

Pseudospectral multireference single and double excitation configuration interaction

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We present a pseudospectral formulation of the multireference single and double excitation configuration interaction method. A formal scaling advantage is achieved and practical timings are presented. The accuracy of the pseudospectral approximation within this method is probed for a variety of test cases. The method is typically accurate to within 1 mhartree while being up to six times faster than conventional codes. © 1995 American Institute of Physics.

INTRODUCTION

For the past few years, we have been exploring the suitability of the pseudospectral method for treatments of electron correlation.^{1,2} The impetus for this study is quite clear. While the predictive power of *ab initio* quantum chemistry is well-documented,³ the computational cost can be prohibitive. This is especially true for large molecules given the constraining scaling behavior of *ab initio* methods. The cheapest method for treating electron correlation, second-order perturbation theory, scales as $O(N^5)$, and most such methods scale as $O(N^6)$ or worse, where N is proportional to the size of the molecule. The pseudospectral method provides some relief here, reducing the scaling properties of a method by roughly a factor of N . Most recently we have shown the pseudospectral approximation to be profitable when applied to perturbation theory in second and third order.² Unfortunately, perturbation theory has some severe limitations. First, it is generally not at all appropriate (in the common Møller–Plesset partitioning) for excited states. Second, concerns about the underlying convergence of the series can rarely be adequately addressed. Finally, it is fair to say that multireference^{4,5} and spin-restricted open-shell^{6–8} versions are still areas of active research, where the future remains uncertain although quite promising.

This last point is quite important since it is well-known that single-reference methods frequently fail except for the ground state of a molecule near its equilibrium geometry. Multireference methods, usually including the configurations required to guarantee proper dissociation, are necessary for a quantitative treatment of electron correlation. Thus, we have now turned our attention to a prototypical multireference method, multireference single and double excitation configuration interaction (MRSDCI). This method was chosen because of its widespread applicability. The method has been shown to be size-consistent to within 2–3 kcal/mol for a number of molecules, provided a large enough reference space is used.⁹ However, ultimately the number of reference configurations required to maintain approximate size consistency will become constraining. In such a case, the various coupled-pair functional (CPF) methods^{10–12} or possibly multireference perturbation theories^{13,14} (MRPT) can be used. Since the dominant computational effort in both CPF and MRPT methods is exactly the same as MRSDCI, our conclusions regarding the magnitude of the pseudospectral advan-

tage should remain approximately unchanged for these variants.

THEORY

We will limit our discussion of the pseudospectral approximation since it has been adequately treated in the existing literature. The method was originally developed in the fluid dynamics work of Orszag,¹⁵ and first applied in the realm of electronic structure theory by Friesner.¹⁶ It uses both a physical space grid and a spectral (function) space basis set. The possibility of transforming between two different representations allows one to use whichever is computationally convenient. Thus local operators, such as the Coulomb potential, are represented in physical space. The locality in physical space manifests itself as a diagonal physical space matrix representation of the operator, with all the concomitant computational advantages of diagonal–matrix–vector multiplication. The price to be paid is the transformation of a function between physical and spectral space representations.

The integrals which comprise the main bottleneck in all *ab initio* methods are the two-electron integrals

$$(ij|kl) = \int \frac{\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\varphi_k(\mathbf{r}_2)\varphi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (1)$$

where φ_i are the basis functions used. The pseudospectral approximation of these integrals is given as

$$(ij|kl) \approx \sum_g Q_{ig} A_{kl}(g) R_{gj}, \quad (2)$$

where g indexes grid points,

$$R_{gj} = \varphi_j(\mathbf{r}_g), \quad (3)$$

$$A_{kl}(g) = \int \frac{\varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_g|} d\mathbf{r}_1, \quad (4)$$

and the matrix \mathbf{Q} is determined through a least-squares fit of $\mathbf{QR}=\mathbf{S}$, where \mathbf{S} is the analytic overlap matrix. The relationship to numerical integration is obvious from Eq. (2), where replacement of \mathbf{Q} with $\mathbf{R}^t \mathbf{w}$ would yield integration with grid weights as given by the diagonal matrix \mathbf{w} . The use of \mathbf{Q} instead of $\mathbf{R}^t \mathbf{w}$ is particularly important when sparse grids are used because \mathbf{Q} is fit using a superset of the final spectral basis. This is known as “dealiasing” and removes much of

the error which otherwise arises from transformation between two finite, incomplete spaces which have different spans.

The MRSDCI method has a long history in *ab initio* quantum chemistry.^{17,18} It consists of generating a set of configuration state functions (CSFs) by zero, single, or double excitation of electrons from a set of reference CSFs. The matrix representation of the Hamiltonian operator in this many-particle basis is then formed and diagonalized. In the following treatment, we will use i, j, k, l to represent internal orbitals (occupied in at least one of the references) and a, b, c, d to represent external (virtual) orbitals. We denote as n the number of internal orbitals, V the number of external orbitals, and N the number of atomic orbitals. Spin-adapted states of arbitrary spin-coupling missing two electrons in the internal orbitals are denoted as S and T .¹⁹ The wave function coefficients of the doubly excited CSFs are thus denoted C_{Sab} , where S denotes the spin-coupling and spatial occupation in the internal space and ab denotes the external orbitals housing the two excited electrons. In an entirely analogous fashion, s and t represent arbitrary spin-adapted $(n-1)$ electron states and singly excited CSFs are represented as c_{sa} . The numbers of internal $(n-2)$ electron and $(n-1)$ electron CSFs are denoted as P and p , respectively. With the advent of modern computers, it was quickly realized that the storage of the Hamiltonian matrix would become impractical for large CI expansions. The direct CI method was developed²⁰ which avoids the storage of the matrix by using diagonalization schemes which require only the product of the matrix and an arbitrary vector. The first general and efficient formulation of direct MRSDCI is due to Siegbahn,²¹ with later refinements by Saunders and van Lenthe.²² Our spectral formulation incorporates many of these later refinements, which are characterized predominantly by reformulating the basic equations to use matrix multiplication wherever possible.

A brief review of some of the MRSDCI equations is given here, with particular emphasis on the pieces which will be treated pseudospectrally and discussed later. The reader is referred to Siegbahn's paper for a detailed listing of all the necessary equations.²¹ Using second quantization, it is easy to show that the matrix elements of the Hamiltonian operator take the following form:

$$\mathbf{H}_{\mu\nu} = \sum_{ij} A_{ij}^{\mu\nu} \langle i|\hat{h}|j\rangle + \sum_{ijkl} A_{ijkl}^{\mu\nu} \langle ij|kl\rangle, \quad (5)$$

where the A constants are related to the generators of the unitary group as

$$A_{ij}^{\mu\nu} = \langle \mu|E_{ij}| \nu \rangle \quad \text{and} \quad A_{ijkl}^{\mu\nu} = \langle \mu|E_{ij}E_{kl} - \delta_{jk}E_{il}| \nu \rangle. \quad (6)$$

The indices μ and ν label CSFs and \hat{h} is the usual one-electron part of the Hamiltonian. For future reference, we remind the reader that the E_{ij} operator is an excitation operator which annihilates an electron from orbital φ_j and creates an electron in orbital φ_i . The most important point in the work of Siegbahn was the realization that the A constants can be written as products of an internal and an external part. The internal part depends only on orbital indices which are occupied in one of the references and has a complicated

structure. The external part depends only on the occupation of orbitals which are unoccupied in all references and takes on only a few values.

A renormalization of the wave function coefficients for doubly excited CSFs, which incorporates the external part of the coupling coefficients, will be assumed in the following formulas and is denoted as

$$(\bar{C}_S)_{ab} = \begin{cases} \sqrt{2^{\delta_{ab}}} C_{Sab}, & S \text{ singlet-coupled} \\ \text{sgn}(a-b) C_{Sab}, & S \text{ triplet-coupled} \end{cases}. \quad (7)$$

Following Meyer's self-consistent electron-pair theory,²³ the renormalized coefficients are arranged in square matrices which are either symmetric (singlet coupling) or antisymmetric (triplet coupling). Only the nonredundant elements are actually stored, and the square matrices are formed from these as needed. The same renormalization, also denoted by an overbar, is applied to the $\sigma = \mathbf{H}c$ (residual) vector where convenient. Thus, the transition from the renormalized residual vector to the residual vector in the conventional normalization without redundant elements is given as

$$\sigma_{Sab} = \begin{cases} \sqrt{2^{\delta_{ab}}} (\bar{\sigma}_{Sab} + \bar{\sigma}_{Sba}), & S \text{ singlet-coupled} \\ (\bar{\sigma}_{Sab} - \bar{\sigma}_{Sba}), & S \text{ triplet-coupled} \end{cases}. \quad (8)$$

Notice that the range of a and b are unrestricted on the right-hand side of Eq. (8), while $a \leq b$ or $a < b$ on the left of the equation (for singlet or triplet coupling of S , respectively).

With these definitions, we can proceed to write the interactions which consume the most computational resources for general MRSDCI as

$$\bar{\sigma}_{Sab}^{2x} = \sum_{Tc} BJ_{ij}^{ST}(ij|ac)\bar{C}_{Tcb} + \sum_{Tc} BK_{ij}^{ST}(ia|jc)\bar{C}_{Tcb}, \quad (9a)$$

$$\bar{\sigma}_{Sab}^{3x,4x} = \sum_{cd} (ac|bd)\bar{C}_{Scd} + \sum_{sc} B_i^{sS}(ia|bc)c_{sc}, \quad (9b)$$

$$\sigma_{sc}^{3x} = \sum_{Sab} B_i^{sS}(ia|bc)\bar{C}_{Sab}. \quad (9c)$$

The superscripts $2x$, $3x$, $4x$ simply label the contributions to the residual vector by the number of external indices in the integrals treated. The BJ and BK constants are the internal coupling coefficients for generalized Coulomb and exchange interactions, respectively. The B_i^{sS} are analogous internal coupling coefficients for interactions between singly and doubly excited CSFs, as defined by Siegbahn.²¹ There is an implicit summation over i and j in Eq. (9a), which is not shown because these indices are constant for a given S and T . Equation (9a) and the first term of Eq. (9b) represent the interaction between doubly excited CSFs, while Eq. (9c) and the second term of Eq. (9b) arise from the interaction between singly excited and doubly excited CSFs.

Equation (9a) does not include all the contributions from the (ia/jb) and (ij/ab) integrals, only the most time-consuming. For example, these integrals also appear in the interaction between reference and doubly excited CSFs. The

terms coupling double excitations to double excitations have operation counts scaling as $O(XV^3)$ and $O(PV^4)$, where X is the number of nonzero B_j^{ST} and B_k^{ST} . These terms comprise the dominant effort in terms of computer time, if we do not consider MRSDCI expansions where many doubly excited CSFs are contracted or excluded from the many-particle basis. Examples of such MRSDCI expansions include internally contracted CI²⁴ and correlation-consistent CI.²⁵ For these methods, it is the coupling of singly and doubly excited CSFs through the (ij/ka) integrals which consumes the lion's share of the computer time. These interactions arise when a single external index is shared, e.g., the contribution to σ_{sa} from C_{Sab} .

The integrals (ac/bd) and (ia/bc) represent the most oppressive disk storage requirement. As pointed out by Ahlrichs,²⁶ this can be avoided by writing their contribution in the atomic orbital basis. The cost of treating the (ac/bd) contribution then becomes $O(PN^4)$, typically a twofold increase because there are more atomic orbitals than virtual orbitals. Also, the integrals must be regenerated with each iteration, preferably ordered by the indices c and d [see Eq. 9(b)]. Unfortunately, the most efficient way to generate the integrals is in order by the indices b and d . These conflicting requirements will increase the iteration time by an amount greater than simply the time required to generate the integrals.

The application of the pseudospectral approximation to the equations presented thus far involves the insertion of the expression in Eq. (2) into Eqs. (9a)–(9c). Thus, we have

$$\begin{aligned} \bar{\sigma}_{Sab}^{2x} = & \sum_g Q_{ag} \sum_T A_{ij}(g) B_j^{ST} \sum_c R_{gc} \bar{C}_{Tcb} \\ & + \sum_{i,g} A_{ia}(g) \sum_T Q_{jg} B_k^{ST} \sum_c R_{gc} \bar{C}_{Tcb}, \end{aligned} \quad (10a)$$

$$\begin{aligned} \bar{\sigma}_{Sab}^{3x,4x} = & \sum_g Q_{ag} \sum_d A_{bd}(g) \sum_c R_{gc} \bar{C}_{Scd} \\ & + \sum_g Q_{bg} \sum_s B_i^{Ss} A_{ia}(g) \sum_c R_{gc} \bar{C}_{sc}, \end{aligned} \quad (10b)$$

$$\sigma_{sc}^{3x} = \sum_g Q_{cg} \sum_{Sa} B_i^{Ss} A_{ia}(g) \sum_b R_{gb} \bar{C}_{Sab}. \quad (10c)$$

These equations are in direct correspondence with Eqs. (9a)–(9c) for clarity. Again, recall that X is the number of nonzero matrix elements $\langle S | E_{ia} E_{bj} | T \rangle$, where a and b are dummy indices since the $(n-2)$ electron CSFs S and T have occupations specified only in the internal space. Therefore, X is the number of $(n-2)$ electron CSFs, P , multiplied by the number of ways to annihilate and subsequently create an electron in the internal orbital space for the average $(n-2)$ electron CSF. The scaling behavior in the first equation is reduced from $O(XV^3)$ to $O(PMV^2 + XMV)$, where M is the number of gridpoints. The two inner and two outer summations of Eq. (10a) scale as $O(PMV^2)$ and the two middle summations scale as $O(XMV)$. Since M is proportional to V , we will replace M with V in determining any scaling advantage. This yields spectral and pseudospectral scalings of $O(XV^3)$ and $O(PV^3)$, respectively.

In order to quantify the advantage of X/P , we examine the closed-shell single-reference case. Ignoring spin-coupling, there are n^2 ways to remove two electrons from the internal space, therefore $P \approx n^2$. For each of these P internal configurations, there are n ways to annihilate an electron. Because the reference is closed-shell, there are always less than four orbitals in which to create an electron and therefore $X \approx Pn$. This implies that a scaling advantage of n is achieved.

TABLE I. Spectral and pseudospectral HF*SDCI total energies for selected molecules in equilibrium geometries with a 6-31G** basis set.

Molecule	Energy ^a			SCC energy ^a		
	Spectral	Pseudospectral ^b	Error ^c	Spectral	Pseudospectral ^b	Error ^c
HCN	-93.157 964	-93.157 807	0.157	-93.183 320	-93.183 191	0.129
HNC	-93.133 781	-93.133 910	-0.129	-93.157 669	-93.157 884	-0.215
<i>cis</i> -HOOH	-151.123 112	-151.122 798	0.314	-151.155 545	-151.155 141	0.404
<i>trans</i> -HOOH	-151.135 647	-151.134 941	0.706	-151.168 112	-151.167 133	0.979
HOOH	-151.136 946	-151.136 272	0.674	-151.169 275	-151.168 359	0.916
Acetylene	-77.085 583	-77.084 760	0.823	-77.109 857	-77.108 888	0.969
Ethylene	-78.330 503	-78.330 160	0.343	-78.358 742	-78.358 487	0.255
Ethylene oxide	-153.319 117	-153.318 765	0.352	-153.375 538	-153.375 298	0.240
<i>cis</i> -Difluoroethylene	-276.283 402	-276.283 469	-0.067	-276.362 793	-276.362 557	0.236
<i>trans</i> -Difluoroethylene	-276.283 107	-276.283 192	-0.085	-276.362 446	-276.362 155	0.311
Butadiene	-154.448 884	-155.447 748	1.136	-155.538 175	-155.536 870	1.305
Tetrafluoroethylene	-474.221 628	-474.224 018	-2.390	-474.370 155	-474.373 796	-3.641
Glycine	-283.556 231	-283.555 941	0.290	-283.694 102	-283.693 733	0.369

^aTotal energy in hartrees with and without size-consistency correction (SCC).

^bGrids used are the coarse grids of PSGVB v1.00.

^cError = $E_{ps} - E_{sp}$ in units of mhartree, where E_{ps} is the pseudospectral total energy and E_{sp} is the spectral total energy.

TABLE II. CPU times in seconds on a HP9000/735 for spectral and pseudospectral HF*SDCI calculations using 6-31G** basis sets.

Molecule	No. of CSFs	G92	Spectral	Pseudo-spectral ^a	Speedup ^b
HCN	19 503	78	111	48	2.3(1.6)
Acetylene	27 028	116	141	61	2.3(1.9)
Ethylene	56 953	297	397	157	2.5(1.9)
Ethylene oxide	203 203	2 072	2 418	812	3.0(2.5)
Difluoroethylene	374 545	3 984	5 797	1830	3.2(2.2)
Butadiene	634 501	7 931	15 570	3423	4.5(2.3)
Tetrafluoroethylene	1 256 905	22 613	24 940	9182	2.7(2.5)
Glycine	1 282 401	25 027	36 026	9794	3.7(2.6)

^aGrids used are the coarse grids of PSGVB v1.00.

^bSpeedup of pseudospectral code relative to our spectral implementation. Speedup with respect to GAUSSIAN92 is given in parentheses.

It is important to point out that the apparent extra summation over i in the second term of Eq. (10a) does not actually range over all internal orbitals, and therefore does not affect the scaling. This is because the coupling coefficient BK_{ij}^{ST} is zero if the orbital i is doubly occupied in S . The range of this index for the purpose of counting floating-point operations is the average number of empty or singly occupied internal orbitals among the doubly excited CSFs. While this obviously increases for reference spaces with more open shells, X also increases.

Consider the limit of a complete active space (CAS,²⁷ also known as FORS²⁸) reference with n electrons in n active orbitals. Then the range of i for a given S becomes at most n . An estimate of X for this case is $\frac{4}{9}\bar{\lambda}Pn^2$, where $\bar{\lambda}$ denotes the average number of spin couplings for each ($n-2$) electron internal orbital spatial occupation. This estimate is derived by assuming that an electron can be annihilated or created in any of n active orbitals with probability $2/3$. The factor of $\bar{\lambda}$ in the operation count can be removed by using the “internal spin driven” scheme suggested by Saunders and van Lenthe.²² Substituting the appropriate value for X in the scaling of $O(XV^3)$, the scaling for the spectral MRSDCI method with a CAS reference becomes $O(Pn^2V^3)$. Since the range of i is n , we must include it in the pseudospectral scaling of $O(PV^3)$, which yields a scaling of $O(PnV^3)$. Comparing this to the spectral scaling, we see that the pseudospectral advantage of n is unchanged.

In Eq. (10b), the pseudospectral method reduces the scaling of Eq. (9b) from $O(PV^4)$ to $O(PMV^2)$, an advantage of V by the above arguments. The terms represented in the second half of Eqs. (9b) and (9c) which couple singly excited and doubly excited CSFs are rarely important in terms of CPU time, usually accounting for less than 5% of the iteration time. The primary reason for treating them pseudospectrally is to avoid storing the (ia/bc) integrals. Nevertheless, with proper coding the scaling advantage for the contribution from (ia/bc) integrals is a factor of V .

Since V is typically much greater than n , one expects the greatest advantage to come from the pseudospectral treatment of the (ab/cd) integrals. Unfortunately, for medium quality basis sets such as the 6-31G** basis sets of Pople and co-workers,²⁹ the contribution of these integrals is not particularly time-consuming. Instead, the contribution of the

(ia/jb) integrals represents as much as 60% of the CPU time per iteration. However, the importance of the (ab/cd) integrals grows rapidly as the quality of the basis set is increased. Therefore, we expect the overall pseudospectral advantage to grow with the size of the basis set.

IMPLEMENTATION AND RESULTS

We have written both spectral and pseudospectral MRSDCI codes in order to assess the practical advantages of the pseudospectral approximation in the MRSDCI equations. The coupling coefficients BK_{ij}^{ST} , BK_{ij}^{ST} , and B_i^S are generated by the program GUGA2³⁰ and stored on disk for later use by the CI codes. The spectral MRSDCI implementation follows Siegbahn’s prescriptions quite closely, deviating only to implement selected improvements suggested by Saunders and van Lenthe. The pseudospectral code can accommodate arbitrary grids, but the ones we have used are the “coarse” and “medium” grids of PSGVB v1.00.^{31,32} These grids have approximately 70 and 100 points per atom, respectively.

In order to ensure that the reference energy is reproduced exactly, we use spectral (ij/kl) integrals, i.e., the integrals with all indices in the internal space. Our experience with perturbation theory showed that accuracy was much improved if the second-order energy was computed spectrally. In direct analogy, we use spectral (ij/ka) integrals wherever they are required, and, optionally, spectral (ia/jb) and (ij/ab) for all interactions except those between doubly excited CSFs. If spectral (ia/jb) and (ij/ab) integrals are available, they are also used in the computation of diagonal elements and for the interaction between doubly excited CSFs with the same internal ($n-2$) electron CSF. This is simply done for convenience in the code. The amount of time expended in this part of the code is entirely negligible, so if the spectral (ia/jb) and (ij/ab) already exist on disk, one may as well use them.

The interactions between doubly excited CSFs with different internal ($n-2$) electron CSFs are evaluated according to Eq. (10a). In order to do this efficiently, the internal coupling coefficients must be sorted by the internal ($n-2$) elec-

TABLE III. Disk usage for various codes in megawords (1 Mw=8 million bytes). All calculations are HF*SDCI.

Molecule	Basis set	G92 ^a	Pseudospectral ^b	Spectral ^c
Difluoroethylene	6-31G**	18	9	16
Butadiene	6-31G**	30	15	37
Difluoroethylene	6-311G+ +**	43	25	69
Tetrafluoroethylene	6-31G**	53	27	44
Glycine	6-31G**	54	29	59
Glycine	6-311G+ +**	129	76 ^d	254 ^d

^aMaximum memory usage was set to 4 Mw. The program was run in “semi-direct” mode, so (ab/cd) and (ab/ci) integrals are not stored on disk.

^bDisk usage for our pseudospectral MRSDCI code. This includes the spectral (ai/bj) and (ab/ij) integrals as well as the CI vectors used in the Davidson procedure and the $A_{kl}(g)$ integrals. Coarse grids are assumed for the 6-31G** basis sets and medium grids for the 6-311G+ +** basis sets.

^cDisk usage for our spectral MRSDCI code. This code stores the (ab/cd) and (ab/ci) integrals on disk in addition to the storage required by the pseudospectral code.

^dEstimated.

TABLE IV. Spectral and pseudospectral HF*SDCI total energies for selected molecules using a 6-311G++** basis set.^a

Molecule	Energy ^b			SCC energy ^b		
	Spectral	Pseudospectral ^c	Error ^d	Spectral	Pseudospectral ^c	Error ^d
HCN	-93.225 190	-93.224 657	0.533	-93.254 337	-93.253 784	0.553
HNC	-93.203 290	-93.202 708	0.582	-93.231 261	-93.230 679	0.582
<i>cis</i> -HOOH	-151.248 990	-151.248 894	0.096	-151.288 004	-151.288 009	0.005
<i>trans</i> -HOOH	-151.261 477	-151.260 808	0.669	-151.300 525	-151.299 740	0.785
HOOH	-151.263 164	-151.262 611	0.553	-151.302 149	-151.301 499	0.650
Acetylene	-77.144 026	-77.143 755	0.271	-77.172 082	-77.171 772	0.310
Ethylene	-78.386 696	-78.386 783	-0.087	-78.419 572	-78.419 860	-0.288
Ethylene oxide	-153.431 598	-153.431 739	-0.141	-153.497 917	-153.498 455	-0.538
<i>cis</i> -Difluoroethylene	-276.506 515	-276.504 108	2.407	-276.602 069	-276.599 066	2.003
<i>trans</i> -Difluoroethylene	-276.507 815	-276.505 569	2.246	-276.603 226	-276.600 504	2.722

^aHartree–Fock equilibrium geometries in the 6-31G** basis set are used.

^bTotal energy in hartrees with and without size-consistency correction (SCC).

^cGrids used are the medium grids of PSGVB v1.00.

^dError = $E_{ps} - E_{sp}$ in millihartrees. See Table I, footnote c.

tron CSF. This is in contrast to spectral MRSDCI, where the integrals and coupling coefficients are sorted by internal orbital indices i and j . The sorting of the coupling coefficients takes at most a few seconds for all the cases we show here. The (ia/bc) and (ab/cd) integrals are treated pseudospectrally, as written in Eqs. (10b) and (10c), wherever they appear in the code. Thus, they never exist as four-index quantities and $O(N^4 + nN^3)$ disk storage is removed relative to a spectral implementation which does not regenerate atomic orbital integrals every iteration.

The lack of index symmetry of the pseudospectral integrals entails a nonsymmetric Hamiltonian matrix which prohibits the use of the Davidson diagonalization procedure. Therefore, we use a modification appropriate for nonsymmetric matrices as suggested by Rettrup.³³ The deviation of the pseudospectral Hamiltonian matrix from being symmetric is usually quite small, however we have found the Davidson procedure to be extremely sensitive to this. The modified version we use for the pseudospectral code usually converges in exactly the same number of iterations as the Davidson procedure for the spectral code. Occasionally, one extra iteration is performed. The extra overhead incurred in the modified Davidson procedure is negligible.

The test cases we present all use either 6-31G** or 6-311G++** basis sets^{29,34} and the s combination of the d functions is never removed. The geometries are restricted Hartree–Fock equilibrium geometries using the 6-31G** basis set as determined by GAUSSIAN92.³⁵ Symmetry was used to determine equilibrium geometries, but is never used in the CI. All calculations were performed on an HP 9000-735, which we have found to be approximately the same speed as a Cray Y-MP.

In Table I, we compare total energies obtained using spectral or pseudospectral methods for closed-shell single-reference HF*SDCI with 6-31G** basis sets. The energies obtained before and after application of Pople's size-consistency correction³⁶ are shown. With the exception of tetrafluoroethylene, the pseudospectral approximation reproduces spectral HF*SDCI energies to within 1.3 mhartree. Since we have previously observed difficulty treating mol-

ecules containing fluorine in pseudospectral correlated methods, this implies that further optimization of grids and dealiasing functions for fluorine is necessary. As expected, the errors are only slightly affected by the application of the size-consistency correction. This implies that the errors incurred in a pseudospectral implementation of one of the coupled-pair functional methods would be similar to those shown here.

One of the reasons we show HF*SDCI results is to compare practical CPU times with GAUSSIAN92. GAUSSIAN92 uses the unrestricted Hartree–Fock formalism for SDCI on open-shell molecules and cannot perform MRSDCI calculations at all. Therefore, these test cases allow us to compare practical CPU timings with a well-established code that regenerates integrals every iteration for the (ab/cd) contribution. GAUSSIAN92 has an advantage here in that it is specific to the closed-shell single-reference case. This means the coupling coefficients can be hard-coded and there are special tricks to reduce floating-point operations by about 50%.³⁷ With these caveats in mind, we refer the reader to Table II for the CPU time used by GAUSSIAN92, our pseudospectral MRSDCI, and our spectral MRSDCI codes. Convergence in all three codes is reached when the energy difference between iterations is less than 10^{-8} hartree or the norm of the residual vector is less than 10^{-6} . The pseudospectral code is up to 4.5 times faster than our spectral implementation. We argue that this is the appropriate comparison because both codes are general MRSDCI codes and are in comparable states of optimization. While our codes were written in less than six months, GAUSSIAN92 has been written and optimized over a period of more than two decades. Nevertheless, the primary difference between the comparison with GAUSSIAN92 and that with our own spectral code is the break-even point for the pseudospectral method. The pseudospectral code is up to 2.6 times faster than GAUSSIAN92.

The other precious resource for large calculations is the amount of disk space used. GAUSSIAN92 has been run in the default "semidirect" mode, where the transformed (ab/cd) integrals are not stored on disk. Therefore, it requires $O(n^2N^2)$ disk space. Since our pseudospectral implementa-

TABLE V. CPU times in seconds on a HP9000/735 for spectral and pseudospectral HF*SDCI calculations using 6-311G++** basis sets.

Molecule	No. of CSFs	G92	Spectral	Pseudo-spectral ^a	Speedup ^b
HCN	52 326	188	592	159	3.7(1.2)
Acetylene	69 378	433	810	216	3.8(2.0)
HOOH	106 030	837	965	366	2.6(2.3)
Ethylene	140 185	1 104	2 566	549	4.7(2.0)
Ethylene oxide	521 731	7 831	13 858	3293	4.2(2.4)
Difluoroethylene	1 038 961	17 658	39 333	6289	6.3(2.8)

^aGrids used are the medium grids of PSGVB v1.00.

^bSpeedup with respect to our spectral implementation. Speedup with respect to GAUSSIAN92 is given in parentheses.

tion stores the transformed $A_{kl}(g)$ integrals on disk, it requires $O(MN^2 + n^2N^2)$ disk space. For the grids we are using, this is not important and our code actually uses about half as much disk space as GAUSSIAN92. Table III lists disk usage for several of the HF*SDCI test cases. Compared to GAUSSIAN92, the pseudospectral method is up to 2.6 times faster in CPU time while consuming half as much disk space. The last entry in Table III shows disk requirements for glycine in a 6-311G++** basis set and stresses the importance of minimizing disk usage for workstation computations. Few workstations would have the disk space to perform that calculation using GAUSSIAN92 or a spectral code which stored transformed (ab/cd) integrals. The requirements of the pseudospectral code are more modest. Further optimization should increase the CPU time advantage, and it is possible to regenerate the $A_{kl}(g)$ integrals each iteration and remove all cubic disk storage requirements. Since the cost of transforming these integrals is at worst $O(MN^3)$, one can use the decreased loop limits of the MO basis without storing the transformed integrals. Furthermore, in the context of parallel architectures, it will be much easier to achieve linear speedups when there is no need to consider parallelizing four-center integral generation simultaneously with the parallelization of the CI.

Since the greatest advantage is achieved in the treatment of the (ab/cd) integrals, we also present results for mol-

TABLE VII. CPU times in seconds on a HP9000/735 for spectral and pseudospectral MRSDCI calculations using 6-31G** basis sets.

Molecule	Reference	No. of CSFs	Spectral	Pseudo-spectral ^a	Speedup
HCN	RCI(1/2)	69 723	460	331	1.4
Ethylene	RCI(2/4)	803 633	9 992	6 488	1.5
Difluoroethylene	GVB(2/4)	1 485 064	27 599	13 137	2.1
Difluoroethylene	RCI(1/2)	1 522 525	30 759	14 002	2.2

^aGrids used are the coarse grids of PSGVB v1.00.

ecules using 6-311G++** basis sets.³⁴ These basis sets are more extended than the 6-31G** basis sets, and thus the (ab/cd) contribution becomes more important (over 50% of the iteration time for ethylene oxide with our spectral code). Therefore, the pseudospectral advantage becomes more important. We observed slower convergence in the CI procedure when the coarse grids were used. This is not entirely unexpected, since all the grids and dealiasing functions in PSGVB v1.00 are optimized for 6-31G** basis sets. Therefore, we used the medium grids for these results, which led to the same convergence behavior as seen when using spectral integrals. Since the energies obtained using the coarse grids were almost identical (within 0.2 mhartree for all cases tested) to those from the medium grids, we expect that optimization of grids and dealiasing functions for extended basis sets should allow the use of grids with as few points as the coarse grids. The accuracy obtained for the extended basis sets is shown in Table IV. The errors are very similar to those shown in Table I for the cases with 6-31G** basis sets. As in the previous cases, there are some difficulties with molecules containing fluorine atoms, but apart from these molecules the errors are less than 0.8 mhartree. This is very encouraging, since it suggests that extension of the basis set requires little extra effort in grid and dealiasing optimization. The magnitude of the pseudospectral advantage does increase, even though we have also increased the prefactor by using larger grids. These timings are shown in Table V. Note that the relative advantage with respect to GAUSSIAN92 is increased

TABLE VI. Spectral and pseudospectral MRSDCI total energies for selected molecules at their equilibrium geometries with a 6-31G** basis set.

Molecule	Reference ^a	Bond	No. of CSFs	Energy		
				Spectral	Pseudospectral ^b	Error
HCN	RCI(1/2)	H-C	69 723	-93.161 219	-93.161 073	0.146
HNC	RCI(1/2)	H-N	69 723	-93.137 262	-93.137 104	0.158
Ethylene	RCI(2/4)	C=C	803 633	-78.344 721	-78.344 773	-0.052
<i>cis</i> -Difluoroethylene	GVB(2/4)	C=C	1 485 064	-276.297 648	-276.299 176	-1.528
<i>trans</i> -Difluoroethylene	GVB(2/4)	C=C	1 485 064	-276.297 146	-276.298 770	-1.624
<i>cis</i> -Difluoroethylene	RCI(1/2)	C-F	1 522 525	-276.288 174	-276.288 561	-0.387
<i>trans</i> -Difluoroethylene	RCI(1/2)	C-F	1 522 525	-276.287 883	-276.288 476	-0.593

^aGVB=Generalized Valence Bond. RCI=Restricted configuration interaction. The GVB wave function uses two orbitals to describe a bond. The GVB(x/y) reference thus has x electron pairs distributed in y orbitals in all possible ways consistent with the restriction that exactly one of the two orbitals in each bond is doubly occupied. The RCI(x/y) reference has x electron pairs distributed in y orbitals in all possible ways consistent with the restriction that the sum of the occupations of the two bond orbitals in each bond is exactly two.

^bGrids used are the coarse grids of PSGVB v1.00.

TABLE VIII. Spectral and pseudospectral isomerization energies (kcal/mol) using HF*SDCI wave functions with size-consistency corrections.

	<i>trans</i> -Difluoroethylene – <i>cis</i> -difluoroethylene	HNC –HCN	<i>trans</i> -HOOH –HOOH	<i>cis</i> -HOOH –HOOH
HF*SDCI/6-31G**				
Spectral	0.21	16.16	0.73	8.65
Pseudospectral	0.25	15.94	0.77	8.33
Error	0.04	0.22	0.04	0.32
HF*SDCI/6-31G++**				
Spectral	–0.73	14.54	1.02	8.91
Pseudospectral	–0.91	14.56	1.11	8.50
Error	0.18	0.02	0.09	0.41

by a factor of 1.3 for difluoroethylene on progressing from the 6-31G** basis set to the 6-31G++** basis set.

Results of true MRSDCI calculations are of practical interest, and the energies (with no size-consistency correction) are shown in Table VI. These cases all use 6-31G** basis sets, and therefore are performed on the coarse grids of PSGVB v1.00. The accuracy is very similar to that obtained for the HF*SDCI test cases. Again, we sometimes see an increased error for molecules containing fluorine. Discounting these two results, the error incurred by the pseudospectral approximation is less than 0.5 mhartree. Timings are shown in Table VII, and GAUSSIAN92 times are not shown because the code cannot do these calculations. The magnitude of the pseudospectral advantage decreases for the multireference cases. This is primarily due to two factors. First, the percentage of time which is spent in the common spectral part of the code increases. The dominant culprit here is the treatment of the (*ij/ka*) integrals and their increased importance in multireference cases has been noted by Saunders and van Lenthe.²² Second, we have been unsuccessful so far in optimizing the part of the code which scales as $O(XMV)$, consisting of the partial sums involving the coupling coefficients BJ_{ij}^{ST} and BK_{ij}^{ST} in Eq. (10a). As X increases, the lack of optimization here becomes more important.

We explored the use of localized internal orbitals as a means of reducing the effort in the $O(XMV)$ portion of the code, the middle sums in each of the two terms of Eq. (10a). This did not work successfully because of the “orthogonalization tails” of the localized internals. If one demands that the energy difference between the calculations with and without grid-based cutoffs be less than a microhartree, it is necessary to keep all terms in the sum where \mathbf{Q}_{ig} is greater than 10^{-5} . Even though the internal orbitals may be well localized as determined by, e.g., a contour plot, the orthogonalization tails cause the magnitude of \mathbf{Q}_{ig} to be greater than 10^{-5} over almost the entire molecule. We tried interchanging the positions of \mathbf{Q} and \mathbf{R} in Eq. (10a), since one expects \mathbf{R} to be more localized than \mathbf{Q} . This gives little improvement—on average less than 15% of the gridpoints can be ignored for each internal orbital. At least for the medium-size molecules we present as test cases here, it must be concluded that there is little to gain from truncating sums based on localization of internal orbitals. Such cutoffs may be useful if they are based on atomic orbitals, as we have shown in previous work.²

Somewhat surprisingly, performance can be improved by

using cutoffs based on the magnitude of the \mathbf{RC} product in Eqs. (10). We have found that it is sufficient to keep only terms of magnitude greater than 10^{-5} here, and after the first few iterations the cutoff can be increased to 10^{-3} . The ability to increase the cutoff is a direct result of the iterative refinement nature of the Davidson diagonalization—later iterations require less accuracy in the \mathbf{Hc} product. This fact suggests a multiple grid strategy using a fine grid for the first few iterations and a coarse grid with cutoffs on the \mathbf{RC} product for the majority of the iterations.

Efficient use of cutoffs on the actual pseudospectral quantities \mathbf{Q} , \mathbf{R} , and $\mathbf{A}_{kl}(g)$ requires formulation of Eqs. (10) in the atomic orbital basis. In general, this will lead to inefficiencies because the number of terms in a sum will increase from V^2 to N^2 , typically a factor of 50%. Furthermore, the efficient rearrangement of terms in Eqs. (10) can no longer be performed because the atomic orbital overlap matrix will appear in Eq. (10a) while remaining absent in Eq. (10b). However, the use of cutoffs in the formation of the \mathbf{RC} product can be done efficiently by half-transforming the double-excitation portion of the molecular orbital CI vector into a mixed AO/MO basis. Thus,

$$(\mathbf{RC})_{Sgc} = \sum_c R_{gc} \bar{C}_{Scb} = \sum_\gamma R_{g\gamma} \left(\sum_c U_{\gamma c} \bar{C}_{Scb} \right), \quad (11)$$

where γ denotes an atomic orbital and \mathbf{U} is the coefficient matrix of the molecular orbitals. The partial transformation of the CI vector is of negligible expense. Using a threshold of 10^{-5} for elements $R_{g\gamma}$ affects the final energy by less than a microhartree and typically saves half the time used to form the \mathbf{RC} product. Since the formation of the \mathbf{RC} product is approximately one-fifth of the total effort, this represents a 10%–15% improvement in CPU time.

We have used the total energies presented above to calculate several isomerization energies, which are shown in Table VIII. These are accurate to within 0.5 kcal/mol, which is clearly sufficient for many purposes. Note the cancellation of error in the *cis*–*trans* isomerization energy difference for difluoroethylene, which bolsters our argument that the errors in the total energies for fluorine-containing molecules are a simple consequence of poor grids and dealiasing functions for fluorine.

DISCUSSION

It is quite clear that the pseudospectral MRSDCI method is capable of sufficient accuracy for many chemical applications. However, further attention to the grids and dealiasing functions for fluorine is necessary. Unfortunately, the scaling advantage of n is rather small, which makes the prefactor very important. Part of this prefactor is the size of the grid relative to the number of basis functions. It is possible that this may be decreased through further optimization. However, this will be very difficult because it is hard to imagine an integration grid with less than 70 points/atom. More likely, decreasing the size of the grid must be done by choosing the gridpoints more intelligently. Such schemes exist in other related contexts, e.g., the “backward-trimming” approach of Perez-Jorda³⁸ and the “potential-optimized DVR” of Echave and Clary.³⁹ These schemes deserve closer attention with regards to a pseudospectral MRSDCI method.

Another part of the prefactor is the efficiency of the implementation. This means that the observed advantage is quite sensitive to the degree of optimization of the code. We have implemented the method on an HP 9000-735, which is one of the new breed of “superscalar” architectures. This machine is quite sensitive to cache issues, and our inexperience in writing for these architectures is likely a large factor in the decreased pseudospectral advantage seen here relative to our experience with the MP3 method.

Recently, Rendell and Lee⁴⁰ have proposed the use of a method very similar to the pseudospectral method in the treatment of the coupled-cluster CCSD and CCSD(T) equations. They propose the use of a “resolution of the identity” method,^{41,42} which entails the approximation

$$\phi_i \phi_j \approx \sum_{\kappa} C_{ij\kappa} \phi_{\kappa}, \quad (12)$$

where ϕ are the molecular orbitals and $C_{ij\kappa}$ are determined by fitting. This leads to an expression for the two-electron integral of Eq. (1) which is very similar to the pseudospectral expression of Eq. (2):

$$(ij|kl) \approx \sum_{\kappa} C_{ij\kappa} (\kappa|kl), \quad (13)$$

where $(\kappa|kl)$ is a three-center electron repulsion integral. In this approximation, there is no possibility of decreasing the cost of the method because the integrals can only be separated based on the two charge distributions. This precludes any advantage in treating the exchange-type interactions which dominate the CPU time. Rendell and Lee have proposed the method as a means of reducing the amount of disk storage required. From a formal perspective, this method is inferior to the equivalent pseudospectral method. The formation of the (ab/cd) integrals from the three-center quantities scales as $O(NV^4)$, and the worst scaling encountered in the CCSD method is, like SDCI, $O(n^2V^4)$. Since V and N are usually much greater than n , one expects the formation of the (ab/cd) integrals will become a new bottleneck. Pseudospectrally, the disk space reduction is achieved *and* the cost of the calculation is *lowered*. Note that the application of

the pseudospectral method to the CCSD equations is straightforward and follows our development of the pseudospectral MRSDCI method in this work.

In practice, one must also ask which approach is more accurate. The answer to this is not entirely clear, since there is no common method for which results can be compared. However, there is no reason to believe that the errors will be much different for CCSD and HF*SDCI. With this assumption, we can make a few comments here. The total energies in the pseudospectral method are almost certainly more accurate. The largest error reported here is 3.6 mhartree, compared to 12.2 mhartree for the RI-CCSD(T) method. Further, if the outlier results of the fluorine-containing molecules are discounted, the pseudospectral error is less than 1.3 mhartree. While an error of several millihartrees may be on the verge of acceptability, an error of 12.5 mhartree is far too large for most *ab initio* quantum chemists. Nevertheless, the performance of the RI method with respect to energy differences is astounding. Even though the errors in the total energy are never less than a millihartree for the cases they show, the error in selected energy differences when the correlation consistent (cc) basis sets are used is always less than 0.1 mhartree. If atomic natural orbital (ANO) sets are used, the maximum error increases to over 15 mhartree. This suggests that the performance of the RI method with respect to energy differences cannot be counted on in general. Indeed, reliance on such a delicate cancellation of errors must be approached with great trepidation.

Perhaps the most exciting application of the pseudospectral MRSDCI method is in conjunction with localized procedures, as developed by Saebo and Pulay.⁴³ They have shown that the bottleneck in localized MP3 and MP4 methods is in the evaluation of the “external exchange” operator—the contribution of the (ab/cd) integrals. Because of the similarity of the MP3 and SDCI equations, this assessment is almost certainly true for a localized MRSDCI method as well. As the calculation of the (ab/cd) contribution is precisely where the pseudospectral method exhibits the greatest advantage, we expect that a pseudospectral localized MP3/MP4 or MRSDCI method will be quite successful.⁴⁴

CONCLUSIONS

We have presented a new MRSDCI method incorporating the pseudospectral approximation. Formal scaling advantages of n (number of internal orbitals) and V (number of virtual orbitals) are achieved in the treatment of integrals with two and four virtual orbital indices, respectively. The total energies resulting are typically in agreement with the corresponding spectral energies to within a millihartree, although the error is as high as 3.6 mhartree for one of the test cases. We suspect this is due to inadequate optimization of the grids and dealiasing functions for fluorine atom. Performance advantages of up to a factor of 6.3 are observed relative to our own implementation of the spectral MRSDCI method. Some comparisons with GAUSSIAN92 were also presented and our code is up to 2.8 times faster while using half the disk storage. Unfortunately, the largest scaling advantage of V applies to the treatment of the (ab/cd) integrals. Since this is not the most time-consuming part of the MRSDCI

method unless highly extended basis sets are used, the practical advantages we show here are not as large as might have been expected.

The method removes the integral storage bottleneck and allows significant reduction of CPU time at little cost in accuracy. We have compared our approach to that of Rendell and Lee,⁴⁰ who achieve the first goal of removing the integral storage bottleneck in the CCSD method. As Rendell and Lee point out, this is expected to be particularly beneficial on parallel architectures. We report elsewhere the parallel implementation of the pseudospectral MRSDCI equations.⁴⁵

We have also pointed out the suitability of the pseudospectral method for localized MP3/MP4 and MRSDCI approaches, and we are beginning the development of such methods.⁴⁴

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