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A new method for diagonalising large matrices

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of eigenvalues sought: even if only the lowest few eigensolutions are needed, the computational effort involved is close to that required for *all* eigensolutions.

There are many problems of physical interest for which such difficulties with the CH method can become acute. Many quantum mechanical Hamiltonian problems require only the lowest few eigensolutions to very large matrices whose elements $\langle \phi_i | \boldsymbol{H} | \phi_j \rangle$ are easy to calculate, but which possess no simple systematics (e.g. they are not diagonally dominant or sparse). Such is the case, for example, in ground-state electronic structure calculations for molecules, solids and surfaces, where our relative [illegible]

2. Iterative methods for large matrix diagonalisation

2.1. Background

[redacted]

where we have used the linearity of the residual operator. Unfortunately, the formal solution

$$|\delta A\rangle = -(\boldsymbol{H} - E^{\mathrm{ap}}\boldsymbol{S})^{-1}|R(|A^{\mathrm{ap}}\rangle, E^{\mathrm{ap}})\rangle \tag{2.8}$$

is no easier to solve than the original eigenproblem because of the need for matrix

The expansion set $\{|b_i\rangle\}$ requires further explanation. Like the other basis expansion methods, DIIS uses a Newton step, equation (3.3), to generate a new vector $|\delta A\rangle$ which is then added to $\{|b_i\rangle\}$. The elements of this set are thus the $|\delta A\rangle$ generated in each of the preceding iterations, so that DIIS clearly incorporates information from the entire iteration history for the given eigenvector being refined. Since the vectors $\{|\delta A^{(i)}\rangle\}$ are

using the stored values of the $\{\boldsymbol{H}|\delta\boldsymbol{A}^{(k)}\rangle\}$. Note that the new residual $R^{\text{new}} = (\langle R_{\text{new}}|R_{\text{new}}\rangle)^{1/2}$ is usually much less than $(\rho^2)^{1/2}$ in equation (3.6) because the energy (3.9) has been updated.

(iv) Check for convergence: if the residual R^{new} is less than some predetermined

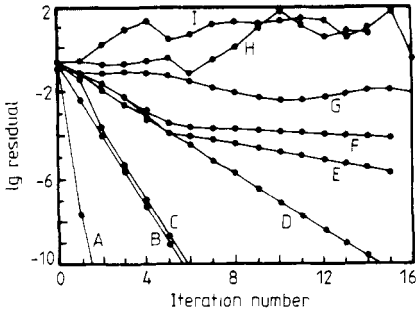


Figure 1. Iteration histories for the modified Nesbet matrix: A, block Davidson ($m = n = 4$), $\varepsilon = 10^{-7}$; B, Davidson; C, DIIS; D, E, F, simultaneous coordination relaxation for $m = 5$,

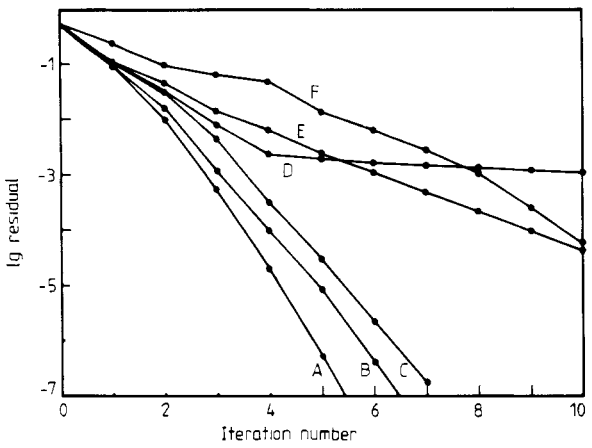
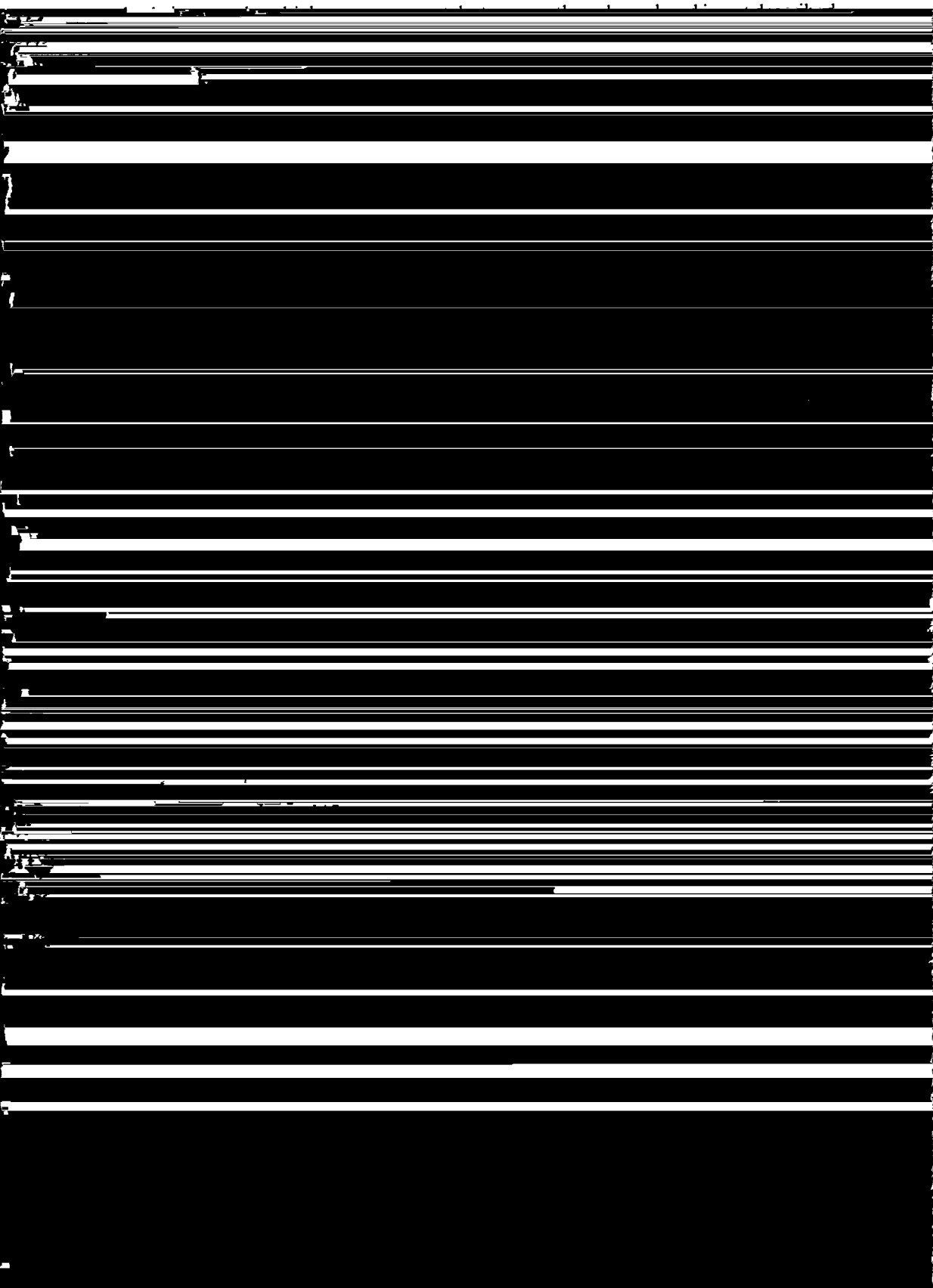
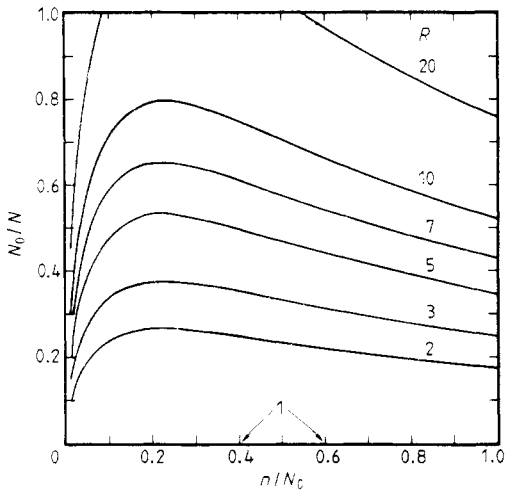
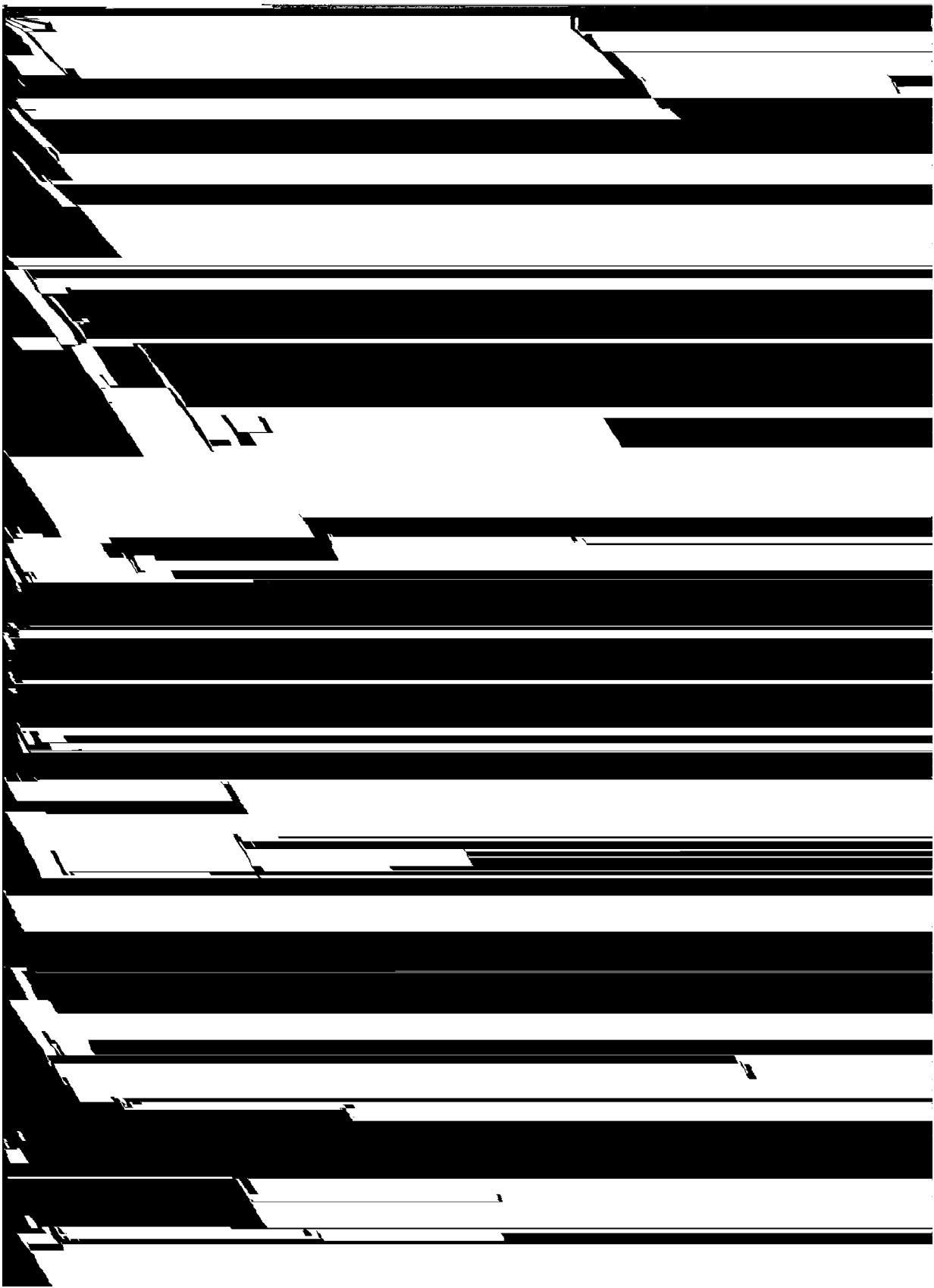


Figure 2. Iteration histories for the complex Hermitian ZnSe matrix: A, block Davidson




1.0
0.8
0.6
0.4
0.2
0
N_0/N
0.2
0.4
0.6
0.8
1.0
n/N_0
R
20
10
7
5
3
2
1



Acknowledgments

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