LETTER TO THE EDITOR

Convergence improvement for coupled cluster calculations

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Abstract. Convergence problems in coupled-cluster iterations are discussed, and a new iteration scheme is proposed. Whereas the Jacobi method inverts only the diagonal part of the large matrix of equation coefficients, we invert a matrix which also includes a relatively small number of off-diagonal coefficients, selected according to the excitation amplitudes undergoing the largest change in the coupled cluster iteration. A test case shows that the new IPM (inversion of partial matrix) method gives much better convergence than the straightforward Jacobi-type scheme or such well-known convergence aids as the reduced linear equations or direct inversion in iterative subspace methods.

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The coupled cluster (CC) method is widely used in electronic structure calculations. The CC theory has been described in many reviews (see, e.g., [1, 2, 3, 4, 5]), and will not be presented here. The basic equation for the CC method is the Bloch equation

\[ \Omega H \Omega = H \Omega, \]  

(1)

where \( H \) is the Hamiltonian and \( \Omega \) is the wave operator. The resulting equations have the general algebraic form

\[ A_i + \sum_{j=1}^{N} B(t)_{ij} t_j = 0, \quad i = 1, 2, \ldots, N, \]  

(2)

where \( t_j \) are the cluster or excitation amplitudes to be determined, \( N \) is the number of the unknown amplitudes, \( A \) is a vector and \( B(t) \) is a square matrix which in general depends upon \( t \). For simplicity, we consider the case when \( B \) does not depend upon \( t \),

\[ A_i + \sum_{j=1}^{N} B_{ij} t_j = 0, \quad i = 1, 2, \ldots, N. \]  

(3)

The generalization for the case of \( B(t) \) is straightforward (and implemented in the relativistic CC code employed for the test examples below). The direct solution of equations (3) using the Gauss elimination method is feasible only for systems with a few thousand cluster amplitudes at most, whereas problems encountered in our relativistic CC may involve millions of such amplitudes. A Jacobi-type iterative method is usually applied to solve these equations. Using the fact that \( B \) is normally a diagonally dominant matrix, the method involves direct inversion of the diagonal part \( D \) of \( B \). The system (3) is rewritten in the form

\[ t_i = -(D^{-1})_{ii}[A_i + \sum_{j=1}^{N} (B - D)_{ij} t_j], \quad i = 1, 2, \ldots, N \]  

(4)

and is solved iteratively.

The coupled cluster calculations are often beset by convergence difficulties. This is particularly true for multireference CC methods, such as the Fock-space approach [2, 3]. Several methods for improving convergence have been proposed; the most commonly used are the reduced linear equations (RLE) [6] and direct inversion in the iterative subspace (DIIS) [7, 8] approaches. These help in some, but not all, cases. Most severe convergence problems may be traced to the existence of intruder states. While increasing the model (or \( P \)) space improves the quality of the calculation by including a larger part of the correlation, it also increases the probability of encountering intruder states and getting no valid results at all. New methods for improving convergence are therefore highly desirable. One such method is presented in this Letter.

The problem may be illustrated by an example taken from recent work [9], where ground and excited state energies of \( \text{Hg} \) and its ions were calculated by the relativistic coupled cluster method. The 5\( d^{10} \) ground state of the \( \text{Hg}^{2+} \) ion served as the reference state, and the Fock-space CC scheme was

\[ \text{Hg}^{2+}[(0)\text{sector}] \rightarrow \text{Hg}^+[(1)\text{sector}] \rightarrow \text{Hg}[(2)\text{sector}], \]  

(5)
with electrons added in the 6s and 6p orbitals, designated as valence particles. While the calculations in [9] were relativistic, the nonrelativistic notation will be employed for brevity. The model space in the (1) sector, with one valence particle, consisted of determinants with $5d^{10}6s^1$ and $5d^{10}6p^1$ configurations. Adding the 7s, 7p, and 6d orbitals to the list of valence particles would yield more state energies in the (1) sector, as well as better description of the 6s 16p 1 configurations. Adding the 7s, 7p, and 6d orbitals to the list of valence particles would yield more state energies in the (1) sector, as well as better description of the 6s 16p 1 configurations. The calculation of all matrix elements will therefore cause large changes in the amplitudes on the left hand side, leading to divergence.

Analysis shows that the divergence is caused by the 5d 6s 16p 1, 5d 6s 2 and other intruder states from the complementary Q space, which are close in energy to certain P states (5d 10 7p 1, 5d 10 6d 1, and others). The diagonal elements $B_{ii}$ of the matrix $B$ correspond to differences between the total energies of the $P$ and $Q$ determinants connected by the $t_i$ excitations. Some of these elements will be very small in this case, leading to large elements in $D^{-1}$. Small changes in $t$ amplitudes on the right hand side of equations (4) will therefore cause large changes in the amplitudes on the left hand side, leading to divergence.

We propose to overcome this problem by replacing the $D$ matrix by $D'$ which includes, in addition to the diagonal elements of $B$, those nondiagonal $B$ elements which are large in comparison with corresponding diagonal elements. The calculation of all $B$ matrix elements is impractical, and a selection procedure for nondiagonal elements to be included in $D'$ is described below. This new matrix is constructed so that its matrix elements, $D'_{ij}$, are equal to or approximate the $B_{ij}$ matrix elements both for $i = j$ and for $i, j \in I$, where $I$ is some small subset of the amplitudes. The other nondiagonal $D'_{ij}$ matrix elements ($i \notin I$ or $j \notin I$) are set to zero. The method involves the inversion of the partial matrix (IPM) $D'$. A modified form of the system of equations (4),

\[
t_i = - \sum_{k=1}^{N} (D'^{-1})_{ik} [A_k + \sum_{j=1}^{N} (B - D')_{kj} t_j], \quad i = 1, 2, \ldots, N
\]  

(6)

is obtained and solved iteratively. Equations (6) can be divided into two sets,

\[
t_i = - \sum_{k \in I} (D'^{-1})_{ik} [A_k + \sum_{j=1}^{N} (B - D)_{kj} t_j - \sum_{j \in I} (D' - D)_{kj} t_j], \quad i \in I, \quad (7)
\]

\[
t_i = -(D'^{-1})_{ii} [A_i + \sum_{j=1}^{N} (B - D)_{ij} t_j - (D' - D)_{ii} t_i], \quad i \notin I, \quad (8)
\]

where the second part is similar to equations (4).

The size of the subset $I$ must be kept small, so that the calculation (the most time-consuming step), storage and manipulation of the non-zero off-diagonal $D'$ elements remains feasible. Careful selection of the amplitudes to be included in $I$ is therefore of paramount importance. The algorithm followed here starts with calculating the $t_i$ amplitudes by the standard iteration scheme (4). The amplitudes which have undergone the largest changes are included in $I$, the corresponding $D'_{ij}$ matrix elements are evaluated, and the $t_i$ amplitudes in $I$ are recalculated by equations (7). The dimension
$M$ of the $I$ subset was kept at 1000, which makes the calculation and manipulation of $D'$ feasible. Optimal algorithms for determining $M$, selecting excitations to be included in $I$, and calculating the $D'$ matrix will be studied in the future.

It should be noted that the system (3) is equivalent to the standard equations (4) in the limit $M = 0$; in the limit $M = N$, scheme (3) converges in one iteration, if one takes $D'_{ij} = B_{ij}$,

$$t_i = -\sum_{k=1}^{N} (B^{-1})_{ik} A_k, \quad i = 1, 2, \ldots, N.$$  \hspace{1cm} (9)

Formally, one can always achieve convergence of the iterations (3) by increasing $M$. The IPM method proposed here may be combined with other procedures for accelerating convergence, such as the reduced linear equations [3] and direct inversion in the iterative subspace [4, 5] methods. This has not been done in the present application, and will be tried in the future. It should be mentioned that the identification of the resulting high-lying levels may require careful analysis of the $t$ amplitudes, particularly if some of the latter are large, indicating large contributions of $Q$ configurations. Finally, it should be noted that the IPM scheme described above may be regarded as adopting the Gershgorn-Shavitt $A_k$ perturbation theory approach rather than that of $A_0$ [10].

The different iteration schemes were tested for the 33-electron relativistic Fock-space CC calculation with single and double cluster amplitudes of Hg$^+$ levels in the $(spdfg)$ basis from [3] in the framework of the Dirac-Coulomb Hamiltonian. Two model spaces were used, one consisting of determinants with $5d^{10}6s^1$ and $5d^{10}6p^1$ configurations, the other including in addition the $5d^{10}7s^1$, $5d^{10}7p^1$, and $5d^{10}6d^1$ configurations. All iterations involved 1:1 damping (the input amplitudes for iteration $n + 1$ were taken as the average of input and output amplitudes of iteration $n$). The IPM scheme is compared with the standard scheme (4) and with the RLE [3] and DIIS [4, 5] methods in tables 1 and 2. The RLE and DIIS methods used the output of the last five iterations to form the new input vector. All methods led to convergence for the small model space (table 1). The RLE, DIIS, and IPM schemes were about equally effective in reducing the number of iterations required. The large model space (table 2) shows markedly different behavior for the different methods. Straightforward iteration by the Jacobi-type method blows up almost immediately; the large excitation amplitudes may be traced to the intruder states mentioned above. The RLE and DIIS schemes exhibit better behavior, but could not achieve convergence even after several hundred iterations. Only the IPM approach proposed in this Letter led to convergence (in the 29th iteration), showing the potential of the method.

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Tables and table captions

**Table 1.** The largest change in the single and double cluster amplitudes $(\max_{i=1}^{N} |t_i^{(n+1)} - t_i^{(n)}|)$ at iteration $n$. The changes are obtained by equations (4) in the RCC calculations with the Jacobi-type, RLE, DIIS and IPM iteration schemes. The model space consists of determinants with $5d^{10}6s^1$ and $5d^{10}6p^1$ configurations. The convergence threshold is $10^{-6}$.

| Iteration | Jacobi       | RLE          | DIIS         | IPM          |
|-----------|--------------|--------------|--------------|--------------|
| 0         | $1.62 \cdot 10^{-1}$ | $1.62 \cdot 10^{-1}$ | $1.62 \cdot 10^{-1}$ | $1.62 \cdot 10^{-1}$ |
| 3         | $2.99 \cdot 10^{-2}$  | $2.99 \cdot 10^{-2}$  | $2.59 \cdot 10^{-2}$  | $1.30 \cdot 10^{-2}$  |
| 6         | $1.39 \cdot 10^{-2}$  | $1.41 \cdot 10^{-3}$  | $1.10 \cdot 10^{-3}$  | $1.38 \cdot 10^{-3}$  |
| 9         | $6.65 \cdot 10^{-3}$  | $6.81 \cdot 10^{-4}$  | $1.21 \cdot 10^{-4}$  | $2.01 \cdot 10^{-4}$  |
| 12        | $3.19 \cdot 10^{-3}$  | $1.69 \cdot 10^{-5}$  | $1.12 \cdot 10^{-5}$  | $3.60 \cdot 10^{-5}$  |
| 15        | $1.54 \cdot 10^{-3}$  | $8.42 \cdot 10^{-6}$  | $5.15 \cdot 10^{-6}$  | $7.01 \cdot 10^{-6}$  |
| 18        | $7.53 \cdot 10^{-4}$  | $9.47 \cdot 10^{-7}$  | $2.43 \cdot 10^{-6}$  | $1.43 \cdot 10^{-6}$  |
| 21        | $3.72 \cdot 10^{-4}$  | convergence    | $1.15 \cdot 10^{-6}$  | convergence    |
| 24        | $1.86 \cdot 10^{-4}$  | convergence    | convergence    |              |
| 27        | $9.46 \cdot 10^{-5}$  |              |              |              |
| 30        | $4.87 \cdot 10^{-5}$  |              |              |              |
| 33        | $2.53 \cdot 10^{-5}$  |              |              |              |
| 36        | $1.34 \cdot 10^{-5}$  |              |              |              |
| 39        | $7.11 \cdot 10^{-6}$  |              |              |              |
| 42        | $3.82 \cdot 10^{-6}$  |              |              |              |
| 45        | $2.07 \cdot 10^{-6}$  |              |              |              |
| 48        | $1.13 \cdot 10^{-6}$  |              |              |              |
| convergence|              |              |              |              |
Table 2. Same as Table 1, except that the model space is larger, consisting of determinants with $5d^{10}6s^1$, $5d^{10}6p^1$, $5d^{10}7s^1$, $5d^{10}7p^1$, and $5d^{10}6d^1$ configurations.

| Iteration | Jacobi     | RLE        | DIIS       | IPM        |
|-----------|------------|------------|------------|------------|
| 0         | $2.14 \cdot 10^{-1}$ | $2.14 \cdot 10^{-1}$ | $2.14 \cdot 10^{-1}$ | $2.14 \cdot 10^{-1}$ |
| 3         | $7.54 \cdot 10^{-1}$  | $7.54 \cdot 10^{-1}$  | $6.93 \cdot 10^{-1}$  | $9.38 \cdot 10^{-2}$  |
| 6         | $2.61$      | $5.18 \cdot 10^{-1}$ | $1.22 \cdot 10^{-1}$ | $1.21 \cdot 10^{-2}$ |
| 9         | $9.31$      | $1.82$      | $5.75 \cdot 10^{-2}$ | $1.25 \cdot 10^{-3}$ |
| 12        | $3.42 \cdot 10^{1}$ | $2.73 \cdot 10^{-1}$ | $3.20 \cdot 10^{-2}$ | $3.19 \cdot 10^{-4}$ |
| 15        | $1.24 \cdot 10^{2}$ | $5.65 \cdot 10^{-1}$ | $2.90 \cdot 10^{-2}$ | $7.39 \cdot 10^{-5}$ |
| 18        | $4.45 \cdot 10^{2}$ | $1.80 \cdot 10^{1}$  | $2.87 \cdot 10^{-2}$ | $1.61 \cdot 10^{-5}$ |
| 21        | $1.54 \cdot 10^{3}$ | $2.77 \cdot 10^{-1}$ | $3.06 \cdot 10^{-2}$ | $1.04 \cdot 10^{-5}$ |
| 24        | $5.00 \cdot 10^{3}$ | $1.01$      | $2.55 \cdot 10^{-2}$ | $9.55 \cdot 10^{-6}$ |
| 27        | $1.49 \cdot 10^{4}$ | $1.46 \cdot 10^{-1}$ | $2.19 \cdot 10^{-2}$ | $3.64 \cdot 10^{-6}$ |
| 30        | $3.93 \cdot 10^{4}$ | $5.51 \cdot 10^{-1}$ | $2.23 \cdot 10^{-2}$ | convergence |
| 33        | $9.08 \cdot 10^{4}$ | $2.40 \cdot 10^{-1}$ | $1.93 \cdot 10^{-2}$ |            |
| 36        | $1.88 \cdot 10^{5}$ | $1.73 \cdot 10^{-1}$ | $1.99 \cdot 10^{-2}$ |            |
| 39        | $3.61 \cdot 10^{5}$ | $4.91 \cdot 10^{-1}$ | $1.36 \cdot 10^{-2}$ |            |
| 42        | $6.70 \cdot 10^{5}$ | $2.95 \cdot 10^{-1}$ | $1.62 \cdot 10^{-2}$ |            |
| 45        | $1.22 \cdot 10^{6}$ | $6.04 \cdot 10^{-1}$ | $1.44 \cdot 10^{-2}$ |            |
| 48        | $2.22 \cdot 10^{6}$ | $5.00 \cdot 10^{-1}$ | $1.45 \cdot 10^{-2}$ |            |

divergence  no convergence  no convergence