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Fast ESR Matrix Diagonalization

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The Gaussian condensation (GC) method of numerical matrix diagonalization is described, and some of its advantages and limitations discussed. It is particularly useful as an aid to the fast precise calculation of ESR line positions and intensities, and is especially suitable when large complex Hermitian ESR spin-Hamiltonian matrices are involved in iterative fitting procedures.

1. INTRODUCTION

Line positions and strengths need to be calculated when analyzing ESR spectra. The magnetic field at which a resonance occurs is associated with the eigenvalues of an appropriate spin-Hamiltonian matrix, and the transition probability is obtained from the dipole moment matrix. Both matrices are usually set up in a nondiagonal representation, and the eigenvectors of the spin-Hamiltonian are needed for transformation of the dipole moment into a diagonal representation.

Reported methods of numerically computing eigenvalues and eigenvectors for ESR purposes involve standard procedures [1] such as Jacobi [2] or the faster Householder [3]. If the spin-Hamiltonian matrix is real, these have been applied directly; if it is complex Hermitian, they have been used [2, 3] with the augmented (doubled order) matrix formed from the real and imaginary parts [1, 4], thus avoiding complex arithmetic but at the cost of increased computation time.

Householder's method for complex matrices has been described by Mueller [5]. His procedures "Householder Hermitian" and "Reverse," together with procedures for the QR algorithm as described by Businger [6] and Welsch [7], have been used for some time in this laboratory to handle complex Hermitian matrices. Programmed (by Joan D. Hayhurst, CSIRO Division of Computing Research) as a FORTRAN routine named HERMQR, the combination is general and efficient, provides accurate eigenvalues and eigenvectors, and is capable of handling degeneracies. As discussed below, it has also been used to complement the method which is the main topic of this paper and whose performance will be compared with it.

For relatively large problems—in particular, Mn^{2+} ESR spectra [8] involving 36×36 irreducible complex Hermitian matrices—computation methods substantially faster than HERMQR are required. Speed is important because successive-approximation methods (as usually applied to fitting spin-Hamiltonian parameters) involve repetition of the calculation of a whole spectrum (or set of spectral lines), while the basic process of calculating single ESR line positions and intensities itself requires iterative procedures and hence multiple diagonalizations.

The main computational load arises because in ESR spectroscopy the stimulating radiation frequency ν is fixed, and resonance is achieved by varying the external magnetic field H and, with it, the energy levels. Thus H appears explicitly in the Hamiltonian matrix, and for *each* individual transition observed (or required to be calculated) a fresh matrix has to be formed and the relevant eigenvalues computed. In the Mn^{2+} case, with $S = I = 5/2$, there are 15 possible fine-structure transitions ($\Delta M = -1$ through -5, with $\Delta M = 0$ not counted), each with 36 possible hyperfine components, so that a total of 540 field-determining calculations may have to be made for one set of spin-Hamiltonian parameters.

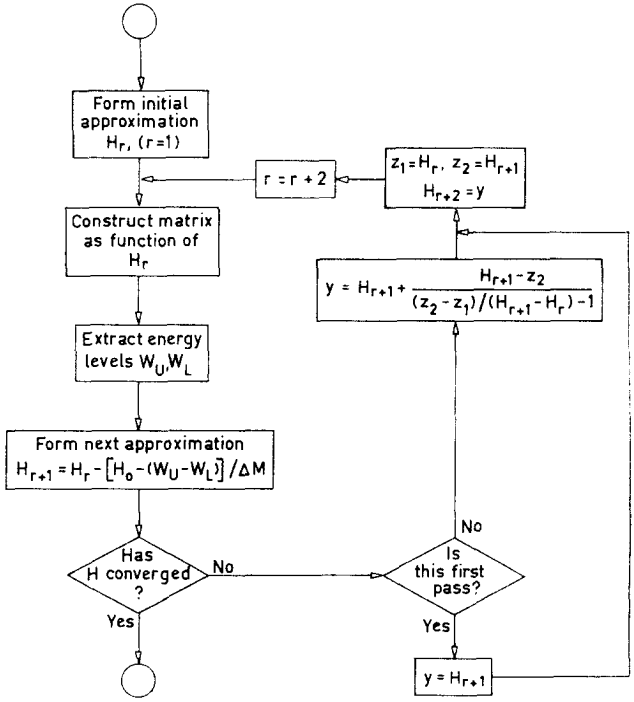

FIG. 1. Basic procedure, including convergence acceleration, for finding line position H as $(r + 1)$-th successive approximation.

Furthermore, iterative procedures are required for each individual line, whose position H is such that the corresponding upper and lower energy levels W_U and W_L (each a function of H) satisfy the resonance condition $W_U - W_L = W_0$, with $W_0 = H_0 = h\nu/g\beta$, where energy is measured in magnetic field units and H_0, h, g, and β have their usual meanings. Determination of H may be carried out by the successive-approximation method indicated in the flowchart of Fig. 1, with convergence accelerated by a variation of the Aitken technique [1]. The initial approximation to H is conveniently obtained from closed perturbation theory formulas.

Only when the line position H finally has been found do the eigenvectors associated with the energy levels need to be computed, so that line strengths can then be calculated.

For computing eigenvalues and eigenvectors, this paper describes procedures that are simpler and faster than those previously reported in ESR studies, and which may also be used in similar types of problems.

2. The GC Method

The key to improving computation speed is the fact that only two eigenvalues are required from a single matrix; some standard diagonalization methods provide a complete solution, most of which is irrelevant to the usual ESR problem. Further, good initial approximations to the ESR eigenvalues can frequently be obtained by perturbation theory.

A single specified eigenvalue may be obtained by an adaptation of the Gaussian elimination method of solving simultaneous equations (described in most books on numerical analysis), and will be referred to here as the "GC method" (for Gaussian condensation). The principle was suggested originally by Badger (quoted in Ref. [10]) and evolved into the "continued-fraction method," well known in molecular spectroscopy [9].

Applied to the determination of the n-th eigenvalue of the m-th order matrix $X = [X_{jk}]$, the basic algorithm [10] of the GC method is: (1) A trial eigenvalue λ is subtracted from all diagonal elements except the n-th; (2) the resulting matrix is effectively reduced to triangular form by Gaussian elimination, in such a fashion as to condense the off-diagonal contributions on to the n-th diagonal element. The ultimate value X'_{nn} of the latter is then the required eigenvalue, provided X'_{nn} equals λ to within an acceptable small factor ϵ, say. If X'_{nn} is not close enough to λ, then X'_{nn} is used as a new trial value, and the process iterated until convergence is achieved.

The analytical basis of the method follows from the fact that if the n-th eigenvalue λ_n is subtracted from all diagonal elements of X, the resulting secular deter-

minant vanishes. Triangularization in the manner just described then requires that $X'_{nn} - \lambda_n = 0$, i.e., that $X'_{nn} = \lambda_n$.

Further detail is indicated in the flowchart of Fig. 2. Complex arithmetic operations on off-diagonal elements, as required for complex Hermitian matrices, are easily included. Operations (in CLEAR of Fig. 2) on zero off-diagonal elements may be skipped readily if time for computer logical testing is significantly shorter than for arithmetic operations, and thus needless work on sparse ESR matrices can be avoided. All operations are carried out in the manifold of X, and no auxiliary storage space is needed. The matrix is destroyed by each iteration. For real nonzero elements, there are approximately $m^3/3$ subtractions and $m^3/3$ multiplications plus divisions involved per iteration. Convergence of the process may be accelerated by using techniques described elsewhere [11].

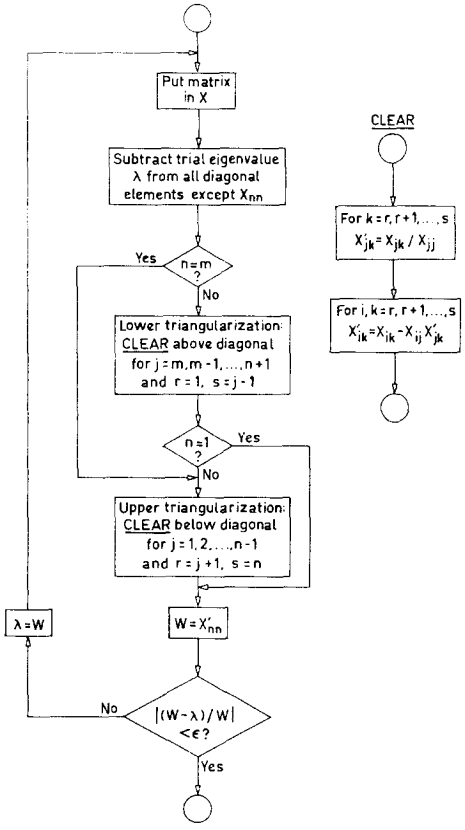

FIG. 2. Basic GC routine for extracting n-th eigenvalue W, to precision ϵ, from m-th order matrix X.

When the eigenvalue has been obtained, back-substitution in the triangulated matrix gives the associated eigenvector, if required.

EIGHERM is the name given to a FORTRAN routine (of which a listing is available from the author) incorporating the above simple processes. For a 36×36 complex Hermitian matrix, with about two-thirds of the elements nonzero, HERMQR requires, on a CDC3600 computer, about 25 sec to extract all the eigenvalues and eigenvectors. EIGHERM needs about 0.5 sec per iteration, with 4–6 iterations (total, to obtain a pair of eigenvalues and eigenvectors) predominating under favorable conditions (good initial perturbation approximations), thus providing a most useful timesaving factor of about 10. On a CDC6600, the times are reduced by a factor of 4 to 5.

3. Use of the GC Method

Matrices having degenerate eigenvalues cannot be handled directly, but this does not cause any difficulties with ESR problems.

In ESR spectroscopy, the Hamiltonian matrix is usually constructed in a representation in which the Zeeman energy is diagonal and where the principal contribution to the nuclear interaction is also diagonal except for terms connecting different fine-structure states. States are labeled by the expectation values of the electron and nuclear spin angular momenta along their respective axes of quantization in this representation. These labels are good quantum numbers in a high-field situation where, for large H, the predominant energy contribution is the diagonal Zeeman term. In high-field, the matrix is then nearly diagonal, the diagonal elements are good approximations to the eigenvalues and may be used as initial trial values λ in applying the GC method, and the convergence is fast; better λ's for initial approximations are, however, readily obtained by perturbation theory.

The number of iterations required for convergence depends on the precision demanded, that is, the value of ϵ chosen. For most ESR work, values of 10^{-4}–10^{-6} are quite adequate for comparison with experimental observations.

When the representation is not a good one, such as in low- and intermediate-field cases where considerable mixing of states occurs (sometimes leading to level crossing), even second-order perturbation theory may not give a sufficiently good initial approximation to the eigenvalue to allow the GC method to converge to the wanted level. Incorrect convergence can be detected manually by comparison of results with a rough energy-level diagram (or table) obtained by using a safe method (such as HERMQR); this is worthwhile when iterative fitting processes are involved and exploratory calculations form only a small part of the overall computing load. Automatic checking can be done by using EIGHERM to carry

out the bulk of the calculation, its final answer then being checked against HERMQR (or similar). In practice, with the Mn^{2+} problem mentioned, it was found that incorrect convergence was associated with an excessive number of GC iterations, and the empirically chosen iteration-count value 5 was used to indicate whether EIGHERM should be abandoned in favor of HERMQR. In regions where EIGHERM was known to fail occasionally, a mixed procedure, outlined in the flowchart of Fig. 3 and guaranteeing a correct result, was then always able to provide significant overall timesaving.

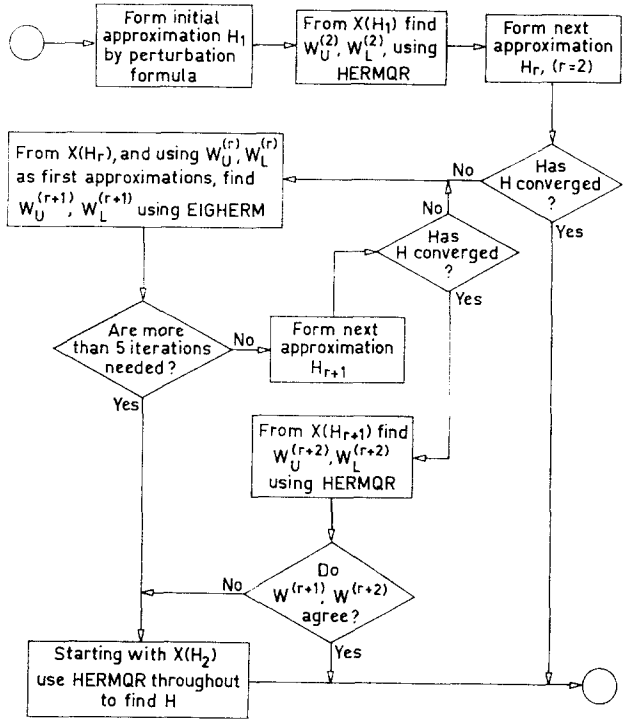

FIG. 3. Outline of mixed procedure for finding line position H, using EIGHERM where possible, and HERMQR for checking and backup (other checking/backup routines could be employed).

For high-field cases, the GC method on its own is a simple, fast, and accurate aid to the computation of ESR line positions and strengths. When the usual Hamiltonian representation is not a good one, the GC method can still be employed efficiently, in a mixed procedure, on problems where computing load is an important factor.

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