the selected-space eigenvectors $\mathbf{c}^k$ as zeroth-order solutions:

$$\Delta E_I^k = \frac{|\langle I|\hat{H}|\mathbf{c}^k\rangle|^2}{E^k - \langle I|\hat{H}|I\rangle}. \tag{136}$$

The set of all configurations I with $|\Delta E_I^k| > \eta$ is added to the reference space, and the new Hamiltonian is diagonalized; this process is repeated until no new important configurations are found. The reference selection is thus self-consistent, and Harrison notes[223] that typically only two iterations are required. The sum of the estimated energy lowerings (136) provides a perturbative correction for excluded configurations, and the total energy (variational energy plus perturbative correction) is an approximation to the full CI energy. An increasingly accurate sequence of wavefunctions is generated by repeating this whole process for a series of thresholds η with decreasing values. Note, however, that those configurations which do not interact directly with any reference function are completely neglected. Although the individual contributions of such configurations should be very small, there are a large number of them. Harrison finds that the CI+PT method approaches the full CI energy from above, suggesting that the error due to the neglect of noninteracting configurations is greater than the error due to the perturbative estimates of configurations which are interacting but not included in the reference space (the latter correction, being nonvariational, could conceivably lead to energies below the full CI limit). Harrison's approach is similar to the original two-class CIPSI algorithm,[92] but it selects references based on their contributions to the energy rather than to the first-order wavefunction; Harrison notes that for properties other than the energy, this might not be the optimal choice.[223] An advantage of his program was that it could handle larger variational spaces than the versions of the CIPSI and MRD-CI programs available at that time (recent improvements in these programs are described above). Results for H_2O, O, and O^- were compared to full CI and indicate that the perturbation theory energy correction rapidly accelerates convergence to the full CI energy. For example, the full CI energy for H_2O at three different geometries was obtained within 0.1 kcal mol^{-1} with a variational reference space and perturbative interacting space spanning less than 0.23% and 25%, respectively, of the full CI space (these results correspond to a selection threshold of $\eta = 4 \times 10^{-7}$).

The wavefunction operator (WFO) approach of Luzanov, Wulfov, and Krouglov (1992)[224] seems to be the same as Harrison's CI+PT approach, although it is formulated differently and implemented using determinants. This method appears to involve the same amount of work as other determinant-based sparse CI methods,[215,220,221] but it uses rather different intermediate arrays. Explicit algorithms for the WFO method were presented in 1996 by Wulfov,[225] who obtained results for HF dimer in a 4s3p1d/2s1p basis using a personal computer (PC) equipped with only 16 megabytes (MB) of RAM and 50 MB of disk space. The largest computation, with threshold $\eta = 10^{-7}$, considered 65,751 determinants variationally and treated an unreported number of interacting determinants perturbatively.

Perturbation theory corrections to variational energies have also been considered recently by Mitrushenkov and Dmitriev (1995),[216] who express the second-order energy correction as

$$\begin{aligned} \Delta E &= \sum_{I_\alpha I_\beta} \frac{\sigma_0(I_\alpha, I_\beta)[\sigma_0(I_\alpha, I_\beta) - E_0 c_0(I_\alpha, I_\beta)]}{E_0 - H^D_{sa}(I_\alpha, I_\beta)} \\ &= (\mathbf{c}_0, \hat{H}\Delta\mathbf{c}), \end{aligned} \tag{137}$$

where $\mathbf{c}_0$ is the current CI vector and $\Delta\mathbf{c}_0$ is the correction vector. The term $H^D_{sa}(I_\alpha, I_\beta)$ is the diagonal element of the Hamiltonian for determinant $|I_\alpha I_\beta\rangle$, and the subscript *sa* indicates an average over all determinants with the same spatial orbital configuration (cf. section 3.2.1). This correction is essentially the same used by Harrison[223] and others. Rather than employ this expression exactly as it is, Mitrushenkov and Dmitriev note[216] that for a converged full CI vector $\mathbf{c} = \mathbf{c}_0 + \Delta\mathbf{c}$, the full CI energy can be expressed as:

$$\begin{aligned} E &= \frac{(\mathbf{c}_0, \hat{H}\mathbf{c})}{(\mathbf{c}_0, \mathbf{c})} \\ &= \frac{E_0 + (\mathbf{c}_0, \hat{H}\Delta\mathbf{c})}{1 + (\mathbf{c}_0, \Delta\mathbf{c})}. \end{aligned} \tag{138}$$

Mitrushenkov and Dmitriev designate this the norm-consistent zero threshold full CI estimate. When $\Delta\mathbf{c}$ is orthogonal to $\mathbf{c}$, this is the second-order perturbation theory estimate (137). However, since selection in the dynamic CI occurs during the subspace iteration process, $\Delta\mathbf{c}$ and $\mathbf{c}$ are not orthogonal. Of course the exact σ_0 and $\Delta\mathbf{c}$ must be used in the evaluation of (138); these are evaluated for fixed I_β as described above. Mitrushenkov and Dmitriev demonstrated this zero threshold energy (ZTE) estimate for Ne, NH_3, Mg, and H_2O; for Ne, comparisons with full CI indicate that the ZTE estimates approach the correct energy much faster than the variational energies with respect to decreasing threshold, but the approach is not monotonic and can occur from below. Very recently, Mitrushenkov has extended this approach to perform the dynamic CI+ZTE in the active space and to treat the external space using only second-order perturbation theory.[226]

In order to compare some of these selected CI methods, we present results for DZP NH_3 in Table 5. These results were obtained in point group C_s with the 1a′ core orbital frozen (i.e., constrained to remain doubly occupied). The

Table 5: Selected and Full Configuration Interaction Benchmarks for NH_3 with an ANO DZP Basis Set.[a]

Threshold	N_{CI}	E_{CI}	E_{CI}- E_{FCI}	N_{PT} $\times 10^6$	E_{CI+PT}	E_{CI+PT}- E_{FCI}
Knowles and Handy, Ref. 218:[b]						
2.0×10^{-4}	171 867	-56.4219	0.0021	n/a	-56.4220	0.0020
1.0×10^{-4}	393 666	-56.4229	0.0011	n/a	-56.4230	0.0010
5.0×10^{-5}	450 763	-56.4232	0.0008	n/a	-56.4234	0.0006
4.0×10^{-5}	665 247	-56.4235	0.0005	n/a	-56.4236	0.0004
Harrison, Ref. 223:[c]						
1.0×10^{-4}	786	-56.390631	0.033376	0.61	-56.422854	0.001153
1.3×10^{-5}	1 889	-56.411996	0.012011	1.04	-56.423766	0.000241
1.6×10^{-6}	5 814	-56.417497	0.006510	2.93	-56.423748	0.000259
3.9×10^{-7}	18 921	-56.420203	0.003804	5.92	-56.423719	0.000288
2.0×10^{-7}	32 288	-56.421211	0.002796	7.68	-56.423737	0.000270
Povill *et al.*, Ref. 123:[d]						
6.0×10^{-6}	1.00×10^6	-56.423659	0.000348	2.49	-56.423681	0.000326
0.4×10^{-6}	1.17×10^6	-56.423785	0.000222	6.55	-56.423824	0.000183
0.1×10^{-6}	1.25×10^6	-56.423825	0.000182	15.10	-56.423875	0.000132
Mitrushenkov and Dmitriev, Refs. 183, 216:[b,e]						
1.0×10^{-3}	2 000	-56.4085	0.0155	n/a	-56.42397	0.00004
1.0×10^{-4}	34 000	-56.4195	0.0045	n/a	-56.42392	0.00009
1.0×10^{-5}	590 000	-56.4235	0.0005	n/a	-56.42400	0.00001

[a] Basis set and geometry of Ref. 218. Only valence electrons are correlated. N_{CI} denotes the size of the variational space, and N_{PT} denotes the size of the interacting space treated by second-order perturbation theory. All energies are given in hartree.

[b] Number of nonzero elements in final CI vector.

[c] Dimensions are given in CSFs instead of determinants.

[d] The CIPSI algorithm uses two thresholds, η and τ. η is given, and $\tau = 10^{-10}$.

[e] Mitrushenkov reports the number of nonzero elements in the CI vector as a percentage of the full CI space (209 626 425 determinants); the N_{CI} values given are thus only approximate.

first highly accurate NH_3 benchmark using a basis set this large was that of Knowles and Handy in their 1989 demonstration of their new selected CI method.[218] Hence, most subsequent selected CI benchmarks on this system have used their geometry and atomic natural orbital basis set. An exception is the wavefunction operator (WFO) benchmark,[224] which employed a different basis set; that method is therefore excluded from the table. The exact full CI energy of NH_3 with this basis set was unavailable when these selected CI benchmarks were published, and the Knowles-Handy[218] extrapolated selected CI estimate of -56.4236 hartree has sometimes been used in place of the full CI value. The apparent convergence of this estimate led Knowles and Handy to propose error bars of ±0.0001 hartree. However, in 1994 Povill *et al.*[123] used the 3-class CIPSI method[93] to select the most important 1.25 million determinants and obtained a variational energy of -56.423825 hartree using the DISCIUS algorithm.[215] This energy is lower than the lowest estimate of Knowles and Handy, including the error bar. This difficulty was cleared up in 1995 by Evangelisti *et al.*,[50] who used the full CI program of Bendazzoli and Evangelisti[48,49] to obtain an energy of -56.424007 hartree (this same value was obtained independently by Olsen[80]). This demonstrates that the energy of Knowles and Handy was not converged as tightly as expected, and that it is easy to underestimate the importance of a large number of neglected determinants.

The data in Table 5 show that the perturbation theory corrected energies are better approximations to the full CI energy than the purely variational results, and that the full CI energy is always approached from above; these conclusions are in general agreement with previous benchmarks for smaller systems.[93,216,223,224] However, we note that the perturbation theory corrections become less effective for large variational spaces, and conversely, the CI+PT energies are slowly convergent (and not monotonic) with the relatively small CI spaces used in Harrison's study[223] (note, however, that Harrison's N_{CI} values are in CSFs rather than determinants, making his variational space look smaller than it actually is). The norm-consistent zero threshold energies of Mitrushenkov and Dmitriev[216] appear particularly effective, although they do not approach the full CI energy monotonically.

Table 5 demonstrates that it is difficult to establish the convergence of the energy for selected CI methods. Another problem which has received relatively little attention is the convergence of properties other than the energy. It would be expected that other properties should not converge as quickly with respect to the size of the CI space as the energy (cf. section 2.2), particularly for selected CI methods which use an energy selection criterion rather than a coefficient criterion. However, a 1992 study by Cave, Xantheas, and Feller[227] used a selected CI method which is similar to the two-class CIPSI[92] method but uses energy-based selection. These authors came to the remarkable conclusion that most one-electron properties considered in their study (including isotropic hyperfine values and dipole and quadrupole moments) converged even more rapidly than the energy.[227] Additionally, Wulfov[228] has recently considered the convergence of the equilibrium geometries and harmonic vibrational frequencies of several diatomic molecules as a function of the selection threshold value.[224,225] The convergence of these properties could not be firmly established due to the lack of corresponding exact full CI values; however, a recent full CI benchmark study by our group[229] on C_2 and CN^+ finds only very small errors in Wulfov's best CI+PT geometries and frequencies (less than 0.001 Å and 4.0 cm^{-1}, respectively).

4.8 Restricted Active Space CI

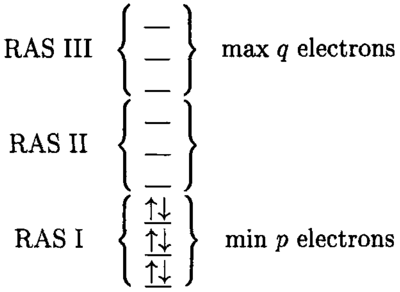
Rather than select individual determinants based on computational estimates of their importance, one might instead select entire classes of determinants which are expected *a priori* to be important based on their partitioning of electrons among various orbital subspaces. This is the motivation behind the truncation of the CI space according to "excitation level" (how many electrons are placed in the virtual subspace) and the second-order CI (SOCI),[13] which includes all determinants with at most two electrons in the external subspace. Such CI selection schemes were described in general terms by Shavitt,[57] who defined the *full class CI* as one which partitions the orbitals into an arbitrary number of orthogonal subsets and includes all or none of the N-electron functions which have a given partitioning of electrons among the subspaces. As Shavitt points out, a full-class CI wavefunction is invariant to separate, nonsingular linear transformations within any of the orbital subspaces.

A benefit of such class selection schemes is that the CI space exhibits a regular structure which can be used to advantage in computational implementations. Additionally, it appears to be easier to gauge the general reliability of wavefunctions obtained using class selection schemes as opposed to individual selection. However, class selection methods will invariably include some less important determinants and therefore cannot yield wavefunctions as compact as those from an individual selection method.

A specialization of the full class CI which uses only three orbital subspaces is the Restricted Active Space (RAS) CI approach introduced by Olsen *et al.*[46] in 1988 along with the string-based full CI algorithm already discussed (section 4.4). The three subspaces are labeled I, II, and III, and the CI space is limited by requiring a *minimum of p electrons in RAS I* and a *maximum of q electrons in RAS III* (cf. Figure 14). There are no restrictions on the number of electrons in RAS II, and thus it is analogous to the complete active space

(CAS). There may be an additional frozen core subspace in which each orbital is constrained to remain doubly occupied; these core electrons and orbitals need not be treated explicitly in the RAS procedure (cf. section 2.4.7). The full CI space may be obtained as the maximum limit of the RAS space. The focus of Olsen's paper was on the utility of the RAS method in limiting the size of CI calculations, but thus far its maximum impact has been on the development of determinant-based full CI algorithms.[83,183]

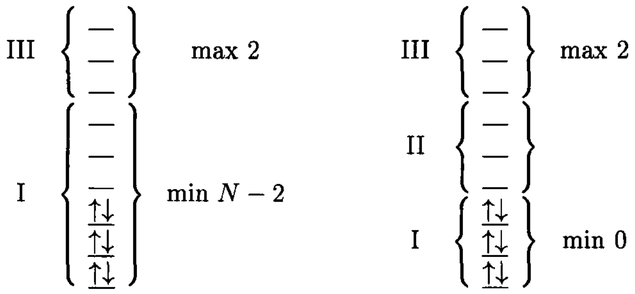
Figure 14: Orbital partitioning and configuration selection in the Restricted Active Space Configuration Interaction method. The CI space includes all determinants in which at least p electrons are in RAS I and at most q electrons are in RAS III.



Any CI space truncated according to excitation level may be formulated within the RAS CI framework: the occupied orbitals are placed in RAS I, and the unoccupied orbitals are placed in RAS III, and the RAS II subspace is absent. The maximum number of electrons in RAS III is set equal to the maximum excitation level, and the minimum number of electrons in RAS I is simply the total number of electrons N minus the maximum excitation level. A full CI can be obtained by applying trivial restrictions, such as a minimum of zero electrons in RAS I and a maximum of N electrons in RAS III.

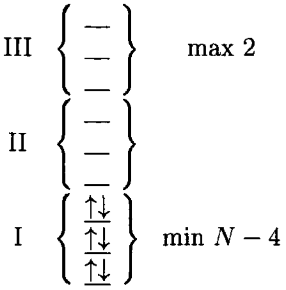
One may also formulate excitation class selected MR-CI spaces within the RAS framework. A SOCI can be obtained by setting RAS I equal to the active space, deleting RAS II, allowing a maximum of two electrons in RAS III, and requiring a minimum of $N-2$ electrons in RAS I. Alternatively, this same CI space may be constructed by placing the virtual orbitals of the active space in RAS II, allowing a maximum of two electrons in RAS III, and requiring zero electrons in RAS I. To obtain the CISD[TQ] wavefunction mentioned in section 2.4.2, one places occupied orbitals in RAS I and virtual active space

Figure 15: Two formulations of the SOCI wavefunction within the RAS CI method.



orbitals in RAS II. A maximum of two electrons are allowed in RAS III, and a minimum of $N - 4$ electrons are required in RAS I (cf. Figure 16). Some possibilities of extending the RAS selection scheme are discussed in section 4.8.3.

Figure 16: Formulation of the CISD[TQ] wavefunction within the RAS method.



The RAS CI algorithm of Olsen *et al.*[46] relies on Handy's separation of determinants into alpha and beta strings (cf. section 4.2). As in other determinant-based CI methods, the determinants are restricted to those having a given value of M_s. Since the number of electrons N is also fixed, this means that the alpha and beta strings always have constant lengths of N_α and N_β, respectively. For a full CI, one forms all possible alpha and beta strings for a given N_α and N_β, and the determinants employed are all possible combinations of these alpha and beta strings. In a RAS CI wavefunction, the CI space is restricted in two ways: first, not all alpha and beta strings are allowed, and secondly, not all combinations of alpha and beta strings to form determinants are accepted. This is best understood from an example: consider the case of 6 orbitals, with $N_\alpha = N_\beta = 3$. If orbitals 4, 5, and 6 constitute RAS III, with a maximum of 2 electrons allowed, then clearly alpha strings such as $a^\dagger_{4\alpha}a^\dagger_{5\alpha}a^\dagger_{6\alpha}$ are not allowed. Similarly, even though $a^\dagger_{1\alpha}a^\dagger_{4\alpha}a^\dagger_{5\alpha}$ and $a^\dagger_{1\beta}a^\dagger_{4\beta}a^\dagger_{5\beta}$ are allowed alpha and beta strings, these strings cannot be combined with each other because the resulting determinant would place four electrons in RAS III.

If the CI coefficient vector is viewed as a matrix, $c(I_\alpha, I_\beta)$, then these restrictions, as well as those due to point-group symmetry, can be implemented by allowing only certain blocks of c to be nonzero. If strings with the same irreducible representation are numbered consecutively, then only those blocks of the CI coefficient matrix with the correct overall symmetry (determined as the direct product of the alpha and beta string irreducible representations) are allowed to be nonzero. For the RAS restrictions, it is convenient to assign a particular code to each alpha and beta string which represents the distribution of electrons among the RAS orbital subspaces. This means that the allowed combinations of strings may be determined directly from their respective codes. In Olsen's nomenclature,[46] these codes correspond to different string graphs; string representation and addressing is discussed further in section 4.9. If strings with a given code (or within a given graph) are numbered consecutively, then the allowed combinations of strings become allowed subblocks of the symmetry blocks in the CI coefficient matrix. These are referred to henceforth as the RAS subblocks. For a full CI, one can group all strings belonging to the same irreducible representation in the same graph, so that the RAS subblocks are the same as the symmetry blocks.

4.8.1 RAS CI σ Equations

The products of shift operators in equations (113) and (114) mean that some alpha/beta strings can contribute to the σ vector even if they are not necessary to describe the CI space. Therefore the string lists must include all valid strings and all the singly substituted strings derived from them. For a full CI, all possible strings for a given number of alpha/beta electrons are allowed, so all singly substituted strings are automatically present. For a restricted CI, however, including all singly substituted strings is an inefficient procedure.

Olsen *et al.* showed[46] how to eliminate the contributions from these "out-of-space" strings for the case of a RAS CI wavefunction. Since the equation for σ_3 (115) contains no products of shift operators, only σ_1 and σ_2 can contain contributions from out-of-space strings. Moreover, since σ_2 is analogous to σ_1 (and can be derived from it for $M_s = 0$ cases), it is sufficient to focus on σ_1. Olsen's approach is to change the sum over i, j, k, l into a restricted sum, $(ij) \geq (kl)$, where (ij) and (kl) are canonical indices defined as

$$(ij) = in + j, \tag{139}$$

if there are n orbitals and the numbering starts from zero. Consider the term

$$\sum_{J_\beta} \sum_{(ij)\geq(kl)} \langle \beta(J_\beta)|\hat{E}^\beta_{ij}\hat{E}^\beta_{kl}|\beta(I_\beta)\rangle (ij|kl) c(I_\alpha, J_\beta). \tag{140}$$

An out-of-space string K_β can only contribute if it is produced by $\hat{E}^\beta_{kl}|\beta(I_\beta)\rangle$, and if $\hat{E}^\beta_{ij}$ transforms it back into an allowed string (J_β). But if the orbitals are numbered consecutively within each RAS space, and if equation (139) is used to define the canonical index (ij), such contributions are impossible. For example, consider the case where a maximum of two electrons are allowed in RAS III. If string I_β already contains two electrons in RAS III, then a single replacement $\hat{E}^\beta_{kl}|\beta(I_\beta)\rangle$ which promotes a third electron to RAS III will yield an out-of-space string. The shift operator $\hat{E}^\beta_{ij}$ could produce an allowed string again if it moves any of the three electrons in RAS III back down into RAS I or RAS II. However, if the summation over orbitals is restricted to $(ij) \geq (kl)$, this is impossible, since $k > i$.

Using the commutation relationship

$$\left[\hat{E}^\beta_{ij}, \hat{E}^\beta_{kl}\right] = \delta_{kj}\hat{E}^\beta_{il} - \delta_{il}\hat{E}^\beta_{kj}, \tag{141}$$

one can rewrite (113) to employ this restriction. The result[46] is:

$$\begin{aligned}\sigma_1(I_\alpha, I_\beta) &= \sum_{J_\beta}\sum_{kl}\langle \beta(J_\beta)|\hat{E}^\beta_{kl}|\beta(I_\beta)\rangle g_{kl} c(I_\alpha, J_\beta) &(142)\\ &+ \sum_{J_\beta}\sum_{(ij)\geq(kl)} \langle \beta(J_\beta)|\hat{E}^\beta_{ij}\hat{E}^\beta_{kl}|\beta(I_\beta)\rangle (ij|kl) c(I_\alpha, J_\beta)(1+\delta_{(ij),(kl)})^{-1},\end{aligned}$$

where g is an asymmetric matrix defined as

$$g_{kl} = \begin{cases} h_{kl} - \sum_{j<k}(kj|jl) - (kk|kl)(1+\delta_{kl})^{-1} & k \geq l \\ h_{kl} - \sum_{j<k}(kj|jl) & k < l. \end{cases} \tag{143}$$

4.8.2 Algorithms for Computing σ

The full CI algorithms must be modified to treat the more general RAS case. Most significantly, the σ_1 and σ_2 equations for RAS CI spaces differ from the full CI equations: (142) requires that the summation over orbitals obey $(ij) \geq (kl)$ (recall that introducing this restriction into the full CI algorithm is one way to reduce effort when $M_s = 0$). The other required modification is that the innermost loops must sum over allowed combinations of alpha and beta strings only. For instance, the loop over I_α near the end of the σ_1 algorithm in Figure 7 must be split into two loops: one over alpha string graphs, and another over strings within each graph. This allows for the sum over J_β to run over only those beta strings which are allowed to combine with strings from the current alpha string graph. Similar modifications must be made to the σ_2 and σ_3 algorithms.

It is perhaps not entirely obvious what is the most efficient way to adapt Olsen's algorithms to account for point group symmetry and RAS restrictions. Although it is a relatively simple matter to introduce a loop over graphs in the multiplication of F by c or c', it is also necessary to introduce loops over graphs in earlier parts of the algorithm; otherwise, F can contain irrelevant entries. When the CI vector is processed a symmetry block at a time or a RAS subblock at a time, it seems best to place these loops over graphs within the σ_1, σ_2, and σ_3 routines. However, when the CI vector is processed a RAS subblock at a time, these loops over graphs may be placed outside the σ subroutines. Further details are presented in section 4.9.

4.8.3 Beyond RAS: More Flexible *a priori* CI Space Selection

Although many useful CI spaces can be obtained in the RAS CI method, it may nevertheless be beneficial to employ more complex CI spaces. Olsen has begun to investigate CI spaces formed as the union of two RAS spaces,[80] while we have considered the addition of another orbital subspace.[18] As first pointed out by Grev and Schaefer,[16] the most weakly occupied CISD natural orbitals contribute almost exclusively to singly and doubly substituted configurations, rather than to triples, quadruples, etc. This suggests the utility of extending the RAS method to include another orbital subspace, formed from the most weakly occupied natural orbitals. Labeling this new orbital set as "RAS IV" may be somewhat misleading, in the sense that the orbital index restriction $(ij) \geq (kl)$ is no longer sufficient to remove out-of-space contributions from (142): we have alternatively referred to this new orbital set as the "tertiary virtual subspace".[18]

Let us assume that the occupied orbitals are collected in RAS I, and that if an electron occupies RAS IV, the determinant must represent a single or double substitution of the reference determinant. Out-of-space contributions arise if one electron occupies RAS IV and another electron occupies RAS II or RAS III: such strings are allowed, but the promotion of another electron from RAS I results in a disallowed string $|\beta(K_\beta)\rangle = \hat{E}^{\beta}_{kl}|\beta(I_\beta)\rangle$. Application of the other shift operator in the σ_1 equation, $\hat{E}^{\beta}_{ij}$, can result in an allowed string $|\beta(J_\beta)\rangle$ with $(ij) \geq (kl)$ if the electron in RAS IV is moved into one of the lower RAS subspaces, as long as it occupies an orbital $i > k$. Thus it is necessary to include in the string space all allowed strings, plus the disallowed strings which have one electron in RAS IV and two electrons in (RAS II + RAS III). Once these strings are included, the RAS σ equations can be used for σ_1 and σ_2. As in the standard RAS method, no out-of-space strings can contribute to σ_3. By definition, the out-of-space strings are not allowed to combine with other strings to form RAS subblocks of the c or σ matrices. Alternatively, in some cases these out-of-space contributions might be dealt with by employing the $(N-2)$-electron reduced space of Zarrabian *et al.*[47,217] (cf. section 4.5).

4.9 Implementation of Determinant-Based Algorithms

In this section we discuss some of the practical issues relevant to the actual implementation of the determinant-based CI algorithms. We also describe our experience with our own fully direct CI program, DETCI, which is capable of evaluating any CI wavefunction which can be formulated as a RAS CI, subject to memory and disk limitations. This program is based in part on the alpha and beta string formalism of Handy[44] and the algorithms of Olsen *et al.*[46,83] It has been modified to allow more complex CI spaces, as described in sections 4.8.3 and 5.4.

Our program requires at least two memory buffers for CI vectors, where a buffer can be either the length of the entire vector, or a spatial symmetry block, or a RAS subblock. Using the fastest algorithm, the program also requires a smaller memory buffer to hold a portion of the CI coefficients in a given RAS subblock. An additional buffer the size of the largest RAS subblock may also be required for taking transposes of the c subblocks if $M_s = 0$ symmetry is employed (this is determined by the core memory option, and if possible the same buffer is used for transposes and gathered CI coefficients). For diagonalizing the Hamiltonian, we have implemented many of the iterative methods described in section 3.2.

4.9.1 Graphical Representation of Alpha and Beta Strings

As discussed in the previous section, it is necessary to have a method for numbering the alpha and beta strings and a reasonable way of grouping these strings together so that allowed combinations of strings can be determined a group at a time. Olsen *et al.* use a graphical method to compute string addresses, and they group strings together by placing them on the same graph.[46]

We have employed a similar method.

The present approach is based on the work of Duch, who has described[230] the graphical representation of CI spaces in considerable detail. First, we consider the simple two-slope directed graphs ("digraphs") which represent alpha or beta strings without consideration of point group symmetry. Figure 17 presents a digraph representing all strings with five electrons in seven orbitals. Each string is represented by a "walk" on the graph, from the head (at $e = o = 0$) to the tail (at $e = N_{\alpha/\beta}$, $o = n$). Moving straight down from vertex (e, o) to vertex $(e, o+1)$ indicates that orbital $o+1$ is unoccupied in the current string, while moving down diagonally from vertex (e, o) to vertex $(e+1, o+1)$ indicates that orbital $o+1$ is occupied. Each vertex on the graph is assigned a weight $x(e, o)$, and each arc connecting two vertices is assigned an arc weight $Y(e, o)$ for the arc leaving vertex (e, o). Since, in general, two different arcs can leave a given vertex, we write $Y_0(e, o)$ for the arc originating from vertex (e, o) which leaves orbital $o+1$ unoccupied, and $Y_1(e, o)$ for the arc which occupies orbital $o+1$.[‡] The index or address of a string or walk is obtained by adding weights for each arc contained in the walk, i.e.,

$$I_\alpha(L^\alpha) = X(L^\alpha) + \sum_{i=0}^{n} Y_{L_i}(e_i, i), \tag{144}$$

where L_i is the occupation (0 or 1) of the ith arc, and (e_i, i) are the coordinates of the vertices crossed by L^α. The term $X(L^\alpha)$ gives the offset of a given graph, if more than one graph is employed. The relative index for a determinant in a block may be given by $I(L^\alpha, L^\beta) = I_\alpha(L^\alpha)S_\beta + I_\beta(L^\beta)$, where S_β is the number of beta strings in the block.

There are several different methods for assigning the arc weights by which one evaluates the index of a string according to equation (144). Under the *lexical ordering* scheme, the tail (N_α, n) of an alpha string graph is assigned a weight $x = 1$. Other vertex weights are computed according to the recursive formula

$$x(e, o) = x(e+1, o+1) + x(e, o+1). \tag{145}$$

Using lexical ordering, typically all arc weights $Y_0(e, o)$ are set equal to zero, and the arc weights $Y_1(e, o)$ are determined according to

$$Y_1(e, o) = x(e+1, o+1) + x(e+1, o) + \cdots + x(e+1, e+1). \tag{146}$$

Figure 17a features vertex and arc weights computed in this manner. A result of the lexical ordering scheme is that paths with a fixed upper part and an

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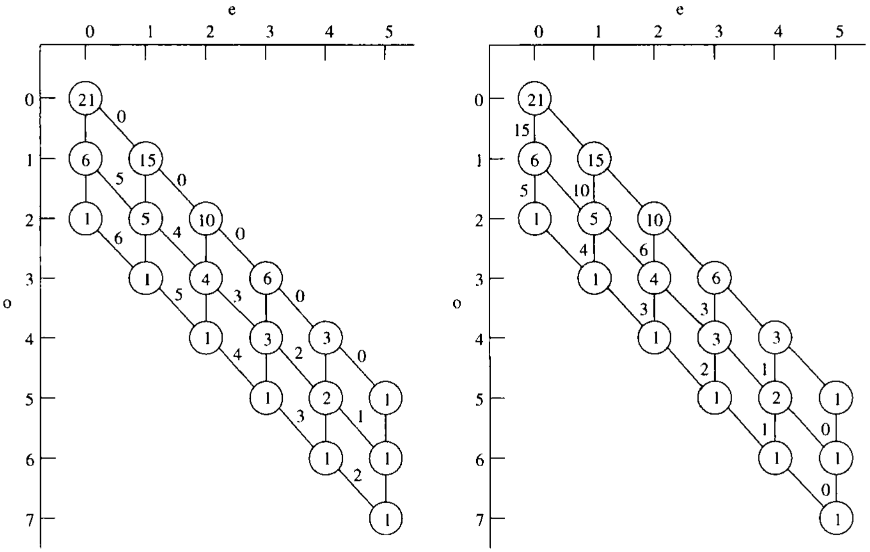
[‡] This differs somewhat from Duch,[230] who sometimes uses $\bar{Y}(e, o)$ to denote the arc *entering* vertex (e, o) in reverse-lexical addressing.

Figure 17: Alpha string graph for $n_\alpha = 5, n = 7$. Vertex weights are determined according to lexical ordering, and arc weights are given so that the rightmost path has index zero. (a) All unoccupied arc weights $Y_0(e, o)$ are zero. (b) All occupied arc weights $Y_1(e, o)$ are zero.



(a)

(b)

arbitrary lower part have consecutive indices. The particular choice of Y values above is appropriate if the rightmost path is to have an index of zero. The same effects can be achieved using

$$\begin{aligned} Y_1(e,o) &= 0 && (147) \\ Y_0(e,o) &= x(e+1,o+1), && (148) \end{aligned}$$

as illustrated in Figure 17b. Any walk has the same index in Figures 17a and 17b. For instance, the walk $a^\dagger_{2\alpha}a^\dagger_{3\alpha}a^\dagger_{4\alpha}a^\dagger_{5\alpha}a^\dagger_{7\alpha}$ has an index of 5+4+3+2+2 = 16 (equation 144) from Figure 17a, and an index of $15+1=16$ from Figure 17b.

In the so-called "reverse-lexical" ordering scheme, all upper paths for a fixed lower path have consecutive indices. Vertex weights are now determined as

$$\bar{x}(e,o) = \bar{x}(e,o-1) + \bar{x}(e-1,o-1), \qquad (149)$$

where the overbar indicates reversed-lexical ordering. Figure 18a depicts a reversed-lexical graph with all non-occupied orbital arcs set to zero. The occupied orbital arcs are computed as

$$\bar{Y}_1(e,o) = \bar{x}(e+1,o). \qquad (150)$$

Figure 18b is the same except that now all occupied arcs have weights of zero. The non-occupied arc weights are

$$\bar{Y}_0(e,o) = \bar{x}(e,o) + \bar{x}(e+1,o+1) + \cdots + \bar{x}(N-1,o+N-e-1). \qquad (151)$$

Note that string indices for reverse-lexical ordering are not necessarily the same as indices for lexical ordering. For the string $a^\dagger_{2\alpha}a^\dagger_{3\alpha}a^\dagger_{4\alpha}a^\dagger_{5\alpha}a^\dagger_{7\alpha}$ considered previously, the index is calculated as $1+1+1+1+6=10$ from Figure 18a, or as $5+5=10$ from Figure 18b.

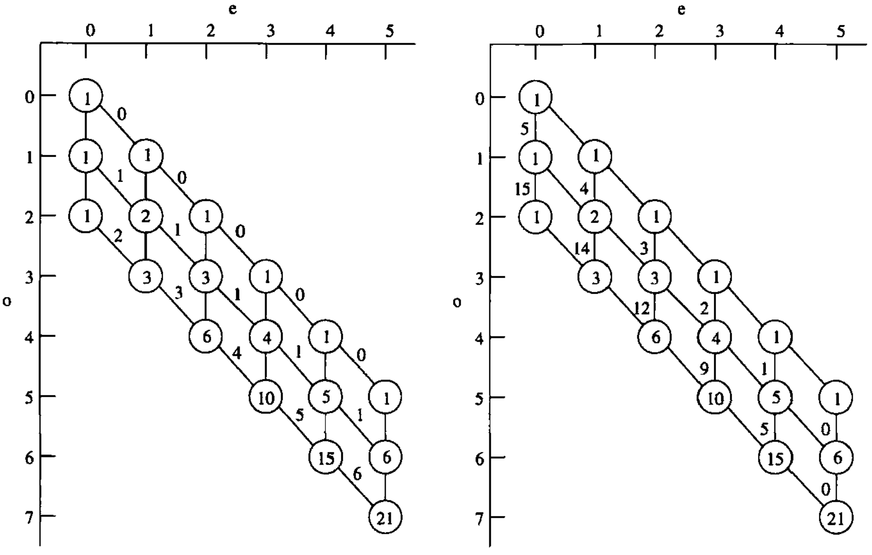
The arc weights given in Figures 17 and 18 cause the rightmost path to have an index $I(R_m)=0$. If we change the arc weights so that the leftmost path has index $I(L_m)=0$, we obtain four more addressing schemes. The two simplest schemes for $I(L_m)=0$ are

$$\begin{aligned} Y_0(e,o) &= 0 \quad Y_1(e,o) = x(e,o+1) && (152) \\ \bar{Y}_1(e,o) &= 0 \quad \bar{Y}_0(e,o) = \bar{x}(e-1,o) && (153) \end{aligned}$$

where the overbars indicate that reversed-lexical vertex weights have been used. Alpha strings for 5 electrons in 7 orbitals employing these addressing schemes are depicted in Figure 19.

If we add another coordinate Γ to each vertex, we can extend these simple digraphs to include point group symmetry. However, this procedure is not

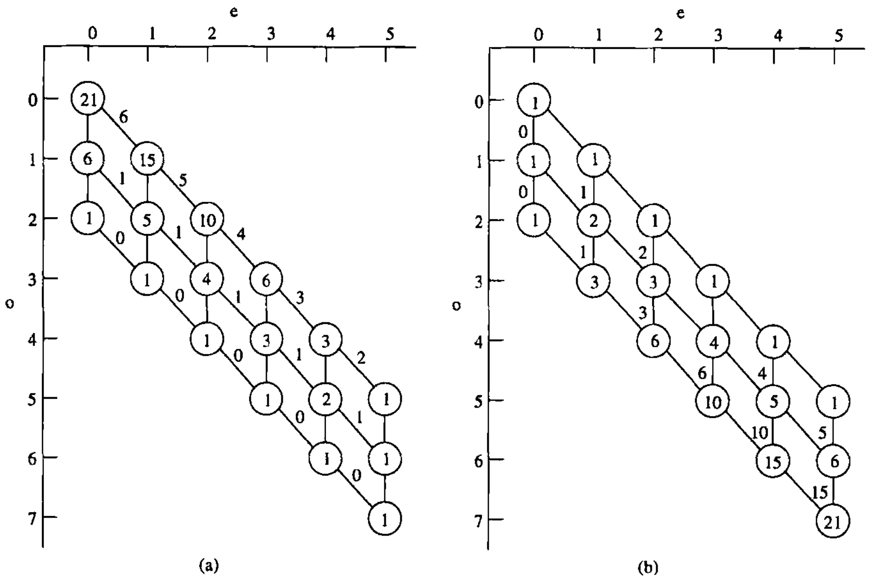
Figure 18: Alpha string graph for $n_\alpha = 5, n = 7$. Vertex weights are determined according to reverse-lexical ordering, and arc weights are given so that the rightmost path has index zero. (a) All unoccupied arc weights $Y_0(e,o)$ are zero. (b) Occupied arc weights $Y_1(e,o)$ are set to zero.



(a)

(b)

Figure 19: Alpha string graph for $n_\alpha = 5, n = 7$, with arc weights determined so that the leftmost path has index zero. (a) Vertex weights for lexical ordering, and arc weights according to $Y_0(e,o) = 0$, $Y_1(e,o) = x(e, o+1)$. (b) Vertex weights according to reverse-lexical ordering, and arc weights according to $\bar{Y}_1(e,o) = 0$, $\bar{Y}_0(e,o) = \bar{x}(e-1,o)$.



really necessary as long as strings with different irreps are placed on different graphs. These two-slope digraphs are actually simpler versions of the four-slope digraphs first used by Shavitt to compute the addresses of configuration state functions (CSFs) in the graphical unitary group approach.[41] The indexing scheme used by DETCI is the reverse-lexical ordering with all unoccupied arc weights set to zero, as depicted in Figure 18a. Olsen *et al.*[46] use the lexical ordering of Figure 17a.

In order to make the CI coefficient matrix block diagonal according to irreducible representation, it is necessary to number the strings consecutively within each irrep. This is accomplished by grouping strings with the same irrep into the same graph. For RAS CI spaces, it is also useful to number the strings such that only certain subblocks of each symmetry block are nonzero. This is accomplished by forming a different string graph for each different distribution of electrons among the RAS subspaces; for example, all strings with irrep a_1 having four electrons in RAS I and two electrons in RAS III are grouped together, whereas strings with irrep a_1 but five electrons in RAS I and one electron in RAS III are grouped together in a separate graph. In this way, the allowed combinations of strings become allowed combinations of graphs, and each allowed pair of alpha and beta graphs becomes a RAS subblock.

4.9.2 Nongraphical Methods for String Addressing

In their full CI program, Bendazzoli and Evangelisti[48,49] dispense with the graphs entirely and compute string addresses directly from their bit patterns, with one bit for each orbital; set bits (ones) represent occupied orbitals. Strings of N_α ones and $n-N_\alpha$ zeroes are a common representation of the combinations of n objects taken N_α at a time, and there exist standard numerical methods of computing lexical addresses for such bit patterns.[231]

Knowles and Handy present an explicit formula for computing a string's address from a list of its occupied orbitals.[109] They employ an auxiliary array defined according to

$$
\begin{aligned}
Z(k,l) &= \sum_{m=n-l}^{n-k-1} \left[\binom{m}{N-k-1} - \binom{m-1}{N-k-2} \right] \\
&\qquad n-N+k \geq l \geq k; k < N-1 \\
Z(k,l) &= l+1-N \quad n \geq l \geq N; k = N-1
\end{aligned}
\tag{154}
$$

where k labels electrons, l labels orbitals, n is the number of orbitals, and N is the number of electrons (we have modified the equation so that electron and orbital numbering starts from zero). The address of a string is then computed according to:

$$I_\alpha = \sum_{i=0}^{N_\alpha - 1} Z(i, \phi_i). \tag{155}$$

Unfortunately, generalizing this formula to assign consecutive indices to strings with the same irrep becomes complicated. Bendazzoli *et al.* note that, since their strings are generated in the desired order, they can write the string's address to intermediate arrays and thus obviate the need to compute string addresses on-the-fly. Such considerations are also true of Olsen's program and of ours. However, storing all strings with their single replacement information can require a very large amount of memory, as discussed in section 4.9.4. In this case, it becomes useful to compute string addresses on-the-fly as rapidly as possible.

If only occupied orbitals are assigned arc weights in the graphical procedure, it is possible to obtain an equation similar to (155), but using the graphical numbering scheme instead of the Knowles-Handy numbering. This is easily seen by comparing equation (155) to equation (144) when only occupied arcs have nonzero weights:

$$I_\alpha(L^\alpha) = X(L^\alpha) + \sum_{i=0}^{N_\alpha - 1} Y(i, \phi_i). \tag{156}$$

This method of evaluation can be very efficient if the matrix Y (with dimension $N_\alpha \times n$) is stored for each of the string graphs. The memory requirement for this approach will generally be manageable, and far preferable to storing the string replacement lists or Bendazzoli and Evangelisti's OV and $OOVV$ lists.[48,49] In the worst case, each excited string would then require N_α matrix lookups and $(N_\alpha - 1)$ additions to determine its address. However, note that a single excitation changes the occupancy of perhaps one and at most two RAS subspaces. It can be seen from eq. (156) that the contribution of unchanged RAS spaces to the string address are *constant* and need only be computed once. Graphically, this means that certain RAS spaces are traversed by the same segment of a walk. Finally, unless fast access to the arc weights is required, it is preferable to keep the arc weights and other graph information in a compact form which stores only allowed vertices.

4.9.3 Example of CI Vector and String Addressing

This section applies the CI vector and string addressing methods just discussed to the specific case of a CISD for H_2O in a minimal basis. Assume that the calculation is performed in C_{2v} symmetry, and that the core orbital has been frozen. The orbitals are then ordered according to Figure 20. Note that the

Figure 20: Orbital ordering for minimum basis CISD H_2O in C_{2v} symmetry.

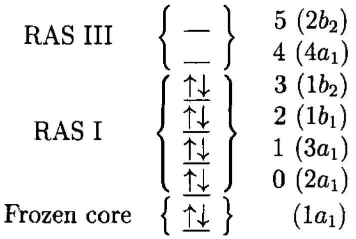


Table 6: Allowed strings for minimum basis CISD H_2O in C_{2v} symmetry.

Graph	Γ	N_{III}	Strings
0	a$_1$	1	(0 1 3 5)
1	a$_1$	2	(0 3 4 5), (1 3 4 5)
2	a$_2$	0	(0 1 2 3)
3	a$_2$	1	(0 2 3 4), (1 2 3 4), (0 1 2 5)
4	a$_2$	2	(0 2 4 5), (1 2 4 5)
5	b$_1$	1	(0 1 2 4), (0 2 3 5), (1 2 3 5)
6	b$_1$	2	(2 3 4 5)
7	b$_2$	1	(0 1 3 4)
8	b$_2$	2	(0 1 4 5)

frozen core orbital is not assigned a number by DETCI because the frozen core electrons are treated implicitly (cf. section 2.4.7).

The distribution of electrons among RAS subspaces can be determined simply from the number of electrons in RAS III, since there are only two RAS subspaces in this particular example. For a given string, there can be 0, 1, or 2 electrons in RAS III, and since there are four irreps in C_{2v}, there can be up to twelve string graphs. For this closed-shell case, the same set of graphs can be used to represent both alpha and beta strings. Table 6 lists all 15 allowed strings. Note that some strings transform as a_2 even though there are no a_2 orbitals; as a general rule for larger cases, strings are almost evenly distributed among irreps. The strings in Table 6 are listed in increasing index order. For the few graphs containing more than one string, it is straightforward to verify using the techniques of section 4.9.1 that the relative addresses within the graph are in the order shown if reverse-lexical ordering is used.

Table 7: Single replacement list for the first string in minimum basis CISD H_2O. J^g is the graph of the target string and J is the target string's relative index.

i	j	J^g	J	Sgn
0	0	0	0	+
1	1	0	0	+
3	3	0	0	+
5	5	0	0	+
4	0	1	1	+
4	1	1	0	−
2	5	2	0	−
2	3	3	2	+
2	0	5	2	−
2	1	5	1	+
4	5	7	0	+
4	3	8	0	+

As discussed later in section 4.9.4, it is necessary to compute lists of all singly excitations from each string. These excitations can be written in the form $|\alpha(J_\alpha)\rangle = \mathrm{sgn}(ij)\hat{E}^{\alpha}_{ij}|\alpha(I_\alpha)\rangle$, and for each string I_α, the lists need to contain the address of J_α, the sign, and the pair of orbitals ij. The string replacement lists for string 0 are given in Table 7.

Finally, it is helpful to show how this string ordering determines the addressing of the CI vector. There are two restrictions on the pairing of alpha strings with beta strings: first, the direct product of the two string irreps must be the irrep of the electronic state of interest (a_1); second, the total number of electrons in RAS III must be two or less. Due to the arrangement of the graphs, these restrictions can be satisfied for pairs of graphs rather than for pairs of strings. Each allowed pair of graphs becomes a RAS subblock. Table 8 lists the allowed RAS subblocks. An interesting feature of this unusually small CI space is that not all allowed strings contribute to allowed determinants: there are no beta strings which can be combined with alpha strings from graphs 1, 6, or 8 which give allowed determinants.

4.9.4 String Replacement Lists

One of the first steps in implementing Olsen's algorithm is the construction of string lists which hold the information needed to generate all single replace-

Table 8: Allowed RAS subblocks for minimum basis CISD H_2O.

Block	α Graph	β Graph	Dets
0	0	0	1
1	2	2	1
2	2	3	3
3	2	4	2
4	3	2	3
5	3	3	9
6	4	2	2
7	5	5	9
8	7	7	1

ments for each string; for example, $|\beta(J_\beta)\rangle = \mathrm{sgn}(ij)\hat{E}^{\beta}_{ij}|\beta(I_\beta)\rangle$ in Figure 9. For each excited string, one needs i, j, (or a composite index ij), the string address J_β, and $\mathrm{sgn}(ij)$, which tells whether $\hat{E}^{\beta}_{ij}$ sends $\beta(I_\beta)$ into plus or minus $\beta(J_\beta)$. The sign is most easily derived using the rules of second quantization, recalling that the phase convention is defined by always listing alpha/beta strings according to increasing orbital number (cf. section 4.2). Note that the equations require the inclusion of operators $\hat{E}_{ii}$, which might not normally be considered "single substitutions."

In the innermost loop of Olsen's σ_3 algorithm, $V(I) = \sum_{J_\beta} F(J_\beta)c'(I, J_\beta)$, the summation should be restricted to only allowed pairs of strings (I, J_β). If loops over graphs are introduced, then one loops over J_α belonging to a given alpha string graph (J^g_α) and J_β belonging to a given beta string graph (J^g_β), where (J^g_α, J^g_β) is an allowed combination of graphs. Now the problem of summing over all substituted strings becomes one of summing over all substituted strings belonging to a given graph. Thus DETCI divides the list of single replacements into multiple lists, one for each target graph. A counter array is used to store how many singly substituted strings there are for each graph. For a large number of graphs (there can be several hundred), this method of storage can be very memory intensive, since the number of pointers for each string is proportional to the number of graphs; however, this method also provides very fast access to the relevant replacement information in the innermost loops.

It is important to point out that the string lists can become very large if there are more than a few thousand strings. For a full CI, the number of strings is approximately equal to the square root of the number of determinants, so quite large full CI spaces can be described using only a small number of strings.

Table 9: Number of strings and determinants for selected CI problems.

CI problem	Fzc	Strings	Dets	Str/Det
cc-pVDZ+ Ne full CI[a]	0	8 568	9 185 280	9.3×10^{-4}
DZ H_2O full CI	0	2 002	1 002 708	2.0×10^{-3}
DZ H_2O full CI	1	715	128 829	5.5×10^{-3}
DZP H_2O CISDTQ	1	10 626	558 823	1.9×10^{-2}
DZP H_2O CISD[TQ][b]	1	4 326	78 895	5.5×10^{-2}
DZP H_2O CISDT	1	5 781	50 187	1.2×10^{-1}
DZP H_2O CISD	1	1 221	2 349	5.2×10^{-1}

[a] Using the basis set of Koch *et al.*[7]

[b] The RAS II space consists of the $2b_2$,$4a_1$,$2b_1$, and $5a_1$ orbitals.

However, it is perhaps not well appreciated that for RAS CI spaces, the number of strings can grow much faster with the number of determinants: this is illustrated in Table 9. Such considerations indicate that any method of storing the string replacement lists whose memory requirements are proportional to the number of strings (with a large coefficient, no less) is unmanageable for large-scale RAS CI procedures.

If the number of determinants remains much larger than the number of strings for a given case, one might consider storing the string lists to disk and loading them as needed. Indeed, such an approach would probably work in conjunction with the σ_3 algorithm. However, this strategy is not amenable to the σ_1 algorithm as implemented by Olsen *et al.*,[46] because one must consider single replacements from *all* graphs which can be reached from the graph containing the strings I_β. It seems preferable to form the string replacement information on-the-fly. A prototype method for doing this exists in DETCI, but it is inefficient: walking down graphs to add up arc weights is rather slow with our current storage scheme for the graphs. However, if the arc weights are stored in a slightly different format, it is possible to compute string addresses much more quickly; indeed, it is possible to compute addresses a RAS space at a time, meaning that arc weight contributions from RAS spaces with fixed orbital occupancies are constant. This strategy was discussed in section 4.9.2 and is currently being implemented in DETCI. Another option is to use an entirely different implementation for restricted CI where storage of string replacement information becomes a problem. Malmqvist *et al.*[56] have implemented RAS CI using a split-graph unitary group approach, and this algorithm may be more efficient for CI spaces which are not close to the full CI.

4.9.5 Algorithms for σ_2 and σ_3 Used by DETCI

Assuming that the string replacement lists are available in-core, the algorithms used by our program for computing σ_2 and σ_3 (simplified somewhat for clarity) are presented in Figures 21 and 22 for the case in which σ is computed a RAS subblock at a time, where the loops over combinations of strings allowed by symmetry and CI space restrictions are placed outside the σ_2 and σ_3 subroutines. The symbol γ in Fig. 22 represents an irreducible representation of the molecular point group. These are the same algorithms used by our program for full CI; if enough memory is available to hold a symmetry block of $\mathbf{c}$ and σ in core, then the RAS subblocks are the same as the symmetry blocks for a full CI. Otherwise, one can use a larger number of string graphs and smaller subblocks. For $M_s = 0$ cases, it is possible to compute only the lower (or upper) triangle of σ, according to (119). Thus only one of each pair of off-diagonal subblocks is determined explicitly. For diagonal blocks, (119) is used to impose the restriction $(ij) \geq (kl)$ in the evaluation of σ_3 (cf. section 4.4.2). In FORTRAN, presumably it is best to eliminate redundant subblocks from the upper triangle, since blocks with only a few rows will typically be found in the upper triangle (assuming that larger indices are assigned to strings with more electrons in RAS III): these blocks do not vectorize well due to short vector lengths. In C, exactly the opposite holds: it is presumably most efficient to eliminate the lower triangle subblocks. However, it is also true that longer vector lengths require more time to set up the lists L, R, and Sgn.

The signs are actually taken care of by very fast bitwise logic operations. σ_2 is computed instead of σ_1 because the preferred direction of vectorization is reversed in c as compared to FORTRAN. In the present context, this means that the step $[\sigma_2(I_\alpha, I_\beta) = \sigma_2(I_\alpha, I_\beta) + F(J_\alpha) * c(J_\alpha, I_\beta)]$ is performed with unit-stride access to σ_2 and c. Note that this is in fact a DAXPY operation, which could be performed by calling the **daxpy** function from the BLAS library. For the IBM RS/6000 POWER2 implementation, calling the BLAS library from the σ_2 or σ_3 routines resulted in no real savings. In fact, this slowed down the σ_3 subroutine, presumably due to the overhead of placing the function call within nested loops.

Note that the σ_2 routine is actually quite close to Olsen's σ_1 routine (swapping alphas for betas, of course), except that the adaptation to point group symmetry and RAS restrictions is now explicit. The σ_3 routine is also similar to Olsen's (with alphas swapped for betas), although the intermediate vector F has been eliminated (see below). Note that this particular version of the σ_3 routine takes advantage of the $(ij) \geq (kl)$ simplification possible for $M_s = 0$ cases; this restriction cannot be used for off-diagonal RAS subblocks if only unique subblocks of σ are computed.

Figure 21: DETCI algorithm for σ_2.

```
Enter subroutine for block $(I_\alpha^g, I_\beta^g)$ of $\sigma_2$ and block $(J_\alpha^g, I_\beta^g)$ of $c$
 loop $I_\alpha = 1$, number of strings in $I_\alpha$ graph $I_\alpha^g$
    zero $F(J_\beta)$
    loop over alpha string graphs $K_\alpha^g$
       $Kcnt = cnt(I_\alpha, K_\alpha^g)$
       $Kidx = idx(I_\alpha, K_\alpha^g)$
       $Kij = ij(I_\alpha, K_\alpha^g)$
       loop $K = 1, Kcnt$
          $kl = Kij(K)$
          $K_\alpha = Kidx(K)$
          $S_1$ = sign associated with $K_\alpha$
          if $(K_\alpha^g = J_\alpha^g)$
             $F(K_\alpha) = F(K_\alpha) + S_1 * h(kl)$
          $Jcnt = cnt(K_\alpha, J_\alpha^g)$
          $Jidx = idx(K_\alpha, J_\alpha^g)$
          $Jij = ij(K_\alpha, J_\alpha^g)$
          loop $J = 1, Jcnt$
             $J_\alpha = Jidx(J)$
             $S_2$ = (sign associated with $J_\alpha$) $* S_1$
             $ij = Jij(J)$
             $F(J_\alpha) = F(J_\alpha) + 0.5 * (ij|kl) * S_2$
          end loop over $J$
       end loop over $K$
    end loop over $K_\alpha^g$
    loop $J_\alpha = 1$, number of alpha strings in $J_\alpha^g$
       if $(F(J_\alpha) = 0)$ skip to next $J_\alpha$
       loop $I_\beta = 1$, number of beta strings in $I_\beta$ graph $I_\beta^g$
          $\sigma_2(I_\alpha, I_\beta) = \sigma_2(I_\alpha, I_\beta) + F(J_\alpha) * c(J_\alpha, I_\beta)$
       end loop over $I_\beta$
    end loop over $J_\alpha$
 end loop over $I_\alpha$
```

Figure 22: DETCI algorithm for σ_3.

```
Enter subroutine for block $(I^g_\alpha, I^g_\beta)$ of $\sigma_3$ and block $(J^g_\alpha, J^g_\beta)$ of $c$
 loop over $ij$
    if $(\gamma(i) \otimes \gamma(j) \otimes \gamma(J^g_\beta) \otimes \gamma(I^g_\beta) \neq 0)$ skip to next $ij$
    $jlen$ = form_list($I^g_\beta$, $J^g_\beta$, $ij$, $L$, $R$, $Sgn$)
    if $(jlen = 0)$ skip to next $ij$
    loop $I_\alpha = 1$, number of alpha strings in $I^g_\alpha$
       loop $J = 1, jlen$
          $c'(I_\alpha, J) = c(I_\alpha, L(J)) * Sgn(J)$
       end loop over $J$
    end loop over $I_\alpha$

    loop $I_\alpha = 1$, number of strings in graph $I^g_\alpha$
       $Jacnt = cnt(I_\alpha, J^g_\alpha)$
       $Jaidx = idx(I_\alpha, J^g_\alpha)$
       $Jaij = ij(I_\alpha, J^g_\alpha)$
       zero $V$
       loop $Ja = 1, Jacnt$ AND $((kl = Jaij(Ja)) <= ij)$
          $J_\alpha = Jaidx(Ja)$
          $S_1$ =sign associated with $J_\alpha$
          $VS = 0.5 * \delta_{ij,kl} * (ij|kl) * S_1$
          loop $Jb = 1, jlen$
             $V(Jb) = V(Jb) + VS * c'(J_\alpha, Jb)$
          end loop over $Jb$
       end loop over $Ja$

       loop $Jb = 1, jlen$
          $\sigma_3(I_\alpha, R(Jb)) = \sigma_3(I_\alpha, R(Jb)) + V(Jb)$
       end loop over $Jb$
    end loop over $I_\alpha$
 end loop over $ij$
```

The figures clearly indicate that an efficient algorithm should take advantage of the sparsity of F in both the σ_2 and σ_3 routines. Although it is possible to ignore this sparsity in order to obtain more highly vectorized algorithms, this results in a slower code due to the large number of multiplications by zero. Attempts to formulate the σ_3 algorithm as a standard matrix multiplication resulted in a program which was slower by a factor of at least four (and usually more) on the IBM RS/6000 model 3CT. The reader may wonder whether further reductions in the overall operation count might increase efficiency: after all, formulating the innermost loop as a DAXPY requires a certain amount of overhead work (namely, the gather and scatter operations). Indeed, a very simple algorithm which performs the minimum number of operations has already been presented in Fig. 8. However, there are a number of reasons to think that this algorithm should be less efficient than that in Figure 22 for workstation computers. One reason is that indirect addressing in the innermost loop causes cache misses and thus longer waits for elements of c. Another is that the simple algorithm takes no advantage of the pipelining features of current workstations, discussed in section 4.3. For DZ H_2O full CI (1 million determinants), using the algorithm in Fig. 22 instead of the simple algorithm in Fig. 8 results in a speedup by a factor of five on the IBM 3CT. However, it is also important to point out that the smaller block sizes in a RAS CI (as opposed to a full CI) mean that the payoff for vectorization is less.

A few remaining comments should be made about our σ_3 algorithm in Fig. 22. First, note that the intermediate vector F has been eliminated. Storage to and retrieval from this array requires several extra operations, yet the efficiency of the DAXPY operation is not enhanced by the use of F, since F is sparse (the only work saved is for excitations which map a string into itself). Second, writing the innermost loop of this routine (and also of the σ_1 routine) as a DAXPY is particularly efficient on the RS/6000 architecture, which performs each pair of floating point multiplications and additions in the *same* machine instruction, the floating point multiply-add (FMA).

In order to gauge the efficiency of our new determinant-based CI program, several timing comparisons have been made between DETCI and the standard Schaefer group CI program GUGACI. Table 10 presents averaged CPU and total times for several full CI test cases. Both programs used the standard Davidson method, keeping on disk the c and σ vectors for every iteration; this lead to noticeable I/O delays for some of the larger test cases. Our new program is also capable of using iteration methods which require fewer vectors on disk (cf. section 3.2). Although we do not have access to Olsen's code, he has reported that his program takes about 40s per iteration for the 1 million determinant DZ H_2O full CI calculation,[232] whereas DETCI requires 30s per iteration on the same model workstation (IBM RS/6000 model 590).

Table 10: CPU and total times per iteration to evaluate several benchmark full CI wavefunctions using the IBM RS/6000 model 3CT. Fzc/Fzv denote the number of frozen core/frozen virtual orbitals.

				Time/Iter (seconds)			
				GUGACI		DETCI	
Molecule	Fzc/Fzv	CSFs	Dets	CPU	Tot	CPU	Tot
DZ H_2O	1/0	37 353	128 829	77	79	3	3
DZ H_2O	0/0	256 473	1 002 708	1430	1465	28	33
cc-pVDZ+ Ne[a]	0/0	2 083 968	9 185 280	13788	14007	282	532
DZP C_2	2/2	6 571 116	27 944 940	32489	34831	1329	3160

[a] Using the basis set of Koch *et al.*[7]

5 Applications of Highly Correlated CI

Most studies limit the CI space to single and double substitutions from a single reference (CISD). Occasionally, when one reference does not provide a sufficient zeroth-order wavefunction, the multi-reference CISD method will be employed. The applications of such methods are too numerous to discuss here; their general performance has already been described in section 2. We consider studies which go beyond CISD for one or a few references; such highly correlated wavefunctions are useful when very accurate results are desired or when several electron configurations are needed for a qualitatively correct reference wavefunction (such as when multiple bonds are broken). We will limit our attention to methods which select the CI space in an *a priori* fashion based on the distribution of electrons among various orbital subspaces.

5.1 Full CI

The most highly correlated configuration interaction method is of course full CI, which solves the Schrödinger equation exactly within the space spanned by the single-particle basis set (section 2.1). Unfortunately, as explained in section 2.4.1, the full CI space grows factorially with the number of electrons or single-particle basis functions; currently, full CI is limited to very small molecules (one or two heavy atoms with a few hydrogen atoms) described by a basis set of double-ζ or perhaps triple-ζ quality. Furthermore, errors due to the incompleteness of the single-particle basis set are generally more severe than those introduced by the neglect of triple, quadruple, etc., substitutions in the treatment of electron correlation. Hence full CI is useful primarily as a benchmark method for evaluating approximate treatments of correlation. Given their extreme computational requirements, it is perhaps surprising how many full CI benchmarks have been reported. Here we will focus primarily on the more noteworthy or more recent benchmarks, and on systems containing more than four electrons.

The early (1980) full CI algorithm of Handy[44] enabled Saxe, Schaefer, and Handy to obtain the exact variational solution for the ground state of H_2O within a modest double-ζ (DZ) basis set; this represented the first CI wavefunction to include more than one million determinants.[213] In 1983, Harrison and Handy used this same algorithm, along with the loop-driven graphical unitary group approach CI (LD-GUGACI) program of Brooks and Schaefer,[43] to report full CI results for H_2O and NH_3 with a DZ basis and for BH and HF in a double-ζ plus polarization (DZP) basis.[38] These two studies, which also gave results for the CISD, CISDT, and CISDTQ methods, clearly demonstrated that triply and quadruply substituted configurations account for nearly all of the error in the CISD correlation energy (cf. Table 2). Moreover, by comparing to Harrison and Handy's results for H_2O, Bartlett, Sekino, and Purvis demonstrated that fourth-order many-body perturbation theory [MBPT(4)] performs poorly when both O–H bonds are stretched,[19] even though it partially accounts for quadruple excitations. This occurs because the restricted Hartree-Fock determinant provides an inadequate zeroth-order wavefunction as the bonds are stretched too far from their equilibrium lengths, and it emphasizes the need for multireference approaches.

The subsequent (1984) vectorized full CI algorithm[109] of Knowles and Handy allowed Bauschlicher, Taylor, Langhoff, and others to carry out a series of important benchmark calculations. In 1986, these authors, along with Partridge, presented full CI results for the Ne atom using a triple-ζ plus double polarization (TZ2P) basis set.[233] Once again, the CISDTQ wavefunction yielded more than 99% of the basis set correlation energy; furthermore, the contribution of quintuple and higher substitutions decreased with increasing basis set size. Subsequent benchmark results using a DZP basis were presented for HF and NH_2;[234] H_2O, F, and F^-;[235] the $^1A_1$–$^3B_1$ separation in CH_2;[236] the barrier height to the reaction $F + H_2 \rightarrow HF + H$;[237] the $^1A_1$, $^1B_1$, and $^3B_1$ states of SiH_2;[238] the 2 $^1A_1$ states of CH_2 and SiH_2 and the $^2A_1$ and $^2B_2$ states of CH_2^+;[239] the low-lying states of C_2;[240] N_2, NO, and O_2;[241] the CH_3 radical;[242] and Be_3.[243] Bauschlicher and co-workers have also investigated transition metals. They estimated the ^5D–^5F energy separation for the Fe atom using a 5s4p2d1f basis set,[244] excitation energies and oscillator strengths for the ^{2}D Rydberg series in the Al atom with a 7s6p4d3f ANO basis,[245] the ^3F–^5F separation for the Ti atom, and the $^4\Phi$–$^2\Delta$ separation for TiH in a 5s4p3d1f/2s basis set.[246] Illas, Rubio, Ricart, and Bagus used the

Knowles-Handy program to obtain full CI energies for the first row atoms and their hydrides in 4s3p1d/2s1p basis sets; these benchmarks were used to evaluate the CIPSI method[219] and the performance of ANO basis sets versus more traditional segmented basis sets.[247] Casanovas, Rubio, and Illas have also performed full CI studies on the interaction of H atom with Cu_5 and Ag_5 cluster models to investigate the transferability of the correlation contribution to the chemisorption bond for different pseudopotentials.[248]

Several of these studies considered molecules at three geometries, with equivalent bonds simultaneously stretched to 1.0, 1.5, and 2.0 times their equilibrium lengths; hence, approximate methods could be judged not only by what fraction of the correlation energy they recovered, but also by how well they paralleled the full CI potential energy surface. The MR-CISD method was found to parallel full CI very well, particularly when CASSCF orbitals are used and all configurations present in the CASSCF are used as references. More recently, these authors have used large basis set full CI benchmarks to examine core-core and core-valence correlation effects[249] and to calibrate more approximate MR-CISD approaches for the dissociation energy of BH.[250] Many of these results are summarized in a 1990 review article by Bauschlicher, Langhoff, and Taylor.[15]

Most of the full CI studies just discussed involved CI spaces spanning tens of millions of determinants. More recent full CI algorithms, which follow Olsen *et al.* in sacrificing some degree of vectorization for reduced operation counts,[46,48,49] have allowed for CI spaces including hundreds of millions of determinants. Indeed, Olsen, Jørgensen, and Simons reported a full CI calculation on the Mg atom using a 5s3p2d1f ANO basis and requiring more than one billion determinants; unfortunately, it was not possible to fully converge the wavefunction due to the extreme amount of CPU time required.[83] The first *converged* full CI benchmark requiring more than one billion determinants was reported recently by Evangelisti, Bendazzoli, Ansaloni, Durí, and Rossi, who presented an out-of-core adaptation of their full CI program for distributed-memory parallel computers and used it to obtain the full CI energy of Be_2, with all electrons correlated, in a 4s2p1d ANO basis set partially uncontracted to 9s2p1d.[84]

In 1995, these workers used an in-core version of this algorithm to resolve an uncertainty concerning the full CI energy of NH_3 with an ANO DZP basis set.[50] Knowles and Handy had in 1989 presented an energy of -56.4236 ± 0.0001 hartree using their approximate full CI method which truncates the σ vector; 665,247 of 209,626,425 determinants were treated variationally, and the convergence limit was estimated perturbatively.[218] This value underestimates the importance of the large number of neglected determinants, as was first demonstrated by Povill, Rubio, Caballol, and Malrieu.[123] The true full CI energy was shown to be -56.424007 hartree.[50,80] The program of Bendazzoli and Evangelisti[48] has also been applied to DZ H_8 and N_2[49] and to $C_{18}H_{18}$ using a simple Pariser-Parr-Pople (PPP) Hamiltonian.[48]

In 1996, Olsen, Jørgensen, Koch, Balková, and Bartlett presented DZP full CI results for H_2O at three geometries, where all ten electrons were correlated. Although the basis set was not designed to describe core correlation, these results are valuable in that they are fully invariant to orbital rotations, whereas they would not have been if the 1s-like orbital on oxygen were frozen.[22] As shown by Handy and co-workers,[20] it is fairly straightforward (and valuable) to generalize a full CI program to produce many-body perturbation theory (MBPT) energies order by order. Hence, Olsen *et al.* considered MBPT through 15th order and examined the convergence of the series as the two OH bonds are simultaneously stretched, causing the zeroth-order wavefunction to become progressively worse. In another 1996 study, Olsen, Christiansen, Koch, and Jørgensen examined the convergence of MBPT for several small molecules using DZP and larger basis sets. These authors concluded that perturbation theory corrections grow with increasing basis size and that, remarkably, the inclusion of diffuse functions can cause the perturbation series to diverge even for well-behaved molecules such as HF.[23,251] Olsen's algorithm has also been used to provide benchmark full CI excitation energies for CH^+;[252] BH, CH_2, and Ne atom;[7] H_2O, N_2, and C_2;[37] and H_2O^+.[22]

Most full CI studies have focused solely on energies. A few papers, however, have presented full CI results for other molecular properties. In 1987 Bauschlicher and Taylor presented full CI dipole moments and polarizabilities for HF, CH_2, SiH_2, and F^- with a DZP basis.[253] Moreover, Bauschlicher and Langhoff gave full CI equilibrium geometries, dissociation energies, and harmonic vibrational frequencies for CH, NH, and OH using flexible ANO basis sets.[254] The following year, these authors presented full CI and SOCI transition moments for two transitions in CH_2 and selected dipole and quadrupole transitions in BeO,[255] and Bauschlicher presented geometries, frequencies, and the dipole moment for the $^4\Phi$ and $^2\Delta$ states of TiH.[246] Later, Bauschlicher and Taylor also presented full CI transition moments for H_2 and BH in a comparison of the length and velocity representations for the transition moment.[256] Full CI transition moments and polarizabilities for CH^+ have been presented by Olsen and co-workers.[252] Koch and Bauschlicher have presented a method for computing analytically the frequency dependent linear and quadratic response functions for full CI wavefunctions; they have considered Be atom in a 9s9p5d basis set and have reported transition energies and dipole moments for several states, the first polarizability at real and imaginary frequencies, and the static second hyperpolarizability.[257] Bauschlicher *et al.* have determined the full CI isotropic hyperfine coupling constant for the nitrogen atom using basis sets as large as 8s4p2d.[258] Spin-orbit coupling has been investigated at the full CI level for CH_2 by Vahtras *et al.*[259] and for LiBe by Marino *et al.*[260]

Researchers have even obtained exact full CI equilibrium geometries for a few polyatomic systems with a DZP basis: the linear transition state for the reaction $F + H_2 \rightarrow HF + H$;[237] the systems H_6, H_7^+ and $H_5^+\cdot$ He;[17,261] the $\tilde{X}\ {}^2B_1$ and $\tilde{A}\ {}^2A_1$ states of NH_2;[262] BH_3;[39,262] H_5^+;[263] and the four lowest-lying states of methylene[262,264] and NH_2^+.[265] For the latter four molecules, full CI dipole moments and harmonic vibrational frequencies have been reported at the full CI equilibrium geometries.[39,263–265] The DZP full CI studies of methylene clearly demonstrate the need to use larger basis sets: predictions for the singlet-triplet energy gap[236,262,264] are at least 2.5 kcal mol^{-1} too large compared to experiment.[264] We have recently completed a considerably more challenging full CI benchmark study of the four lowest states of methylene using the more reliable TZ2P basis set.[266]

In the past few years, full CI benchmarks have been used to calibrate methods for systems featuring weak interactions. Woon has obtained the full CI well-depth, equilibrium separation, and harmonic vibrational frequency for He_2 with basis sets as large as augmented correlation-consistent polarized quadruple-ζ (aug-cc-pVQZ).[267] In a subsequent study, van Mourik and van Lenthe used the full CI program of Harrison and Zarrabian[47] to obtain dimer energies at two separate geometries using large basis sets including h-type polarization functions and bond functions.[36] One interesting conclusion of this study, which could only be determined using highly correlated wavefunctions, was that the usually-reliable CCSD method is unsuitable for obtaining accurate potential energy curves for He_2. Other recent full CI studies have also focused on helium dimer,[268–271] as well as the dimer of two H_2 molecules[268–270] and the He–H_2 system.[268,269] Such benchmarks have been helpful in examining the problem of basis set superposition error.[270]

5.2 Second-Order CI

One important conclusion from the full CI benchmark studies of Bauschlicher, Taylor, Langhoff, and others in the 1980's is that the MR-CISD method based on CASSCF orbitals provides potential energy surfaces which accurately parallel the full CI surfaces.[14,15,234,238–240,242,254] For example, the CASSCF MR-CISD method predicts singlet-triplet energy separations in CH_2 and SiH_2 within 0.01 kcal mol^{-1} and 0.03 kcal mol^{-1}, respectively, of the full CI results.[236,238] The best results are obtained when no threshold is used for reference selection: that is, when all CSFs in the CASSCF wavefunction are used as references. This CAS-ref MR-CISD procedure is intimately related[107] to second-order configuration interaction (SOCI), which distributes electrons in all possible ways as long as no more than two electrons are allowed in external orbitals at once (of course, spatial symmetry and spin symmetry may also be imposed on the final N-electron basis functions). For closed-shell systems these procedures are identical, but they can differ for open-shell systems. In cases where all occupied orbitals which are correlated in the SOCI are included in the active space, one can guarantee that the SOCI space is generated by using as references all CSFs arising from CASSCF wavefunctions of all possible spatial symmetries.[107] SOCI wavefunctions are invariant to orbital rotations within the active space, whereas this is not necessarily the case for CAS-ref MR-CISD when the references are symmetry-restricted. In cases where there are "inactive" orbitals (occupied orbitals which are correlated in the SOCI but not included in the CASSCF), Bauschlicher has recommended that the SOCI be defined according to the RAS CI scheme, such that one places inactive orbitals in RAS I, active orbitals in RAS II, and external orbitals in RAS III;[15] this maintains the desired orbital invariance properties. This SOCI can alternatively be generated an MR-CISD in which the references are now all CSFs arising from all CASSCF wavefunctions of every spatial and spin symmetry.

The reliability of SOCI, coupled with its essentially *a priori* selection of the CI space, makes it an attractive alternative to full CI. Unfortunately, for reasonable active spaces the dimension of the SOCI grows very rapidly with system size and thus the method is applicable only to small molecules. Nevertheless, for quite a few molecules it is possible to use the SOCI method in conjunction with large one-particle basis sets and hence to obtain wavefunctions very close to the exact nonrelativistic Born-Oppenheimer limit. Below, we will attempt to give the reader a sense of the types of problems to which the SOCI method has been applied. Bauschlicher, Langhoff, and Taylor have already given[15] an excellent review of the related CASSCF MR-CISD method, and we refer the reader to their article for a discussion of additional important studies.

The SOCI method has been applied primarily to diatomics and triatomics. Two of the early applications of SOCI were studies of Be_2 by Blomberg, Siegbahn, and Roos[272] (1980) and by Lengsfield, McLean, Yoshimine, and Liu[89] (1983). With only four active electrons, a SOCI for this system is identical to the CISD[TQ] method discussed in the following section. The Be_2 molecule is challenging to theory because of the near degeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ configurations in the the Be atom and because the bonding in the dimer is dominated by dispersion forces. The latter study[89] used a 6s4p3d1f Slater basis set to yield a SOCI dissociation energy of $D_e = 1.87$ kcal mol^{-1} (2.04 ± 0.21 kcal mol^{-1}, including estimates of core correlation and basis set errors), in contradiction to previous coupled-cluster studies[273] giving $D_e \leq 0.2$ kcal mol^{-1}; the experimental value[274] is 2.26 ± 0.09 kcal mol^{-1}, signaling a success of the SOCI method and a failure of coupled-cluster models which neglect connected triple substitutions. A SOCI study of the related Mg_2 molecule using large ANO basis sets was reported[275] in 1990 by Partridge *et al.* Other SOCI studies on the ground states of diatomic molecules include an investigation of the potential energy curves of NeN^{2+} and NeN^+ by Koch, Liu, and Frenking,[276] and of N_2 and O_2 by Langhoff, Bauschlicher, and Taylor.[277] The latter study used a 5s4p3d2f1g basis and reported equilibrium bond lengths, harmonic vibrational frequencies, and dissociation energies of (1.101 Å, 2343 cm^{-1}, 9.723 eV) for N_2 and (1.209 Å, 1561 cm^{-1}, 5.139 eV) for O_2, in excellent agreement with experimental values of (1.0977 Å, 2358 cm^{-1}, 9.905 eV) and (1.2075 Å, 1580 cm^{-1}, 5.214 eV), respectively. The multi-reference Davidson correction for size extensivity (section 2.4.6) improves the SOCI dissociation energies but worsens the predicted bond lengths and vibrational frequencies. A subsequent study by Almlöf *et al.*[278] considered even larger basis sets (including *i* polarization functions), core-valence correlation, and basis set superposition effects in an investigation of remaining sources of error in the dissociation energy of N_2; their best theoretical estimate was within about 2 kcal mol^{-1}, or 1% of the experimental dissociation energy.

Several studies have used the SOCI method to describe excited electronic states of diatomic molecules. In 1988, Partridge *et al.*[279] reported SOCI potential energy curves for the $A'\ {}^5\Sigma_g^+$ and $C''\ {}^5\Pi_u$ states of N_2; these results had important implications for theories of the N_2 afterglow and for the first time allowed an assignment of the Hermann infrared system. Also in 1988, Bauschlicher *et al.*[280] reported SOCI spectroscopic constants (r_e, T_e, and ω_e) for several low-lying quartet states of AlC; this study indicated that the SOCI results based on CASSCF orbitals optimized separately for each state were nearly identical to SOCI using a common set of state-averaged CASSCF orbitals. Balasubramanian has used the SOCI method along with relativistic pseudopotentials to study diatomics incorporating elements below the second row of the periodic table. His work has included studies of the low-lying electronic states of InSb;[281] Ga_2, Ga_2^-, and Ga_2^+;[282] GeH and GeH^+;[283] WH;[284] GaH;[285] TlH and InH;[286] and GeCl.[287] Another study by Balasubramanian considers the low-lying states of the transition metal hydrides YH-CdH.[288]

The SOCI method has also been used for a number of triatomics, including the much-studied[264] methylene molecule (CH_2). An early application of the SOCI method to methylene was presented by Saxe, Schaefer, and Handy,[289] who used Handy's 1980 string-based determinant CI program[44] to obtain an estimate of $T_e = 10.5$ kcal mol^{-1} for the singlet-triplet energy gap using a 8s5p3d/4s1p basis set. More recently, Bauschlicher, Taylor, and Langhoff have used the SOCI method in conjunction with a 5s4p3d2f1g/4s3p2d ANO basis set to predict[290] optimized geometries for the $\tilde{X}\ {}^3B_1$ and $\tilde{a}\ {}^1A_1$ states of

CH_2 of (1.079 Å, 133.6°) and (1.110 Å, 102.0°), which compare to experimentally derived estimates of (1.0753 Å, 133.93°) and (1.116 Å, 101.8°), respectively. McLean *et al.*[291] used the SOCI method with a 4s3p2d1f/3s2p basis to obtain 37 energy points which were fit with a nonrigid bender Hamiltonian model to yield $\nu_1 = 2985 \pm 20$ cm^{-1} and $\nu_3 = 3205 \pm 20$ cm^{-1} for the fundamental stretching frequencies, compared to experimentally derived values of 2992 and 3213 cm^{-1}. For the singlet-triplet energy splitting (T_e), the 5s4p3d2f1g/4s3p2d ANO SOCI estimate of 9.13 kcal mol^{-1} by Bauschlicher *et al.*[290] and the TZ3P(2f,2d)+2diff SOCI estimate of 9.02 kcal mol^{-1} by Yamaguchi *et al.*[86] compare very favorably with the best nonrelativistic Born-Oppenheimer-corrected experimental estimate of 9.372 kcal mol^{-1}.[264,292–294] Yamaguchi *et al.* also report[86] SOCI excitation energies for the $\tilde{b}\ {}^1B_1$ and $\tilde{c}\ {}^1A_1$ states which will hopefully guide further experimental efforts.

Among the numerous other studies of polyatomic molecules using the SOCI method, Balasubramanian has reported energies and optimized geometries for low-lying states of SnH_2;[139,295] PbH_2;[139] GaH_2, GaH_2^+, GaH_3, and GaH_3^+;[285] YH_2^+ and ZrH_2^+;[296] AsH_2, AsH_2^+, SbH_2^+, and BiH_2^+;[297] GeH_2;[139,283] HfH_2;[298] TlH_2, TlH_2^+, InH_2, and InH_2^+;[286] and PH_2, PH_2^+, and PH_2^-.[299] Yarkony *et al.* have used SOCI wavefunctions as zeroth-order solutions in first-order perturbation theory treatments of the full Breit-Pauli spin-orbit Hamiltonian; in this fashion, these workers have studied the spin-forbidden decay of systems including $\tilde{X}\ {}^2\Pi$ HS^{2+},[300] $\tilde{a}\ {}^3\Sigma_1^+$ NO^+,[301] and $\tilde{a}\ {}^4\Sigma^-$ CH.[302] SOCI has also been used to assess the quality of the CCSD(T) method for electron affinities,[303] to obtain accurate barrier heights for the termolecular reaction of $3H_2$,[261] and to yield transition moments.[138,255]

Finally, we note that it may be advantageous to use natural orbitals (NOs) rather than the CASSCF orbitals usually employed in SOCI studies. Grev and Schaefer[16] have shown for a number of small molecules (NH_2, CH_3, SiH_2, N_2) that a SOCI procedure based on CISD natural orbitals yields energies which are very close to the CASSCF SOCI energies, even when several bonds are simultaneously stretched to twice their equilibrium length. Blomberg and Liu have also observed similar performance of MCSCF orbitals and SOCI natural orbitals for energies and transition moments of CH and CH^+,[138] although we note that CISD NOs are much less expensive to obtain than SOCI NOs. CISD NOs are also easier to obtain than CASSCF orbitals, and they are better suited to orbital truncation; that is, the energy lost by deleting a few of the most weakly occupied NOs will typically be smaller than that lost by deleting a few of the highest-lying CASSCF orbitals. This allows for an effective reduction in the number of determinants included in a SOCI wavefunction with minimal loss in accuracy. Moreover, the energy lost by deleting these weakly occupied NOs is primarily due to neglected singly and doubly substituted determinants which occupy these orbitals, and not to neglected triples, quadruples, etc.[16,17] This suggests a strategy of using a smaller NO basis to treat higher-than-double substitutions, and this idea has been implemented in the CISD[TQ] method described in section 5.4.

5.3 Restricted Active Space CI

As already discussed, many commonly encountered CI spaces can be formulated within the RAS CI scheme. However, at the moment our attention is focused on CI calculations using the RAS CI program of Olsen and co-workers.[46] Examples of full CI calculations using Olsen's program have already been discussed above, so here we limit our attention to truncated CI wavefunctions.

The RAS CI method can be very valuable when used in conjunction with the multiconfigurational linear response (MCLR) method, which allows calculation of excitation energies, transition moments, and second-order properties such as polarizability. In 1989, Olsen and co-workers compared MCLR and full CI results for CH^+ and found that for highly accurate results, it is necessary to provide more extensive treatments of electron correlation than the valence CAS. Furthermore, these authors found that the RAS method provides an accurate means of reducing the size of the CI space in these MCLR studies. Jensen *et al.* were able to show that the RAS MCLR calculations which include dynamical correlation give very reliable frequency-dependent polarizabilities for the nitrogen molecule.[304] Sanchez de Merás *et al.* found that the polarizabilities of H_2O and CO_2 obtained using the RAS MCLR method with polarized basis sets were within 5% of experiment.[305] More recently, Sundholm and Olsen have used the RAS approach as part of a finite element multiconfigurational Hartree-Fock method for determining the atomic quadrupole moment of Ca (3d4s; ^1D) and the electron affinity of the ^1S ground state.[306,307]

5.4 CISDTQ and CISD[TQ]

Few studies have employed configuration interaction with all singles, doubles, triples, and quadruples (CISDTQ) because the number of triple and quadruple substitutions grows very rapidly with the number of electrons and basis functions (cf. Table 3). CISDTQ results are most commonly reported in benchmark full CI studies to indicate the fraction of the basis set correlation energy recovered by triples and quadruples.[17,22,39,80,234,241,264] Nevertheless, the CISDTQ method has occasionally been used for benchmarking in cases where the full CI was not technically feasible, because the CISDTQ results are expected to be very close to full CI for small molecules. For systems with eight electrons or less at their equilibrium geometries, the CISDTQ method recovers more than 99.8% of the correlation energy for a DZP basis set (cf. Table 2). One benchmark study by Lee *et al.* examined the effects of triple and quadruple excitations on equilibrium geometries, harmonic vibrational frequencies, and infrared intensities of several small molecules.[308] A similar study by Scuseria, Hamilton, and Schaefer[309] used CISDTQ equilibrium geometries and harmonic vibrational frequencies to evaluate the performance of the CCSDT method for several diatomic molecules.[4]

Chemical applications of the CISDTQ method include the 1988 study by Scuseria and Schaefer[310] on the barrier height for the F + H_2 → FH + H reaction, which is very sensitive to the level of theory employed. By truncating the CI space at quadruples, these authors were able to increase the basis set from 28 functions (in Bauschlicher and Taylor's full CI study[237]) to 47 basis functions and enabled them to consider the effects of correlating the fluorine 2s orbital. Additionally, Tanaka and Nishimoto have used CISDTQ to examine the reaction mechanism for 1,3 hydrogen transfer in excited states of formamide,[311] and Du, Hrovat, and Borden[312] have used CISDTQ as part of a study on singlet-triplet gaps in diradicals.

Multireference CISD methods generally offer a more economical treatment of the dominant effects of triple and quadruple substitutions and allow the use of larger one-particle basis sets. The primary disadvantage of MR-CISD compared to CISDTQ is that the choice of references (and truncation, if any, of the generated singles and doubles space) must be performed carefully so as not to bias the results. An *a priori* selection scheme for MR-CISD which has been investigated in our laboratory is the CISD[TQ] method,[16] which selects as references all single and double substitutions in the active space. This is equivalent to a CISDTQ in which no more than two electrons are allowed into external orbitals, or to a second-order CI (SOCI) in which greater-than-quadruple substitutions have been eliminated. This method was used by Saxe *et al.* in a 1982 study of ethylene using a DZP basis and the shape-driven graphical unitary group approach (SD-GUGA) CI program.[91] The resulting wavefunction (spanning more than 1 million CSFs) was considered a benchmark result. In 1992 study of NH_2, CH_3, SiH_2, C_2, and N_2, Grev and Schaefer[16] found that the CISD[TQ] method provides results which are very close to SOCI when a single reference function dominates. A subsequent study of several other small molecules by Fermann *et al.*[17] reinforced these conclusions. Some results from these studies which indicate the ability of CISD[TQ] to parallel the SOCI and full CI surfaces are presented in Table 11. The CISD[TQ] and SOCI wavefunctions were based on CISD natural orbitals, which perform as well as CASSCF orbitals for SOCI.[16] Although the savings in the number of CSFs for CISD[TQ] compared to SOCI in Table 11 is relatively modest, this savings increases very rapidly with basis set and number of electrons: for

Table 11: Errors in Total Energies (millihartree) Relative to Full CI for Several Molecules Using a DZP Basis.[a]

Method	No. CSFs	$E(r_e)$	$E(1.5 \cdot r_e)$	$E(2.0 \cdot r_e)$
$^2B_1$ NH_2 (Ref. 16):				
CISD	898	9.003	23.475	69.168
CISD[TQ]	18 396	2.897	2.630	4.957
SOCI	21 687	2.853	2.107	1.703
Full CI	2 435 160	0.000	0.000	0.000
$^2A_2''$ CH_3 (Ref. 16):				
CISD	1 385	8.384	23.216	70.646
CISD[TQ]	51 818	2.156	2.065	4.910
SOCI	76 660	2.090	1.254	0.889
Full CI	9 591 312	0.000	0.000	0.000
$^1A_1$ H_2O (Ref. 17):				
CISD	926	12.851	30.421	75.644
CISDTQ	151 248	0.397	1.547	6.280
CISD[TQ]	32 361	1.630	2.537	6.867
SOCI	76 660	1.276	1.058	1.020
Full CI	6 740 280	0.000	0.000	0.000

[a] CISD[TQ] and SOCI methods employed CISD natural orbitals.

DZP ethylene, a CISD[TQ] description requires over 1 million CSFs, whereas a SOCI requires over 42 million. In addition to these results, Grev and Schaefer[16] also demonstrate that the CISD[TQ] method yields reliable dissociation energies for the difficult N_2 and C_2 molecules.

More recent work has explored the quality of CISD[TQ] equilibrium geometries and harmonic vibrational frequencies. King *et al.*[313] have found that for H_2O with a TZ2P basis, the equilibrium geometry predicted by CISD[TQ] differs from that of CISDTQ by less than 0.0001 Å in the bond length and 0.2° in the bond angle. Furthermore, the CISD[TQ] harmonic vibrational frequencies differ from those of the complete CISDTQ by an average of only 5 cm^{-1}. Such agreement is outstanding, particularly in view of the fact that the CISD[TQ] wavefunction contains 45 times fewer CSFs than CISDTQ. In related work, Hoffman *et al.*[314] have found similar results for H_2S. Another study by Leininger and Schaefer[315] considers the ozone molecule, which is challenging to theory because of the unusual importance of triple and quadruple substitutions. It is not currently feasible to obtain the complete CISDTQ wavefunction with a DZP basis, but the DZP CISD[TQ] equilibrium geometry differs from experiment by only 0.009 Å, and the harmonic vibrational frequencies differ by an average of 2.4%, with the treacherous antisymmetric stretching frequency predicted within 4.5%.

Finally, even though the computational cost of a CISD[TQ] procedure is substantially reduced compared to CISDTQ, the scaling with system size (cf. section 2.4.5) remains unfavorable. Hence, it is necessary to seek further reductions in the CI expansion with a minimal loss in the quality of the wavefunction. One promising strategy was suggested by Grev and Schaefer's 1992 study[16] on the use of CISD natural orbitals (NOs) in the CISD[TQ] and SOCI methods. This work indicated not only that CISD NOs are as effective as CASSCF orbitals at providing good correlating orbitals in the active space, but also that the most weakly occupied NOs contribute almost negligibly to the energy. Furthermore, the errors in the energy caused by deleting weakly occupied orbitals are almost entirely due to the neglect of singles and doubles occupying these orbitals, and not to triples or quadruples. This suggests a more compact CISD[TQ] wavefunction[17] which splits the external orbital space into two sets. If the unoccupied (virtual) orbitals of the active space are labeled the primary virtual subspace, then the external orbitals are divided into secondary and tertiary virtual subspaces, where the tertiary subspace comprises the set of the most weakly occupied NOs. One may then modify the CISD[TQ] method to eliminate those triple and quadruple substitutions which place an electron in one of the most weakly occupied orbitals.[17,18,90] In effect, one uses a larger basis set for the singles and doubles than for the triples and quadruples.

This "split-virtual" CISD[TQ] method has been implemented in our de-

Table 12: Correlation Energy Recovered (Relative to CISDTQ) by the Split-Virtual CISD[TQ] Method for H_2O in a cc-pVTZ Basis Set.[a]

Method/ Secondary Space	NO Cutoff	Number of Dets	%SDTQ Energy
CISD		15 939	93.1
CISDT		938 679	95.8
CISDTQ		28 085 271	100.
CISD[TQ] w/ primary space $2b_2 4a_1 2b_1 5a_1$			
(18 7 9 15)	none	984 789	98.8
(9 4 6 8)	10^{-4}	320 531	98.6
(3 1 1 2)	10^{-3}	41 261	96.5
(0 0 0 0)		16 713	94.7

[a] CISD[TQ] methods employed CISD natural orbitals (NOs). The secondary orbital space selects all virtual orbitals with NO occupation numbers greater than the given cutoff and is identified according to how many orbitals of each irrep of C_{2v} it contains, in the order (a_1, a_2, b_1, b_2). Only valence electrons are correlated.

terminant based CI program (cf. section 4.8.3), and we have presented some preliminary results[18] for the neon atom and for H_2O. Table 12 gives some of our results for H_2O with a cc-pVTZ basis set. We find the NO-based selection scheme to be effective in obtaining the dominant effects of triple and quadruple substitutions while using fewer CSFs, and we believe this promising strategy should be even more effective in the coupled-cluster approach, where the connected triples ($\hat{T}_3$ operator) could be evaluated using a smaller NO space.

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