Pseudospectral full configuration interaction

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A pseudospectral formulation of the full configuration interaction method is presented in this paper. This represents the first application of the pseudospectral approximation to configuration interaction expansions. It is shown that a formal scaling advantage of n, the number of molecular orbital basis functions, is achieved. The spectral and pseudospectral total energies obtained for a series of first-row atoms and ions are compared. The relative operation counts of the spectral and pseudospectral methods are also discussed in this paper. Finally, two hybrid spectral/pseudospectral approximations that vastly improve the accuracy of the pseudospectral total energies are presented.

INTRODUCTION

The method of configuration interaction (CI) is one of the most successful methods of recovering the correlation energy in electronic structure calculations. The underlying mathematics is simple, yet there are many practical problems associated with its application, primarily due to difficulties related to the often extensive length of the CI expansion. Originally, programs would construct the Hamiltonian matrix in the CI basis and diagonalize the matrix explicitly.[1] However, the dimension of the matrix quickly becomes so large that its storage is difficult. The answer to this problem was to use diagonalization methods that only needed the vector resulting from the product of the Hamiltonian matrix and another vector. The Nesbet,[2] Shavitt,[3] and Davidson[4] methods are examples of these. By using these methods, one can store the integrals that make up the matrix and combine them during the diagonalization procedure without ever explicitly constructing or storing the matrix.[5] Since the number of integrals required increases much less rapidly than the number of configurations for all but the most trivial CI expansions, this leads to much less stringent storage requirements. The unitary group approach[6] allowed the efficient generalization of this direct CI method, as the fundamental equations are naturally written in terms of integrals and coefficients whose meaning will be discussed later.

For full-CI calculations, another problem surfaced— the storage of the spin coupling coefficients. Siegbahn[7] proposed the use of the resolution of the identity for the construction of the two-body coupling coefficients, thereby eliminating the need to store them. This method takes advantage of the fact that modern computers are much faster at matrix multiply operations than other operations, and hence casts the required operations in terms of matrix multiplications.

Interestingly, both of these advances involve blurring the distinction between assembly of the required quantities and diagonalization. Using direct CI, one loses the ability to distinguish between construction of the matrix and diagonalization. With Siegbahn's method, one loses the ability to distinguish between construction of the two-body spin coupling coefficients and diagonalization. We present a pseudospectral[8] approach which, as we will see later, forms the two-electron integrals during the diagonalization process, leading to further blurring of assembly and diagonalization.

The pseudospectral method of Friesner and co-workers[9–11] uses both basis functions and a physical space grid to form two-electron integrals. The method has been tested for Hartree–Fock[10] (HF) and generalized valence bond[11] (GVB) methods. In all cases tested so far, agreement with purely spectral (conventional) approaches to HF and GVB has been extremely good. For HF, the pseudospectral method scales as Mn^2, compared to n^4 for spectral methods, where M is the number of grid points, and n is the number of basis functions. Using cutoffs changes the asymptotic scaling to Mn. Since M is proportional to n, the pseudospectral formulation gains a factor of n in scaling, and a factor of n^2 in the limit of infinitely large molecules.

One of the keys to the success of the pseudospectral approach is that the basis functions are used to analytically integrate out the Coulomb singularity. Historically, this has been the bane of numerical approaches to electronic structure calculations, because one requires a very dense grid to integrate over the singularity numerically. Friesner's recognition of and solution to the problems caused by aliasing were also fundamental in making pseudospectral calculations agree sufficiently with spectral calculations.

In this paper, we outline a pseudospectral theory for the full-CI problem which synthesizes Siegbahn's method for spectral full CI and Friesner's pseudospectral technique. We show that a scaling advantage of n is achieved, and examine the floating-point operation count for representative grid and basis set sizes. We also present the results of test calculations which probe the accuracy of the pseudospectral approximation for the CI method.

THEORY

By now, the second-quantized form of the molecular Hamiltonian is well known to be

$$\mathbf{H} = \sum_{ij} \mathbf{E}_{ij}(i|\mathbf{h}|j) + \tfrac{1}{2}\sum_{ijkl}[\mathbf{E}_{ij}\mathbf{E}_{kl} - \delta_{jk}\mathbf{E}_{il}](ij|kl), \quad (1)$$

where the $\mathbf{E}_{ij}$ are the spin-averaged excitation operators given by

$$\mathbf{E}_{ij}= \sum_{\sigma=\alpha\beta} a_{i\sigma}^{+}a_{j\sigma}, \tag{2}$$

with $a_{i\sigma}^{+}$ and $a_{i\sigma}$ being the creation and annihilation operators for spin orbital $i\sigma$, respectively. The $(i|\mathbf{h}|j)$ and $(ij|kl)$ are the usual one- and two-electron integrals over spatial molecular orbitals. Here and in the following we adopt the convention that i, j, k, and l denote molecular orbitals and μ, ν, and κ denote configuration state functions (CSF's), which we take to be eigenfunctions of spin. We label the element of the CI vector corresponding to the CSF ν as c_ν. Given (1), it is straightforward to show that the result of the matrix–vector product $\sigma=\mathbf{H}c$ is

$$\sigma_\mu= \sum_{ij\nu} \langle\mu|\mathbf{E}_{ij}|\nu\rangle (i|\mathbf{h}|j)c_\nu$$

$$+\tfrac{1}{2}\sum_{ijkl\nu} \langle\mu|\mathbf{E}_{ij}\mathbf{E}_{kl}-\delta_{jk}\mathbf{E}_{il}|\nu\rangle (ij|kl)c_\nu. \tag{3}$$

Inserting the resolution of the identity and rearranging, Siegbahn showed that for full CI this could be written as

$$\sigma_\mu^{(1)}= \sum_{ij\nu} \langle\mu|\mathbf{E}_{ij}|\nu\rangle [(i|\mathbf{h}|j)-\tfrac{1}{2}\sum_k (ik|kj)]c_\nu, \tag{4}$$

$$\sigma_\mu^{(2)}=\tfrac{1}{2}\sum_{ijkl\kappa\nu} \langle\mu|\mathbf{E}_{ij}|\kappa\rangle\langle\kappa|\mathbf{E}_{kl}|\nu\rangle (ij|kl)c_\nu, \tag{5}$$

$$\sigma_\mu=\sigma_\mu^{(1)}+\sigma_\mu^{(2)}. \tag{6}$$

Siegbahn then defined the following matrices:

$$D_{kl,\kappa}= \sum_\nu \langle\kappa|\mathbf{E}_{kl}|\nu\rangle c_\nu, \tag{7}$$

$$I_{ij,kl}=(ij|kl), \tag{8}$$

$$A_{\kappa,ij}^{\mu}= \langle\mu|\mathbf{E}_{ij}|\kappa\rangle, \tag{9}$$

and wrote

$$\sigma_\mu^{(2)}=\tfrac{1}{2}\operatorname{Tr}(\mathbf{A}^\mu\mathbf{ID}). \tag{10}$$

The $\mathbf{ID}$ product is independent of μ, so it is performed once per iteration. The trace of $\mathbf{A}^\mu(\mathbf{ID})$ is computationally trivial because $\mathbf{A}^\mu$ is extremely sparse. $\mathbf{D}$, on the other hand, is typically quite dense (provided c is sufficiently dense). Since the dominant operation in this algorithm is the matrix multiplication $\mathbf{ID}$, the algorithm scales as Cn^4 [$\mathbf{I}$ is $(n^2\times n^2)$ and $\mathbf{D}$ is $(n^2\times C)$], where n is the number of CI basis functions (molecular orbitals) and C is the number of CSF's.

The pseudospectral method is a hybrid scheme which allows integrals to be calculated partly in physical space and partly in spectral space. Essentially, one defines a matrix $\mathbf{R}$ which acts on a spectral vector to give a physical space vector, and a matrix $\mathbf{Q}$, given most simply as $\mathbf{R}^{-1}$, which performs the inverse transformation. Then, the action of a spectral operator $\mathbf{O}_{\mathrm{sp}}$ is given as

$$\mathbf{O}_{\mathrm{sp}}=\mathbf{QO}_{\mathrm{ps}}\mathbf{R}, \tag{11}$$

where $\mathbf{O}_{\mathrm{ps}}$ is the physical space equivalent of the operator $\mathbf{O}_{\mathrm{sp}}$. In practice, $\mathbf{Q}$ is more complicated because dealiasing functions are used to project out spurious effects caused by the incompleteness of the basis set. The sole purpose of the dealiasing functions is to improve the accuracy of the pseudospectral approximation, and they appear only implicitly in $\mathbf{Q}$. In other words, they are used during the least-squares fitting of $\mathbf{Q}$ and then projected out.[12]

For our purposes, we can regard the pseudospectral approximation as follows:[13]

$$(ij|kl)= \sum_g Q_{ig}R_{jg}B_{kl}(g), \tag{12}$$

where $\mathbf{Q}$ and $\mathbf{R}$ are the matrices described above, the sum is over the grid points g, and $B_{kl}(g)$ is

$$\int \frac{\phi_k(\mathbf{r})\phi_l(\mathbf{r})}{|\mathbf{r}-\mathbf{r}_g|}d\mathbf{r}, \tag{13}$$

where ϕ_i is the ith basis function and $\mathbf{r}_g$ is the vector describing the position of the gth grid point. These are similar to three-center electron–nuclear attraction integrals, and methods for computing them are well known.

The two approaches described above can be combined to give a new way of calculating $\sigma_\mu^{(2)}$

$$\sigma_\mu^{(2)}=\tfrac{1}{2}\sum_{ijklg\kappa\nu} Q_{ig}R_{jg}B_{kl}(g) \langle\mu|\mathbf{E}_{ij}|\kappa\rangle\langle\kappa|\mathbf{E}_{kl}|\nu\rangle c_\nu. \tag{14}$$

Following Siegbahn, we define

$$I_{ij,g}^{1}=Q_{ig}R_{jg}, \tag{15}$$

$$I_{g,kl}^{2}=B_{kl}(g), \tag{16}$$

$$\sigma_\mu^{(2)}=\tfrac{1}{2}\operatorname{Tr}[\mathbf{A}^\mu\mathbf{I}^1\mathbf{I}^2\mathbf{D}]. \tag{17}$$

The $\mathbf{A}^\mu$ and $\mathbf{D}$ matrices remain the same as those defined in Eqs. (7) and (9). This scales as CMn^2, where M is the number of gridpoints used. As in the pseudospectral formulation of HF and GVB, since M is proportional to n, a scaling advantage of n is achieved.

IMPLEMENTATION AND RESULTS

We have implemented the algorithm specified by Eqs. (14)–(17) above. We use the algorithm of Shavitt[14] to generate the matrix elements between CSF's, $\langle\mu|\mathbf{E}_{ij}|\nu\rangle$. In order to overcome the difficulties associated with the lack of index symmetry in the pseudospectral integrals, Eq. (17) is rewritten as

$$\sigma_\mu^{(2)}=\tfrac{1}{4}\operatorname{Tr}[\mathbf{A}^\mu(\mathbf{I}^1\mathbf{I}^2\mathbf{D}+(\mathbf{I}^2)^t(\mathbf{I}^1)^t\mathbf{D})], \tag{18}$$

where the superscript t denotes matrix transposition, and Eq. (15) is rewritten as

$$\mathbf{I}_{ij,g}^{1}=\tfrac{1}{2}(Q_{ig}R_{jg}+R_{ig}Q_{jg}). \tag{19}$$

With these modifications, diagonalization schemes applicable to symmetric matrices may be used without difficulty. We have chosen to use the Davidson diagonalization scheme.[4] All calculations have been performed using the 6-31G** basis sets[15,16] in conjunction with the grids devel-

oped by Friesner and co-workers. The pseudospectral quantities $\mathbf{Q}$, $\mathbf{R}$, and $B_{kl}(g)$ were calculated in the atomic basis using the pseudospectral HF code of Friesner and co-workers,[17] and then transformed to the molecular basis using standard techniques. We have programmed Eqs. (4) and (7)–(10) for the spectral results[18–20] and Eqs. (4), (16), (18), and (19) to obtain the pseudospectral results.[21]

Unfortunately, although a formal scaling advantage of n is achieved, the pseudospectral code is slower than the spectral code for all cases presented here. The reason for this is apparent when one counts floating-point operations for the two algorithms. Firstly, the integral matrix $\mathbf{I}$ is really $[[n(n+1)/2]\times[n(n+1)/2]]$, not $(n^2\times n^2)$. This is because of the index symmetry of the integrals, which is incorporated into the algorithm for calculating $\sigma^{(2)}$ by calculating the matrix element $\langle\mu|E_{ij}|\nu\rangle$ as $\langle\mu|E_{ij}+[(1-\delta_{ij})E_{ji}]|\nu\rangle$.[7] Additionally, we require four matrix multiplications to form the properly symmetrized $\mathbf{ID}$ matrix. Therefore, the pseudospectral algorithm requires $4CM[n(n+1)/2]$ operations. The spectral algorithm requires $C[n^2(n+1)^2/4]$ operations. The break even point for the pseudospectral algorithm is reached when

$$M=\frac{n(n+1)}{8}. \qquad (20)$$

In the cases we report here, the number of molecular orbitals is 14 or 15. This requires M to be less than 30 for any reduction in the number of floating-point operations. The grids used are typically 200–300 points (these are referred to as the medium grids by Friesner and co-workers). The pseudospectral code takes the same number of iterations to reach convergence as the spectral code for all cases tested. Thus, we expect the pseudospectral code to be approximately 10 times slower than the spectral code, and this is in fact the case. Although this is very disappointing, we expect advances in pseudospectral methodology will lead to decreased grid sizes in the future, at which point the algorithm presented here will become viable for common full-CI calculations.

Given the above, it is useful at this point to distinguish between two types of CI calculations. First, there is the complete active space CI (CASCI) which is generally used to account for the dominant correlation effects. This philosophy mandates a full-CI expansion in a small space of active orbitals, generally not exceeding $O(10)$ orbitals. Secondly, there are benchmark full-CI calculations. These are meant to provide exact answers subject only to the neglect of relativistic effects, the Born–Oppenheimer approximation, and the incompleteness of the basis set. It is clear that the pseudospectral full-CI method will rarely be of interest for CASCI calculations. The exception to this is when a pseudospectral HF calculation is performed on a molecule with $O(100)$ basis functions, and a CASCI calculation is desired. This situation could easily arise if one were studying some chemical process involving a large molecule. A spectral CASCI calculation would require the formation of all the spectral integrals, which would take a prohibitive amount of CPU time. With our method, there is no need to

calculate the spectral integrals. The CI calculation would take longer pseudospectrally, but the combined time of integral calculation and solution of the CI problem would be less. On the other hand, if the original HF calculation was done spectrally, and the integrals are available on mass storage, it would be impractical to use the pseudospectral full-CI algorithm presented here.

Benchmark full-CI calculations have been performed with up to 30 orbitals.[22] Our algorithm is mainly designed for these types of calculations, but without further reductions of the grid size, it will still show no benefits at 30 orbitals. We have not attempted to optimize atomic grids for full-CI results, but this might allow the use of much smaller grids for a given accuracy.

Given that this new algorithm is only appropriate in special situations at present, we must ask whether it is accurate enough. Comparison of the spectral and pseudospectral total energies for a number of first-row atoms are given in Table I, along with the overlap of the pseudospectral and spectral CI vectors. It is evident that the pseudospectral approximation is quite good for carbon, but deteriorates going to the right of the periodic table. Although this is almost certainly not fortuitous, we are not sure of the cause. Possibly, it is simply a reflection of the fact that the grid for carbon has been much more extensively optimized than others. It may also be related to the contraction of the SCF atomic orbitals as one progresses to the right of the periodic table. Like all numerical integration schemes, the pseudospectral method has the most difficulty integrating rapidly varying functions. However, this has not caused serious problems for pseudospectral HF, so we are unsure of the relevance of that argument here.

We have investigated two ways to improve the accuracy of the pseudospectral method at relatively little cost. The first involves the calculation of the core–valence interaction spectrally. The core–valence interaction is added to the one-electron integrals, and the resulting effective one-electron potential integrals are conventionally calculated as

$$F_{ab}^{C-V}=(a|h|b)+\sum_{\gamma=1}^{N_F}[2(\gamma\gamma|ab)-(\gamma a|\gamma b)], \qquad (21)$$

where N_F is the number of frozen core orbitals. This can be calculated pseudospectrally as

$$F_{ab}^{C-V}=(a|h|b)+\sum_{g}\sum_{\gamma=1}^{N_F}[I_{\gamma\gamma,g}^1 I_{g,ab}^2+I_{ab,g}^1 I_{g,\gamma\gamma}^2$$
$$-\tfrac{1}{2}(I_{\gamma a,g}^1 I_{g,\gamma b}^2+I_{\gamma b,g}^1 I_{g,\gamma a}^2)]. \qquad (22)$$

When we calculate the core–valence interaction spectrally, we mean to say that we have used Eq. (21) instead of Eq. (22). In principle, this requires the calculation of all of the spectral two-electron integrals (because a, b, and γ are all molecular orbital indices), but in practice $O(N^2m^2)$ integrals must be evaluated, where N is the total number of atomic orbitals, and m is the number of atomic orbitals which contribute to one of the frozen core molecular orbitals. Since frozen core orbitals are typically quite localized, m will usually be significantly less than N. For benchmark type full-CI calculations, the calculation of spectral

TABLE I. Spectral and pseudospectral full-CI total energies for various atoms and ions. The energies are in hartrees and all calculations employed a 6-31G** basis set.

| Species | | #SEFs[b] | Spectral | Pseudospectral | | $E^{(1)}$ [d] | | $\langle \Psi^P | \Psi^S \rangle$ [e] |
				Error	Error (mH)[c]	Energy	Error (mH)[c]	
^3P C	(all orbitals)	98 280	−37.756 50	−37.756 74	−0.24	−37.756 50	<0.01	0.999 999 4
^3P C	(1s frozen)[a]	4 095	−37.752 90	−37.752 61	0.29	−37.752 90	<0.01	0.999 999 4
^2P C+	(all orbitals)	27 300	−37.359 34	−37.359 30	0.04	−37.359 33	0.01	0.999 999 5
^2P C+	(1s frozen)[a]	910	−37.356 07	−37.356 06	0.01	−37.356 07	<0.01	0.999 999 5
^4S C−	(all orbitals)	240 240	−37.742 34	−37.742 01	0.33	−37.742 33	0.01	0.999 999 4
^4S C−	(1s frozen)[a]	12 012	−37.738 51	−37.738 18	0.33	−37.738 51	<0.01	0.999 999 4
^4S N	(all orbitals)	240 240	−54.476 29	−54.480 36	−4.07	−54.476 27	0.02	0.999 993 6
^4S N	(1s frozen)[a]	12 012	−54.473 55	−54.477 68	−4.13	−54.473 54	0.01	0.999 993 8
^3P N+	(all orbitals)	98 280	−53.952 04	−53.956 85	−4.81	−53.952 03	0.01	0.999 995 4
^3P N+	(1s frozen)[a]	4 095	−53.949 58	−53.954 44	−4.86	−53.949 57	0.01	0.999 995 5
^3P O	(1s frozen)[a]	63 063	−121.817 55	−121.810 20	7.35	−121.817 31	0.24	0.999 970 4
^1S Ne	(1s frozen)[a]	273 273	−128.628 63	−128.599 42	29.21	−127.627 51	1.12	0.999 866 0
^2P Ne+	(1s frozen)[a]	182 182	−127.857 53	−127.826 91	30.62	−127.856 38	1.15	0.999 803 2

[a] The 1s orbital was constrained to be doubly occupied in all configurations.
[b] #SEFs=number of spin eigenfunctions in the full CI expansion.
[c] 1 mH = 10^{-3} hartree. Error=E(pseudospectral)−E(spectral).
[d] $E^{(1)}$ = First order perturbation theory total energy. See text for details.
[e] Ψ^P is the pseudospectral CI vector and Ψ^S is the spectral CI vector.

integrals is not a disadvantage, since the CPU time required for the CI will far outweigh the cost of the integral evaluation. However, it would be difficult to use Eq. (21) for CASCI calculations in a severely truncated orbital subspace, because the number of integrals that need to be evaluated is dependent on the size of the full orbital space. The time required for the actual CI calculation does not depend at all on which of Eqs. (21) or (22) is used, as this is part of the integral transformation. We have done this only for the calculations where the 1s atomic orbital was kept doubly occupied in all configurations. The results are given in Table II. We find the error decreases by an order of magnitude, which implies that the CI energy is very sensitive to the accuracy of the integrals involving the tight 1s function. Friesner and co-workers have observed similar behavior for HF and GVB applications.[23] The procedure works very well, but is rather arbitrary since the extent to which the spectral results are mimicked depends on the orbital set chosen to remain doubly occupied.

The second approach is to calculate the energy in the first order of perturbation theory, where the perturbation is the difference between the pseudospectral and spectral

Hamiltonians. Thus, we simply calculate the spectral energy of the pseudospectral CI vector, $\langle \Psi^P | H^S | \Psi^P \rangle$, as the energy correct through first order in the perturbation. This procedure is aesthetically pleasing and the resulting energy is a rigorous upper bound. The results are in Table I, under the heading $E^{(1)}$. The drawbacks to this procedure are that one iteration of a spectral direct CI must be performed and the full set of spectral integrals must be evaluated. Since it usually takes about ten iterations for a direct full-CI calculation, this perturbed pseudospectral full-CI method will never be more than 10 times faster than a spectral calculation, regardless of grid or basis set size. For now, this is of no concern, but when calculations with large basis sets are attainable, it will be a severe disadvantage. Unlike the calculations which used the spectral core–valence interaction, there are no significant economies possible in spectral integral evaluation, and this correction is therefore not at all suited to CASCI calculations in severely truncated orbital spaces.

SUMMARY

We have presented a direct full-CI approach in a pseudospectral formalism. A formal scaling advantage of n is achieved, but our calculations are slower pseudospectrally because of the large grids we have used. The method is accurate to about a millihartree if first-order perturbation theory is subsequently applied, with errors ranging from 0.01–1.15 millihartrees in the cases tested. Without the first-order correction, the energy is not a rigorous upper bound and the error with respect to the spectral calculation ranges from 0.01–30.62 millihartrees. We have also explored the use of spectral integrals to calculate the core–valence interaction for cases where the 1s orbital was kept doubly occupied. The error for this level of approximation ranges from 0.01–2.77 millihartrees.

TABLE II. Spectral and pseudospectral full-CI total energies for various atoms. The energies are in hartrees and all calculations employed a 6-31G** basis set. The core–valence interaction for the pseudospectral cases is calculated using spectral integrals. In all cases, the 1s molecular orbital is kept doubly occupied in all configurations.

Species	Spectral	Pseudospectral	Error (mH)
^3P C	−37.752 90	−37.752 74	0.16
^2P C+	−37.356 07	−37.356 05	0.02
^4S C−	−37.738 51	−37.738 34	0.17
^4S N	−54.473 55	−54.472 92	0.63
^3P N+	−53.949 58	−53.949 06	0.52
^1S Ne	−128.628 63	−128.631 22	−2.59
^2P Ne+	−127.857 53	−127.860 30	−2.77

The accuracy attained with the perturbative calculations suggests that the pseudospectral method shows promise for other types of CI expansions that do not exhibit the factorial dependence of the number of configurations on n. Development of such methods is in progress.[24] While the method at present is of limited use, we expect that advances in pseudospectral methodology will lead to smaller grids for a given accuracy, at which point the method may become viable for general use.

ACKNOWLEDGMENTS

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