

Pseudospectral double excitation configuration interaction

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We present a pseudospectral formulation of the single reference, closed shell double excitation configuration interaction method using a generator state self-consistent electron pair approach. The method scales as $O(n^2N^3)$, compared to the conventional scaling of $O(n^2N^4 + n^3N^3)$. In no case tested does the pseudospectral energy differ by more than 0.35 mhartree from the conventional result.

INTRODUCTION

Recently, we have presented¹ a pseudospectral formulation of the full configuration interaction (FCI) problem. The method was accurate to a mhartree after corrections, but the size of the numerical grids required made it impossible to realize any computational advantage for systems feasible with today's hardware. In this paper, we present the first application of the pseudospectral method to truncated configuration interaction, the double-excitation configuration interaction (DCI) method. Since the scaling of the conventional DCI method is not combinatorial like full CI, it is easier to realize the pseudospectral advantage.

The method we present here has several striking characteristics. First, the method will be faster than conventional DCI approaches for sufficiently large cases, as the scaling is decreased from $O(n^6)$ to $O(n^5)$, where n is the number of molecular orbitals. This scaling advantage will be realizable for cases of rather modest dimension, where we consider modest to mean the calculation would take <10 min of cpu time on a CRAY YMP or equivalent using conventional methods. Second, it provides a framework within which "direct,"² in the sense of "direct self-consistent field (SCF),"³ correlated techniques can be realized. By "direct," we mean that neither the Hamiltonian matrix nor the two-electron integrals are stored on disk. This approach will become necessary as correlation treatments are applied to large systems, and the pseudospectral method is well-suited to it because of the ability to organize the required data (which will be combined to form the two-electron integrals) by blocks of gridpoints. Finally, it allows one to take advantage of locality without introducing the approximations suggested by Pulay and Saebo.⁴ This can be done by using "cutoffs" where the requisite summations are restricted to a subset of the physical space grid. Note that the approximations of Pulay and Saebo may be used along with "cutoffs" to gain even greater advantage. At this point, we have only coded the equations for the molecular orbital basis, and therefore we provide numerical evidence supporting only the first of these claims. A forthcoming paper will address the last two issues.

SELF-CONSISTENT ELECTRON PAIR THEORY FOR DOUBLES CI

Self-consistent electron pair (SCEP) theory⁵ provides a matrix-oriented formalism for a number of correlation methods, including configuration interaction with double excitations. The generator state formulation of Pulay, Saebo, and Meyer⁶ is an efficient modification for the special case of a closed-shell reference state. We review the essential equations for the DCI method, but refer the reader to the original reference for more detail. Our notation conventions are that i, j, k, \dots denote molecular orbitals occupied (internal) in the reference state, ψ_0 . Orbitals unoccupied in ψ_0 (external) are denoted as a, b, c, \dots , while p, q, r, \dots denote arbitrary orbitals, and boldface quantities denote matrices.

The generator state formalism is distinguished by a particular choice for the configuration state functions (CSF's) which removes all coupling coefficients from the equations. The CSF's chosen are pairwise nonorthogonal and are given as follows:

$$\psi_{ij}^{ab} = \phi_{ij}^{ab} + \phi_{ij}^{a\bar{b}} + \phi_{ij}^{a\bar{b}} + \phi_{ij}^{a\bar{b}}, \quad i > j, \quad (1a)$$

$$\psi_{ii}^{ab} = \phi_{ii}^{a\bar{b}}, \quad (1b)$$

where $\phi_{ij}^{a\bar{b}}$ represents a determinant with two electrons excited from spin orbitals $i\alpha$ and $j\beta$ to $a\alpha$ and $b\beta$. The ansatz for the DCI wave function, assuming intermediate normalization ($\langle \Psi | \psi_0 \rangle = 1$), is therefore

$$\Psi = \psi_0 + \sum_{i>j, a, b} C_{ij}^{ab} \psi_{ij}^{ab}. \quad (2)$$

The reciprocal basis is defined by the criterion $\langle \psi_I | \psi_J \rangle = \delta_{IJ}$, where I and J denote the collective orbital indices. Explicitly,

$$\tilde{\psi}_{ij}^{ab} = \frac{1}{\delta} (\phi_{ij}^{ab} + \phi_{ij}^{a\bar{b}} + 2\phi_{ij}^{a\bar{b}} + 2\phi_{ij}^{a\bar{b}} + \phi_{ij}^{b\bar{a}} + \phi_{ij}^{b\bar{a}}), \quad i > j, \quad (3a)$$

$$\tilde{\psi}_{ii}^{ab} = \phi_{ii}^{a\bar{b}}. \quad (3b)$$

The fundamental quantities in the DCI problem are the doubles residuum matrices,

$$(T_{ij})_{ab} = \langle \tilde{\psi}_{ij}^{ab} | \hat{H} - E_0 + E_{\text{corr}} | \Psi \rangle, \quad (4a)$$

which are zero when $|\Psi\rangle$ is an eigenvector of \mathbf{H} with eigenvalue $E_0 - E_{\text{corr}}$. We follow the standard practice of designating the energy of the reference wave function as

E_0 , and the DCI correlation energy as E_{corr} . Given the previously stated choice for the CSF's and the wave function ansatz, the crucial formula for the residuum matrices can be written as

$$\mathbf{T}_{ij} = \mathbf{K}_{ij} + \mathbf{K}[\mathbf{C}_{ij}] + \mathbf{F}\mathbf{C}_{ij} + \mathbf{C}_{ij}\mathbf{F} + \mathbf{Q}_{ij} + \mathbf{Q}_{ji}^\dagger + \mathbf{G}_{ij} + \mathbf{G}_{ji}^\dagger + E_{\text{corr}}\mathbf{C}_{ij}, \quad (4b)$$

where the superscript \dagger denotes matrix transposition and the following matrices have been used:

$$(\mathbf{C}_{ij})_{ab} = (\mathbf{C}_{ji})_{ba} = C_{ij}^{ab}, \quad i > j, \quad (5)$$

$$(\mathbf{K}_{ij})_{ab} = (ia|jb), \quad (6)$$

$$(\mathbf{J}_{ij})_{ab} = (ij|ab), \quad (7)$$

$$(\mathbf{K}[\mathbf{C}_{ij}])_{ab} = \sum_{cd} (ac|bd) C_{ij}^{cd}, \quad (8)$$

$$\mathbf{Q}_{ij} = \sum_k [(K_{ik} - \frac{1}{2}J_{ik})(2C_{kj} - C_{jk}) - \frac{1}{2}J_{ik}C_{jk} - J_{jk}C_{ik}], \quad (9)$$

$$\mathbf{G}_{ij} = \sum_{k>l} (1 + \delta_{kl})^{-1} [(ik|jl) - \delta_{lj}F_{ik} - \delta_{kl}F_{jl}] C_{kl}. \quad (10)$$

The matrix \mathbf{F} is the closed-shell Fock matrix. The first term in Eq. (4b) represents the interaction between doubly-excited configurations and the reference, while the remainder of the terms describe interactions among the doubly-excited configurations. The external exchange matrix, $\mathbf{K}[\mathbf{C}_{ij}]$, contains all the contributions from integrals with four external indices, describing the interactions $\langle \psi_{ij}^{ab} | \hat{H} | \psi_{ij}^{cd} \rangle$. Analogously, $\mathbf{G}_{ij} + \mathbf{G}_{ji}^\dagger$ represents the interactions involving integrals with four internal indices, $\langle \psi_{ij}^{ab} | \hat{H} | \psi_{kl}^{cd} \rangle$. The remaining interactions of the form $\langle \psi_{ij}^{ab} | \hat{H} | \psi_{ik}^{ac} \rangle$ are treated in the $\mathbf{Q}_{ij} + \mathbf{Q}_{ji}^\dagger$ term. The final wave function is found by iterating the perturbation theoretic formula

$$(\mathbf{C}_{ij}^{ab})^{n+1} = (\mathbf{C}_{ij}^{ab})^n + \mathbf{T}_{ij}^{ab} / (\langle \psi_{ij}^{ab} | H | \psi_{ij}^{ab} \rangle - E_{\text{corr}}) \quad (11)$$

to convergence.

PSEUDOSPECTRAL TREATMENT OF TWO-ELECTRON INTEGRALS

The pseudospectral method is closely related to numerical integration schemes. It was originally developed in the context of fluid dynamics⁷ and first applied to electronic structure calculations by Friesner.⁸

The two-electron integral

$$(pq|rs) = \int \frac{\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)\phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \quad (12)$$

can be represented via quadrature as

$$\sum_g \phi_p(\mathbf{r}_g)w(\mathbf{r}_g)\phi_q(\mathbf{r}_g) \int \frac{\phi_r(\mathbf{r})\phi_s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_g|} d\mathbf{r}, \quad (13)$$

where w represents a weighting function, and g indexes gridpoints whose location is given by \mathbf{r}_g . This expression can be rewritten in matrix notation as

$$\mathbf{I}^{rs} = \mathbf{R}^\dagger \mathbf{w} \mathbf{A}^{rs} \mathbf{R}, \quad (14)$$

where

$$(\mathbf{I}^{rs})_{pq} = (pq|rs), \quad (15)$$

$$w_{g'g} = \delta_{g'g} w(\mathbf{r}_g), \quad (16)$$

$$(\mathbf{A}^{rs})_{g'g} = A_{rs}(\mathbf{r}_g) = \delta_{g'g} \int \frac{\phi_r(\mathbf{r})\phi_s(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_g|} d\mathbf{r}, \quad (17)$$

$$\mathbf{R}_{gp} = \phi_p(\mathbf{r}_g). \quad (18)$$

The pseudospectral method interprets the matrix equation (14) as a transform from spectral (function) space to physical space, multiplication by the physical space representation of the Coulomb potential operator, and subsequent back-transform to spectral space. From this vantage point⁹ it becomes clear that \mathbf{R}^\dagger should be replaced by \mathbf{R}^{-1} , provided the number of gridpoints equals the number of basis functions.

Friesner further improved the method by using a least-squares technique allowing the use of more gridpoints than basis functions and through the use of dealiasing functions. The dealiasing functions are included because of the recognition that the range of the physical space operator is not limited to the space spanned by the basis set. Therefore, a filtering procedure of some sort is necessary to remove the components outside of the basis set prior to the back-transformation to spectral space. This is conceptually equivalent to the phenomenon of the same name in the theory of discrete Fourier transforms. The use of a least-squares matrix \mathbf{B} in place of $\mathbf{R}^{-1}\mathbf{w}$ accomplishes the desired result.¹⁰ The reader is referred to the papers of Friesner and co-workers for details of the construction of this matrix.¹¹

PSEUDOSPECTRAL FORMULATION OF SCEP FOR DOUBLES CI

We introduce the pseudospectral approximation in the calculation of the two most costly terms of the residual vector, $\mathbf{K}[\mathbf{C}_{ij}]$ and $\mathbf{Q}_{ij} + \mathbf{Q}_{ji}^\dagger$. Spectral calculation of these terms scales as $O(n^2N^4 + n^3N^3)$, where n is the number of internal orbitals and N is the number of external orbitals. Although the scaling behavior suggests that the first term would dominate (generally $n < N$), experience shows that this is not the case for most problems. We submit as an example the calculation on carbon dimer detailed later in this paper. With six internal orbitals and 24 external orbitals, 45% of the time is spent calculating the first term, and 50% is required for the second term. The remaining terms in Eqs. (4) consume only 5% of the cpu time. Of course, this behavior is a consequence of a larger prefactor multiplying the scaling for the $\mathbf{Q}_{ij} + \mathbf{Q}_{ji}^\dagger$ term.

The pseudospectral formula for the external exchange matrix $\mathbf{K}[\mathbf{C}_{ij}]$ is

$$(\mathbf{K}[\mathbf{C}_{ij}])_{ab} = \sum_g B_{ag} \sum_d A_{bd}(g) \sum_c R_{gc} C_{ij}^{cd}. \quad (19)$$

This scales as $O(Mn^2N^2)$, where M is the number of gridpoints. Since M is generally proportional to the total num-

ber of orbitals ($n+N$), and N is usually significantly larger than n , this is roughly equivalent to $O(n^2N^3)$. The corresponding formula for Q_{ij} requires some rearrangement of the spectral term in Eq. (9)

$$Q_{ij} = \sum_k K_{ik}(2C_{kj} - C_{jk}) - J_{ik}C_{kj} - J_{jk}C_{ik}. \quad (20)$$

This requires two additional matrix multiplications when forming the combined quantity $Q_{ij} + Q_{ji}^\dagger$ but is necessary because explicit formation of the matrix $K_{ik} - \frac{1}{2}J_{ik}$ would obviate the pseudospectral advantage. Given this rearrangement, the final formula becomes

$$\begin{aligned} (Q_{ij})_{ab} = & \sum_g A_{ia}(g) \sum_k B_{kg} \sum_c R_{gc} (2C_{kj}^{cb} - C_{kj}^{bc}) \\ & - \sum_g B_{ag} \left[\sum_k A_{ik}(g) \sum_c R_{gc} C_{kj}^{cb} \right. \\ & \left. + \sum_k A_{jk}(g) \sum_c R_{gc} C_{ik}^{cb} \right]. \quad (21) \end{aligned}$$

This scales as $O(Mn^2N^2)$, being equivalent by the previous arguments to $O(n^2N^3)$.

IMPLEMENTATION AND RESULTS

We have written a spectral generator-state SCEP DCI program, defined by Eqs. (1)–(11), as well as a pseudospectral version wherein Eqs. (19) and (21) replace Eqs. (8) and (9). In the pseudospectral version, we use spectral integrals for all terms other than $K[C_{ij}]$ and $Q_{ij} + Q_{ji}^\dagger$. Thus the appropriate E_0 is the conventional one constructed spectrally. Although we have completely ignored the lack of index symmetry in the pseudospectral integrals, we have encountered no serious convergence difficulties. The molecular orbital basis was used exclusively, and the pseudospectral quantities were generated in the atomic orbital basis using the PSGVB (Ref. 12) program and then transformed to the molecular orbital basis using standard techniques. Note that the transformation of the pseudospectral quantities scales as $O(MN^3)$ in contrast to the $O(N^5)$ scaling of the conventional two-electron integral transformation.

The primary purpose of this paper is to show that the pseudospectral DCI method is capable of chemical accuracy on very sparse grids. Therefore, we present no timing information other than to report that the pseudospectral code is $\sim 10\%$ faster for the C_2 test case and up to two times slower for the smaller cases. As neither code is optimized, this information is provided only to show that the method is viable in practice. Analysis of the efficiency of the method must await optimization of the codes and tests on the larger systems for which the pseudospectral method is designed. Nevertheless, we can provide a rough estimate of 30 basis functions as the point where the pseudospectral DCI method becomes cheaper than the spectral one. An efficient code can easily perform calculations of this magnitude using < 10 min of cpu time on a CRAY YMP computer.

TABLE I. DCI results for various atoms using pseudospectral and spectral formulations. Basis sets are all 6-31G**, double excitations are included from all occupied orbitals to all virtual orbitals, and all are in 1S states.

	E_{corr}^a		E_0^b	Error (μH) ^c	Grid size ^d
	Pseudo-spectral	Spectral			
Ne	0.149 305	0.149 312	-128.350 862	7	222
H ⁻	0.015 598	0.015 605	-0.422 441	7	192
F ⁻	0.174 549	0.174 662	-99.350 481	113	222

^aDCI correlation energy in atomic units. DCI total energy = $E_0 - E_{\text{corr}}$.

^bReference energy in atomic units.

^c1 $\mu\text{H} = 10^{-6}$ hartree. Error = $E_{\text{corr}}(\text{spectral}) - E_{\text{corr}}(\text{pseudospectral})$.

^dNumber of points in grid used.

The calculations were performed on an FPS 521-EA computer, taking advantage of the vector processor. The pseudospectral method allows for efficient vectorization over the gridpoints and thus the pseudospectral code is slightly faster than we expected from counting floating-point multiplications. This implies that the estimate of the break-even point might change when using a computer without vector processing capability.

The test cases all use 6-31G** basis sets,¹³ where the s combination of the Cartesian d functions has not been removed. The grids used are the "medium" grids of the PSGVB program. Reference wave functions ψ_0 were obtained from spectral closed-shell Hartree-Fock calculations. The CSF's include all double excitations out of all internal orbitals and into all external orbitals.

We compare the spectral and pseudospectral energies for a few atomic species in Table I. The accuracy is seen to be quite satisfactory, even for F^- , where the error is < 0.1 kcal/mol. More interesting are the diatomic cases shown in Table II. Again, the accuracy is certainly sufficient for this level of theory, with the error never exceeding 0.35 mhartree (0.2 kcal/mol). However, the error varies an order of magnitude over the range of internuclear distances shown. Explanation of this requires knowledge of the behavior of the scheme used to merge atomic grids.¹⁴ Each atom carries its own grid, and these grids are superimposed to form the molecular grid. Then points which are too close are coalesced. This is done in order to avoid approximate linear dependencies which would make it difficult to invert \mathbf{R} accurately. Finally, some points are added to the bonding region in order to improve the quality of the quadrature in the area where the wave function is expected to have considerable amplitude. Clearly, we expect that as the internuclear distance is reduced, the quality of the quadrature will decrease unless one takes pains to replace the deleted points by ones which do not cause linear dependence. Likewise, as the internuclear distance increases, one must ensure that enough points are added to the bonding region such that the quality of the quadrature in this region remains roughly constant. Generating grids of uniform quality for arbitrary molecular geometries is a difficult task, and it is no wonder that the scheme used is not perfect. Part of the problem stems from the fact that we use exclu-

TABLE II. DCI results for various molecules using pseudospectral and spectral formulations. Basis sets are all 6-31G**, double excitations are included from all occupied orbitals to all virtual orbitals, and all molecules are in $^1\Sigma^+$ states.

	r^a	E_{corr}^b		E_0^c	Error (μH) ^d	Grid size ^e
		Pseudospectral	Spectral			
H_2	0.50	0.032 284	0.032 212	-1.061 482	-72	312
	0.60	0.032 822	0.032 789	-1.113 933	-33	320
	0.74	0.033 646	0.033 664	-1.131 292	18	330
	0.80	0.034 144	0.034 162	-1.128 434	18	338
	0.90	0.035 286	0.035 294	-1.116 516	8	338
	1.00	0.036 914	0.036 926	-1.099 475	12	354
	1.10	0.039 153	0.039 176	-1.079 944	23	354
	1.20	0.042 097	0.042 137	-1.059 423	40	362
	2.00	0.092 579	0.092 736	-0.916 740	157	378
HF	0.50	0.161 471	0.161 692	-99.307 194	221	332
	0.60	0.167 269	0.167 586	-99.732 978	317	346
	0.70	0.172 529	0.172 869	-99.921 098	340	355
	0.80	0.177 325	0.177 632	-99.994 570	307	360
	0.91	0.182 030	0.182 292	-100.011 576	262	380
	1.00	0.185 699	0.185 886	-100.001 470	187	380
	1.10	0.189 539	0.189 645	-99.978 492	106	380
	1.20	0.193 407	0.193 422	-99.950 123	15	389
	2.00	0.201 464	0.201 489	-99.890 528	25	399
C_2	1.10	0.231 427	0.231 329	-99.747 453	-98	408
	1.10	0.278 112	0.278 140	-75.335 397	28	446
	1.20	0.278 733	0.278 748	-75.375 661	15	456
	1.24	0.278 805	0.278 809	-75.378 991	4	456
	1.26	0.278 766	0.278 771	-75.378 683	5	456
	1.28	0.278 698	0.278 707	-75.377 268	9	456
	1.29	0.278 665	0.278 682	-75.376 186	17	456
	1.30	0.278 582	0.278 601	-75.374 878	19	456

^aInternuclear distance in angstroms.

^bDCI correlation energy in atomic units. DCI total energy = $E_0 - E_{\text{corr}}$.

^cReference energy in atomic units.

^d1 $\mu\text{H} = 10^{-6}$ hartree. Error = $E_{\text{corr}}(\text{spectral}) - E_{\text{corr}}(\text{pseudospectral})$.

^eNumber of points in grid used.

sively the "medium" grid, while Friesner and co-workers use a strategy with both a "medium" and a larger "fine" grid. The "fine" grid is used to refine the results obtained with the medium grid, and this grid is sufficiently dense to be less sensitive to changes in size and shape.

Although the error incurred by using the pseudospectral approximation in DCI is not as constant as we would like, it is nevertheless true that the approximation is of chemical accuracy. In light of the corrections necessary to achieve this level of accuracy in our previous work on full CI, this deserves further comment. Therefore, we point out that these results are corrected in a sense, since all integrals involving four internal indices and also the Fock matrix are evaluated analytically. As the internal orbitals include those which are most rapidly-varying, this is analogous to the correction we proposed for pseudospectral full CI using spectral integrals for the calculation of the core-valence interaction when core orbitals were constrained to remain doubly-occupied. Thus, our results further validate the approach of using analytic integrals wherever possible for the most rapidly-varying basis functions.

SUMMARY

We have presented a pseudospectral formulation of the generator state SCEP method applicable to DCI wave functions. The scaling is improved by a factor of n , the number of internal molecular orbitals. The method has been shown to be sufficiently accurate for a number of test cases, with errors not exceeding 0.35 mhartree for any case tested. Our pseudospectral code is slightly faster than the spectral version for C_2 with 30 basis functions, and thus we expect the method to be useful for DCI calculations on systems with 30 or more basis functions (molecular orbitals). As DCI calculations of this size are not difficult, we expect the pseudospectral DCI method to open the doors to correlated calculations on molecules of unprecedented size in the near future. In particular, we are excited about the ease with which the generator-state formalism for DCI may be cast in terms of atomic orbitals. This will allow the use of "cutoffs," and it will also make the implementation of "atomic corrections" trivial.¹⁵ We are currently formu-

lating the code in terms of atomic orbitals in order to implement these improvements and further reduce the grid size for a given accuracy.

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¹⁰Friesner and co-workers designate the matrix \mathbf{B} as \mathbf{Q} . We have followed our previous paper in altering the pseudospectral notation where there is conflict between the notation used in the spectral CI methods and that used to denote the fundamental pseudospectral quantities.

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