1.03	1.12	1.25	1.33
quadruples	2.30	2.38	2.18	2.32
quintuples–octuples	0.07	0.08	0.11	0.08

Table 3
Comparison of correlation energies and methods of estimating higher excitations

Basis	[4s2p]	[5s3p]	[6s4p]	[4s2p1d]
E(SD)	−129.621884	−128.658764	−128.682712	−128.696487
E(SD) − E(SCF)	0.099530	0.134751	0.138889	0.174133
E(SDT) − E(SD)	0.001406	0.001836	0.002041	0.001898
E(SDTQ) − E(SD)	0.003735	0.005112	0.005537	0.005779
E(FCI) − E(SD)	0.003907	0.005247	0.005687	0.005975
E(SDTQ) − E(SDT)	0.002329	0.003276	0.003496	0.003881
E(CPF) − E(SD)	0.001617	0.002157	0.002400	0.003539
E(DVD) [a] − E(SD)	0.002114	0.002808	0.003101	0.004675

	[5s3p1d]	[6s4p1d]	[4s2p2d]	[5s3p2d]
E(SD)	−128.735002	−128.759855	−128.719125	−128.759746
E(SD) − E(SCF)	0.210989	0.216032	0.196771	0.235733
E(SDT) − E(SD)	0.002242	0.002518	0.002557	0.003258
E(SDTQ) − E(SD)	0.007266	0.007850	0.006996	0.008928
E(FCI) − E(SD)	0.007429	0.008034	0.007219	0.009131
E(SDTQ) − E(SDT)	0.005024	0.005332	0.004402	0.005270
E(CPF) − E(SD)	0.004329	0.004670	0.004402	0.005276
E(DVD) − E(SD)	0.005606	0.006004	0.005728	0.006823

[a] Davidson's estimate of higher excitations, ref. [3].

quadruples contribution for the [4s2p] basis. For the larger basis sets including polarization functions, this picture changes somewhat. The CPF now accounts for about 60% of the correlation from higher than double excitations, since it now accounts for the dominant portion of the correlation contribution from quadruple excitations. Also, for the larger basis sets the Davidson correction considerably overestimates the contribution from quadruple excitations.

The largest basis set considered in this study, [5s3p2d], accounts for about 75% of the valence-shell correlation energy. The difficulty in extending the FCI technique to still larger basis sets is illustrated by the following numbers. For the [5s3p2d] basis in D_{2h} symmetry, there are 462 CSFs through double excitations, 6706 CSFs through triple excitations, 62234 CSFs through quadruple excitations, and 2360757 CSFs through octuple excitations. In addition, 2360757 CSFs result in 9805897 determinants and 78411025 "intermediate states" [7,8], and the addition of a single f basis function would increase this to about 20 million CSFs. The 2.36 million SCF calculation presently takes about 22.8 min per iteration on the CRAY 2. The present rate limiting step is matrix multiply (MXM) which is currently running at more than 250 Mflops. Recently Calahan and coworkers [16] have implemented an unrolled matrix multiply which has achieved 385 Mflops on our system, thus we expect improved performance in the future.

4. Conclusions

Full CI calculations have been performed for ^{1}S Ne atom using Gaussian basis sets of up to triple-zeta plus double polarization quality. These calculations should supplement existing full CI benchmark calculations in that they account for a significantly larger amount of correlation energy. Presently we are performing additional full CI calculations on such systems as H_2O, HF, O and O^- using the NAS CRAY 2; this should supply further insight into the magnitude and nature of higher excitations.

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