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TOPICAL REVIEW

The Bloch wave operator: generalizations and applications: Part I. The time-independent case

John P Killingbeck^{1,2} and Georges Jolicard²

¹ Mathematics Department, University of Hull, Hull HU6 7RX, UK

² Observatoire de Besançon (UMR-CNRS 6091), Université de Franche-Comté,
41 bis, Avenue de l'Observatoire, 25000 Besançon, France

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Abstract

This is part 1 of a two-part review on wave operator theory and methods. The basic theory of the time-independent wave operator is presented in terms of partitioned matrix theory for the benefit of general readers, with a discussion of the links between the matrix and projection operator approaches. The matrix approach is shown to lead to simple derivations of the wave operators and effective Hamiltonians of Löwdin, Bloch, Des Cloizeaux and Kato as well as to some associated variational forms. The principal approach used throughout stresses the solution of the nonlinear equation for the reduced wave operator, leading to the construction of the effective Hamiltonians of Bloch and of Des Cloizeaux. Several mathematical techniques which are useful in implementing this approach are explained, some of them being relatively little known in the area of wave operator calculations. The theoretical discussion is accompanied by several specimen numerical calculations which apply the described techniques to a selection of test matrices taken from the previous literature on wave operator methods. The main emphasis throughout is on the use of numerical methods which use iterative or perturbation algorithms, with simple Padé approximant methods being found sufficient to deal with most of the cases of divergence which are encountered. The use of damping factors and relaxation parameters is found to be effective in stabilizing calculations which use the energy-dependent effective Hamiltonian of Löwdin. In general the computations suggest that the numerical applications of the nonlinear equation for the reduced wave operator are best carried out with the equation split into a pair of equations in which the Bloch effective Hamiltonian appears as a separate entity. The presentation of the theoretical and computational details throughout is accompanied by references to and discussion of many works which have used wave operator methods in physics, chemistry and engineering. Some of the techniques described in this part 1 will be further extended and applied in part 2 of the review, which deals with the changes which are required to extend wave operator theory to the case of a time-dependent Hamiltonian such as that which describes the interaction of a laser pulse with an atom or molecule.

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Contents

1. Introduction	107
1.1. Some notational conventions	107
1.2. Introduction to the Bloch wave operator concept	109
1.3. General theory: selected references	111
1.4. Computational methods: selected references	113
2. The matrix partitioning approach	114
2.1. Method 1. Elimination of Y	115
2.2. Method 2. Elimination of E	116
2.3. Method 3. A full space approach	118
2.4. The matrix transformation approach	120
2.5. Alternative forms of the effective Hamiltonian	123
2.6. An implicit equation for HB	127
2.7. The use of three subspaces	129
2.8. Partitioning methods in engineering	130
2.9. The wave operator in atomic and molecular theory	132
2.10. A comment on intermediate Hamiltonians	134
3. A selection of useful techniques	136
3.1. Matrix diagonalization by the single cycle method	136
3.2. Generalized inverses and square roots	139
3.3. Gaussian elimination and the folding transformation	141
3.4. The Wynn epsilon algorithm and perturbation theory	142
3.5. Real arithmetic for complex matrices	144
3.6. The spectral representation of HB	145
3.7. Some other techniques	145
4. Some selected test matrices	146
4.1. The test matrices	146
4.2. A direct search method	148
4.3. The single cycle method (SCM)	150
4.4. Constructing HD from HB and F	151
4.5. Iteration with the E -dependent effective Hamiltonian. HL with a one-dimensional model space	152
4.6. HL with a multi-dimensional model space	154
4.7. Expectation value calculations	155
4.8. Comments on the HL calculations	156
4.9. Some iterative calculations for F	157
5. Some numerical perturbation calculations	160
5.1. Rayleigh–Schrodinger methods	161
5.2. Brillouin–Wigner Gauss–Seidel methods	165
5.3. Calculations of second order	168
5.4. A deflation method	169
5.5. An adjustable BW calculation	170
6. Conclusion	172
Dedication	173
Appendix	173
References	174

1. Introduction

This present work is part 1 of a two-part work which deals with the theory and applications of wave operator methods. Part 1 sets out the basic theory and history of the time-independent wave operator concept and part 2 proceeds to some more advanced and relatively recent developments which use and apply a time-dependent form of the wave operator to deal with problems such as the theory of molecular dissociation by laser pulses. To make part 1 more accessible to the non-specialist reader several of the concepts of the wave operator approach have been presented in terms of a partitioned matrix formalism and several illustrative calculations have been performed on finite test matrices which have previously been used in the literature to develop new computational techniques. The reader acquainted with matrix techniques should thus find part 1 to be a gentle introduction to the area of the theory and applications of wave operator methods. The authors hope that even specialists in the field will be able to find some useful ideas and methods in the review; several of the methods set out in the text and the trial calculations were either devised during the writing of the review or were discovered by a lengthy study of corners of the mathematical literature which are not well known to scientists. One fact which emerged from a wide-ranging study of the literature was that several useful ideas or methods have been developed in parallel (with frequent rediscoveries) in the literature of mathematics, chemistry, physics and engineering.

The authors have made no attempt to give an exhaustive bibliography. The number of references has been limited to just a few hundred, although many of the papers cited are key works and so contain references which will allow the reader to trace back the development of any particular topic of interest. Because of the many thousands of works which could have been cited it was necessary for the authors to impose some restrictive guidelines, the principal ones being: that cited works should have been studied in fair detail by one or both authors; that they should make some use of the wave operator concept; and that they should contain some degree of originality or clarity of exposition which make them useful either to general readers or to specialists. Despite the year or so spent in researching the literature the authors are sure to have missed several valuable works which would have qualified under these tests and apologize in advance to any author whose contribution has been inadvertently overlooked. The tests described above could not, of course, be applied with full rigour, since many works which deal with effective Hamiltonian theory were necessarily included despite the fact that their use of the wave operator concept was sometimes more implicit than explicit. This general introduction refers only to a limited number of works, since it has been judged more useful to give those references which deal with a particular concept or technique in the sections of the text which specifically treat the technical topic concerned.

1.1. Some notational conventions

This two-part review is a joint work which has arisen out of several years of research visits by JPK to the research group of GJ at the Observatory of Besancon, University of Franche-Comté. In the initial writing of the review the large amount of material to be surveyed and sifted meant that a division of labour was necessary, with JPK dealing mainly with part 1 on the time-independent wave operator theory and GJ dealing mainly with part 2 on the time-dependent wave operator and its applications to calculations on various dynamical processes. This coverage of two topics and of a wide range of literature has made it necessary to find some kind of compromise in matters of notation. As a simple example, the projection operator

for the model space has been denoted by various authors by at least the three different symbols P , Q and O , with the meanings of P and Q being exactly opposite from one author to another. The present authors have thus felt free to introduce some clear but slightly unorthodox notation in the two parts of the work. Given the great variety of notations used in the literature to denote various entities and also the slightly different traditions in the subject areas of parts 1 and 2, it has not always been possible to keep exactly the same notation in both parts while attempting to review a wide range of past works as well as making some worthwhile original contributions. Accordingly, some of the conventions adopted in the present part 1 are set out below to give some advance warning to the reader.

The usual abbreviations Brillouin–Wigner (BW) and Rayleigh–Schrodinger (RS) are used in the perturbation sections, with Gauss–Seidel (GS) being used in the sections dealing with iterative methods. The abbreviations RDWA (recursive distorted wave approximation) and SCM (single cycle method) are used to refer to two of the methods for wave operator calculation which are based on matrix similarity transformations. The abbreviation SPD (symmetric positive definite) is used for matrices. Capital letter symbols such as HL , HB , HBV , etc are used for some of the effective Hamiltonians, with appropriate explanation in the text. This simple labelling seems to the authors to be much neater than the affixing of multiple subscripts which is common in the literature. In the sections dealing with partitioned matrix methods and with several simple illustrative computations a notation devoid of subscripts has been tried, following the conventions more typical of high level imperative computing languages. This approach not only makes the nature of variables clearer but also permits a much condensed description of several iterative procedures. It is of special value in making clear the particular shape (square or rectangular) of the various matrix sections which arise in the theory of the reduced wave operator. Thus, for example, the N th order estimate of the J,K element of an effective Hamiltonian can be represented by a clear symbol such as $HB(J, K; N)$. This notation allows several indices to be used without a proliferation of small subscripts and superscripts.

Mathematical equations use the normal $=$ sign for the standard equality of algebra. However, to describe calculations the Algol–Pascal assignment statement symbol $:=$ is useful. The standard computing convention ‘old on right and new on left’ is used. For example, the statement $A := A + 5$, which would be nonsense with an $=$ sign, simply means ‘let the new A value be 5 plus the old value’. When a calculation involves two or three short assignment statements these are sometimes placed together on a line, with a colon $:$ as the separating sign (borrowed from QBASIC). The conventions described above, although not standard, have been used previously by JPK and lead to a clear and simple way of describing those mathematical topics which involve matrix or perturbation methods and which naturally lead to computational algorithms and programs. The authors hope that readers will quickly adjust to this notational style and will find that it provides a simple and clear way to represent many of the calculations which are set out throughout part 1.

Given the long history of applied quantum mechanics it is not surprising that various ideas and methods have been rediscovered from time to time; a few examples of this are mentioned throughout the text. Ambiguities of naming have also sometimes arisen. For example the name ‘intermediate Hamiltonian’ used in wave operator theory was also used long ago for some inner projections of the Hamiltonian which were used to find lower bounds to energies (see, e.g. Sack 1972, Almasy and Patkos 1989, Seto and Stankevich 1999). In modern molecular theory ‘partitioning’ can refer to the partitioning of a Hilbert space into A and B parts or to the partitioning of the Hamiltonian into an unperturbed part plus a perturbation (usually by the Møller–Plesset (MP) or the Epstein–Nesbet (EN) methods). Such ambiguities can sometimes cause a surfeit of output in a database search but are quickly resolved by the

context when a particular paper is studied. However, from experience JPK can testify that the greatest surfeit of database output is obtained by a naive search under the heading ‘wave operator’!

1.2. Introduction to the Bloch wave operator concept

Wave operator concepts of various kinds have a long history. Many authors have used the notion of a formal operator which transforms the incident wavefunction into the outgoing wavefunction in a scattering process or which transforms the unperturbed state into the perturbed state in perturbation theory. The formal mathematical proof that such an operator exists does not, of course, remove the difficult task of actually calculating it for specific problems. For example, the Møller wave operator of formal scattering theory, which acts over the time interval $-\infty$ to 0 and which transforms the noninteracting state into the interacting state at $t = 0$ was proved to exist formally under certain conditions by Møller (1945), yet the ways in which it can be modified and actually applied to a variety of numerical scattering problems are still being developed (e.g., Snider 1988, Johnson and Reinhardt 1983, Viswanathan *et al* 1989, Baute *et al* 2001). If a time-dependent point of view is adopted in perturbation theory, then the perturbed states of a system can be regarded as being produced from the unperturbed ones by an adiabatic switching on of the perturbing potential between $t = -\infty$ and $t = 0$; indeed, several of the early works on many-body perturbation theory started from this time-dependent approach. Within the context of the methods of Bloch wave operator theory the method of sequential similarity transformations which is used in the RDWA and SCM approaches was originally treated by a time-dependent approach which used the adiabatic theorem and a sequence of intermediate representations to describe the evolution of the wavefunctions (Jolicard and Grosjean 1985)

The Møller wave operator of formal scattering theory has what Wittgenstein would have called a ‘family resemblance’ to the Bloch wave operator which figures largely in the present review. Since the Møller wave operator refers to an integrated effect between $t = -\infty$ and $t = 0$, it is a time-independent operator and its theory has been treated in various papers (e.g., Møller 1945, Lippmann and Schwinger 1950, Gell-Mann and Goldberger 1953, Stanton 1971) as well as in books such as those of Roman (1965) and Levine (1999). Roman’s account makes it clear that the Møller operator is appropriate to describe scattering processes, which mainly involve a continuous spectrum; indeed, the types of Møller operator defined by Roman have the property of giving zero when they act on bound state functions. By contrast, the time-independent Bloch wave operator of part 1 of this review has been applied almost exclusively to the calculation of bound states in the literature of chemistry and physics. Reed and Simon (1978) and Thirring (1979) discussed the Møller wave operator in a wider context but the principal concern in all the cited works was to establish conditions under which the propagator product $\exp(itH/\hbar)\exp(-itH_0/\hbar)$ will converge in the limits $t \rightarrow \pm\infty$, leading to the Møller wave operators Ω_{\pm} . For Hermitian perturbed and unperturbed Hamiltonians H and H_0 , respectively, the Ω_{\pm} operators are unitary, whereas the Bloch wave operator of the present review is a non-unitary operator associated with a similarity transformation. Perhaps the closest analogy between the Møller and Bloch wave operators arises if the Bloch wave operator is used in conjunction with a special basis in which the basis functions are the eigenfunctions of an unperturbed operator to which the potential V is added to give the full Hamiltonian (this then corresponds to the use of two such operators in the propagators which give the Møller wave operator). If the model space to be used is then chosen to be one of these basis functions, the Bloch reduced wave operator of this review is then simply proportional to the eigencolumn with the first element excluded. For this very special case

some of the equations of the formal scattering theory associated with the Møller wave operator (e.g., the Lippmann–Schwinger equation) resemble those of the wave operator theory for the Löwdin effective Hamiltonian HL of this review, with the difference that complex energies appear in the scattering theory case. Brandas and Micha (1972) described a variational approach which establishes a link between the scattering theory methods of Lippmann and Schwinger and the wave operator techniques described in the works of Löwdin. The book by Levine (1999) treats the Møller wave operator of scattering theory but also has a chapter on operator partitioning theory which includes the same wave operator as that used with the Löwdin effective Hamiltonian for bound states in section 2.1 of the present review. The Møller wave operator, although time-independent, is formally defined using a product of exponential propagation operators involving the perturbed and unperturbed Hamiltonians; Roman (1965) gave a detailed treatment in the context of the theory of the time-dependent Schrödinger equation. This theoretical approach via time-dependent theory carries over into numerical work. Numerical calculations of Møller wave operators often use finite difference or wavepacket techniques within a time-dependent approach (e.g., Viswanathan *et al* 1989). By contrast the Bloch wave operator is mainly used for bound state energies and within that context lends itself directly to the simple finite matrix approach which is described in the rest of this section and which is used throughout part 1 of this review.

The calculation of the energy levels of a system is often carried out by using a Rayleigh–Ritz approach which approximately represents a Hilbert space calculation by using a large but finite set of basis functions. This common method of calculation directly sets various perturbation and variational techniques in the context of traditional matrix algebra. It is the use of the partitioned matrix approach in this context which has led to many of the developments in the definition and use of various wave operators. Within matrix eigenvalue theory itself the most important notions of wave operator theory are fairly easy to set out. They are quite general, although in many applications they are specifically applied to the Hermitian or real symmetric matrix H which represents the quantum mechanical Hamiltonian operator in some large basis set. The basic premise behind the wave operator concept is that in physical applications it is often only necessary to know exactly a relatively small number M of the eigenvalues and eigenvectors of a large $N \times N$ matrix H . In many cases it is the lowest M levels which are required. For simplicity it can be supposed (as is often the case) that the elements of H are arranged with the diagonal elements in increasing numerical order. Using only the ‘lowest’ M basis functions of H will lead to approximate solutions for the lowest M states, but the coupling to all the other $(N - M)$ basis functions will modify the results. However, by suitably modifying the numerical elements in the $M \times M$ matrix it should be possible to produce the exact eigenvalues for the lowest M states. The technical task is to find the rules which give the appropriate modified matrix elements of this $M \times M$ matrix (the effective Hamiltonian). It is easily seen that there are infinitely many of these effective Hamiltonians, since from any given one another one with the same eigenvalues can be generated by means of a similarity transformation. A consideration of the eigenvector problem helps to cut down the number of possible useful effective Hamiltonians. Any eigenvectors calculated in the small space of dimension M are lacking in a considerable amount of information, since they make no mention of the large number $(N - M)$ of components of the true full eigenvector in the larger space. It is now assumed that there exists a wave operator W (in this case a rectangular matrix) which will produce the full eigenvector components when acting on the M components which have been found for each eigenvector by using the effective Hamiltonian in the small space. At first sight the assumption that there exists such an operator which is simultaneously effective for M different states might appear to be extreme. However, by incorporating this assumption as a postulate in the algebra of the matrix eigenproblem in partitioned matrix form it is found

that the wave operator should obey a nonlinear equation (which actually has solutions) and that the knowledge of the wave operator leads directly to the construction of an associated effective Hamiltonian. Thus a formal scheme is set up which can in principle lead to full knowledge of the lowest (or a selected set of) M levels in the spectrum of H . In the modern history of the subject there have been two main traditions in the literature associated with the use of effective Hamiltonians. One of them seeks to set up the elements of the effective Hamiltonian directly by means of rules which involve the matrix elements of H , often with the assumption that the off-diagonal elements are regarded as a small perturbation and so give contributions which can be expressed by means of a perturbation series. The second tradition (with which the present work is mainly concerned) takes the wave operator as the central theoretical entity which has to be found by perturbation or iterative methods, with the effective Hamiltonian being a subsequent auxiliary derived quantity. In many cases this ‘indirect’ approach via the wave operator concept has led to fruitful developments both in the theory and in the computational applications of effective Hamiltonians.

The aim of the present part 1 of the review is to set out some of the main distinctive features of this wave operator approach and to use a few simple illustrative calculations to make them more understandable to readers who might not be familiar with their use. Some methods and ideas which have arisen during the writing of part 1 seem to merit further investigation and might be of some interest to specialists. The individual sections of the review contain many such ideas but a few of the methods which have been explored in the simple test calculations are of particular interest and so are listed below. They are:

- (i) The use of the energy-dependent effective Hamiltonian HL to construct the energy-independent reduced Bloch wave operator F for a group of states.
- (ii) A simple iterative method for calculating matrix square roots without matrix inversion or diagonalization, thus simplifying the construction of the canonical effective Hamiltonian HD from the Bloch version HB .
- (iii) The application of the simple formula for the first-order Bloch wave operator in the SCM algorithm, which is shown to have a range of applications, from square root calculation to full matrix diagonalization.
- (iv) The simple derivation of variational partners of the standard effective Hamiltonians (HBV with HB , HDV with HD , etc).

1.3. General theory: selected references

Several hundreds of works have adopted a partitioned matrix approach to perturbation theory (with or without the wave operator concept) and so in this general introduction only those few of them are mentioned which are regarded as accessible to a general reader who has a standard knowledge of matrix methods. The most prolific writer in this area was undoubtedly the late Per-Olov Löwdin. Löwdin (1962) gave a detailed account of the main ideas of the partitioning approach to perturbation theory, while Löwdin (1965a, 1965b) described the use of that approach to calculate both upper and lower bounds to bound state energies. Löwdin (1982) set out various links between the partitioning approach and the use in quantum mechanics of a type of rational approximant which is similar to the Padé approximant and which is useful for divergent series. Löwdin’s lower bound techniques were further developed by Choi and Smith (1966), Wilson (1967a, 1967b) and Wilson and Read (1967). Hoffmann-Ostenhof and Mark (1973) made some interesting observations about the use of partitioning for various functions $f(H)$ of the Hamiltonian. Choi (1975) used a partitioning approach to derive an algorithm which leads to a perturbation expansion of an effective Hamiltonian which appears to be essentially that of Des Cloizeaux (1960). Although set out almost entirely in terms of

the mathematical context of the simple and generalized matrix eigenvalue problem (so that they are little known by chemists and physicists) the works by Coope (1970) and by Coope and Sabo (1977, 1981) developed several techniques and concepts which are very effective in connection with the wave operator approach. A later study by Cederbaum *et al* (1989) on the block diagonalization of Hermitian matrices gave some useful insights into the properties of the effective Hamiltonians which are associated with wave operator methods.

Several classic works are regarded as having established the main concepts of the theory of the wave operator and of the effective Hamiltonian; they are well worth studying, although the general reader should be warned that several of them used methods and points of view which can appear to be over-complicated to modern workers who have found more direct and simple ways to re-derive some of the most useful parts of the theory. One of the earliest works was that of Kato (1949). He used a resolvent operator method to derive an effective Hamiltonian which leads to the perturbed energies of a group of levels arising from an initially degenerate level. Finding the levels requires the solution of a generalized eigenvalue problem and the terms in the effective Hamiltonian are expressed as a perturbation series. The textbook of Messiah (1960) gave a clear exposition of Kato's approach. Within the context of nuclear theory Bloch (1958) re-examined Kato's work and produced a perturbation series for the non-Hermitian effective Hamiltonian which is nowadays usually named after him. Bloch and Horowitz (1958) treated the energy contribution due to a few particles outside a closed nuclear core and derived an energy-dependent effective Hamiltonian which is of the typical BW form associated with the Löwdin effective Hamiltonian denoted by HL in this review. Huby (1961) gave a clear exposition of the relationship between Bloch's theory and that of Brueckner (1955) and gave some rules for constructing the perturbation terms of various orders in the expansions of the Bloch wave operator and of the perturbed energy. Huby's work was for a non-degenerate state; Silverstone (1971) later generalized it to obtain perturbation series for the effective Hamiltonian associated with an initially degenerate level. Des Cloizeaux (1960) applied a formula due to Lagrange in a derivation of a perturbation series for an Hermitian form of effective Hamiltonian which is nowadays often called the canonical form. Silverstone and Holloway (1971) apparently overlooked this work when they also treated the problem by using a similar formula of Lagrange, although they started from a BW approach to develop their formulae. In a set of three papers Soliverez (1969, 1980, 1981) extended Bloch's theory and set up a general formalism which included the effective Hamiltonians of Bloch and Des Cloizeaux as particular cases. Of the various other works which set out to include the known effective Hamiltonians in a general formalism the works of Lindgren (1974), Klein (1974), Jorgensen (1975) and Kvasnicka (1975a, 1975b) all made important contributions to the subject and made clearer the extent to which some of the concepts could be developed from what appeared to be quite different points of view.

The present review concentrates on matrix and iterative numerical methods, but it will be clear from a study of the works cited above that the diagrammatic approach played a large role in the early history of wave operator theory. It still does so in those parts of quantum chemistry in which it is regarded as important to use formalisms which correspond to the use of linked clusters in an approach via perturbation theory. Authors who developed the diagrammatic approach to perturbation theory included Goldstone (1957), Katz (1962) and Langhoff and Hernandez (1976), while authors such as Kelly (1963, 1969), Ellis (1975), Bartlett and Shavitt (1977) and Finley (1998a, 1998b) applied it to atomic or molecular systems. The works of Primas (1961, 1963) and Goodman (1965) set out to present general perturbation theory in a manner such that it automatically produced linked clusters in its representation in terms of diagrams. They did this by writing the theory in terms of operator commutators and made use of mathematical techniques such as superoperator theory and an original type of operator

commutator analysis. The majority of the works using diagrams which have been cited above, however, used their diagrammatic approach in conjunction with an algebraic approach which is understandable in its own right, since the diagrams were usually set up in order to give a visual description of the contributions which arose from an application of the algebraic formulae. Hose and Kaldor (1979) also described algebraically derived results in terms of diagrammatic rules, but Meissner and Bartlett (1989) later showed that they had omitted some classes of diagrams when formulating their rules. Cullen *et al* (1985) emphasized that using diagrams needs only orbital matrix elements rather than state ones. The papers of Katz (1960), Mavromatis (1973) and Bartlett and Silver (1975) gave readable accounts of the time-independent diagrammatic approach which related it to standard perturbation theory and to the use of illustrative matrix models. In particular Mavromatis pointed out that the obtaining of upper bounds to eigenvalues in matrix diagonalization approaches necessarily corresponds to the use of some unlinked diagrams. Kansa (1974) described the link between the linked cluster perturbation theory and the method of configuration interaction for the Be atom. Apart from his better-known (1967) long work on the diagrammatic approach Brandow (1970, 1979) also wrote several more readable works which gave a good critical account of the basic theory of wave operators and of its applications in nuclear and molecular theory. Freed (1974) and Durand and Malrieu (1987) gave long reviews of the value of the effective Hamiltonian concept in a range of problems in the theory of molecular structure and of magnetism.

1.4. Computational methods: selected references

Many of the works cited above concentrated on the formal aspects of the theory or applications of wave operator and effective Hamiltonian methods, often producing their results in the form of general algebraic formulae. It is also worthwhile to cite some of the works which have paid more special attention to the construction of algorithms for the numerical calculation of various quantities, either by evaluation and summation of perturbation series or by the use of various iterative algorithms. Hegarty and Robb (1979) and Baker *et al* (1981) treated the RS perturbation formalism, starting from a partitioned matrix approach, and then devised and applied a numerical technique to evaluate the low-order terms appearing in the series for the effective Hamiltonian. The first paper used a GS method to solve some associated sets of linear equations while the second used a Lanczos method, with particular attention to the effectiveness of the calculations in the presence of intruder states and to methods of summing some perturbation terms to infinite order. The Toulouse group and its co-workers have produced many works which combine developments in basic theory (e.g., the intermediate Hamiltonian concept) with the use of efficient numerical algorithms. Durand (1983) used projection operator algebra to give a powerful synthesis of the theory of several types of effective Hamiltonian and a simple derivation of the generalized Bloch equation. He also proposed several iterative methods for the numerical calculation of the wave operator and his later work on algorithms, well represented by Durand *et al* (1994), concentrated on the development of methods which have second-order convergence and so serve to reduce the amount of computational time required for large scale problems. Durand *et al* (2000) applied such methods to the case of a large matrix which has complex elements and is non-Hermitian (as stressed in later sections the wave operator formalism applies generally, without restrictions on the symmetry of the matrix being treated). Gadea (1987, 1991) used a projection operator formalism to give a detailed analysis of the relationship between the model and target spaces in wave operator theory, devising some new algorithms which were tested on simple test matrices; the concept of the variational partners of some standard effective Hamiltonians was

developed in detail in these works (and arises in the partitioned matrix section of the present review).

Although the work of the Besancon group and its co-workers has tended to emphasise the concept of the time-dependent wave operator and so is appropriate to part 2 of this review (along with other work by the Toulouse group) the group has produced several works which have devised and applied calculational methods for matrices within a time-independent wave operator approach. The techniques used included a GS–Bloch method (Périé *et al* 1993), a spectral filter matrix eigenvalue method (Jolicard *et al* 1996) and a trial state method for a complex matrix (Jolicard *et al* 2001). The first of these papers made use of the SCM approach, which is used for various purposes in some of the trial calculations in part 1 of this review. Amongst other works which developed numerical algorithms mention should be made of the recursive approach to RS degenerate perturbation theory which was formulated and applied to Zeeman effect calculations by Silverstone and Moats (1981) and of the iterative techniques based on the generalized Bloch equation which were developed and applied by Meissner and Steinborn (1997a, 1997b, 1997c). Kowalski and Piecuch (2000a, 2000b) used a homotopy method to obtain a large number of solutions of the generalized Bloch equation and then examined the problem of how many of these solutions had relevance for physical problems. Andreozzi (1996) not only clarified and related some existing methods for the numerical calculation of wave operators but also constructed new methods which were more general by making use of the effective Hamiltonians of both the A space and the B space (to use the terminology of this review).

2. The matrix partitioning approach

The matrix partitioning approach described in this section has been constructed by taking the most simple and direct blend of various methods which have appeared in the literature. It is mainly inspired by the approaches of Löwdin and of Coope but represents an original variation on their methods. Method 1 as described here is by far the most common one adopted in the literature, while Method 2 represents a particularly compact form of derivation of the reduced Bloch wave operator, which is frequently derived using projection operators in the standard literature. Method 3 gives an elementary approach to the variational forms of several effective Hamiltonians which are not yet widely used in the literature. The initial procedure involves writing the eigenvalue equation for the Hamiltonian as a matrix eigenvalue problem, using some basis set for which it is possible to evaluate the required matrix elements. A small subspace spanned by some of the basis functions is then chosen as the model space (with the label A), while the rest of the basis functions are grouped into the orthogonal complement of A (with the label B). The set of basis functions used to set up the Hamiltonian matrix is assumed to be orthonormal. The resulting matrix eigenvalue equation can then be written in a partitioned form which shows the A and B space components:

$$\begin{pmatrix} H(AA) & H(AB) \\ H(BA) & H(BB) \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = E \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (2.1)$$

Here X and Y are the projections into spaces A and B , respectively, of the eigencolumn with eigenvalue E . Using partitioned matrix multiplication to work out (2.1) leads to the simultaneous matrix equations

$$H(AA)X + H(AB)Y = EX \quad (2.2)$$

$$H(BA)X + H(BB)Y = EY. \quad (2.3)$$

There are several ways to proceed with the solution of this partitioned eigenvalue problem; three of the most useful ones are set out below.

2.1. Method 1. Elimination of Y

The obvious (and most commonly followed) approach is to eliminate Y by using the second equation and then to substitute the result in the first equation to obtain an equation for X alone. Eliminating Y gives

$$Y = F(BA)X \quad (2.4)$$

where

$$F(BA) = [EI(BB) - H(BB)]^{-1}H(BA). \quad (2.5)$$

Substituting in equation (2.2) then gives

$$HL(AA)X = [H(AA) + H(AB)F(BA)]X = EX. \quad (2.6)$$

In calculations the inverse on the right of (2.5) is not usually found directly; the equation is simply recast to become one involving a set of simultaneous linear equations which can be solved by various methods. This particular way of writing the traditional equations makes it easy to compare the results of methods 1 and 2 in the subsequent discussion. It is clear from the equations above that the problem has been reduced to an eigenvalue problem for the effective Hamiltonian $HL(AA)$ in the small model space A , with the X component as the eigenvector (The symbol HL stands for ‘Löwdin Hamiltonian’). Inspection of (2.6) shows that the situation is not as simple as might appear at first sight, since the second term in $HL(AA)$ involves the unknown sought eigenvalue E ; this means that an iterative self-consistent method of numerical solution has to be used, with E being adjusted until it equals an eigenvalue of HL . Whatever the dimension of the model space, the several eigenvalues have to be found one at a time, with a separate self-consistent calculation for each one. The situation is that which is usually described in the existing literature by the statement that the effective Hamiltonian HL is energy-dependent. The self-consistent method of solution which is required is equivalent to a state by state application of an approach within the Brillouin–Wigner tradition, although the calculation of $F(BA)$ can be made either by a Gauss–Seidel method (which is closer to a fully perturbative approach) or by a direct non-perturbative matrix calculation using Gaussian elimination or some other method. The symbol HL has been used here in honour of the many contributions made to the theory by Per-Olov Löwdin. The same mathematical formalism was also used by Bloch and Horowitz (1958) in their work on the energy contribution due to a few nucleons outside a closed shell in nuclear theory, and by Feshbach (1948, 1962) in the theory of nuclear reactions. Hagston *et al* (2002) have recently found a similar approach useful in the quantum theory of solids.

Even without detailed numerical calculation equations (2.5) and (2.6) make it clear that the effective Hamiltonian HL has formal singularities at the eigenvalues of $H(BB)$. The presence of the alternating rising and falling asymptotes at these singularities implies that there should be an eigenvalue of the full H between each eigenvalue of $H(BB)$, together with the extra ones at the bottom of the spectrum which are below the lowest eigenvalue of $H(BB)$. Although the theory described here is quite general, references to the ‘top’ or ‘bottom’ of the spectrum are, of course, based on the commonly used convention that the matrix is ordered with its diagonal elements in an order of increasing magnitude.

2.2. Method 2. Elimination of E

The unorthodox way of writing the equations for method 1 above gives a clue about how to use a different strategy in approaching the partitioned eigenvalue problem. The quantity $F(BA)$ is retained, so that equation (2.4) still holds (i.e., so that Y can be simply calculated once X is known) but the particular expression for $F(BA)$ given by equation (2.5) is not retained. The partitioned eigenvalue problem then takes the form

$$H(AA)X + H(AB)F(BA)X = EX \quad (2.7)$$

$$H(BA)X + H(BB)F(BA)X = EF(BA)X. \quad (2.8)$$

The first equation can now be multiplied from the left by $F(BA)$, so that the right-hand sides of both equations become $EF(BA)X$. The result is then an equality between the two resulting left-hand sides. This can be written in a form with a zero on the right;

$$f(F, H)X = 0 \quad (2.9)$$

with

$$f(F, H) = H(BA) + H(BB)F(BA) - F(BA)H(AA) - F(BA)H(AB)F(BA). \quad (2.10)$$

The logical basis of Bloch wave operator theory can then be explained as follows. The rectangular matrix $F(BA)$ is chosen so as to render zero the rectangular matrix $f(F, H)$ appearing in the equations above, so that the equation $f(F, H)X = 0$ will be true for *every* vector in the A subspace and not just for those particular X which are eigencolumn projections. The matrix F is thus associated with the whole of the A space. When F has been chosen to obey (2.9) then the effective Hamiltonian

$$HB(AA) = H(AA) + H(AB)F(BA) \quad (2.11)$$

can be formed in the A subspace (Here the symbol HB has been used, to stand for ‘Bloch Hamiltonian’). Whenever an eigenvalue and eigencolumn of $HB(AA)$ are found, it then follows not only that (2.7) will be obeyed but also that (2.8) will be obeyed. Thus the full space eigenvalue problem will have been solved and the B space part of the eigencolumn will be found simply by forming the product $Y = FX$, with the rectangular matrix F having the same fixed form for all of the eigencolumns.

The compact approach given above uses less algebra than is common in the literature but puts more emphasis on the logical understanding of the interpretation and use of the quantities which appear in the theory. Method 2 clearly leads to an effective Hamiltonian HB which is energy-independent, so that any convenient method of diagonalization can be used to extract all the eigenvalues associated with space A in one calculation, thus avoiding the self-consistent calculation of the eigenvalues one at a time. When the matrix H is Hermitian there is a technical difference between the types of eigenvalue problem associated with HL and HB ; HL is an Hermitian matrix while HB is not and so requires an appropriate diagonalization method. The apparent advance in the treatment of the problem is bought at a price, however, since the appropriate rectangular matrix $F(BA)$ has to be found by solving the nonlinear equation $f(F, H) = 0$, where $f(F, H)$ is a rectangular matrix of the same type as $F(BA)$. A careful study of the derivation which has been presented above shows that the single nonlinear equation for $F(BA)$ can be rewritten as a pair of equations which in essence reinstates the partitioned form which originally led to that equation:

$$HB(AA) = H(AA) + H(AB)F(BA) \quad (2.12)$$

$$H(BB)F(BA) = F(BA)HB(AA) - H(BA). \quad (2.13)$$

Subtracting $eF(BA)$ from both sides of the second equation, where e is an arbitrary number, leads to the alternative form

$$[H(BB) - eI(BB)]F(BA) = -H(BA) + F(BA)[HB(AA) - eI(AA)] \quad (2.14)$$

where the symbol I denotes a unit matrix of the appropriate dimension. In the derivation of all of the equations presented in this section great care has been taken to indicate with clarity the exact type of square or rectangular matrix which represents every quantity in the theory. In a full matrix notation $F(BA)$ would have three zero sections. A comparison of equations (2.5) and (2.14) now reveals that the $F(BA)$ which appears in method 1 (with an energy-dependent effective Hamiltonian) is a special case of the $F(BA)$ of method 2 for which the parameter e is set equal to E and only the term $-H(BA)$ is retained on the right in equation (2.14). This means that it is possible to set up a computational approach in which either the energy-dependent or energy-independent effective Hamiltonian cases can be chosen at will.

The particular approach which has been adopted here is similar in spirit to that adopted using operator algebra by Bloch (1958) and the rectangular matrix $F(BA)$ which plays the central role in the formalism presented above is equivalent to what is usually termed the Bloch reduced wave operator, actually in a form which is slightly generalized, since the original Bloch theory referred to an initially degenerate level and used perturbation expansions to form the effective Hamiltonian for the perturbed levels. In the literature F is sometimes called the decoupling operator or the correlation operator, depending on the type of problem which is being treated and depending on whether an operator or a finite matrix approach is used. Since equation (2.14) has $F(BA)$ on both sides of it, a direct approach to its solution will usually involve an iterative procedure. Test calculations given in later sections have shown that both iterative and perturbation methods for the calculation of $F(BA)$ are more efficiently carried out when the single nonlinear equation $f(F, H) = 0$ is replaced by the pair of equations (2.12) and (2.13) or (2.12) and (2.14). From the discussion of methods 1 and 2 given above it is clear that there are two ways of approaching the calculation of $F(BA)$. One way is to find a solution of the nonlinear equation for F and then to find HB and the associated eigencolumns; this is the approach widely adopted in the literature, although in many chemical applications the problem of nonlinearity is avoided by using only the lowest-order approximation for F (which is given by a simple linear formula). A second way to find F is to revert to first principles. It might be that for some difficult cases (such as those involving the so-called intruder states) a calculation of one state at a time making use of HL is the easiest one to perform. Once the X and Y components of a group of eigenstates have been found using HL it is then possible to construct the F and thence the HB which would have produced the known results in the energy-independent approach. Evangelisti *et al* (1987, 1991) made use of this first principles approach in a study of avoided crossings and of intruder state effects in general. They studied the Li_2 system with variable interatomic distance r , using full matrix diagonalization to find the spectrum and then constructing the HB which would describe low-lying states. Their particular interest was in tracing the behaviour of the elements and eigencolumns of HB at avoided crossings. The standard type of HB effective Hamiltonian was found to have various defects in handling avoided crossings and intruder states. The 1987 paper proposed the use of an intermediate Hamiltonian to give a better description of the Li_2 system and the 1991 paper proposed an approach which leads to the solution of generalized rather than ordinary eigenvalue problems to find the few low-lying eigenvalues which are to be followed as the interatomic distance is varied.

It is important to note here that, since the emphasis of this review is on numerical rather than algebraic methods, no specific choice of the orthonormal basis set for the Hamiltonian

matrix has been imposed. In the work of authors (e.g., Bloch 1958) who set out to obtain algebraic formulae for the terms in a perturbation series for the energy a specific choice is imposed; the basis functions are the eigenfunctions of an unperturbed Hamiltonian and the full Hamiltonian is obtained by the addition of a perturbing potential V , so that the matrix elements of V will appear in the terms of the perturbation series. The choice of an A space composed of H_0 eigenvectors was made in the works of Kvasnicka (1977) and Svrcek and Hubac (1987), which used a wave operator approach to derive algebraic expressions for the low order terms in the perturbation expansion of some effective Hamiltonians. In a numerical approach, once the matrix is formed it is in principle possible to choose the ‘unperturbed’ matrix in any way which facilitates the numerical calculation and many of the possible choices for the ‘perturbation’ will not correspond to the matrix elements of any local potential operator of the type which appears in the Hilbert space quantum mechanical operators initially used to describe the system being treated.

2.3. Method 3. A full space approach

On passing from method 1 to method 2 in the preceding discussion the principal step was to retain the concept of the F matrix but to remove the constraint that F should be given by an E dependent equation. It was then found that by making F obey a nonlinear matrix equation it was possible to find several different eigenstates using one effective Hamiltonian HB . In method 3 the generalization is taken one step further, yielding several results which are useful when H is an Hermitian matrix. A full space calculation of the spectrum of the H matrix is carried out under the assumption that a matrix F exists but with the single property that it acts as a constraint on the basis functions used; in the special case in which F is actually the same one as that of method 2 then the constraint will in effect vanish, leading to exact eigenvalues in the A space. Accordingly, a full space calculation is performed in which each basis vector consists of the unit vector $e(J)$ in the A space plus a B space component which is obtained by forming the product $F(BA)e(J)$. No assumption is made about the matrix $F(BA)$ apart from the obvious one about its necessary shape. For an A space of dimension M there will then be M basis functions. The matrices of the full space Hamiltonian H and of the full space unit operator I must be set up to give the appropriate matrix eigenvalue problem. A typical (J, K) matrix element of H will take the form

$$[e(J) \quad Fe(J)]^* \begin{pmatrix} H(AA) & H(AB) \\ H(BA) & H(BB) \end{pmatrix} \begin{pmatrix} e(K) \\ Fe(K) \end{pmatrix} \quad (2.15)$$

while the matrix elements of I are found by using the partitioned unit matrix instead of the partitioned Hamiltonian matrix in the triple product. On noting that the complex conjugate term on the left will produce an Hermitian conjugate term F^\dagger in the formal matrix algebra, it then follows that the resulting matrix eigenvalue equation is in fact a generalized eigenvalue equation of the form

$$[H(AA) + H(AB)F + F^\dagger H(BA) + F^\dagger H(BB)F]X = E[I + F^\dagger F]X \quad (2.16)$$

which refers to the A space only (as a result of having constrained the B space components to be equal to $F(BA)$ times the A space components).

The operators on both the left and right of (2.16) are manifestly Hermitian, but appear in a generalized eigenvalue equation for which the eigencolumns will not be orthonormal with respect to the usual unit matrix metric. Because of the special way in which the basis set was constructed it follows that the eigenvalues obtained will be upper bounds to the M lowest eigenvalues of the full H , if the A space has dimension M . This result is true for any choice of $F(AB)$ and will be inherited by any form of effective Hamiltonian problem which arises

from (2.16) by means of a similarity transformation. If the operator on the left of (2.16) is provisionally denoted by HKV (variational Kato Hamiltonian) then by direct multiplication using some of the results of the preceding section it can be seen that the equality

$$[I + F^\dagger F][H(AA) + H(AB)F(BA)] = HKV(AA) \quad (2.17)$$

holds for the special case in which F exactly obeys the nonlinear equation for the Bloch reduced wave operator. For that special case equation (2.16) can be written in the apparently redundant form which introduces the Kato effective Hamiltonian

$$[I + F^\dagger F]HB(AA)X = HK(AA)X = E[I + F^\dagger F]X. \quad (2.18)$$

This is equivalent to the generalized eigenvalue equation of Kato (1949), although he used a perturbation expansion and a quite different notation based on the algebra of projection operators on the model and target spaces. In the notation used here the cancellation of $[I + F^\dagger F]$ from both sides is obviously appropriate, giving the HB eigenvalue equation. If the constraint matrix F does *not* satisfy $f(F) = 0$ however, another form of eigenvalue problem is obtained by multiplying (2.16) from the left by the inverse of $[I + F^\dagger F]$. In the compact notation introduced above this alternative equation takes the form

$$[I + F^\dagger F]^{-1}HKV(AA)X = HBV(AA)X = EX. \quad (2.19)$$

The symbol HBV has been used here to denote what might be called a variational form of HB . This form reduces to HB when F is exact but has guaranteed variational and upper bound properties when F is only an approximation, such as that obtained from a perturbation calculation of low order or from an iterative calculation which has not yet converged.

The method of using a constrained basis set calculation in order to arrive at the variational form of HB (and of other effective Hamiltonians) is direct and natural within the matrix partitioning method. Gadea (1991) derived equivalent versions of these variational forms via a lengthy treatment involving the algebra of projection operators and cited some previous works which had also mentioned these forms of the various effective Hamiltonians. He also gave some test calculations for the Mathieu matrix eigenvalue problem to illustrate the superior performance of the variational forms. Within the projection operator formalism the form of an operator such as HBV is often obscured, since it is expressed by means of a formula which sandwiches the simple symbol H between various groups of projection operators. The terms appearing in equation (2.16) reveal the components of the H matrix which appear in HBV and show that the (AA) effective operator is in fact quite complicated, since, as the simple derivation showed, it represents a procedure for compressing into the A space what is in essence a full space calculation.

Since method 3 involves a comparison of full space and A space calculations it is appropriate at this point to make a comment about the normalization of eigencolumns. The standard approach in using the effective Hamiltonian in the A space would be to normalize the A space eigencolumns to unity; this convention is consistent with the intermediate normalization convention adopted in a perturbation approach and so is used by most authors. However, Hurtubise and Freed (1993a, 1993b, 1994) explored in detail how the normalization convention adopted can complicate or simplify the construction of effective operators for operators other than the Hamiltonian and pointed out the role played by the norm of the A space component when it is the full space eigenvector which is taken to be normalized to unity. The study of the fractional contribution of the A space part X of a full space eigencolumn naturally involves the operator $S(AA) = [I + F^\dagger F]$, although in section (4.7) it is pointed out that for an individual eigenvector this fractional contribution can be found numerically by a simple finite perturbation technique. The conventions adopted in the matrix partitioning approach of this review are consistent with those adopted by most authors; the full wave operator (denoted by

W in this work and Ω by several authors) is defined to have the property that it gives back the full space normalized eigenvector when it acts on the A space component of that eigenvector.

2.4. The matrix transformation approach

Instead of using the indices AB , etc to indicate the shapes of the various matrices appearing in the theory, it is possible to adopt a more visual approach by displaying the matrices which are used in a matrix similarity transformation of the original partitioned Hamiltonian matrix. Equations (2.7) and (2.8) can be written in the form

$$\begin{pmatrix} H(AA) & H(AB) \\ H(BA) & H(BB) \end{pmatrix} \begin{pmatrix} I & 0 \\ F & I \end{pmatrix} \begin{pmatrix} X \\ 0 \end{pmatrix} = E \begin{pmatrix} I & 0 \\ F & I \end{pmatrix} \begin{pmatrix} X \\ 0 \end{pmatrix} \quad (2.20)$$

where F is the $F(BA)$ introduced previously. A short calculation shows that the members of the family of partitioned matrices of the form

$$T(F) = \begin{pmatrix} I & 0 \\ F & I \end{pmatrix} \quad (2.21)$$

have the multiplicative property $T(F)T(G) = T(F + G)$, so that the inverse of $T(F)$ is simply equal to $T(-F)$. It thus follows that the triple matrix product $T(-F)HT(F)$ will give a similarity transformation of the H matrix which leaves the eigenvalues unchanged. Equation (2.20) already has $HT(F)$ on the left; left multiplication by $T(-F)$ gives a transformed partitioned Hamiltonian matrix with the components:

$$\begin{aligned} (AA) & H(AA) + H(AB)F \\ (BB) & H(BB) - FH(AB) \\ (AB) & H(AB) \\ (BA) & H(BA) + H(BB)F - FH(AA) - FH(AB)F. \end{aligned} \quad (2.22)$$

Choosing F so as to render the (BA) portion of this transformed matrix zero requires the solution of exactly the same nonlinear equation which was derived previously. The (AA) portion of the matrix will then be uncoupled from the rest of the matrix, so that the (AA) submatrix will produce some of the eigenvalues for the original full matrix. This (AA) submatrix is, of course, precisely the effective Hamiltonian HB obtained previously. It is clear from equation (2.20) that each eigenvalue of the effective Hamiltonian has an associated eigencolumn with components X and $Y = FX$ when regarded as a solution of the untransformed problem. Thus the main features of the results of matrix partitioning theory are reproduced in this alternative approach which displays the relevant matrix similarity transformations. This approach will be applied in some of the later illustrative calculations. Although the algebra and the calculations of the present work concentrate on the eigenvalues associated with the small model space, it is worth noting in passing that the (BB) term in the transformed matrix terms of (2.22) is an effective Hamiltonian with eigenvalues associated with the larger B subspace. The A and B space effective Hamiltonians both appear in the algorithms of Andreozzi (1996).

In the specialist literature of wave operator theory many authors set out the theory by using the algebra of projection operators. Since the present discussion has been set out in terms of matrix theory for the benefit of a more general readership, it is of interest to give a short example of a translation between the two approaches, using some algebra given by Kowalski and Piecuch (2000b). The following ‘dictionary’ sets out several of the operators in partitioned matrix form. P and Q are the projection operators on the A and B spaces and W is

the (full) wave operator. The Hamiltonian H takes its standard partitioned form as in earlier equations. The principal quantities are

$$P = \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix} \quad Q = \begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix} \quad W = \begin{pmatrix} I & 0 \\ F & 0 \end{pmatrix}. \quad (2.23)$$

By matrix multiplication the reader will be able to check that the wave operator W satisfies the equations (with 0 interpreted to be the null matrix)

$$PW = P \quad WP = W \quad WQ = 0. \quad (2.24)$$

Armed with these results one can then proceed by algebra (or by explicit matrix multiplication) to obtain results such as

$$W^2 = WPW = WP = W. \quad (2.25)$$

What is clear about this approach is that it explicitly sets to zero various sections of the matrices. For example, the F matrix has been a principal quantity in the previous discussion. The equations above show it as the B space part of a full wave operator W which acts *only* on the A space and gives a result which has both A and B space components. To ensure that the resulting AB vector is an eigenvector in the full space (i.e., that it belongs to the desired target space) W must be constrained to obey some equation which is equivalent to the nonlinear equation which has already been derived for the Bloch reduced wave operator. The required equation is

$$WH = WHW \quad (2.26)$$

which is usually called the generalized Bloch equation. Constructing the appropriate matrix products on the left and the right of (2.26) leads to zero AB and BB submatrices on both sides, together with identical AA submatrices equal to $H(AA) + H(AB)F$. The (BA) sections on the left and right are equal to $H(BA) + H(BB)F$ and $FH(BA) + FH(BB)F$, respectively. Requiring these two (BA) sections to be equal simply gives again the nonlinear equation for F which was previously derived using a matrix partitioning approach. Another equation which is sometimes used in wave operator theory or calculations directly involves HB :

$$HW = W(HB). \quad (2.27)$$

The validity of this equation also follows on working out the products of the partitioned matrices on both sides; the AB and BB portions are zero, while the AA and BA portions on both sides can be seen to be equal because of the equations which are obeyed by $F(BA)$ and $HB(AA)$. Logrado and Vianna (1997) used an approach in which the initial model space is an eigenfunction of the full perturbed Hamiltonian. Their resulting nonlinear equation for the wave operator has an unorthodox appearance but a careful analysis of the definitions of the potential terms used in it shows it to be another way of writing the standard generalized Bloch equation which has been used by other authors.

In the work of Durand (1983) and other authors the projection operators for the model space were given the symbols P_o and Q_o and an associated target space was introduced explicitly and assigned the projection operators P and Q . Various effective Hamiltonians were then described using the formal operator $P_o P P_o$, which is, of course, unknown at the start of a calculation. The link of this approach with that described above was that $(P_o P P_o)^{-1}$ was equal to the product $W^\dagger W$, where W was the wave operator matrix which was defined in equation (2.23) above; this product also equals the matrix $[I + F^\dagger F](AA)$ introduced earlier. Durand (1983) derived the generalized Bloch equation (2.26) and also transformed the formulae involving the unknown P to obtain expressions for the various effective Hamiltonians which involve only P_o and the full or reduced wave operator. If the labels A and B are

suppressed in the various submatrices inside the product then the nonlinear equation for the reduced wave operator can be written in the full matrix factorised form

$$Q[I - F]H[I + F]P = 0. \quad (2.28)$$

The work of Meissner and Nooijen (1995) used this equation as well as a partitioned matrix approach where the projection operators P and Q are taken to be the projection operators for the A space and the B space, as in equations (2.23). This factorised form displays more clearly that a matrix similarity transformation is involved, since the terms in square brackets represent the transformations $T(-F)$ and $T(F)$ introduced previously. In equation (2.28) the full matrix form of the matrix H includes all its four submatrices and the full form of matrix F has three zero submatrices as well as the $F(BA)$ submatrix which has been studied previously. The appendix gives an example of how equation (2.28) is modified for the time-dependent case, as a foretaste of the subject matter of part 2 of this review.

A careful study of the projection operator formalism used by Durand and other authors yields two useful translations between that formalism and the simple approach via partitioned matrices which is used throughout part 1 of the present review. In the operator approach the composite operator $(P_o P P_o)^{-1}$ plays a prominent role but has to be explained as operating only in the model space, so that it is not an inverse in the usual matrix sense. The corresponding quantity in the partitioned matrix approach described here is just the matrix $[I + F^\dagger F](AA)$, which is given the shorter symbol $S(AA)$ or simply S in some parts of the discussion. The projection operator onto the target space is denoted by P in Durand's work, whereas in the present work P is the projection operator onto the fixed model A space (that operator being the P_o of Durand). In the notation of the present work the projection operator onto the target space (i.e., the space of the actual full eigenvectors) corresponds to the partitioned matrix which has the four non-zero sections

$$(AA)S^{-1} \quad (BA)FS^{-1} \quad (AB)S^{-1}F^\dagger \quad (BB)FS^{-1}F^\dagger. \quad (2.29)$$

Matrix multiplication quickly shows this partitioned matrix to be equal to its own square. When the matrix acts on an eigencolumn with the A part X and the B part $Y = FX$ then it simply reproduces that eigencolumn. With these two translations and the ones for W (denoted Ω by Durand) and P and Q (the P_o and Q_o of Durand) it is possible to translate much of the operator theory in the literature into the partitioned matrix language of the present work; the identity $P + Q = I$ can be used to work out unusual terms.

Using the symbol P of Durand for the operator described by equation (2.29) and remembering the previous comment about the meaning of the symbol $(P_o P P_o)^{-1}$, the reader can confirm that the wave operator W of equation (2.23), the Ω of Durand, can be written in the product form $P(P_o P P_o)^{-1}$, which is used by several authors.

An interesting example of the way in which the matrix or the operator notation can be the more appropriate depending on the circumstances is provided by section 3 of the chapter by Löwdin (1966) on partitioning methods. That work contains the projection operators P and Q of equation (2.23) (although they are O and P in Löwdin's notation) and also an operator T which is easy to see in matrix form; it has three zero sections and a non-zero BB section which contains the inverse of $[EI(BB) - H(BB)]$. To express this in operator terminology is not totally straightforward; Löwdin produced the operator expression (translated into the notation of the present review) $T = Q[aP + Q(E - H)Q]^{-1}Q$ for it, where a is any non-zero number, and then established that $dT/da = 0$. Direct study of the matrix with $[EI(BB) - H(BB)]$ in the BB block and with all other sections zero shows that putting $aI(AA)$ in the AA block leads to an invertible matrix and that the BB block of the inverse is just the inverse $[EI(BB) - H(BB)]^{-1}$, for any value of a , provided that it is non-zero. Thus Löwdin's operator result is easily seen by a visual inspection of the matrix representation, which further

shows, incidentally, that taking the limit of a tending to infinity also gives a zero AA block in the inverse and thus matches to the full T matrix and not just to its BB portion. Löwdin used the operator formalism to derive what is essentially the HL theory of this review, except that he used a one-dimensional A space and so produced an energy expectation value rather than an effective Hamiltonian. He then applied the operator formalism to obtain various perturbation results; to do this he took the single A space function to be an eigenfunction of the unperturbed Hamiltonian, so that his wave operator W simply converts that single unperturbed wavefunction into the perturbed one.

The present review stresses the matrix approach to transformations. In an approach which uses the underlying Hilbert space operators rather than their matrix representations a transformation approach usually leads to a formalism involving operator commutators, particularly when the formalism of second quantization is employed. Two recent examples are the work of Alexian and Moreno (1999) on coupled oscillators and the work of White (2002) on molecular systems. Matrix commutator algebra also appears in the equations of motion approach to many-body theory (Dalgaard and Simons 1977). However, probably the best known form of perturbation theory which involves commutators is the Van Vleck perturbation theory, which uses a transformation operator of the form $\exp(G)$, where G is an anti-Hermitian operator. G is usually taken to be a perturbation series in the perturbing potential V and is chosen so as to produce a transformed Hamiltonian in which the terms up to some specified order in V have been removed. Jordahl (1934) gave one of the first accounts of the low-order theory for a non-degenerate level. A detailed account of Van Vleck theory was given by Kemble (1958). Kirtman (1968) gave the low-order theory for an initially degenerate level, treating the hydrogen atom Stark effect. Jorgensen, Pedersen and Chedin (1975) gave a detailed modern development of the Van Vleck theory, with references to earlier work. Much of this earlier work did not use a wave operator approach and so is not central to the point of view adopted in the present review; however, the more recent works of Hoffmann (1996) and Khait *et al* (2002) on generalized Van Vleck perturbation theory did stress a wave operator approach.

2.5. Alternative forms of the effective Hamiltonian

It should be emphasised that the brief account given here of various effective Hamiltonians is, like several modern accounts, based on ‘wisdom after the event’. The original works of the various authors who created the central concepts of wave operator theory were often conceived in a spirit quite different from that of modern interpretations of their work. For example, some of the early work was based on a perturbation approach to various projection operators or was restricted to the case of an A space with exactly degenerate unperturbed energies. An overall view which unifies large portions of the earlier work has only been achieved in fairly recent times and even then there are several competing forms of synthesis, each one stressing some central concept (e.g., transformations, resolvents) in terms of which earlier work can be systematized. One example of some importance is provided by the Des Cloizeaux effective Hamiltonian HD (described below). Many Hermitian effective Hamiltonians had been proposed in the literature of perturbation theory but it required a detailed analysis to show that several of them were identical to HD , so that HD is nowadays often referred to as the canonical effective Hamiltonian in the family of Hermitian effective operators derivable from an Hermitian H . The work of Klein (1974) was one of the early ones to investigate the links between various effective Hamiltonians. Klein established that HD is the same as the effective Hamiltonians of various other authors who had used a range of apparently quite different techniques to define their own effective Hamiltonians. Although Klein’s work

contained a few technical defects which were later pointed out and rectified by other authors such as Jorgensen (1978) and Brandow (1979) his main conclusions were confirmed by later work. In particular, Klein's 'proximity' test was both explored and modified by later workers (Jorgensen 1975, Brandow 1979, Cederbaum *et al* 1989). The technical details of the various forms of the test can be found in the cited works but the main thrust of them is that the unitary transformation T which produces pre-assigned diagonal blocks in the transformed H matrix and which itself remains as close as possible to the unit matrix (in an appropriate matrix norm) will lead to the canonical form of the Hermitian effective Hamiltonian. A similar kind of 'proximity' result holds for the canonical orthogonalization method of Löwdin (1950) and, indeed, helps to explain the role which it plays in one of the approaches to the construction of the canonical effective Hamiltonian HD ; Mayer (2002) gave a succinct modern derivation of some aspects of the theory.

The concentration on unitary transformations necessarily leads to HD ; in the present work HD is only approached indirectly via the quantities F and HB and the approach via HB only requires that the (BA) portion of the H matrix shall be rendered zero, whereas the approach via unitary transformations aims at a total decoupling in which the (AB) portion is also rendered zero. The most obvious result which emerges in any numerical application of the techniques described above is that the Bloch effective Hamiltonian HB which arises from the reduced wave operator F is non-Hermitian. This feature arises from the requirement that the subspace eigenvectors shall be the exact A space components of the full space eigenvectors. If the full matrix is Hermitian, then the fact that the eigenvectors must be orthogonal in the full space means that the components within the A space will in general not be orthogonal when the inner products are restricted to the A space. Thus the effective Hamiltonian within the model space will not in general be Hermitian. This does not change the eigenvalues, which are still a selection of those for the full space problem. From a linguistic point of view it is perhaps unfortunate that the term 'effective Hamiltonian' has become standard, first since there is an intuitive expectation that a Hamiltonian should in principle be Hermitian and secondly since the mathematical formalism is very general and does not even specify that the full matrix should be symmetric or Hermitian; the wave operator approach can be (and frequently has been) used for matrices which have complex elements. It is clear that changing the effective Hamiltonian HB to $T^{-1}HBT$ to render it Hermitian will simply change the eigencolumn X to $T^{-1}X$; to restore the original (X, Y) Bloch pair then needs an appropriate modification of the transformations involved. One way to modify the form of the effective Hamiltonian is to multiply equation (2.20) from the left by the Hermitian conjugate of $T(F)$ rather than by the inverse of $T(F)$. The resulting matrix equation has an (AA) component which is exactly the same as that which is obtained by simply multiplying the Bloch effective Hamiltonian equation by the SPD matrix $[I + F^\dagger F]$, which for brevity will be denoted by $S(AA)$ in the rest of this discussion. The resulting (AA) component equation is then just a repetition of the HK generalized eigenvalue equation which has already been introduced and which has been seen to give rise to the effective Hamiltonians HKV and HBV .

In a review of methods of treating the generalized eigenvalue problem in quantum chemistry Ford and Hall (1974) discussed several techniques for converting a generalized eigenvalue equation into an equivalent ordinary eigenvalue problem. Most of them have been used in the wave operator literature. One standard way to produce an eigenvalue equation from a generalized eigenvalue problem has already been applied; HBV was produced from the Kato equation by multiplying by the inverse of $S(AA)$. The resulting operator HBV , although having useful variational properties, was not Hermitian. However, an alternative procedure is to note that the SPD matrix $S(AA)$ will have exactly one SPD square root matrix, which will be denoted by $R(AA)$ in the rest of this discussion. Starting from (2.18) and (2.16)

and multiplying from the left by the inverse of $R(AA)$ produces the following eigenvalue equations:

$$HD(AA)(RX) = R[H(AA) + H(AB)F(BA)]R^{-1}(RX) = E(RX) \quad (2.30)$$

$$HDV(AA)(RX) = R^{-1}HKV(AA)R^{-1}(RX) = E(RX). \quad (2.31)$$

The traditional Bloch effective Hamiltonian HB appears in the central square bracket in equation (2.30); the new transformed effective Hamiltonian arising from it has been denoted by HD and is the canonical Hermitian effective Hamiltonian of Des Cloizeaux (1960), which has been derived by many different routes in the literature. The alternative form in equation (2.31) has been denoted by HDV and equals HD if F is an exact solution of the nonlinear equation for the reduced Bloch wave operator. Clearly, HD is not manifestly Hermitian; that it must be Hermitian follows from the fact that it can be shown to be the transformed form of the effective Hamiltonian when the Löwdin symmetric orthogonalization technique is applied to the A space projections of the full space eigencolumns (*not* to the actual normalized HB eigenvectors) Brandow (1979) suggested that the effective Hamiltonian HD should be rendered manifestly Hermitian by taking one half of the sum of HD and its Hermitian conjugate. However, as can be seen from equation (2.31) HDV involves manifestly Hermitian expressions and, through its equivalence to HD , reveals the Hermitian form of the effective Hamiltonian HD in those cases in which the F used is an exact reduced Bloch wave operator. HDV necessarily inherits the variational and upper bound properties of HBV but also has the property that it maintains its Hermitian form even when the F used in it is only an approximate and not an exact solution of the nonlinear equation for the Bloch reduced wave operator. This property would also hold for Brandow's symmetrized form of HD .

The explicit construction of HD from HB , which has itself been found from F , will require the formation of the matrix $S(AA)$ and of its square root $R(AA)$ and also the inverse of $R(AA)$. In the literature the use of power series expansions or of matrix diagonalization methods has been proposed for the calculation of these matrices. Section (3.2) of this review describes a modern technique which is very effective when the elements of the F matrix are small. If it is only the eigenvalues which are needed then those for the form HB are directly obtainable from the relevant eigenvalue equation while those for HK or HKV can be found by solving the associated generalized eigenvalue equations; as has been noted above, the HKV spectrum will differ from those of HB and HK if F is not exact. It is clear that different but equivalent forms of Hermitian effective Hamiltonian can be constructed by using different orthogonalization techniques on the Bloch eigenvectors. Evangelisti *et al* (1991) have suggested the use of Schmidt orthogonalization in some cases. The canonical orthogonalization process is another possible technique and involves the diagonalization of the matrix $S(AA)$ studied above. Yet another approach (also from the Ford and Hall repertoire!) is to note that S can be expressed not only in the form R^2 but also in the form LL^T where L is a lower triangular matrix, for which the calculation of the inverse is relatively easy. This decomposition of S then leads to an eigenvalue equation for the non-canonical effective Hamiltonian

$$HA = L^T[H(AA) + H(AB)F(BA)](L^T)^{-1} \quad (2.32)$$

which has the variational partner

$$HAV = L^{-1}HKV(AA)(L^T)^{-1}. \quad (2.33)$$

The symbols HA and HAV have been used to denote these two Hermitian effective Hamiltonians, since Andreozzi (1996) noted the value of the LL^T decomposition in his

study of effective Hamiltonians. Orthogonalizing the Bloch eigenvectors by means of the Schmidt process, which Evangelisti *et al* (1991) mentioned as sometimes useful, will give the same HA as the LL^T decomposition (but only if the vectors are selected in the correct order).

Calculations which apply the various formalisms described above involve technical steps such as the extraction of matrix square roots, the solution of generalized eigenvalue equations, etc, as well as the solution of the nonlinear equation for the Bloch reduced wave operator F . Later sections of this review will set out some calculational methods which can be used to deal with these technical problems. Inspection of both the energy-dependent and energy-independent formalisms shows that the E which appears in the equations is not any *particular* specified eigenvalue, except for the proviso that it must be such that it has an eigenvector with a non-zero component X in the A subspace which has been chosen. This means that in principle any eigenvector of the full space problem should be obtainable via the wave operator formalism. F obeys a nonlinear equation and it is well known that in general such equations have many exact solutions and even more approximate solutions. For this particular matrix problem it is clear how the many exact solutions arise. For example, if the subspace A is taken to be one dimensional and the full matrix is of $N \times N$ type, then N eigenvalues would in general be expected and could be regarded as the roots of a polynomial equation of degree N . It would then be expected that there should be N different solutions of the nonlinear equation for F , one solution for each of the eigenvalues, since the 1×1 effective Hamiltonian is directly equal to the eigenvalue. If the A subspace is M dimensional then an even greater number of solutions for F would be expected, corresponding to the possible selections of M eigenvalues at a time from the N possible eigenvalues. In most applications, however, an attempt is made to select the subspace A so that the component X is dominant, with the influence of the B subspace being regardable as some form of perturbation. In such an approach it is often natural to use a perturbation expansion in which the coupling between the A and B subspaces is multiplied by a perturbation parameter λ and the various quantities appearing in the theory are derived as power series in λ . This approach naturally tends to pick out those particular solutions which correspond to an F with small numerical components, leading to those eigenvectors which have the largest components in the A subspace. To emphasise this, most authors in the field have used the concept of a target space as well as that of a model space, with the notion that the model space spectrum should give an accurate description of the group of exact eigenstates which form the target space. Strictly speaking, of course, the exact target space is not known at the start of a calculation, although it enters into the formal algebraic theory via its projection operator P , with the model space projection operator being denoted by P_o .

It should be stressed that in this review the authors have chosen to take what experience suggests to be the most simple route through the theory of effective Hamiltonians. This route first finds the wave operator and then constructs the Bloch effective Hamiltonian. Any desired derivative forms such as the canonical Des Cloizeaux form are then constructed by making appropriate calculations using those two previously constructed quantities. This way of approaching the theory places emphasis on rendering zero the $H(BA)$ portion of the Hamiltonian matrix, thus achieving the decoupling transformation which leads to the Bloch theory. However, there exists another approach in the literature in which a full decoupling is attempted in one direct step; in this approach the $H(BA)$ and $H(AB)$ portions of the Hamiltonian matrix are rendered zero simultaneously by using a unitary transformation which leads directly to an Hermitian effective Hamiltonian (usually the Des Cloizeaux one). Although the work of Des Cloizeaux (1960) is the best known one in this tradition, the work of Choi (1975) and that of Speisman (1957) have some interesting features. Choi's algorithm, although used to produce algebraic expressions, appears to be

capable of a purely numerical implementation which would construct the canonical effective Hamiltonian directly. The present authors have not had sufficient time to investigate the associated programming difficulties but consider Choi's algorithm as an interesting topic for further research. Speisman's work involves some lengthy algebraic manipulations but has the interesting formal feature that it manages to incorporate what is essentially the Bloch F matrix of the present work into a unitary (rather than just a similarity) type of transformation; it thus succeeds in obtaining the canonical effective Hamiltonian directly, rather than incorporating factors involving the $S(AA)$ matrix afterwards to convert HB into HD . Both of the works just cited proceed by deriving algebraic expressions for the low-order terms of the perturbation series for the effective Hamiltonian and they deal only with the case of a set of unperturbed states which initially belong to the same degenerate energy level. Nevertheless this method of approach via the direct construction of an effective Hamiltonian, although not as simple as that via the wave operator concept, appears to compare favourably with the more traditional approaches to degenerate perturbation theory which have to vary their treatment according to the order of perturbation at which the degeneracy is removed; Hirschfelder (1969) gave an account of this traditional approach and Larcher and Chong (1969) gave an account of it in terms of a sequence of operations on appropriately constructed matrices. Choi (1969) treated degenerate perturbation theory by a repeated partitioning approach which reduced the treatment of each level split off from an initially degenerate level to that of a single nondegenerate level.

The approach which is adopted in the present review and in most works on wave operator methods is to keep a fixed set of basis functions in the A space. The eigenvectors of the effective Hamiltonian HB are then termed 'bonne fonctions' by some authors, since they are correctly aligned along the A space components of the full space eigenvectors, so that the F matrix will generate the B space components from them. In the approach adopted by workers such as Certain and Hirschfelder (1970) and Hirschfelder (1978) the initial concept used is that of a small space of exact eigenvectors of H ; the perturbation expansions used are then seeking to produce this space starting from an equal number of unperturbed eigenvectors. At each stage it is the full Hamiltonian H which is used in the matrix diagonalizations associated with each order of perturbation and the calculations can be regarded as being generalized matrix eigenvalue calculations for the matrix of H set up in a basis of RS perturbed eigenfunctions. This appears to set the Certain and Hirschfelder approach in the same tradition as the full space calculation set out as method 3 in this review, which also uses the full H to obtain variational behaviour. However, method 3 condenses the effect of the full space calculation into the variational effective Hamiltonian HBV and this operator acts in the fixed A space. In an appendix of their paper Certain and Hirschfelder (1970) demonstrate that the energies given by their approach at each order are equal to those which can be obtained by a perturbative method based on the use of the Löwdin operator which has been denoted by HL in the present work.

2.6. An implicit equation for HB

Since F and HB are closely related and since F obeys a nonlinear equation in its own right it seems natural to anticipate that HB might also obey some nonlinear equation. Des Cloizeaux (1960) derived such an equation, which turned out to be much less convenient than the one obeyed by F . In several of the iterative and perturbative calculations of the present review the equation for F has been cast in a hybrid form which gives equal emphasis to both F and HB and which has been found to be more useful in numerical work. However, a derivation of the implicit equation for HB is given below, since it gives some extra insight into the

relationship between the effective Hamiltonians HL and HB and also into the common practice of choosing the unperturbed energy levels in the model space to be degenerate.

The first step in the derivation is to assume that all the levels in the model space start off with the common energy e and that both HL and HB have been redefined so that they describe the level shifts and splittings which are produced by adding a perturbing potential V . To emphasise this it is useful to write HB in the form

$$HB = eI(AA) + VB \quad (2.34)$$

and HL in the form

$$HL(E) = eI(AA) + VL(E) = eI(AA) + V(AA) + TV(1, E) \quad (2.35)$$

with

$$TV(N, E) = V(AB)[EI(BB) - H(BB)]^{-N}V(BA). \quad (2.36)$$

For the X component $X(E)$ of an eigenvector with the eigenvalue E the theory developed in the preceding sections makes it clear that the following equality must hold

$$(E - e)X(E) = (VB)X(E) = VL(E)X(E) \quad (2.37)$$

where by definition VB is the same for all the possible eigenvalues E but $VL(E)$ depends on E . $VL(E)$ can be formally expanded about the reference value e to give the result

$$VL(E)X(E) = [VL(e) - TV(2, e)(E - e) + TV(3, e)(E - e)^2 \dots]X(E). \quad (2.38)$$

The crucial point about this expansion is that $(E - e)$ behaves just like a pure number and so can be moved to the right through all the other terms which appear in the expression for $VL(E)$. When the expanded $VL(E)$ acts on $X(E)$ it is thus possible to replace the powers of $(E - e)$ by powers of VB . If it is then assumed that the set of $X(E)$ for varying E forms a basis for the model space then the results above can have the operand $X(E)$ removed in order to obtain an operator equation in which E does not appear

$$VB = VL(e) - TV(2, e)VB + TV(3, e)VB^2 \dots \quad (2.39)$$

This equation can be solved iteratively to give a sequence of solutions:

$$VB(1) = VL(e) \quad VB(2) = VL(e) - TV(2, e)VL(e) \quad (2.40)$$

$$VB(3) = VL(e) - TV(2, e)VL(e) + [TV(2, e)]^2VL(e) + TV(3, e)VL(e). \quad (2.41)$$

In principle the terms $TV(m, e)$ can be obtained by solving a sequence of sets of linear equations. However, although the formal results shown above have sometimes been used to obtain algebraic perturbation expansions they are not well adapted to numerical calculations. In the case in which the initial set of levels in the model space is not degenerate the absence of a common scalar factor $(E - e)$ makes the simple approach used above inapplicable. Durand and Paidarova (1996) gave a formal treatment of the more general case but the apparent simplicity of their implicit equation for the effective Hamiltonian was only obtained by introducing superoperators which reverse the order of some operators acting between the A and B subspaces and which if used in numerical work would in principle involve the inversion of large matrices. Since the first approximation to VB obtained above is $VL(e)$, which will be Hermitian, it seems that a simple way to proceed in the quasidegenerate case would be to use $HL(e)$ for some appropriate average e value, then form the resulting approximate F and use it in the variational effective Hamiltonian HBV to obtain reasonably accurate eigenvalues. Such an approach would be useful if the linear equations appearing in the HL calculation were being solved by a Gauss–Seidel method which does not converge for E values which are towards the top of the model space spectrum.

2.7. The use of three subspaces

The simple theory and calculations set out in the preceding sections use only two subspaces, the model space and its orthogonal complement. In the formal theory of the wave operator the (unknown) target space and its orthogonal complement are also sometimes introduced, so that four subspaces appear in the theory. Most of the numerical test calculations of the present work use only the known A and B subspaces, with various kinds of folding process to incorporate the influence of the B space basis functions into an effective Hamiltonian in the A space. This approach can be extended to a cascading folding process involving more than two subspaces; the most trivial example of this is the folding method for matrix eigenvalues (section 3.3). Several authors have made theoretical or calculational use of three subspaces. Barrett (1974) described the history and use of the doubly partitioned Hilbert space method in nuclear theory. In this approach a few shell model states form the A space and the excited state basis functions which would usually be the B space are partitioned into a B part and a C part, with the C part containing the high energy basis states. Leaving aside highly specialized technical details the calculation can be roughly described as one in which the $C \rightarrow B$ folding produces a less singular effective potential based on the Brueckner reaction matrix (which obeys an implicit equation similar to that in BW theory) and then the $B \rightarrow A$ folding uses this effective potential in an effective Hamiltonian calculation in the A space.

In atomic theory Taylor (1974, 1983) made use of an approach in which three subspaces are used. The A subspace contains the approximate atomic or molecular groundstate, which could be taken to be a determinantal function in which the orbitals have been found by the Hartree–Fock method. Brillouin’s theorem will then ensure that only doubly excited functions will be directly linked to the groundstate function by the residual perturbation which describes correlation effects. In the simple linear equation of perturbation theory with the intermediate normalization convention the energy shift depends only on the coefficients of those directly coupled states in the perturbed wavefunction. However, there will also be a small indirect influence from the singly excited states, which are still coupled to the doubly excited states. If the excited state basis functions are partitioned into a B space of doubly excited functions and a C space of singly excited functions, then the matrix portion (AC) will be zero. This simplifies the form of the partitioned eigenvalue problem. The $C \rightarrow B$ folding gives an extra effective potential term which modifies the effective $B \rightarrow A$ coupling and so gives an extra correlation energy shift at the $B \rightarrow A$ folding stage.

A triply partitioned space was also used by Jolicard and Billing (1990); figure 1 of their paper gives a partitioned matrix view of their procedure. Their iterative calculation makes use of diagonalization in the A space together with first-order recursive distorted wave (RDWA) transformations intended to reduce first the CA coupling and then the BA coupling. The final result is an A space which is decoupled from the B and C spaces; the original feature is that the B space (the intermediate space) is generated during the calculation as being formed by states which (at a given step) still have an appreciable remaining coupling with the evolving A space eigenstates. This B space acts as a kind of ‘buffer space’ which cuts down intruder state problems. The second-order perturbation method of Staroverov and Davidson (1998) also used three spaces, with the inner two spaces being called the reduced and full model spaces; the reduced model space refers to the basis functions which dominate in the wavefunction of the actual state being calculated and an iterative process has to be used to determine effective Hamiltonians in the two spaces. Khait and Hoffmann (1998) also used three subspaces in a process which refines the inner model space by an iterative procedure very similar to that used by Jolicard and Billing (1990). The recent work by Durand *et al* (2000) on resonances in H_2^+ set out a range of useful techniques. The Bloch wave operator approach is applied to a large

non-Hermitian matrix and the space of basis functions is partitioned into three subspaces to improve the convergence of the iterative calculation of the wave operator. Further, the iterative method used is of ‘almost’ second order, being a computationally convenient approximation to a Newton–Raphson calculation.

In this review (and in much of the literature) a matrix or operator point of view is adopted. Although the F matrix obeys a nonlinear equation it is given by a simple linear formula in first order. It is thus of interest to note that Dalgarno and Lewis (1955) introduced a quantity f as the ratio of the first-order perturbed wavefunction to the unperturbed wavefunction in their treatment of the one-dimensional perturbed Schrödinger equation. In their differential equation formalism f then was found to obey a linear differential equation. Young and March (1958) used the notation of Speisman (1957) in giving an account of the relationship between the operator form of perturbation theory and the use of the f function in a differential equation approach. They pointed out that in principle the technique can be extended to higher orders of perturbation theory. Later workers developed much further the original ideas of Dalgarno and Lewis and Young and March, developing logarithmic perturbation theory and other techniques in the differential equation approach to the Schrödinger equation. Au (1997) gave a brief account of the history and recent developments of this area of theory, which is only mentioned here because of the partial resemblance between the f of Dalgarno and Lewis and the F matrix of wave operator theory.

2.8. Partitioning methods in engineering

A search of the engineering literature reveals that the use of matrix partitioning has been widespread in vibration theory for some time; Dong *et al* (1972) cite papers as far back as 1909. They also describe a method of iterative calculation which makes use of the equivalent of the wave operator W of the present work. In some respects it could be said that the partitioning method of vibration theory is more general than that of quantum mechanics, since it has always been formulated in terms of the generalized eigenvalue problem rather than the ordinary eigenvalue problem. However, with a little thought it is not difficult to rewrite the theory associated with the energy-dependent effective Hamiltonian HL in a style which is appropriate to a generalized eigenvalue problem. Using the symbol S temporarily in this paragraph to denote the overlap matrix of the basis function, this generalized eigenvalue equation takes the form

$$\begin{pmatrix} H(AA) & H(AB) \\ H(BA) & H(BB) \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = E \begin{pmatrix} S(AA) & S(AB) \\ S(BA) & S(BB) \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (2.42)$$

The formal device which simplifies the algebra (and which is sometimes useful in calculations) is to rewrite this equation by putting $H - ES$ on the left, with a formal zero eigenvalue on the right. The whole of the partitioning theory presented previously can then be carried out with the matrix H replaced by the matrix $G = H - ES$. The final reduced equation for X can then have its $-ES(AA)$ term separated off to the right-hand side again to give an A space generalized eigenvalue problem of the form

$$[H(AA) - G(AB)G(BB)^{-1}G(BA)]X = ES(AA)X \quad (2.43)$$

which can be used to treat the generalized eigenvalue problem in an iterative calculation similar to that used for HL , provided that it is remembered that for a generalized eigenvalue problem the Rayleigh quotient for a trial column involves division by the expectation value of the metric matrix S (rather than that of the unit matrix). The derivation sketched above is a translation into the present context of a method which has appeared in various guises in the engineering literature, where it is written in terms of load patterns, stiffness and mass

matrices, etc, and where the eigenvalue is the square of a vibrational angular frequency and so is a positive number if the reference equilibrium configuration of the structure considered is a stable equilibrium. (The presence of complex eigenvalues would indicate that the initial equilibrium was unstable.) Multiplying (2.43) from the left by the inverse of $S(AA)$ gives an eigenvalue equation involving an energy-dependent effective Hamiltonian which is the most natural generalisation of HL for the case of a non-orthonormal basis. De Andrade and Freire (2003) have recently given a detailed analysis of this operator and of several other effective Hamiltonians which can be used when the basis is non-orthonormal.

A careful translation of one of the iterative methods described by several authors (Geradin 1971a, 1971b, Dong *et al* 1972, Popplewell *et al* 1973, Shah and Raymund 1982) was made by the present authors, since it is often cited as being of guaranteed convergence. In terms of the concepts of the present work (and posed in terms of the ordinary eigenvalue problem) the method proceeds by starting with an approximate wave operator W , for example from first-order theory, and then solving to find the eigencolumns of the A space generalized eigenvalue problem which arises when the full partitioned H matrix eigenvalue is multiplied from the right by W and from the left by W^\dagger . (This is in effect the use of the operator HBV .) A set of approximate full eigencolumns is then constructed, using the W operator to form the B space components. This set of columns is then acted on by the inverse of the *full* matrix H to give a new W , which is then used in the next cycle, and so on. (With a positive definite H this operation with the inverse could be replaced by a Gauss–Seidel solution of the appropriate linear equations.) The reason for the convergence of the method is clear from this description, since the method is in effect the inverse power method, which would tend to drive any column towards the eigencolumns with eigenvalues at the bottom end of the spectrum. The intervening step of using HBV or its equivalent is simply a means of separating out M columns (for an A space of dimension M) to produce the M lowest levels of the spectrum of H rather than M copies of the groundstate. One of the works in the engineering literature which gave an account of the method in a spirit somewhat similar to that adopted in the translation given above was that of Lam and Bertolini (1994), who modified the inverse iteration part of the calculation in an attempt to speed up the rate of convergence.

For an H which is not positive definite an appropriate shift would have to be used. Alternatively the use of $(H - e)$ would tend to pick out the spectrum in the vicinity of e . A similar technique was used in the variational Rayleigh iteration method of Killingbeck and Jolicard (1996), which used a variational principle which allows the effect of the operator $(H - e)^{-2}$ on a vector to be estimated by using the positive power $(H - e)^2$. The filter diagonalization techniques for matrix eigenvalue calculations have also used various localized functions of H to concentrate attention on specific parts of the eigenvalue spectrum (Iung *et al* 1993, Wyatt 1995, Jolicard *et al* 1996, Minehardt *et al* 1997, Alacid *et al* 1999). Nakatsuji (2002) recently developed a theory for the inverse shifted Hamiltonian based on the traditional theory for the Hamiltonian, with an inverse Schrödinger equation and an associated variational principle. That work was a development of his earlier work on the structure of the exact wavefunction (Nakatsuji 2000), which gave various theorems about the representation of an atomic or molecular wavefunction in terms of single and double excitation functions. Nakatsuji and Ehara (2002) later showed that this approach was efficient in producing full configuration interaction results while using a sequence of iterations in each of which only a small number of variables is involved.

There are methods, however, which directly use positive powers of $(H - e)$ in their own right, usually by varying a trial vector in order to minimize the expectation value of $(H - e)^2$; Feller (1974) described an approach of this type. A few preliminary calculations suggest that for small matrices the random search method used for the wave operator in section (4.2) can

also be used for this type of calculation, although it is obviously far less efficient than other methods.

2.9. *The wave operator in atomic and molecular theory*

A search under the headings ‘perturbation theory’ and ‘wave operator’ on a modern scientific database yields several thousand references. It is thus only possible here to refer to a few selected works which illustrate some typical features of wave operator or perturbation techniques, although further references are scattered throughout other sections. One of the standard models of simple molecular orbital theory is the π electron theory of conjugated planar molecules. The early history of the Huckel and other semi-empirical approaches to this theory are set out in books such as that of Parr (1964). The more modern attempts to justify the earlier work from first principles include that of Harris (1967) using Van Vleck theory and that of Freed (1972), which started from an HL effective operator of the type used in the present work. Probably the most comprehensive work on the topic was that of Brandow (1979), which used several different forms of effective Hamiltonian and also gave a good review of general theory.

Authors who tackled molecular problems by using RS perturbation theory in its traditional form, which requires the sequential calculation of the perturbed wavefunctions of each order, include Laidig *et al* (1985), Knowles *et al* (1985) and Olsen and Fulscher (2000). In the majority of the works dealing with molecules the approach has been to concentrate on producing such a good first approximation to the wavefunction that the use of only the first-order wave operator and of second- or third-order perturbation theory will suffice to give accurate results. A study of the formula for the first-order wave operator shows that it does not involve the off-diagonal Hamiltonian matrix elements in the B space; this serves to make the calculations more easy. Setting these off-diagonal elements to zero to simplify the higher order calculations gives what is called the B_K approximation. When the A space is taken to contain several important basis functions and a preliminary diagonalization has yielded a good first approximation to (say) the ground state, then there are two ways to proceed when considering the second-order effects due to the many basis functions in the B space which are weakly coupled to the chosen one in the A space. The calculation can simply leave the chosen state unchanged and work out the diagonal part of the effective Hamiltonian as an energy shift (if the energy gaps in the A space are already fairly large) or it can allow a readjustment of the original coefficients in the initial state vector because of the second-order coupling terms in the effective Hamiltonian; this second approach is called ‘coefficient relaxation’ by some authors and it sometimes requires very careful reading to ascertain whether it has been used. An early use of second-order perturbation theory was the H_2 calculation of Schulman and Kaufman (1970), while a more recent example was the work of Illas *et al* (1991) in which the A subspace was gradually enlarged to ensure that the effect of the many B space configurations could indeed be described well by second-order theory. Works which carefully showed the sum over states expansions of the effective Hamiltonians which they used include those of Wang and Freed (1989a, 1989b), Graham and Freed (1992), Kozłowski and Davidson (1995) and Nakano *et al* (2001). Works which made explicit use of the Bloch equation and the first-order wave operator include those of Finley (1998a, 1998b), Finley and Hirao (2000) and Choe *et al* (2001). Gwaltney *et al* (2000) derived the terms in their effective Hamiltonian by starting from a matrix partitioning approach and the HL operator. De Graaf *et al* (2001) used second-order perturbation theory to study magnetic couplings in ionic insulators and Chakravorty and Davidson (1996) used it to improve the Z^{-1} expansions for the energy of

atomic ions. Parisel and Ellinger (1996) gave a lengthy account of the use of second-order perturbation theory in molecular calculations, with many references.

Perhaps the best known case of intruder state effects in atomic theory is that provided by the Be atom, for which any reasonable initial approximation shows the $1s\ 2s3s$ singlet state to lie between the $1s2s^2$ and the $1s2p^2$ singlet states, whereas the true ground state is dominated by the latter two configurations. A detailed analysis of this system was given by Finley *et al* (1996), who adopted a wave operator perturbation approach and discussed variants of the MP and EN choice of unperturbed Hamiltonian which can improve the rate of convergence of the energy calculations when the A space involves the $1s2s^2$ and the $1s2p^2$ states. They also gave many references both to earlier work on Be and to alternative theoretical approaches to deal with the intruder state problem. Sawatzki and Cederbaum (1986) showed how varying the choice of the unperturbed Hamiltonian can avoid intruder state problems and applied their methods to calculate the energies of five eigenstates of the H_2 molecule by perturbation theory. Choe *et al* (2001) used a two-state model to analyse the behaviour of possible intruder states in their second-order calculations and then used appropriate shifts in a redefined unperturbed Hamiltonian in order to remove the harmful effects of the intruders. In principle atomic and molecular problems must necessarily involve a B space which is of infinite dimension, which means that the matrix representation of the problem is truncating the B space in some way, although with modern computers the B space can be made to contain many thousands of basis functions. For second-order perturbation calculations of the ground state energy of an atom or molecule it is possible to apply a well-known method from the early history of quantum mechanics, the Hylleraas variational principle, which produces definite lower bounds to the modulus of the second-order energy contribution as the trial function for the first-order perturbed function is varied. It also leads to an estimate of the third-order energy and permits the use of trial functions which can be more complicated than those encompassed by a finite orbital basis, although these two features do not seem to have been much exploited in molecular calculations. An informative paper which used both the Hylleraas principle and the partitioning approach to the eigenvalue problem is that of Cave and Davidson (1988a) and Certain and Hirschfelder (1970) described a generalized Hylleraas approach for multidimensional reference spaces. Meath and Hirschfelder (1964) had much earlier applied variational principles similar to the Hylleraas one in their study of BW perturbation theory.

An obvious candidate for the application of partitioning techniques is the Dirac theory of the electron, since the common case in which the third and fourth components of the relativistic wavefunction are small seems to call for an approach which represents their effects by means of a modified Pauli theory involving only the two large components. Long ago Blinder (1960a) used a partitioning approach to achieve this, in his theory of atomic hyperfine interactions. More modern approaches to the Dirac equation which specifically used wave operator methods were those of Rutkowski and Schwarz (1996), Rutkowski (1999) and Kutzelnigg (1999). Kutzelnigg and Liu (2000) used quasidegenerate perturbation theory and an effective Hamiltonian approach to incorporate relativistic effects in a multiconfiguration self-consistent field calculation.

The coupled cluster approach represents the wave operator in the formalism of second quantization and sets it equal to $\exp(f)$, where f is a sum of creation operators which generate single, double and occasionally higher excitations from the one or more initial functions taken as reference functions. Coester (1958) within nuclear theory and Cizek (1966) within molecular theory are usually regarded as having established the basic concepts of the CC theory and there have been many subsequent works on the theory and applications of it, e.g. Monkhorst *et al* (1981), Kaldor and Haque (1986), Lindgren (1991), Meissner and Bartlett (1991, 1995), Kowalski and Piecuch (2000a, 2000b). In the $\exp(f)$ wave operator of CC

theory f includes a string of creation operators, each with an unknown coefficient which remains to be determined during the calculation. This exponential form adds a further layer of nonlinearity to that which would already be present by virtue of the nonlinear form of the generalized Bloch equation (a similar but milder effect appears in traditional Van Vleck theory). Meissner and Paldus (2000) commented that a CC structure can be incorporated into the theory after performing a more direct treatment via the generalized Bloch equation. Kowalski and Piecuch (2000a, 2000b) used a homotopy approach to find a large number of solutions of the generalized Bloch equation, pointing out the even greater variety of solutions which would arise in a CC formalism in which approximate solutions of the equations were also allowed. Many books have been written on the application of perturbation and other techniques in quantum chemistry. Two which the present authors have found particularly informative are those of Szabo and Ostlund (1996), which set out the principles of Hartree–Fock theory and included an outline of the diagrammatic approach to many-body perturbation theory, including the linked cluster concept, and that of Nooijen (1992), which gave a detailed exposition of the coupled cluster theory, of second quantization and of diagrammatic methods. In a recent work Noga *et al* (2002) started from a coupled cluster approximate wavefunction for a molecule and then improved it by using a perturbation approach based on the connected moments perturbation theory introduced by Cioslowski (1987).

2.10. A comment on intermediate Hamiltonians

Although the test calculations of part 1 of this review do not include any which use the intermediate Hamiltonian concept, it is still worthwhile to see how some of the basic mathematics associated with the intermediate Hamiltonian can be expressed in terms of the simple partitioned matrix approach which has been used throughout the present work. The works of Malrieu *et al* (1985) and Evangelisti *et al* (1987) were the principal ones which explained how the problems of intruder states and avoided crossings led to the introduction of the intermediate Hamiltonian concept. The ideas involved are most easily understood for the case of a matrix for which the matrix elements are all functions of one variable parameter x . As x varies the diagonal elements might cross and the off-diagonal coupling between different states will vary. If the A space used in a wave operator approach for one or two of the lowest eigenstates is a fixed one which gives good results for small x values then as x increases the varying diagonal spacings and couplings might make higher state contributions dominate the lowest energy level eigenvectors. This would reveal itself by the presence of large numerical elements in the reduced wave operator F and F would become difficult to calculate by numerical methods and probably quite impossible to calculate by perturbation methods. Such matrices with one variable parameter appear amongst the test matrices of this review and the type of effect outlined above is discussed whenever it appears in the results of the test calculations of section 4. After describing several chemical systems for which similar problems arise, Malrieu *et al* (1985) introduced the concept of an intermediate Hamiltonian which, while acting in an extended model space, is only required to describe accurately the lowest few states in a main model space. The remaining states in the intermediate space are only given an approximate description but serve to protect the main model states against intruder state effects. If the partitioned matrix notation used so far in this review is extended in an obvious way to allow for the main model space A , the intermediate space B and the remaining large space C , then the two wave operators appearing in the method of Malrieu *et al* are the W which has already appeared in earlier sections and an extra wave operator R . The two operators have the following non-zero portions:

$$W(I(AA), F(BA), F(CA)) \quad \text{and} \quad R(I(AA), I(BB), G(CA), G(CB)). \quad (2.44)$$

Thus W is a standard wave operator for subspace A (with its F column split into two parts) while R is somewhat like a wave operator for the model space $A + B$, except that it does not need to obey the full appropriate nonlinear equation. In order to ensure that the accurate results provided by W are preserved by the new operator R in the extended model space it is necessary to impose the requirement that $RW = W$. Inspecting the possible matrix products of the W and R matrices as displayed above shows that only the CA component gives a non-trivial result, in the form of an equation which relates the portions of the reduced wave operator parts of W and R :

$$G(CA) + G(CB)F(BA) = F(CA). \quad (2.45)$$

This result shows that the constraint imposed on R is not very onerous; once $G(CB)$ has been chosen in some way then $G(CA)$ follows if the A space matrix F is already known. The simple choice $G(CB) = 0$ leads to the result $G(CA) = F(CA)$.

The intermediate effective Hamiltonian in the extended model space $A + B$ is formed by the standard Bloch Hamiltonian rule, which can be written here in the condensed but obvious form

$$HB(AB, AB) = H(AB, AB) + H(AB, C)G(C, AB) \quad (2.46)$$

where, for example, $H(AB, AB)$ is made up of four submatrices. The special choice $G(CB) = 0$, $G(CA) = F(CA)$ makes several of the terms in $HB(AB, AB)$ zero and produces the intermediate Hamiltonian with the non-zero portions

$$\begin{aligned} &(AA)\{H(AA) + H(AC)F(CA)\} (BB)\{H(BB)\} \\ &(AB)\{H(AB)\} (BA)\{H(BA) + H(BC)F(CA)\} \end{aligned} \quad (2.47)$$

Since this simple result shows a marked asymmetry Malrieu *et al* (1985) proposed an approach in which the standard form of the generalized Bloch equation $HW = WHW$ is modified to the form $HR = WHR$ and they gave a perturbative algorithm which produces the series for R if the series for W is known. They also gave an alternative approach in which the whole of the intermediate Hamiltonian is calculated as a perturbation series under the assumption that the unperturbed main model states all have the same energy; that is why test matrix 3, which comes from their paper, has its first five diagonal elements equal. That matrix was later used by Zaitsevskii and Dement'ev (1990) and by Chaudhuri and Freed (1997), who stated (incorrectly) that the standard RS series for the case of a five-dimensional A space and a fifteen-dimensional B space diverges. In the work of the other authors cited and in the calculations of the present review the series for F and for HB were found to converge; Malrieu *et al* simply claimed that their intermediate Hamiltonian approach gave a quicker convergence but commented that the associated series should have the same radius of convergence as the standard RS series.

Malrieu *et al* (1985) asserted that any solution R of the equation $HR = WHR$ must also obey the equation $RW = W$, whereas Zaitsevskii and Dement'ev commented that the only appropriate solution to the equation $HR = WHR$ is the very simple one set out above (with $G(CB) = 0$). The calculations of Malrieu *et al* do in fact give the correct energies for the main model space, which supports their assertion, and appendix 2 of their paper gives what is intended to be a general proof of it. Inspection of their numerical examples show that they both use matrices in which the A and B spaces have the same dimension, so that several of the quantities appearing in the theory are invertible square matrices. The present authors conjecture that the 'theorem' of Malrieu *et al* is valid only in cases for which the A and B spaces have the same dimension. It might also be noted that in such cases it would be possible to assign the values of the $G(CA)$ elements in $F(CA)$ and then find

the values of the $G(CB)$ elements by using the inverse of the square matrix $F(BA)$. In general the concept of an intermediate Hamiltonian which does some things exactly and other things approximately is somewhat imprecise and various authors have devised ways of calculating such operators which do not use the specific formalism employed by Malrieu *et al* (1985). Zaitsevskii and Dement'ev (1990) used a BW iterative approach which gradually constructed the main and model spaces without the need to choose fixed dimensions for them at the start of the calculation. Malrieu *et al* (1994), Zaitsevskii and Malrieu (1997) and Chaudhuri and Freed (1997) all proposed particular ways of defining and calculating intermediate Hamiltonians and Landau *et al* (2000) described a coupled cluster version of the intermediate Hamiltonian. Evangelisti *et al* (1991) took an alternative approach to handling the intruder state problem by using a formalism in which the energies for the desired target space states are found by solving a generalized eigenvalue problem in a model space which contains some extra dimensions, while abandoning the notion of a one-to-one correspondence between model and target space states. Datta *et al* (1996) and Meissner and Malinowski (2000) used coupled cluster theory to define an intermediate Hamiltonian; Datta *et al* used partitioned matrices to explain their approach. Meissner and Nooijen (1995) used similarity transformations to treat both the standard Bloch Hamiltonian and intermediate Hamiltonians and gave an approach to the intermediate Hamiltonian which they stated to be equivalent to the use of the $HR = WHR$ criterion of Malrieu *et al* (1985). In its study of the derivation of the Bloch effective Hamiltonian their work had the interesting feature of first applying a transformation to render zero the BA portion of the Hamiltonian matrix (as in the present work) and then applying a subsequent similarity transformation to the transformed matrix to render zero the AB portion without disturbing the zero nature of the BA portion.

3. A selection of useful techniques

The present section gives an explanation of several techniques, some of them gleaned from the mathematical literature, which are useful in treating either the construction or the diagonalization of the Bloch and other effective Hamiltonians in the A (or model) subspace. The assumption made throughout is that the effective Hamiltonian matrix is of relatively low dimension but, although often real, cannot be assumed to be symmetric. Several of the techniques described are best suited to the perturbative regime (the most common one) in which F has numerically small elements. The problem of solving the nonlinear equation for the reduced Bloch wave operator is not dealt with in this section, since several ways of tackling it are described in later sections.

3.1. Matrix diagonalization by the single cycle method

The SCM was introduced by Périé *et al* (1993) in connection with calculations using the wave operator approach; this application is described in some of the test matrix calculations of this review. The SCM was originally developed as an improvement of the recursive distorted wave approach (RDWA) to the calculation of the wave operator but was later developed (Killingbeck, unpublished) to become a full matrix diagonalization technique which has some resemblance to the traditional Jacobi method and which has found several different applications in the present work. The method uses the similarity transformation approach described in section (2.4) and exploits the multiplicative properties of partitioned matrices. The idea is to start with the matrix H and the unit matrix $C = I$ and to transform them both together, so that H becomes diagonal and C is transformed into the matrix of eigencolumns. The matrix H

need not be symmetric, which makes the method effective for dealing with the Bloch effective Hamiltonian HB . The schema

$$(HX = EX) \rightarrow (U^{-1}HU)(U^{-1}X) = E(U^{-1}X) \quad (3.1)$$

shows how the calculation proceeds, but a little thought reveals that if the initial C matrix is the unit matrix then the transformation $U^{-1}HU$ of the matrix H should be accompanied by the transformation to the right by U of the C matrix in order to produce the matrix of eigencolumns. Each of the transformations used is one for which the U matrix is a unit matrix plus a single non-zero element $F(J, K)$ for which the numerical value w is given by the first-order wave operator perturbation formula

$$w = H(J, K)/[H(K, K) - H(J, J)]. \quad (3.2)$$

The effect of the (J, K) similarity transformation can be summarized by listing the changes to be made (in strictly the specified order) to the elements of H and C

For H and C	add w times column J to column K
Then for H	subtract w times row K from row J .

The most simple procedure is to perform the (J, K) transformations cyclically, covering all the non-diagonal elements in turn, with as many complete cycles as are needed to render the sum of the moduli of the off-diagonal elements of H less than some very small tolerance value. It is clear that a problem arises if $H(K, K) = H(J, J)$. However, in numerical test calculations it has been found effective to simply jump over such (J, K) elements and also to adjust large w values by applying a damping formula

$$w \rightarrow w/[1 + K|w|] \quad (3.3)$$

where K is typically between 0 and 5 and ensures that the w value does indeed give a 'small' transformation. As the (J, K) indices are scanned cyclically, experience shows that a collective effect takes place; elements which when undamped would give large or infinite w values are gradually reduced by the actions of the other transformations and so tend to zero with all the other elements. Perhaps the most dramatic example of this cooperative effect is provided by the 50×50 matrix which is test matrix number 4 of the specimen numerical calculations of this work. That matrix has all diagonal elements equal except the $(1, 1)$ element and yet the method succeeds in giving the full spectrum of the matrix, since the small group of transformations which are initially possible gradually modifies the elements of H and turns on the previously forbidden (J, K) transformations. In the exceptional case that all the diagonal elements of the matrix are initially equal it has been found effective to perform one initial scan using w values which are small random numbers. This separates the diagonals sufficiently for the ordinary algorithm to become effective without changing the final results. The method described here is similar to the standard Jacobi method, although it involves no trigonometric functions or square roots. It shares with the Jacobi method the feature that the final set of diagonal elements of H (i.e., the eigenvalues) need not be in a monotonic numerical order. For small effective Hamiltonian matrices this is not troublesome, but in general it is useful to add an extra step which suitably orders the eigenvalues and their associated eigencolumns.

In the test matrix calculations reported in this work the SCM diagonalization approach was the method of choice for finding the spectrum of the Bloch effective Hamiltonian. In the matrix diagonalization calculation the aim is to render zero all the off-diagonal elements of H , but the method can also be used to calculate the reduced Bloch wave operator by choosing instead to make a chosen rectangular portion of the H matrix zero, in a direct numerical application of the theory described in section 2.4. If the H matrix is complex,

with complex eigenvalues, then a version of the method which uses complex arithmetic can be applied and has been used for several calculations in wave operator and matrix theory. However, since the method is essentially based on a perturbative formula, it should be anticipated that the transformation sequence might not converge if the initial H matrix has very large off-diagonal elements. This point needs further investigation, although the use of a sufficiently large K value in the damping formula (3.3) has so far rendered the method successful for most such cases. The role of the damping formula in this method appears to be analogous to that of the inverse tangent function in the Jacobi method; in both methods the effect is to limit the magnitude of the elements in each individual transformation of the sequence.

Some trial calculations were carried out with a modified SCM (SCJM) which is very close to the Jacobi method. The modification is best explained by displaying the set of four elements with indices J and K which appear in the transforming matrix for the (J, K) step in the two methods. These are

$$(\text{SCM}) \begin{pmatrix} 1 & 0 \\ w & 1 \end{pmatrix} (\text{SCJM}) \begin{pmatrix} u & -w \\ w & u \end{pmatrix} \quad (3.4)$$

where u is the positive square root of $1 - w^2$ so that w and u in effect resemble the sine and cosine appearing in the traditional Jacobi method. The inverse of the SCM form is found by reversing the sign of w , while the inverse of the SCJM form is simply its transpose. The rules for finding w were left unchanged in the test calculations with the SCMJ form, with K being kept sufficiently large to ensure that the square root operation to find u is always permitted. The SCJM approach works well, but was not adopted to replace the more simple SCM for two principal reasons. First, since SCJM uses unitary transformations it is appropriate for use with Hermitian or real symmetric matrices, while the SCM is more general and does not require the initial matrix to be symmetric. Secondly, when the SCJM in the form described above was applied to the calculation of an effective Hamiltonian (as described for the SCM in section 4.3) the resulting effective Hamiltonian was indeed symmetric but was not in the canonical HD form which appears throughout most of the literature of wave operator theory. For both of the above reasons it was decided to stick to the simple SCM, which finds a variety of applications in the test matrix calculations which are reported later. Hoffmann (1996) used a transformation approach which was almost exactly the same as the Jacobi method in his calculations of the wave operator but only went as far as finding the first-order wave operator and the second-order effective Hamiltonian.

The matrices treated in the present work are all real. For a complex matrix it is easy to set up the relevant formulae using complex arithmetic and the forerunner of the SCM, the RDWA, has been used for various calculations on complex matrices (Jolicard and Billing 1990). One difficult corner of matrix eigenvalue calculations is that of finding the small number of complex conjugate eigenvalues which can arise together with many real eigenvalues when a real matrix is strongly asymmetric. The w values given by the SCM formulae will then all be real and so apparently could not lead to any complex results. Several preliminary calculations suggest that this problem can be overcome by using the complex form of the algorithm and by using a first cycle in which the w values are given small random imaginary parts. On later cycles most imaginary parts fall to zero, giving real eigenvalues, while a few of the imaginary parts stay non-zero and generate the imaginary parts of the eigenvalues which are complex. The limits of applicability of this simple procedure remain to be established by later work.

In the present review the simple similarity transformations which form the basis of the SCM are used for various calculations in wave operator theory but they have a long history

in more general matrix theory. Strachey and Francis (1961) used them to transform a general matrix first to lower Hessenberg form and then to tridiagonal form, showing that their method was equivalent to the use of the Lanczos method with a particular choice of starting vector. The rules which they gave to determine the numerical values of the elements (denoted by w here) involved the ratio of off-diagonal elements and produced the desired transformation in a definite number of steps. The simple perturbative choice for w used in wave operator calculations can be used to render zero the appropriate off-diagonal elements (or in principle to shape the matrix in any desired way) by adjusting the set of elements for which the SCM cycles are performed. Several trial numerical experiments showed, however, that the special method of Strachey and Francis is much more speedy and reliable, since the SCM relies on a cooperative effect which is variable from case to case and which is strongly influenced by the size of the off-diagonal elements. The SCM uses only one non-zero element at a time (apart from the implicit unit matrix in the transformation) whereas the RDWA method uses transformations with a full column of non-zero elements. In both cases the inverse of the similarity transformation is very easy to find (involving only a sign change). Collar (1948) used transformations in which every off-diagonal element is non-zero simultaneously, with a value given by the first-order perturbative formula of the present work. However, these transformations did not have a simple inverse and so the inverse needed to find the transformed matrix had to be calculated separately. For this purpose the Schulz method described in section 3.2 was often suitable, since $1 - S$ is a reasonable first estimate of the inverse of $1 + S$ if the elements of S are small. This would certainly be the case if Collar's method were augmented by using the rules for limiting the size of w which are given by equation (3.3).

3.2. Generalized inverses and square roots

The first principles definition of F can be written in the form

$$\begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} I \\ F \end{pmatrix} (X) \quad (3.5)$$

where (X) and (Y) now represent a group of M eigencolumns for an A space of M dimensions, rather than a single eigencolumn as in previous sections, and (X) contains only the A space parts of the group of eigencolumns. Since the columns in (X) can be assumed to be linearly independent the square matrix (X) will have an inverse. Extracting the B space component of equation (3.5) then quickly leads to the result

$$F = (Y)(X)^{-1}. \quad (3.6)$$

This result permits the construction of the energy-independent Bloch reduced wave operator F from the (X) and (Y) which have been found by using (for example) a state-by-state calculation with the energy-dependent effective Hamiltonian HL which uses a different F for each state. Thus an F which obeys a nonlinear equation can be constructed by using a sequence of single column F s which are found without directly solving that equation but rather by resorting to the use of the first principles definition of F . If equation (3.5) is multiplied from the left by the partitioned row (I, F^\dagger) then it is easy to obtain another formal result, this time for (X) :

$$(X) = (I + F^\dagger F)^{-1} (I, F^\dagger) \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (3.7)$$

The composite matrix above produces (X) from the full eigencolumn and acts like an inverse of the wave operator matrix appearing in (3.5), even though that rectangular matrix has no

traditional inverse. It is one of the types of generalized inverse treated in the mathematical literature (Penrose 1955, Ben-Israel 1965). Historically it has been most often used in connection with least-squares fitting, where (X) is a matrix in which all the rows are of the form (x_1, x_2, \dots) and the equation $MX = Y$ gives an incompatible set of linear equations which can only be solved in a least-squares sense. Multiplying Y by the generalized inverse of M then gives the best fit set of x values. The class of problems being studied here, however, falls into a different category, since for this case the matrix (X) can be assumed to be square and non-singular.

The generalized inverse of a rectangular matrix M can be found iteratively from the iterative process of Ben Israel, which can be described by the assignment statement formula

$$Z := Z + Z(I - MZ) \quad (3.8)$$

provided that the initial Z is a sufficiently small multiple of the Hermitian conjugate of M . The process described by (3.8) is an extension to rectangular matrices of the standard process of Schulz (1933) for square matrices. Peters and Wilkinson (1970) reviewed several non-iterative methods for the calculation of generalized inverses, stressing that most of them were natural extensions of standard methods for finding the inverse of a square matrix, just as the Ben-Israel method is a generalization of the Schulz method. Higham (1997) discussed how to modify the Schulz process in order to calculate the square root of a symmetric positive definite matrix S . He gave several algorithms; the most useful one, for the case of a matrix S which is close to the unit matrix, is an iterative one which requires no matrix inversions. Two matrices Y and Z are used, with the initial values $Y = S$ and $Z = I$. The iteration process is then described by the assignment statement cycle (modified slightly by the present authors)

$$T := 3I - ZY \quad Y := YT/2 \quad Z := TZ/2. \quad (3.9)$$

This process gives quadratic convergence of Y to the square root of S and of Z to the reciprocal square root of S . This process will be of obvious value for the case when S is the matrix $S(AA)$ of effective Hamiltonian theory and it has been used in some of the test calculations of this work.

If the operators which appear in equations (3.5) and (3.7) above (and which are in effect inverses of one another) are denoted by K and L , respectively, then the approach of Hurtubise and Freed (1993a, 1993b, 1994) can be used. Those authors pointed out that a variety of such mutually inverse pairs (K, L) can be defined, each such pair leading to a model space effective Hamiltonian of the form LHK . Taking the K and L from the discussion above and the H matrix in its partitioned form leads to a triple product LHK which gives, as the reader can confirm, the variational form HBV of the Bloch Hamiltonian. However this HBV appears on its own in a single (AA) form, since the particular way of writing equation (3.5) has represented only the X part of the eigenfunction. If the more conventional full space column is used, with a zero B space portion below the upper X , then the operators L and K become just the operators $T(F)$ and $T(-F)$ of section 2.4 and the triple product then leads to a full matrix with the usual Bloch operator HB appearing as the (AA) component.

In accord with the notions of perturbation theory the cases in which F has small matrix elements can be described as being perturbative cases, since the F elements can be found by applying some form of perturbation theory to an initial F matrix which is set at zero. In non-perturbative cases in which the F matrix has large matrix elements, the SPD matrix S will be far from the unit matrix and so the iterative algorithm based on Higham's work will not converge. For these more general cases it has been found convenient to make yet another use of the SCM, by diagonalizing S while retaining the square eigencolumn transformation matrix C . Since S is SPD it follows that C will have orthogonal columns (as is indeed found computationally);

each column can be exactly normalized to render C unitary, so that its inverse is found by simply taking its transpose. The desired power of the diagonal form of $S(1/2, -1/2, -1, \dots)$ can then be calculated trivially as another diagonal matrix and the back-transform can be calculated by reversing the original diagonalizing transformation. This procedure would thus be effective both for calculating the square root needed in the conversion of HB into HD and for calculating the inverse which is needed in order to produce the effective Hamiltonian HBV . It has been found to be effective for all of the test matrices treated.

To distinguish the two square root algorithms described here the first one, based on Higham's work, will be referred to as algorithm 1 and the second one (which makes use of the SCM approach) will be referred to as algorithm 2. As a consequence of some of the test calculations reported in this review it was found that algorithm 1 can sometimes converge to a legitimate square root $R(+)$ which is not SPD even though $S(AA)$ is SPD. It was as a response to this behaviour that algorithm 2 was introduced as a checking algorithm. Several works on matrix theory state the theorem: an SPD matrix has a unique SPD square root. The correct interpretation of this slightly ambiguous statement is that amongst the square roots of an SPD matrix there is exactly one which is SPD. This result is made clearer by the use of algorithm 2 as described above, since a variety of plus or minus square roots can be chosen along the diagonal at the diagonal matrix step, with the SPD case corresponding to the 'all positive' choice.

3.3. Gaussian elimination and the folding transformation

The derivation of the energy-dependent effective Hamiltonian (method 1 of section 2.1) involves a partitioned matrix Gaussian elimination process. This is sometimes called a folding transformation, since it folds down a large matrix into a smaller one in the A subspace. This approach is often useful in numerical work. For example, Williams and Weaire (1976) used it in some pseudopotential calculations to fold down a 69×69 matrix to a 12×12 matrix, with the 12×12 matrix being solved in a sequence of self-consistent calculations to locate the e values for which some eigenvalue equals the input e parameter in the term $[eI(BB) - H(BB)]$. They did not use A and B subspaces of dimensions 12 and 57, respectively, but simply folded down the matrix one row and column at a time. This involves using the form of the matrix partitioning formulae which are appropriate for the case in which the B subspace has dimension 1. The resulting $(N - 1) \times (N - 1)$ matrix then has modified elements in which each current element $H(J, K)$ is overwritten with a new modified value which is given by the assignment statement

$$H(J, K) := H(J, K) + H(J, N)H(N, K)/[E - H(N, N)]. \quad (3.10)$$

There is no requirement for the matrix to be symmetric, although for a symmetric matrix or a banded one the folding process can be simplified by noting that folding retains the original symmetry and bandwidth. Williams and Weaire (1976) folded down from dimension 69 to 12. If folding is continued all the way down until a 1×1 matrix is left, then the last (1, 1) element is the reciprocal of the (1, 1) element of the resolvent $[H - EI]^{-1}$ and so is zero if E is an eigenvalue. More usefully, the product of all the diagonal elements $H(N, N)$ which arise during the process is equal to the determinant of the matrix of $H - EI$ and so the E values which make it zero are the eigenvalues of the original matrix which has been folded down to 1×1 size. In the case of a non-orthogonal basis (as for the Kato effective Hamiltonian HK) it is probably best to form the matrix $M = (H - ES)$, where S is the metric matrix and then use the folding method to find the determinant. The appropriate folding formula is then

$$M(J, K) := M(J, K) - M(J, N)M(N, K)/M(N, N) \quad (3.11)$$

and the secant rule can be used to find a zero of the determinant from a sequence of determinant evaluations. Equation (3.11), with $M = H - EI$, is identical in form to that for the variational approximation to the scattering matrix as given by Yang and Miller (1989), except that the basis functions used for the scattering problem relate to the appropriate incoming and open channels and so the matrix will in general have complex elements. When equation (3.11) is used for bound state calculations which require many non-orthogonal basis functions to describe them (e.g., Rydberg states) then problems can arise because of the near linear dependence amongst the basis functions. A formal indicator of such problems is the presence of very small eigenvalues in the diagonalized form of the overlap matrix. Jungen and Kaufmann (1992) discussed ways of handling this problem. Their work has the interesting feature that in one section it has a perturbed eigencolumn which arises by treating as a perturbation the effective potential term (due to the $A - B$ coupling) which appears in the Löwdin effective Hamiltonian HL of the present review.

Since the H matrix is destroyed by the folding operation, a copy of it is actually used in the sequence of foldings with changing E values. This method of calculating matrix eigenvalues has been used for many years (e.g., James and Coolidge (1933), Löwdin (1963), Killingbeck (1991)). Once an eigenvalue has been found then the associated eigencolumn can be found using inverse iteration, i.e. by solving the linear equation system $(H - ES)X = Y$ for a suitable Y column. In the present work the direct calculation of the eigenvalues using the folding transformation approach has been used to check both the complete spectrum of the full matrices in the examples as well as the eigenvalues of the effective Hamiltonian in the A subspace, since the technique works for both symmetric and non-symmetric matrices. Although the test matrices used in this review are small, it should be noted that the folding method is widely applicable; for example it has been used for perturbed oscillator matrix problems with as many as 20 000 basis states (Killingbeck, in preparation) by exploiting the fact that for a banded matrix the folding operation can work out the required determinant by means of a recursive process which only needs to generate a small number of the elements of the matrix at each step. If a real matrix for which eigenvalues are sought is asymmetric to a small extent, then only a small error is made by using the symmetrised version of the matrix. This can be seen as follows. The matrix can be regarded as a symmetric matrix plus a small skew symmetric perturbing matrix of order β . The eigenvalues are found by rendering zero the determinant of $H - EI$. Changing the sign of the perturbing terms is equivalent to taking the transpose of the matrix, which does not change the determinant and so leaves the spectrum the same. It then follows that the perturbation series expansion of any nondegenerate eigenvalue must involve only even powers of β . Taking the symmetrized version of the matrix thus gives eigenvalues with a leading error term of order β^2 . If the elements of F are small, then the symmetric component of HB is a reasonable approximation to HD , as was noted by Kuo *et al* (1993). The folding method (essentially Gaussian elimination) is usually applied in numerical work but the algebraic formalism of Mower (1980), which used nested sets of resolvents, was essentially an algebraic version of the folding transformation approach which eliminates one dimension at a time. Mower's work also included the use of two operators which are equivalent to the operators W and HL of the present review. When the folding method is presented in algebraic form it naturally leads to expressions which resemble continued fractions and Swain (1976) gave a detailed analysis of the link between Hilbert space and continued fraction methods, with particular reference to RS perturbation theory.

3.4. The Wynn epsilon algorithm and perturbation theory

The Wynn epsilon algorithm (Wynn 1956) is a simple lozenge algorithm which is often effective in extrapolating a sequence of partial sums of a perturbation series or a sequence of

terms in an iterative process so as to estimate the sum of the series or the limit of the sequence, even when the sequence of terms being analysed is not convergent. Weniger (1989) has given a review of several of the more modern summation and extrapolation techniques, many of which were developed at Lille (see, e.g. Brezinski (1980, 2002)). In the present work only the original Wynn epsilon algorithm was used and it turned out to be quite effective in some of the model matrix calculations. Killingbeck (1988a) gave a flexible form of the algorithm which incorporates three different summation methods which have appeared in the mathematical literature. The most simple approach is to set up two column (or row) arrays, A and B . The array A is filled with zeros, while array B is filled with the sequence of terms (partial sums or iterates) to be analysed. The arrays A and B are imagined to be set out in a staggered pattern of the form

$$\begin{array}{cccccc}
 & & S(0) & & & \\
 0 & & \times & & & \\
 & S(1) & & \times[1/1] & & \\
 0 & & \times & & \times & \\
 & S(2) & & \times[2/1] & & \times[2/2] \\
 0 & & \times & & \times & \\
 & S(3) & & \times[3/1] & & \\
 0 & & \times & & & \\
 & S(4) & & & & \\
 A & B & A & B & A & B
 \end{array} \tag{3.12}$$

and the new elements of A and B , the crosses on the above diagram, are filled in by the lozenge algorithm of the following diagram

$$W_S^N E = W + (S - N)^{-1}. \tag{3.13}$$

The elements of the successive B columns are then improving estimates of the desired limiting value. When the input elements $S(J)$ are the partial sums of a series the elements of the B columns are the numerical values of Padé approximants to the sum of the series. In the layout shown above $S(J)$ has been taken to be the sum of a perturbation series up to the term λ^J and the B elements have been given labels which indicate their appropriate interpretation as Padé approximants. If at each stage the A column is multiplied by 0 or -1 instead of by 1 before proceeding, then the results obtained relate to two other types of sequence transformation which have appeared in the literature (Killingbeck 1988a).

For a sequence of matrices (for example a sequence of estimates of the Bloch reduced wave operator F) several different procedures are possible. The most simple procedure, which has been followed in the test matrix calculations of this work, is to apply the above algorithm (usually called the scalar algorithm) separately to the sequence of values of each individual matrix element. An alternative is to note that the reciprocal which appears in the algorithm could in principle be interpreted as an inverse if the elements in the A and B arrays were taken to be matrices rather than numbers. The usual interpretation given to this inverse in the literature is that it should be taken to be a (transposed) generalized matrix inverse of the kind introduced in the preceding discussion. Although much work on this theme has appeared in the mathematical literature, the applications to quantum mechanical problems are not yet plentiful. The theory of the traditional scalar Padé approximants has, however, been extended to cover quadratic Padé approximants, which have been applied to some quantum mechanical problems, including some studies of avoided crossing problems in effective Hamiltonian theory (Goodson 2000a, 2000b, Dunn *et al* 1996).

The Wynn epsilon algorithm as described here has been applied in some of the test matrix calculations of the present review but there are several aspects of it which would still merit further exploration. For example, for a square matrix such as HB the generalized inverse is simply the usual matrix inverse. For the simple case in which HB is of 2×2 type it would not be difficult to set up a version of the Wynn algorithm in which the transposed matrix inverse replaced the scalar inverse; this would then allow the performance of the algorithm to be compared with that of one which (as in the present review) simply applies the scalar algorithm to each of the individual elements of HB . Another comparison worth making is that between what might be termed internal and external iterative methods with quadratic rates of convergence. Authors such as Durand (1983) or Dietz *et al* (1993) have concentrated on the internal approach, in which the actual iterative formulae used to calculate a numerical quantity are modified so as to give quadratic convergence. By contrast the external approach sticks to a simple first order iterative process but then treats the output sequence from the iterative process by using the Wynn epsilon (or some other) algorithm; this procedure usually produces a quadratically convergent sequence from the initially linearly convergent sequence. This external approach is in some respects more universal than the internal approach and it would be interesting to make a comparison of the two methods for a suitable test problem. An example of the use of the two types of approach is mentioned in the account of the BWGS method of section 5.2. In an iterative approach to the calculation of the F matrix each column can be regarded as a vector in its own right; Smith *et al* (1987) and Graves-Morris (1992) described methods for the extrapolation of a vector sequence, although in the present review the individual elements have been treated separately using the scalar algorithm. Rissanen (1972) treated Padé approximants for sequences of rectangular matrices. Coleman (1976) and Jamieson (1987) explored the mathematical relationships between Padé approximant methods and several of the iteration-variation techniques of quantum mechanics. Jbilou and Sadok (1995) treated the use of vector extrapolation methods for solving systems of linear equations and gave many references to earlier works using vector extrapolation methods.

3.5. Real arithmetic for complex matrices

Although it is quite feasible to perform complex variable forms of the various calculations associated with wave operator theory, some workers prefer to treat matrix problems involving complex variables by performing a preliminary transformation to a real matrix problem which can then be treated by some pre-existing software. Two such transformation approaches can be summarized by a simple calculation which is somewhat in the spirit of the partitioned matrix approach which has been used throughout the present work. If the complex variable matrix eigenvalue problem for an $N \times N$ matrix is written in the form

$$(C + iD)(X + iY) = (A + iB)(X + iY) \quad (3.14)$$

(where C and D are real matrices and X and Y are column elements) then taking the real and imaginary components on both sides leads to a pair of equations which can then be re-expressed as a $2N \times 2N$ matrix equation:

$$\begin{pmatrix} C & -D \\ D & C \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} A & -B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (3.15)$$

If the original matrix is Hermitian then B must be zero and the operation gives an ordinary real symmetric matrix eigenvalue problem with a dimension which is twice that of the original matrix. The number of eigenvalues is conserved, however, since each eigenvalue of the larger matrix is doubly degenerate; with each eigencolumn (X, Y) is associated a partner $(-Y, X)$. If the original matrix is not Hermitian then the A and B terms in (3.15) can be taken over to the

left to give a $2N \times 2N$ matrix $M(A, B)$ which has both A and B as parameters. The eigenvalue equation then takes the form of the requirement that $M(A, B)$ should have the eigenvalue zero. Thus A and B have to be adjusted in some trial and error process which attempts to make the determinant take the value zero. In many of the applications of this approach B is a small number and so various types of iterative or perturbative techniques can be used to handle the problem. This real matrix approach has been used for resonance state problems by Bylicki (1991), who modified an original technique due to Moiseyev (1983).

3.6. The spectral representation of HB

One way to construct HB is to first find F as the product $(Y)(X)^{-1}$ by using blocks of eigencolumn elements which have been calculated, for example, by using a state-by-state procedure involving the energy-dependent effective Hamiltonian HL , or by any other means of finding accurate eigencolumns. HB and its transpose will have the same eigenvalues but with different eigenvectors $X(J)$ and $Z(J)$, respectively, associated with a given eigenvalue $E(J)$. A little algebra (Wilkinson 1965) shows that $Z^T(J)X(K) = 0$ for $E(J) \neq E(K)$. In the most simple case all the $E(J)$ are different and when scaled to form a biorthogonal set with the $X(J)$ the $Z(J)$ can be defined by the property

$$Z^T(J)X(K) = \delta_{(J,K)} \quad (3.16)$$

or, more informatively, by

$$Z(J) = \sum_K B(J, K)X(K) \quad (3.17)$$

where B is the square matrix which is the inverse of the symmetric matrix with the elements $X^T(J)X(K)$. The effective Hamiltonian HB can then be set out in the form of a spectral decomposition

$$HB = \sum_{J,K} X(J)E(J)B(J, K)X^T(K) = \sum_J X(J)E(J)Z^T(J). \quad (3.18)$$

It can easily be checked that acting with either of the expressions shown above on $X(J)$ correctly produces $E(J)X(J)$. If the reduced wave operator is known then HB can be formed by simply forming the sum $H(AA) + H(AB)F(BA)$. If only HB and the full H matrix are known, then many different $F(BA)$ matrices would give the same HB , since adding any solution of the equation $H(AB)X(BA) = 0$ to $F(BA)$ leaves HB unchanged. Only if $H(AB)$ is square and nonsingular (as it is for some of the test matrices) can $F(BA)$ be found unambiguously from HB . The correct $F(BA)$ must, of course, pass the more stringent test that it obeys the correct nonlinear equation. Malrieu *et al* (1985) wrote a spectral decomposition to involve the projections of the exact full space eigenvectors on the model space. This form stresses the 'correct' direction of the A subspace eigenvectors but seems to the present authors to be equivalent to the forms given above, since an appropriate rescaling of the biorthogonal vectors will be involved.

3.7. Some other techniques

The few techniques which have been described above were chosen because they form the basis of several of the methods used in the test calculations reported later and also fit into the area of matrix algebra with which the majority of general readers will be familiar. Several other interesting matrix techniques which are not used here have been applied in works on wave operator methods. These include the superoperator notation, which has sometimes been

used to describe operators which are themselves functions of other operators (Primas 1963, Durand and Paidarova 1996) and the definition and use of an inner product $\langle A|B\rangle$ for a set of finite matrices of given dimension. This inner product is usually defined to be the trace of the matrix product $A^\dagger B$ and it permits notions such as those of an orthonormal set and of Fourier analysis to be extended to matrices. The tensor operators of angular momentum theory can be regarded as being an orthonormal set when treated in this formalism (Killingbeck 1975) and Nicolas and Durand (1980) used a slightly generalized matrix inner product definition in their treatment of effective operators by a form of matrix Fourier analysis. Becker and Fulde (1989), Polatsek and Becker (1997) and Hubsch *et al* (1999) described an approach which uses cumulant theory. This approach uses a definition of the effective Hamiltonian which involves a partition function in a formalism which is akin to that of statistical mechanics and which is quite different from the simple projection operator formalisms which are traditionally used (since it uses Liouville space rather than Hilbert space). The new method is claimed to give automatic size consistency when applied to many-body systems; Polatsek and Becker (1997) note that up to second order the effective Hamiltonian obtained is that of RS theory, with the cumulant approach only giving different results at higher order.

4. Some selected test matrices

Several test matrices from the literature of wave operator theory have been collected together to provide material for the trial calculations which are reported in the next few sections of this review. This section describes these test matrices and gives some accurate eigenvalues for them; it is hoped that this information will be useful to other workers who require simple test problems while developing new wave operator techniques.

4.1. The test matrices

4.1.1. Matrix 1. A 4×4 matrix (Navratil and Geyer 1993, Navratil *et al* 1993). The matrix is real symmetric and includes an adjustable parameter x . The upper part of the matrix has the (1, 3) and (2, 4) elements zero, while the (1, 2), (1, 4) and (2, 4) elements all equal $5x$. The (3, 4) element is x and the diagonals (from 1 to 4) are $1, 1 + 25x, 3 - 5x$ and $9 - 5x$. This model matrix has been used in the literature to study level-crossing and intruder state problems and to explore the way in which the degree of non-Hermiticity of the effective Hamiltonian depends on the off-diagonal coupling. Most authors have used a two-dimensional A subspace with this model problem but both one and two-dimensional model spaces are used in the present work. For the case $x = 0.08$ which has been used by several authors the eigenvalues are 0.899 093 636 4, 2.381 927 461 8, 3.296 800 662 4, 8.622 178 239 4. As the value of x increases some avoided crossings occur; for example, at $x = 1/15$ the elements $H(2, 2)$ and $H(3, 3)$ are equal, leading to an avoided crossing. For $x < 1/15$ the eigencolumn associated with eigenvalue $E(2)$ of the H matrix will have a dominant contribution from basis state 2, while for $x > 1/15$ the contribution of basis state 3 will dominate.

4.1.2. Matrix 2. A 5×5 matrix (Leinaas and Kuo 1976). This small test matrix was originally derived from a test matrix for the Lipkin model of nuclear theory but was rewritten to involve a pseudo-angular momentum. Close inspection reveals some apparent discrepancies between the published numerical results in the paper of Leinaas and Kuo and the stated Hamiltonian; accordingly in the present work the Hamiltonian has been rewritten to take the following form in terms of angular momentum operators

$$H = [J_z - WJ + 4W] + (3/2)U[J_+ + J_-] + (V/2)[J_+ - J_-]^2 \quad (4.1)$$

where the matrix elements of the operators in the basis of states $|J, M\rangle$ are given by

$$J_z|J, M\rangle = M|J, M\rangle : J_{\pm}|J, M\rangle = [J(J+1) \mp M(M+1)]^{1/2}|J, M \pm 1\rangle. \quad (4.2)$$

When the Hamiltonian is presented in this way it is easy to construct the matrix by matrix multiplication starting from the J_{\pm} matrices. The three numerical parameters obey $W = -x$; $V = 0.3W$; $U = -0.3W$, where x is an adjustable positive parameter. The angular momentum J is variable but the choice $J = 2$ gives a five-dimensional full space. Leinaas and Kuo used a one-dimensional model space and $J = 2$. For the case $x = 0.1$ the energy levels are $-2.016\,205\,863\,3$, $-1.304\,759\,159\,0$, $-0.395\,878\,797\,6$, $0.708\,815\,390\,5$, $2.008\,028\,429\,4$ while for $x = 0.4$ they are $-2.811\,963\,774\,3$, $-1.764\,154\,685\,2$, $-1.421\,295\,395\,7$, $-0.075\,189\,324\,9$, $2.072\,603\,180\,1$.

4.1.3. Matrix 3. A 20×20 matrix (Malrieu *et al* 1985). This symmetric matrix has its first five diagonal elements equal to 1. For J values from 6 to 10 the diagonal (J, J) element is $2 + (J - 6)/10$, while for $J = 11$ to 20 it is $J - 8$. The off-diagonal elements $(J - 1, J)$ are 0.1 (for $J = 2$ to 5) and 0.5 (for $J = 11$ to 20). The elements $(J - 5, J)$ are 0.1 (for $J = 6$ to 10) and 0.5 (for $J = 11$ to 20). The elements $(J - 10, J)$ are 0.1 (for $J = 11$ to 20). Malrieu *et al* used this model matrix in an exploration of the intermediate Hamiltonian concept; their space A was of dimension 5 (and thus initially degenerate if the off-diagonal elements are regarded as being a perturbation), while the intermediate space used was of dimension 10. The lowest seven eigenvalues of the matrix are 0.818 185 353 5, 0.890 035 365 3, 0.990 939 434 3, 1.089 247 492 3, 1.162 869 161 8, 1.679 498 696 7, 1.975 762 742 5.

4.1.4. Matrix 4. A 50×50 matrix (Durand *et al* 1994). The matrix is symmetric and has a $(1, 1)$ element of zero, with all the other elements in row 1 equal to an adjustable parameter λ . All the diagonal elements except $(1, 1)$ are equal to 1. All the $(J, J + 1)$ elements for $J > 1$ are equal to a second adjustable parameter μ . The main interest of this matrix is that it has an eigenvalue near to zero in the middle of a background spectrum with a wide range of negative and positive eigenvalues. The matrix is intended to give a finite matrix simulation of the coupling of a discrete bound state to a continuum. The main interest of Durand *et al* was in finding the perturbed bound state energy (which remains close to zero) by using a wave operator approach. For the particular choice of parameter values $\lambda = 0.005$ and $\mu = 0.6$ this eigenvalue is $-0.000\,561\,527\,8$, as was indicated in a private communication by the original authors, who had inadvertently included the wrong data in table 2 of their paper. The rest of the spectrum is distributed over the region between the lowest level of $-0.197\,632\,079\,1$ and the highest level of $2.198\,094\,148\,6$.

4.1.5. Matrix 5. (Evangelisti *et al* 1987). This is the matrix eigenvalue equation which arises in a matrix approach to the eigenvalue problem for the Mathieu differential equation. If the traditional matrix indices $1, 2, \dots$, are used then the matrix is symmetric and tridiagonal, with the diagonal elements $H(N, N) = 4(N + 1) + x/2$ and the off-diagonal elements $H(1, 2) = x/8$ and $H(N, N + 1) = x/4$ for $N > 1$. The value of the parameter x has been chosen in the range 0 to 16 by various authors. To obtain eigenvalues for the Mathieu differential equation it is necessary to increase the dimension of the matrix until the matrix eigenvalues attain their limiting values to a given number of digits. For the x values 2 and 4 a matrix dimension of 20 is sufficient to reach the limit. The lowest two levels at $x = 2$ are 0.878 234 455 1 and 5.100 900 595 6, while for $x = 4$ they are 1.544 861 395 9 and 6.371 300 982 7.

4.1.6. *Matrix 6. (Coope and Sabo 1977).* This is a real symmetric matrix with off-diagonal elements all equal to 1 and with the diagonal elements given by the formula $H(N, N) = 2N - 1$. The dimension of the matrix can be chosen at will. For the 30×30 case the lowest five eigenvalues are 0.319 736 977 2, 2.368 439 641 1, 4.401 133 876 4, 6.427 419 225 8 and 8.450 274 100 4.

4.1.7. *Matrix 7. A perturbed oscillator matrix.* A real matrix of arbitrary size representing the perturbed Hamiltonian $-D^2 + x^2 + \lambda x^2$ in a basis of eigenfunctions of the Hamiltonian $H_o = -D^2 + \beta^2 x^2$. This perturbed oscillator problem has often been treated in the literature of quantum mechanics. The matrix can be constructed by matrix multiplication (Killingbeck *et al* 2000) starting from the basic matrix element $\langle n|x|n+1 \rangle = \sqrt{(n+1)/2\beta}$ and the fact that the eigenvalues of H_o are equal to $(2n+1)\beta$ for $n = 0, 1, 2, \dots$. Since both H and H_o are of even parity, it is possible to set up two distinct matrix eigenvalue problems by using either the even ($n = 0, 2, 4, \dots$) or the odd ($n = 1, 3, 5, \dots$) eigenfunctions of H_o as the basis functions. By varying β it is possible to control the strength of the coupling between the chosen A and B subspaces. Meissner and Steinborn (1997a) used such an oscillator matrix in their calculations which applied a Bloch wave operator approach to quantum mechanical problems.

4.2. A direct search method

One simple way to tackle a small system of nonlinear equations is to use a direct search approach. For the problem of calculating the wave operator F the system of nonlinear equations takes a simple form; the components of F must be chosen so that all the components of the matrix

$$f(F) = H(BA) + H(BB)F(BA) - F(BA)H(AA) - F(BA)H(AB)F(BA) \quad (4.3)$$

are simultaneously zero. For the 4×4 test matrix 1 given above, with an A subspace of dimension two, the task is to vary the 4 elements of F so as to render zero (or as small as is computationally feasible) an object function which is the sum of the moduli (or the sum of the squares) of the 4 elements of $f(F)$. Two search methods were tried; both of them vary the elements of F over an interval $-a$ to a to find the set of values which minimize the object function, and then repeat this process with a smaller interval (usually $0.9a$) and so on until the object function becomes very small (around 10^{-12}). The first search method used a discrete set of values in the range $-a$ to a , while the second used a random number generator to give a random number distribution of values in that range. Once a solution for F has been found the effective Hamiltonian matrix $H(AA) + H(AB)F(BA)$ can be formed, giving some eigenvalues. As anticipated, there are several different solutions to the nonlinear equations for F . Each one of them is obtained by the search process if the initial trial F chosen is within an appropriate capture region surrounding it. Some calculations were carried out for the parameter value $x = 0.08$ which was used by Navratil and Geyer (1993) and Navratil *et al* (1993). The eigenvalues of the full 4×4 matrix have already been given in section 4.1. The results given here are severely truncated double precision ones. Taking states 1 and 2 to define the A submatrix led to the following typical results, in which the F matrix elements are given in the order (3, 1), (3, 2), (4, 1), (4, 2). The input (0, 0, 0, 0) gives the result (0.1583, 0.5446, -0.1548, -0.012 12) and the eigenvalues numbers 1 and 3. The input (-1, -1, -1, -1) gives the result (-0.3000, -1.7488, -0.0486, 0.0191) and the eigenvalues numbers 1 and 2. The input (-20, 5, 0, 0) gives (-19.9875, 3.9778, 0.2191, -0.0588)

and the eigenvalues numbers 2 and 3. The input $(0, 0.5, 20, -3)$ gives the result $(0.4335, -1, 9622, 19.4724, -5.6591)$ and the eigenvalues numbers 2 and 4.

These results illustrate the variety of solutions which can be obtained for F . Those solutions which contain very large components (such as the last two given above) clearly refer to states for which the associated eigencolumns have their dominant components in the B subspace. Such states lead to strongly non-symmetric HB matrices; for example, the four solutions cited above have the associated HB matrices (in order)

$$\begin{pmatrix} 0.978 & 0.395 \\ 0.463 & 3.218 \end{pmatrix} \begin{pmatrix} 0.980 & 0.408 \\ 0.289 & 2.300 \end{pmatrix} \begin{pmatrix} 1.088 & 0.377 \\ -7.595 & 4.591 \end{pmatrix} \begin{pmatrix} 8.705 & -0.922 \\ 0.484 & 3.214 \end{pmatrix}. \quad (4.4)$$

This strong (indeed, violent) asymmetry is taken in physical applications as a warning that the chosen model space is highly inappropriate to describe the target space states which it is intended to obtain. Such ‘bad’ eigencolumns and their associated F matrices would not be expected to be attainable by means of a perturbation approach which is based on the A subspace basis vectors and treats the $A - B$ coupling as relatively small. Nevertheless, these ‘bad’ solutions are perfectly correct in a mathematical sense. The four widely different solutions obtained above were given to demonstrate that even such non-perturbative results can be obtained by a careful approach. However, it should be clearly noted that for a small problem such as this 4×4 one there is a more easy way to proceed; the basis states can be permuted to put any two functions in the positions 1 and 2. This simple procedure associates different pairs of eigenvalues with subspace A and so produces F matrices which will have small elements for each case.

The search method can also be applied to the present 4×4 problem with a one-dimensional A subspace and an F matrix with the three elements $(2, 1)$, $(3, 1)$ and $(4, 1)$, so that it should produce one eigenvalue at a time from the associated solution for the F matrix. Using the input $(0, 0, 0)$ gives as a result of the search the F column $(-0.1998, 0.0495, -0.0525)$ and thus eigenvalue number 1. Since the eigencolumn is formed by simply augmenting the F column with a first element equal to 1, it is possible to use the full space orthogonality of the eigencolumns to force any later search to go to a different solution. This is done by making the new objective function equal to the sum of the squares of the 3 components of F plus a large multiple (typically 20) of the sum of the squares of the inner products of the trial eigencolumn (i.e., the trial F augmented by a 1 in the first position) with all the previously found eigencolumns. The objective function then has a maximum, rather than a minimum, at the previous solutions and so the minimizing search is repelled from those solutions and finds a different one. When this procedure was carried out for the 4×4 test problem it gave the F solutions $(3.43794, -6.31223, 0.016883)$, $(5.86811, 3.35405, -0.12603)$ and $(0.08950, 0.25789, 18.96595)$, associated respectively with the eigenvalues numbers 2, 3 and 4. The last three F columns obtained are clearly associated with eigencolumns mainly situated in the B subspace and so are far removed from any solution which would be expected using some perturbative method based on the A subspace. Only the first solution, based on $(0, 0, 0)$, would be expected in a perturbative approach, although for this small test matrix the problem could be handled much more easily by simply permuting the basis functions to vary the content of the A subspace.

The calculations reported above are intended to illustrate directly the point which was made earlier, that the general wave operator formalism is so general that in principle it applies equally to all the possible eigenvectors which have a non-zero component in the selected A subspace. The direct search method was also modified to give a gradient form, since the gradient matrix of the matrix $f(H, F)$ is not difficult to obtain and so can be used in a Newton–Raphson type of calculation. However, it was found that these search

methods are comparatively slow and thus only useful for very small test matrices, although (as demonstrated here for test matrix 1) they are useful in demonstrating the range of solutions obtainable for the Bloch reduced wave operator F . Although a simple random search method was employed in some of the calculations reported here, it might be possible to devise more efficient probabilistic methods. Genetic algorithms are becoming increasingly popular and were used for the diagonalization of the Hamiltonian matrix by Nandy *et al* (2002); an adaptation of such a method might turn out to be useful for wave operator calculations of larger dimension than those which could be treated by the simple search methods used in this review.

4.3. The single cycle method (SCM)

The name of this technique was perhaps not particularly well chosen but was originally intended (Périé *et al* 1993) to emphasise that it uses similarity transformations involving one element at a time. Previous works had used the recursive distorted wave approximation (RDWA) described by Jolicard and Grosjean (1985) and Jolicard and Humbert (1991) in which the transformations used fix the elements of a complete column simultaneously by using the first order wave operator formula. It was discovered that by treating the elements one at a time the convergence properties of the method could be improved, since each single element transformation changes the environment for the next one, leading to a cumulative collective effect. The SCM makes use of the similarity transformation method for matrix diagonalization which has been described in section 3.1. For the wave operator applications the aim is to render zero just the BA portion of the Hamiltonian matrix, while simultaneously finding the elements of the Bloch reduced wave operator matrix F . The formulae for the amplitude w associated with the (J, K) transformation and the damping formula to be used to limit w are just as already set out in section 3.1. The rules for modifying the H matrix elements are also those of that section. However, in order to find the F matrix rather than the matrix of eigencolumns the role played by the C matrix has to be modified. The square array of columns C is replaced by a rectangular array F with indices appropriate to the reduced wave operator array to be calculated. As the (J, K) transformations scan the rectangular (BA) region the w value for a particular (J, K) element is simply added to the present value of $F(J, K)$, with the F array being initially set at zero. The origin of this rule will be apparent on looking at the multiplication rule below equation (2.21), which shows that taking the product of similarity transformations involves adding the F submatrices. If only the Bloch effective Hamiltonian matrix is required, then it is not necessary to find F since after convergence the (AA) submatrix which remains is precisely the Bloch HB and can be diagonalized by making a further application of the similarity transformation method. Thus the SCM serves both to construct and to diagonalize the Bloch HB ; it also serves (via square root algorithm 2) in the transformation of HB into HD .

Test matrix 3, the 20×20 matrix of Malrieu *et al* (1985), was employed as a first illustrative example, with the A subspace being taken as that with the basis functions 1 to 5. The task for the sequence of transformations is then to render zero the F matrix region, i.e. the matrix elements $H(J, K)$ with J from 6 to 20 and K from 1 to 5. This will decouple the A and B subspaces and so leave a 5×5 effective Hamiltonian matrix which should give 5 of the eigenvalues. To check the rate of progress of the calculation it is convenient to make the program output the sum of the moduli of all the elements in the F block after each cycle through all the (J, K) single element transformations in that block. For the 20×20 test matrix the process converges very quickly and leads to a transformed 5×5 matrix (the A space effective Hamiltonian) which produces the eigenvalues numbers 1 to 5 as quoted in

the test matrix data. If the A subspace is only one dimensional, so that the transformations have to render zero the first column of the H matrix excluding the $(1, 1)$ element, then the process still converges even though the first 5 diagonal elements are initially equal, and yields the lowest test matrix eigenvalue, with the sequence of transformations gradually changing the diagonals to remove the initial degeneracy. The method also works for an A space of dimension 4 but does not converge for an A space of dimensions 2 or 3, although it does render the (BA) terms small (so that the resulting F could be used together with the operator HBV).

When the transformation method is applied to the 4×4 test matrix number 1 and the (J, K) scan is set to render zero the elements $H(J, K)$ with $J = 3, 4$ and $K = 1, 2$, it leads to the eigenvalues numbers 1 and 3 in the spectrum for the 4×4 matrix. When the method is applied to the 50×50 test matrix number 4 and the value of λ is held at 0.005 several interesting features arise. With μ set equal to 0.6 and a $1 \times 1 A$ submatrix the process diverges, whereas with $\mu = 0.4$ it converges fairly quickly to give an eigenvalue of -0.00068954 . If the process is set to render zero all elements except the diagonals then it converges to give the whole spectrum at $\mu = 0.6$. The lowest eigenvalue is found to be -0.1976321 while the perturbed eigenvalue near zero is calculated to be -0.00056153 , agreeing with the revised result of Durand *et al* (1994). For the test matrix 2 the method using a two-dimensional A subspace correctly leads to the two lowest energies at both $x = 0.1$ and $x = 0.4$. For the test matrix 6 of dimension 30 the use of an A subspace of dimension 5 with the transformation method gives the lowest five eigenvalues.

The numerical test results indicated a characteristic feature of the SCM, namely that the co-operative effect of the successive transformations which it uses is at a maximum when all of the matrix elements are being used, as in a full matrix diagonalization. When only a small selection of the elements is being used, as in the calculation of the F matrix, then the performance of the SCM depends more strongly on the smallness of the off-diagonal matrix elements. The SCM has the obvious limitation that, like transformation methods in general, it needs to have the whole of the matrix present, although this is no problem for some small scale tasks such as diagonalizing HB or finding the square roots needed for the passage from HB to HD .

4.4. Constructing HD from HB and F

The SCM as described here produces both HB and F from a calculation in which the elements in the F region are scanned. A subsequent calculation in which all off-diagonal A space elements are scanned will give the the eigenvalues and eigencolumns for HB . Since the SCM is essentially an improved version of a perturbative technique, it tends to give the best convergence for states which have large A space eigenvector components and thus have relatively small F components. For such cases it is possible to perform an auxiliary calculation which produces the canonical effective Hamiltonian HD without first needing to perform any kind of matrix spectral analysis. This is done by using square root algorithm 1, which was described in section 3.2 and which produces both the $+1/2$ and $-1/2$ powers $R(+)$ and $R(-)$ of the matrix $S = [1 + F^\dagger F]$ in a single process involving matrix products. Formation of the triple product $R(+)(HB)R(-)$ then gives HD .

The SCM program used to carry out the calculations which were reported in the previous section was modified by the addition of a small subroutine to work out $R(+)$ and $R(-)$ and then construct HD . The calculation was successful for all the calculations in which the SCM converged to give F and HB . For example, for test matrix 1 at $x = 0.08$ and with an A space of dimension 2, the HB and HD effective Hamiltonians were found to be

$$\begin{aligned}
 HB &= \begin{pmatrix} 0.978\,048\,70 & 0.395\,150\,32 \\ 0.463\,310\,29 & 3.217\,845\,60 \end{pmatrix} \\
 HD &= \begin{pmatrix} 0.979\,328\,16 & 0.431\,209\,11 \\ 0.431\,209\,11 & 3.216\,566\,14 \end{pmatrix}
 \end{aligned}
 \tag{4.5}$$

(after truncation of the double precision results). A check using the SCM correctly gave the same eigenvalues for both HB and HD . In a case for which a technique yields an F matrix with large elements (i.e., a non-perturbative case) then the square root algorithm 2 can be used; this proceeds via a spectral analysis of the matrix $[1 + F^\dagger F]$ and is used in some of the later test calculations.

4.5. Iteration with the E -dependent effective Hamiltonian. HL with a one-dimensional model space

Inspection of the mathematical theory of section 2.1 shows that one way to calculate the eigenvalues of the full matrix would be to solve the linear equations

$$[eI(BB) - H(BB)]F(BA) = H(BA) \tag{4.6}$$

for $F(BA)$, using some trial value e and then find the eigenvalues of the effective Hamiltonian matrix $H(AA) + H(AB)F(BA)$, adjusting e until one of these eigenvalues equals e and thus must be an eigenvalue of the full matrix. It is clear that the procedure is essentially a Brillouin–Wigner type of iterative one, with the eigenvalues having to be found one at a time, although a quick approximate set of eigenvalues for those eigencolumns which are predominantly in the A subspace can be found by using some appropriate average value e . In an iterative approach the obvious method would be to apply some rootfinding technique to vary e so as to render zero the difference $E(e) - e$ as a function of e . Several authors have struggled valiantly to render the procedure as effective as possible, despite the unavoidable limitation of having to deal with one eigenvalue at a time if high accuracy is required. Löwdin returned to the problem many times, but several of the most useful aspects of his work for computational purposes are set out in an early paper (Löwdin 1963). Two useful results of his work can be summarized as follows: first, there is always at least one true eigenvalue between e and a computed eigenvalue (in practice this leads to upper and lower bound results as e is varied); and secondly, that applying a Newton–Raphson process to find a zero of $E(e) - e$ leads to a correction formula which can be expressed in terms of a Rayleigh quotient when the matrix is symmetric or Hermitian. Since the second result was used directly in the construction of the algorithm used in the test calculations of this work it is worthwhile to set it out briefly. The usual Newton–Raphson formula, when applied to find a root of the equation $f(x) = 0$, gives the next approximation in the form $x - f(x)/g(x)$ with the function f and the derivative g being worked out at the present estimate. Löwdin showed that for the matrix problem considered here, where a zero of $f(e) = E(e) - e$ is being sought and where the A subspace is taken to be one dimensional, the Newton–Raphson formula leads to the result that the next estimate of e is given by the Rayleigh quotient formed by using the H matrix and a column in which the first element is 1 and the other elements are the current F elements obtained from the solution of equation (4.6) above. In retrospect this result is not too surprising, since it has some affinity with the traditional Rayleigh iteration procedure, which projects out an eigencolumn by acting on an approximate eigencolumn with the operator $[eI - H]^{-1}$, adjusting e at each step to be the Rayleigh quotient for the current refined approximate eigencolumn.

The majority of the original works of Löwdin applied to the case of a one-dimensional A subspace. In the first calculations reported here the A subspace was taken to be one dimensional, so that only one eigenvalue could be estimated at a time. The point of interest was

to see how many of the eigenvalues could be found by varying the parameter e . Computational experience showed that the effectiveness of the calculation was much enhanced by the use of a device similar in spirit to that used to control the magnitude of the w parameter in the single cycle method described previously. In a direct application of Löwdin's formula the next e value would be set equal to the Rayleigh quotient $RQ(e)$ for the current approximate eigencolumn. The expectation value is taken using the full H matrix and a full version of the eigencolumn in which the first element is 1 and the other elements are the elements of the current F column. With this approach it was found that over a wide range of input e values the process converged to the same eigenvalue. To prevent this behaviour the new trial value of e was not set equal to $RQ(e)$ but was changed gradually, so that the spectrum was explored slowly without jumping over some of the eigenvalues near which the function $E(e) - e$ has large magnitude. This damping process can be summarized by the sequence of assignment statements

$$SH := RQ - e : SH := SH(1 + |SH/SHM|)^{-1} : e := e + SH \quad (4.7)$$

where SHM is a maximum allowed shift which is set by the operator along with the initial trial e value. With this extra feature the calculation was even able to locate eigenvalues which were very close to eigenvalues of the much larger B space and which had only a relatively small A space component. For a specially constructed perturbed oscillator problem, the 40×40 matrix of the Hamiltonian $-D^2 + x^2 + x^4$ set up in a basis of even parity eigenfunctions of $-D^2 + 8x^2$, the method found the lowest five of the even parity eigenvalues fairly easily. Overall, the method was able to find all of the cited eigenvalues for the test problems, except for the case of problem 2, for which $E(5)$ at $x = 0.1$ and $x = 0.4$ seemed to be unattainable directly, but could be found using the diagonal sum rule.

It is worth pointing out that to solve the system of linear equations (4.6) for the F matrix the Gaussian elimination process was used. Once again this illustrates the universal role played by this traditional process at all levels of the theory, as pointed out in section 3.3. By forming the product $(Y)(X)^{-1}$ the eigencolumn blocks (X) and (Y) which are found using these one state at a time method calculations with HL can be used to construct the F matrix appropriate to the energy-independent Bloch reduced wave operator for the set of calculated states. This idea was tested on several of the results obtained for the test problems and did give the correct F matrix. The use of a direct Gaussian elimination method to solve the system of linear equations (4.6) makes the method of this section very effective for the test problems.

An alternative approach which is closer to the spirit of traditional Brillouin–Wigner perturbation theory is to attempt to solve the equations by using an iterative method such as the Gauss–Seidel method. If the calculations outlined above are carried out with basis state 1 as the one-dimensional model space then the lowest eigenvalue can be found for all the test matrices except matrix 4, for which the state associated with basis state 1 is in the middle of the full matrix spectrum rather than at the bottom of it. The reason for the success in calculating the lowest energy is that the matrix $[H(BB) - e1(BB)]$ is positive definite, since deletion of state 1 from the basis leads to a lowest eigenvalue for $H(BB)$ which is above the lowest eigenvalue of the full H matrix. This then means that the Gauss–Seidel iteration process will converge. By repeating the above calculations for $H(BB)$ on its own it was easy to show directly that for the test matrices the lowest eigenvalue of $H(BB)$ is just below the second eigenvalue of the full H matrix, as would be expected from the fact that a one-dimensional A space is being used, with higher eigenvalues necessarily being trapped between the singularities in HL which appear at the eigenvalues of $H(BB)$. Even so, it turned out to be possible to obtain some of the excited state eigenvalues for the test matrices 1, 2, 3 and 5, despite the overlapping of the full spectrum with the $H(BB)$ spectrum.

The most simple way to carry out the HL calculation would be to use the iterative formula $E = F(E)$, where $F(E)$ is simply the numerical value of $HL(E)$ for the one-dimensional A subspace; this would give a first order process for which the convergence theory was given in the chapter by Löwdin (1966) and also in the paper by Hose and Taylor (1982). The basic result is that the iterations converge if the full space normalised eigenvector is such that the sum of the squares of its A space components is greater than $1/2$. Most of the eigenvectors for the test calculations reported here do not satisfy this onerous requirement. Löwdin's 1966 paper gave a review of most of the basic theory scattered throughout Löwdin's papers and described the second-order iterative method (based on the Rayleigh quotient) which was used in the test calculations, except that the present authors added a damping factor which rendered the method more stable when finding eigenvectors with very small A space components.

4.6. HL with a multi-dimensional model space

When the test matrices were treated by using a multi-dimensional model space it was found that the performance of $HL(AA)$ plus Gauss–Seidel iteration was much improved, presumably in part because the eigenvalues of $H(BB)$ are pushed up to even higher energies. The procedure adopted was kept as simple as possible, being essentially an extension of that used for the case of a one-dimensional A space. The $HL(AA)$ effective Hamiltonian was formed by solving the appropriate M linear equations to give $[H(BB) - eI(BB)]^{-1}H(BA)$ by GS iteration and then the resulting $M \times M$ matrix $HL(AA, e)$ was diagonalized to give M approximate eigenvalues and eigencolumns. A particular eigencolumn was then selected to carry out the same iterative process as was used for the case of the one-dimensional A space. When that particular eigencolumn and eigenvalue had been refined another one was treated. Thus a one at a time procedure was used, but with the extra feature that at each stage the Rayleigh quotients for the other approximate eigencolumns gave quite good estimates of their associated eigenvalues. This comparatively simple method has a feature which makes it similar in spirit to the use of the intermediate Hamiltonian in energy-independent wave operator theory. Since the convergence of the Gauss–Seidel calculation of $HL(AA)$ is ensured for any e less than the lowest eigenvalue of $H(BB)$ it follows that adding more 'buffer states' to distance the lowest few states in space A from the spectrum of $H(BB)$ will facilitate convergence of the calculation of $HL(AA)$. Even if the higher eigenvalues of $HL(AA, e)$ are not exactly obtainable by the one state at a time process (because the Gauss–Seidel process diverges for those e values), the exact calculation of the lower eigenvalues will simultaneously produce reasonable approximate eigenvalues for those higher states which are unattainable by the direct procedure.

Since the operator HL is Hermitian for a fixed e value, a set of orthogonal A space eigenvectors is produced during the location of each eigenvalue. On applying the technique to the test matrices it was found that the use of a two-dimensional model space gave a set of two correct eigenvalues for test matrices 1, 5 and 6 and for test matrix 2 at $x = 0.1$. At $x = 0.4$, however, $E(2)$ is not attainable directly but is well estimated during the calculation of $E(1)$. Changing to a three-dimensional A space leads to converged exact results for the lowest three eigenvalues at $x = 0.4$.

For test matrix 3 the use of a five-dimensional model space with GS iteration gives the five lowest eigenvalues. If the Gaussian elimination method is used to solve the linear equations in the B subspace then, of course, no convergence problems arise at that stage of the calculation, so that all the eigenvalues can be found equally well. If the effect of the B space states on the A space spectrum is small then it is sometimes possible to use a rough approximation which neglects the off-diagonal elements in $H(BB)$. This renders the solution of the linear equations

in the B space trivial for every trial E value. This method, called the B_K method, has been applied in some calculations on molecules. Nitzsche and Davidson (1978) and Davidson *et al* (1981) described this approximation in the context of a matrix partitioning formalism.

4.7. Expectation value calculations

The present paper deals mainly with the use of effective Hamiltonians for the calculation of energy levels but several authors have looked at the use of effective operators which can be used within the model subspace in order to find the matrix elements of an arbitrary operator between the exact full space eigenvectors. It is an obvious preliminary requirement that the matrix elements of the operator must be known in the basis set being used to set up the Hamiltonian matrix, and the results for the effective operators are often stated in the form of a perturbation series which uses the matrix elements. For the special case of an operator G which does not lift any of the degeneracies of the energy levels which are represented by the effective Hamiltonian there is a simple numerical way to find the expectation value $\langle G \rangle$ for an eigenstate. A small term gG is added to the Hamiltonian and the eigenvalue problem for $H + gG$ is solved after that for H . Each energy level will then have an energy shift equal to g times the $\langle G \rangle$ value for the associated eigencolumn. In this approach the g value must, of course, be sufficiently small for first-order perturbation theory to be applicable. This application of the Hellmann–Feynman theorem can be made to involve analytic derivatives in some techniques of quantum mechanics (e.g., Killingbeck 1985, 1988b). For the present calculations it is of interest to make use of a perturbing operator which is not given as a function of coordinates but is quoted directly in terms of its matrix elements. The most simple perturbation is to add the small number g to the matrix element $H(1, 1)$ of the full matrix of H ; working out $\langle G \rangle$ then shows that the energy shift produced is g times the squared coefficient of the basis state 1 in the *full normalized* eigencolumn which goes with the eigenvalue considered. This energy shift approach avoids the specific forming and normalisation of the full space eigencolumn and was used by Killingbeck *et al* (2000) in some matrix diagonalization calculations. Adding g to all the diagonal elements of H which refer to the basis states in the A subspace will reveal the degree to which any specific eigenstate overlaps with that subspace. For the simple Löwdin method which sticks to basis state 1 throughout, as in the HL calculations described above, adding $g = 0.001$ to $H(1, 1)$ and then monitoring the subsequent change in the eigenvalue quickly reveals that the use of the damping equations (4.7) has made it possible to find some eigenvalues which are far outside the perturbative regime and have very small A space components. For test matrix 3 the squared coefficient of the basis state 1 is found to vary from 0.0310 for the first eigenvalue to 0.0010 for the seventh eigenvalue.

An algebraic application of the principle behind this numerical use of energy shift ideas makes it possible to give an alternative derivation of one of the formulae which appear in the work of Löwdin (1963). The aim of the HL calculation is taken to be that of varying e so as to render zero the function $f(e) = E(e) - e$, where $E(e)$ is the calculated eigenvalue. The gradient of f with respect to e at an e value which renders $f(e)$ zero can be related to other partial derivatives by means of the following formula, in which the symbol h can stand for any particular element of the H matrix which is regarded as being varied:

$$\left(\frac{\partial f}{\partial e}\right)_h = -\left(\frac{\partial f}{\partial h}\right)_e \bigg/ \left(\frac{\partial e}{\partial h}\right)_f. \quad (4.8)$$

For the special choice $h = H(1, 1)$ a glance at the expression for $E(e)$, as given in section 2.1 shows that df/de is equal to 1, since $H(1, 1)$ itself is the (AA) term in the effective Hamiltonian HL . The quantity de/dh means the rate of change of the calculated eigenvalue with respect to the matrix element $H(1, 1)$. As explained above this is the square

of $A(1)$ for the full space eigenvector. The conclusion of the calculation is that at an e value which gives an eigenvalue, i.e. at a zero of $f(e)$, the derivative df/de is equal to $-1/A^2(1)$, where $A(1)$ is the coefficient of basis state 1 in the full space *normalized* eigenvector. This form of the result is very simple but differs from that given in much of the literature, since many authors concentrate on finding dE/de rather than df/de . The result shows that levels with a very small A space component are more difficult to find because the region around them over which f varies is narrow and adjoins a region of low df/de which tends to throw a Newton's method rootfinder out of that region into the vicinity of a distant root. The results of the trial calculations show that this problem can be reduced by using the damping formula (4.7) which constrains the varying e value to scan slowly through the region in which $f(e)$ is varying rapidly. The fact that df/de and dE/de are negative at the zeros of $f(e)$ can be used to prove the straddling theorem, mentioned earlier, which states that there is always an exact eigenvalue of the full Hamiltonian H between e and $E(e)$.

The simple energy shift procedure used above obtains expectation values by applying a small but finite perturbation to the system. This finite perturbation method goes back as least as far as the work of Pople *et al* (1968) but is probably even older. The calculation of expectation values in the coupled cluster formalism was discussed by Nooijen and Snijders (1993) and the more general problem of finding effective operators which will give the off-diagonal matrix elements of an arbitrary operator was discussed in the context of effective Hamiltonian theory by Kassis (1977) and Navratil and Geyer (1993). Perhaps the most detailed combined analysis of general effective operators and effective Hamiltonians was that of Hurtubise and Freed (1993a, 1993b, 1994), which explained how the definition of an effective operator depends on the convention which is used for the normalization of the eigenvectors in the full space and the model space. This point was also emphasised in chapter 5 of the book on nuclear theory by Towner (1977), in which the theory of effective operators was presented in the context of a lengthy exposition of the Bloch-Horowitz derivation of the energy-dependent effective Hamiltonian for a few nucleons outside a filled shell. A short paper by Duan and Reid (2001) summarised some of the results of Hurtubise and Freed and started from the effective Hamiltonian HL and a wave operator formalism to derive (partly in terms of diagrams) an effective operator for the energy (actually HB) as well as effective operators for other observables. The review paper by Ellis and Osnes (1977) gave a lengthy account of the construction of effective operators in nuclear theory, using a combination of algebraic and diagrammatic techniques. The short paper by Navratil *et al* (1993) gave a very clear account of the theory of effective operators by making use of two successive matrix transformations; the first one produces the Bloch effective Hamiltonian and the second one serves to simplify the form of the effective operators which represent operators other than the energy.

4.8. Comments on the HL calculations

Although the calculations using HL would be regarded as within the BW tradition, they show some typical features which appear more widely in wave operator and perturbation theory calculations. For example, when the GS method is used with a given multidimensional reference space it might only be possible to find some of the lowest eigenvalues exactly but the best approximate values for the higher eigenvalues could be found, for example, by diagonalizing the HL associated with the highest exactly calculable eigenvalue. The sandwiching theorem would then give some extra information about bounds on these energies and the use of the approximate F from the HL calculation could be used in a better calculation with HBV , and so on; an endless variety of approaches using HL seems to be possible. The phenomena involved are quite similar to those which arise in the intermediate Hamiltonian

approach (cited earlier), although that approach is within the RS tradition. When HL is used with an accurate method of solution of the linear equations (e.g., Gaussian elimination) then most of the problems associated with intruder states disappear. It then becomes possible to use a sequence of individual HL calculations, each with its own separate F column, in order to construct an F matrix and an operator HB (and thence HD) for the group of states treated, thus transferring from an energy-dependent to an energy-independent formalism. Although the details have not yet been investigated by the authors, it is a plausible conjecture that a similar approach might be able to produce some form of intermediate Hamiltonian in the case for which only the more restricted GS method is used to solve the linear equations (see section 2.10).

The HL calculation necessarily treats accurately one state at a time, even when working in a multi-dimensional model space. This state-specific way of calculating has become increasingly popular as a means of avoiding such problems as the intruder state problem and (in molecular problems) too much complication in the definition of an unperturbed one body Hamiltonian within the BW tradition. Eberhardt *et al* (1974) made some configuration interaction calculations by a method which is the same as that used in section 4.5 except that they took only the diagonal part of the large (BB) section of their matrix. State-specific BW calculations were also used in the calculations of Wenzel and Steiner (1998), Masik *et al* (1998) and Pittner *et al* (1999, 2001) and in the perturbation formalism of Chen *et al* (2002). The calculation of Meath *et al* (1963), although presented in terms of the reaction operator, is equivalent to an iterative BW calculation of the wave operator within a partitioning formalism for a single state. In the RS tradition the number of works which have used a state-specific approach either explicitly or implicitly is large (e.g Adamowicz *et al* (2000), Finley (1998a, 1998b), Duch and Dierksen (1992), Meissner and Paldus (2000)). BW approaches are more simple than RS ones and so make it possible to carry out efficient calculations for a specific system while reducing any problems which might arise from intruder states. However, the BW form of perturbation theory has for long been out of favour in the literature of quantum chemistry because, within the context of general theory, it has the formal feature of being size inconsistent. There is a vast literature on this subject but three works which explained the problem and showed how it can be partially solved in a wave operator approach were those of Sheppard (1984), Heully *et al* (1996) and Hubac and Wilson (2000). The BW approach was shown to be useful in the calculation of the intermediate Hamiltonian by Zaitsevski and Dement'ev (1990) and its value for some atomic and molecular problems was demonstrated by Hubac *et al* (2000), Quiney *et al* (2001) and Hubac and Wilson (2001).

4.9. Some iterative calculations for F

Many authors have proposed iterative methods for the calculation of the wave operator. Some of the methods start from what is essentially a perturbative point of view, assuming that the basis functions used are eigenfunctions of some unperturbed Hamiltonian. Nevertheless the common starting point of the direct iterative methods is a nonlinear equation, which can be that for the Bloch reduced wave operator (the F of this work) or that for the full wave operator, either the generalized Bloch equation or an alternative form which involves a commutator. The methods vary in the degree of complication with which they partition the terms in the nonlinear equation for F into 'left-hand side' and 'right-hand side' terms for the iterative process; some authors have even suggested that the partitioning should be varied as the iterative process progresses. In the calculations of the present work a relatively simple method was applied to the test matrices. In particular, the Bloch effective Hamiltonian was retained as an entity in the iteration equations. For both iterative and perturbative calculations this approach was found

to be computationally effective as well as giving direct access to HB during the calculations. The equations used were those already derived in section 2.2 but with a slight change which permitted the introduction of a relaxation parameter K . It should be noted that the following equations are written in assignment form (new value on the left, old value on right):

$$\begin{aligned}
 HB(AA) &:= H(AA) + H(AB)F(BA) \\
 Y(BA) &:= -H(BA) + F(AB)[HB(AA) - eI(AA)] \\
 Z(BA) &:= [H(BB) - eI(BB)]^{-1}Y(BA) \\
 F(BA) &:= F(BA) + K[Z(BA) - F(BA)].
 \end{aligned}
 \tag{4.9}$$

In the calculations the matrix $Z(BA)$ was found by solving the appropriate system of linear equations in the B space by using Gaussian elimination, although a GS iterative approach would be possible for e values which are below the spectrum of the $H(BB)$ submatrix. The set of equations given above includes a variable parameter e . In terms of pure algebra the equations for F and thus their solutions are unchanged whatever the value of e . However, the convergence properties of the iterative process and the particular solution which is finally obtained are found to be influenced by the choice of both e and of the relaxation parameter K . The role of K in controlling the convergence to particular solutions is analogous to that of the damping formulae which have been used in some of the other test calculations reported in this work. The subroutine which was devised for the SCM calculations and which converts HB into HD was attached to the program which was constructed to implement the iterative procedure.

Square root algorithm 1 succeeded when the elements of F were small. In all the test calculations the initial F matrix was set at zero. For the 4×4 test matrix 1 with an A subspace of dimension 2 and with $x = 0.08$ the use of the e values 0, 3 and 20 gave converged results for F and HB , although the value of K had to be given the small value of 0.2 to constrain the last two iterations to converge. For the cases $e = 3$ and $e = 20$, F contains very large elements and HB is far from symmetric. The eigenvalue pairs obtained from HB are $[E(2), E(3)]$ at $e = 3$ and $[E(3), E(4)]$ at $e = 20$. For these cases the square root algorithm 1 failed and so algorithm 2 had to be used to produce an HD from HB . For the choice $e = 0$ a K value of 1 gave rapid convergence of F and HB , with the associated eigenvalue pair $[E(1), E(2)]$. The calculation of HD using square root algorithms 1 and 2 gave converged but different apparent HD matrices:

$$\begin{aligned}
 HB &= \begin{pmatrix} 0.98054 & 0.40762 \\ 0.28001 & 2.30048 \end{pmatrix} \\
 HD1 &= \begin{pmatrix} 0.9182 & 0.16729 \\ 0.16729 & 2.36282 \end{pmatrix} & HD2 &= \begin{pmatrix} 0.9730 & 0.32331 \\ 0.32331 & 2.30772 \end{pmatrix}.
 \end{aligned}
 \tag{4.10}$$

HB , $HD1$ and $HD2$ were checked to give the same eigenvalues, particularly since $HD1$ has the unexpected property that its off-diagonal element is not close to the average of those for HB . A check of the intermediate results of the computation revealed that it is $HD2$ which is the correct canonical form of HD , while $HD1$ is a non-standard form which is necessarily related to it by a unitary transformation. For this case (in which F has one large matrix element) square root algorithm 1 leads to a legitimate but non-SPD square root $R(+)$. For test matrix 2 at $x = 0.4$, with a model space of dimension 2 the choice $e = -3$, $K = 1$ led to the levels $E(1)$ and $E(2)$ with small F elements, so that HD was directly obtained from HB by using the simple iterative method 1 for $R(+)$ and $R(-)$. The choice $e = 4$, $K = 0.1$ led to the levels $E(4)$ and $E(5)$, with a highly asymmetric HB and large F elements, so

that algorithm 1 for obtaining HD did not work. For the test matrix 3 with an A space of dimension 3 the choice $e = 0$, $K = 1$ gave rapid convergence and produced the lowest 3 levels, with algorithm 1 giving HD from HB . For test matrix 4, with an A space of dimension 1, the choice $e = 0$, $K = 1$ gave rapid convergence to the correct eigenvalue which is stated in the test matrix data. For the 20×20 test matrix 3 with a model space of dimension 2 and $x = 4$ the choice $e = 0$, $K = 1$ gave rapid convergence and produced the lowest two levels, with algorithm 1 giving HD from HB . For test matrix 6 with an A space of dimension 3 the choice $e = 0$, $K = 1$ gave rapid convergence and produced the lowest three eigenvalues, with algorithm 1 again producing HD from HB . Similar success was obtained by using A subspaces of varying dimension for the perturbed oscillator matrix, test matrix 7, with $\beta^2 = 8$.

The results for test problem 1 illustrate a point of more general interest. The iterative process produced the lowest two eigenvalues at $x = 0.08$ but the SCM calculation gave the levels $E(1)$ and $E(3)$, for which the eigenvectors have the largest A space components. This distinction between methods which ‘follow the eigenvalues’ and those which ‘follow the eigenvectors’ (particularly for problems involving avoided crossings) has frequently been made in the literature. The method of Krenciglowa and Kuo (1974), which was originally derived by a diagrammatic approach, gives the states with the largest model space overlap. Suzuki and Lee (1980) gave two methods, one of which gives the states which are nearest in energy to the unperturbed energy. Both of these methods were formulated for the case of a degenerate unperturbed system. Anastasio *et al* (1974) showed how to improve the convergence properties of the Krenciglowa–Kuo method and Suzuki *et al* (1994) extended the Lee–Suzuki method to handle non-degenerate model spaces. Andreozzi (1996) gave new algorithms which were equivalent to the KK and LS ones as well as some which could give the levels in the neighbourhood of any assigned energy. Bogner and Kuo (2001) described both the KK and LS methods in terms of iterative algorithms and related them to the renormalization group method. Both of these last two works used the nonlinear equation for F (section 2.2), which they called the decoupling equation.

The appearance of avoided crossings as the parameter x varies is clear in the case of test matrix 1 and can also appear as the internuclear distance R is varied in calculations on simple diatomics such as H_2 and H_2^+ . The effects associated with avoided crossings are part of a wider category of phenomena which involve intruder states, i.e. states (usually collective ones) which can unexpectedly descend into the model space energy region and spoil the intended description of the low lying levels by means of a small previously selected model space. In atomic theory a simple case of this is provided by the Be atom; the obvious near-degeneracy of the $1s^2 2s^2$ and $1s^2 2p^2$ states with $S = 0$ suggests the use of a two-dimensional model space but the presence of various intruder states involving higher ns type orbitals complicates the calculation. Several other examples are given by Evangelisti *et al* (1987), who apply the intermediate Hamiltonian method of Malrieu *et al* (1985) to deal with the intruder state problem; in particular they refine the distinction (mentioned above) between ‘energy following’ and ‘state following’ types of wave operator by introducing ‘adiabatic’ and ‘diabatic’ wave operators. Three of the early works which explored the intruder state problem by using a theoretical exposition combined with the use of some clear 2×2 and 3×3 matrix examples were those of Schucan and Weidenmuller (1972, 1973) and of Schaefer (1974). In a sequence of connected works Vincent and Pittel (1973), Pittel *et al* (1976) and Vincent (1976) gave a detailed discussion of the methods of constructing an effective Hamiltonians by means of perturbation theory in cases for which intruder state effects are important; Vincent’s paper gave several ways of defining the Bloch wave operator in terms of the projection operators on the model and target spaces. Hose (1986) gave a detailed analysis of the way in which

intruder states affect the choice of model space as the internuclear distance in H_2 is varied. Finley *et al* (1995) used a model of four hydrogen atoms on a rectangular array to show how the choice of the unperturbed Hamiltonian in a perturbation approach could be used to diminish intruder state effects as the length of the rectangle is varied while its width remains fixed. Two works which both used the same perturbed two-dimensional oscillator example to illustrate their approach to avoided crossing phenomena were those of Fried and Ezra (1989) and Dunn *et al* (1996). The second paper looked at the behaviour of Padé approximants of both linear (i.e., traditional) and of quadratic type in describing energy levels near an avoided crossing. The first paper took an alternative approach which is similar to that which makes use of effective Hamiltonians; the authors noted, by using the example of a 2×2 matrix, that the secular equation describing two close energy levels should have a convergent perturbation expansion even if the formal RS series for the individual state energies are divergent because of the avoided crossing. They thus concentrated on obtaining the expansion for the secular equation and found reasonable results for the perturbed oscillator test problem. Cizek *et al* (1996) used the concept of an effective characteristic polynomial in their study of anharmonic oscillators.

In the test matrix calculations above the linear algebra was carried out in the B space, since the matrix $[H(BB) - eI(BB)]$ was placed on the left of the equations to be iterated. The equations can be rewritten to put $[HB(AA) - eI(AA)]$ on the left. This leads to an A space calculation but appears to require a matrix inversion. However, this can be avoided by taking the transpose of the resulting matrix equation and so obtaining another problem involving a system of linear equations (In terms of general algebra, the matrix equation $AX - XB = C$ can be solved iteratively by writing it in the form $AX = C + XB$. If it is written in the alternative form $XB = AX - C$ then the calculation of the inverse of B can be sidestepped by taking the transpose of the equation). At first sight it is tempting to choose the form of the equations which involves linear algebra in the smaller A space but preliminary numerical experiments indicate that this 'easy' alternative does not have such good convergence properties as the B space method. However, for the case of test matrix 3 the use of a relaxation parameter formalism similar to that for the B space approach did give the lowest five levels with an A space of dimension 5, although several hundred iterations and a relaxation parameter of $1/2$ were needed to produce convergence, with the e parameter set at 5 (which is greater than any of the required A space eigenvalues). Clearly, further numerical experiments are required to discover to what extent the A space version of the iterative method can compete with the B space version.

5. Some numerical perturbation calculations

Much of the literature dealing with the theory of wave operator and effective Hamiltonian methods is devoted to the derivation of the expressions for the low-order terms in the perturbation expansion of the various quantities arising in the theory. The expressions are written in terms of sums-over-states which involve matrix elements of the perturbing potential as well as unperturbed energy differences. This approach has long been familiar within non-degenerate Rayleigh–Schrödinger perturbation theory; for several simple problems in that area modern methods such as hypervirial perturbation theory have made it possible to use recurrence relations in a purely numerical approach which bypasses the more cumbersome traditional sum-over-states algebra and permits the calculation of perturbed energies and expectation values without any knowledge of the perturbed wavefunction (Killingbeck *et al* 2001). For matrix eigenvalue problems, however, it is necessary to use more traditional numerical or algebraic perturbation theory expansions which involve sums over states and

matrix elements between basis states. In the present review the emphasis is on numerical perturbation calculations but it should be noted that Kleiner (1972) used a matrix partitioning approach in an algebraic derivation of the RS energy perturbation series up to fourth order, while Marcus (2001) gave the low-order RS perturbation theory for a non-symmetric matrix. The terms of various orders in the matrix perturbation theory of Pakiari and Khalesifard (1997) were presented in the form of matrix products which could be evaluated numerically and so permitted a perturbation calculation for the H_2 molecule.

5.1. Rayleigh–Schrodinger methods

In the present work the various quantities have been expanded in powers of a perturbation parameter λ defined as follows. The unperturbed matrix is taken to be diagonal in both the A and B subspaces and so the notation $D(AA)$ and $D(BB)$ is used for the portions of the unperturbed matrix. The perturbing matrix consists of the remaining terms in the full matrix, whether of AA , BB , AB or BA type. Thus the perturbation can have diagonal contributions. This freedom to vary the diagonal perturbation terms is used in some of the reported test matrix calculations. In the works which give algebraic expressions for low-order terms in effective Hamiltonian theory it has often been used to convert a non-degenerate unperturbed Hamiltonian into a degenerate one (with a necessary change in the perturbing terms) so as to exploit the relatively more simple terms which occur in the perturbation series for the degenerate case. In the work of this section the perturbing terms are multiplied by a perturbation parameter λ ; the value $\lambda = 1$ corresponds to the actual matrix problem and so the various perturbation series arising are summed with $\lambda = 1$ in an attempt to find the perturbed F matrix and Bloch effective Hamiltonian. The terms appearing in the Hamiltonian matrix are thus written as

$$\begin{aligned} H(AA) &= D(AA) + \lambda V(AA) & H(AB) &= \lambda V(AB) \\ H(BA) &= \lambda V(BA) & H(BB) &= D(BB) + \lambda V(BB) \end{aligned} \quad (5.1)$$

and the F and HB matrices are written as perturbation series

$$F(BA) = \sum_M \lambda^M F(BA; M) \quad HB(AA) = \sum_M \lambda^M HB(AA; M). \quad (5.2)$$

The expansion for $F(BA)$ starts at the first order term. The F matrix has to obey the nonlinear equation

$$H(BB)F(BA) - F(BA)H(AA) = F(BA)H(AB)F(BA) - H(BA). \quad (5.3)$$

The perturbation series can be formed by inserting the appropriate expressions from (5.1) and (5.2) in this equation and grouping the terms according to ascending powers of λ . It is clear from (5.3) that the nonlinear term gives a lowest-order contribution of order 3 and so plays no role in the calculation of the first-order term of F . This first-order term arising from (5.3) is quickly seen to be given by

$$[D(AA) - D(BB)]F(BA; 1) = V(BA) \quad (5.4)$$

from which the $F(BA; 1)$ matrix is obtained directly, since the matrices $D(AA)$ and $D(BB)$ are diagonal. This first-order result has already been used to define the small step-by-step transformations which are used in the single cycle method of section 4.3.

Inspection of the higher-order terms appearing in (5.3) will lead to recurrence relations which link the terms of various orders and so will permit the construction of the series for F , from which the series for HB can be constructed in an auxiliary calculation. This procedure based on (5.3) is the most common one in the literature and was implemented in one of the programs written to treat the test matrices of the present work. Another program was written

to implement the slightly different perturbation method of Roussy (1973) which attaches a perturbation parameter to the nonlinear term in (5.3). The numerical calculations revealed that for the test matrices the need to form a matrix triple product (for the FHF term) slows down the speed of the calculations considerably in the higher orders of perturbation theory. It was found that a given order of perturbation theory could be reached more rapidly by using an approach which introduces HB directly into the recurrence relations and so does not involve any direct triple products. Using the facts that $HB(AA) = H(AA) + H(AB)F(BA)$ and that the zeroth and first-order terms of F and HB are known it is straightforward to obtain the recurrence relation which produces the higher order terms:

$$[D(BB) - D(AA)]F(BA; M) = \sum_J F(BA; J)HB(AA; M - J) - V(BB)F(BA; M - 1) \quad (5.5)$$

$$HB(AA; M) = V(AB)F(BA; M - 1).$$

The approach based on these recurrence relations not only leads to faster calculations but also produces the effective Hamiltonian HB along with F , so that either of them can be treated by Padé approximants if desired. The compact matrix notation used here makes the presentation of the equations more easy; in calculations the various elements of the matrix $F(BA; M)$ are, of course, obtained by taking the appropriate elements of the matrix products appearing in the equations. The diagonal form of the unperturbed matrices $D(AA)$ and $D(BB)$ simplifies the calculation and leads to the typical unperturbed energy differences if the results are expressed as algebraic formulae rather than being used numerically. The values of $F(BA)$ and $HE(AA)$ are formed by summing the terms in their perturbation series.

For the test matrix problems the RS perturbation approach described above is quite effective. For the 20×20 test matrix 3 the F and HB series converge by order 25 and produce a 5×5 effective Hamiltonian which gives very accurately the lowest five eigenvalues exactly as found in the preceding calculations. For a 40×40 example of the matrix of $-D^2 + x^2 + x^4$ in a basis with $\beta^2 = 8$ (which cuts down the AB coupling) the perturbation series converge well by order 30 for the case of an A space of dimension 3 and give the lowest three eigenvalues accurately.

The 4×4 example test matrix 1 gave interesting results. With $x = 0.05$ the perturbation series converge to give an effective Hamiltonian with the eigenvalues 0.942 794 6 and 2.190 624 2, which are the lowest two eigenvalues. At $x = 0.08$, however, the perturbation series diverge, although a Wynn–Padé analysis which applies the Wynn epsilon algorithm to each element produces accurate values for the elements of $F(BA)$ and $HE(AA)$. Varying the $V(AA)$ term was also tried. The program was modified to include a variable parameter K which modifies the unperturbed diagonal terms; for example the diagonal unperturbed element $D(J, J)$ becomes $D(J, J) + KV(J, J)$ while the perturbing term $V(J, J)$ is reduced to $(1 - K)V(J, J)$ to render the total diagonal element of the perturbed matrix exactly the same as before. This approach changes the diagonal elements which appear in the perturbation recurrence relations. It was found that for the 4×4 test matrix 1 the choice $K = 2$ is effective for $x = 0.08$. This choice changes the diagonal elements of $D(AA)$ and $D(BB)$ but simply reverses the sign of the diagonal terms of the perturbation. With this change the perturbation series converge, leading to an effective Hamiltonian with eigenvalues 0.899 093 6 and 3.296 800 7. These are the first and third eigenvalues at $x = 0.08$. The two values of x used in the calculations reported above are on opposite sides of an avoided crossing at $x = 1/15$. The wave operator perturbation calculation eigenvalue jumps from the lower eigenvalue branch to the upper one as x is increased through the avoided crossing.

For the 50×50 test matrix 4 with $\lambda = 0.005$, the perturbation series converge at $\mu = 0.2$ and at $\mu = 0.4$ to give the correct energy for the perturbed state arising from the unperturbed zero diagonal in the (1, 1) position. At $\mu = 0.6$ the perturbation series diverge, although a Wynn–Padé analysis gives a perturbed eigenvalue estimate of -0.00057 , which is not too far from the accurate value of -0.000561528 which was given in the test matrix data of section 4. For the 30×30 test matrix number 6 the use of A subspaces of dimension M with M varying from 1 to 5 leads to a strongly divergent sequence of partial sums for the HB matrix elements. However, the application of the Wynn algorithm to each individual element gives well converged values for each element of HB and produces the M lowest eigenvalues to all the digits quoted in the data for the test matrix 6. For test matrix 2 with an A space of dimension 2 the perturbation calculation gives a converged HB matrix and the correct lowest two eigenvalues at $x = 0.1$, while at $x = 0.4$ the sequence of HB elements diverges but leads to the two lowest eigenvalues to 8 digit accuracy when the Wynn algorithm is used. For the 20×20 Mathieu test matrix number 5 with an A space of dimension 2 the perturbation calculation quickly gives a converged HB which yields the two eigenvalues cited in the test matrix data at both $x = 2$ and $x = 4$.

It thus emerges that the perturbation method is successful for the test matrices, even though it sometimes has to be augmented by the use of the Wynn algorithm when the raw sequences of partial sums diverge. The HB matrix alone was treated by the Wynn algorithm in the results cited here, since the HB array is usually much smaller than the F array. A few test calculations showed that a divergent F array is equally well amenable to treatment by the Wynn algorithm; such a treatment would, of course, be needed if the full wavefunction were required for any auxiliary purpose.

Although the test calculations reported above were in the main carried out for standard decompositions of the test matrix into perturbed and unperturbed parts, the formalism is sufficiently flexible to allow the use of other decompositions; for example, one of the most common formal devices used in general theory is to reduce all problems to those of degenerate perturbation theory by adding an artificial extra perturbation which makes all the unperturbed A space levels have the same energy. This way of handling the problem can easily be tested numerically by adjusting the D and V terms in the matrix perturbation approach of the present section. Dietz *et al* (1994) showed how appropriate choices of the unperturbed and perturbed parts of the Hamiltonian can influence the rate of convergence of the perturbation series in RS theory. They gave some examples for molecular calculations.

In atomic and molecular calculations the two traditional ways of choosing the unperturbed Hamiltonian are the Møller–Plesset (MP) one and the Epstein–Nesbet (EN) one. The MP approach uses a sum of one-particle operators (usually a sum of Hartree–Fock operators) as the unperturbed Hamiltonian; this means that the residual perturbing potential has diagonal matrix elements. The EN method by contrast uses the diagonal matrix elements of the total H to define the unperturbed problem and thus the perturbation is defined to have zero diagonal terms. Several authors have proposed choices of the single particle Hamiltonian which can give better low-order perturbation results than those given by the EN or MP approaches. The work of Surjan and Szabados (2000) is of particular interest within the context of the present discussion, since they made essential use of several partitioning methods in their theory. Rosta and Surjan (2002) showed how to construct efficient unperturbed Hamiltonians which include two-body operators. The theory and calculations reported above refer to the common case of an M dimensional A space with an orthonormal set of basis functions as the basis for the full H matrix. Blinder (1960b) described a second-order perturbation theory for the case $M = 1$, with the B space basis functions being orthogonal to the A space function but not to each other. Besalu and Carbo-Dorca (1998) described a compact RS perturbation method for the matrix

eigenvalue problem; in their formalism the unperturbed matrix need not be diagonal but if it is not diagonal then it is necessary to find its eigencolumns in order to start the perturbation calculation. The analogous approach in the method of this section would be to diagonalize the full $H(AA)$ initially, which would then require a recomputation of the matrix elements between the A and B spaces; such a test calculation is reported below. This procedure was also used in a perturbative calculation of configuration interaction wavefunctions by Fortune and Rosenberg (1976), who gave algebraic sum over states expressions for the energy terms up to fifth order. It was also used by Huron *et al* (1973). Their initial states, found by diagonalization within a space of strongly interacting functions of determinantal type, were iteratively modified by mixing in other states which were coupled to them in the first order of perturbation theory, with an iterative sequence of diagonalization and perturbation being carried out to produce accurate eigenfunctions for a few low-lying states. Huron *et al* showed that this approach was particularly effective in finding excitation energies, provided that a particular barycentric modification of the MP definition of the unperturbed Hamiltonian was used to carry out the perturbation calculations; they also discussed various other modified forms of the MP and EN procedures which had previously been proposed in the literature. Bendazzoli *et al* (1987) used an iterative procedure involving diagonalization and perturbation, setting out their method in a manner which is more directly in the tradition of matrix eigenvalue techniques. Segal and Wetmore (1975) also used a matrix perturbation approach to configuration interaction calculations, although their method was based on an iterative BW calculation of low order rather than on an RS approach. Several works have looked at how the MP or EN methods for partitioning the molecular Hamiltonian can be modified to give better convergence of the associated energy perturbation series. Recent works in this spirit include those of Finley and Freed (1995), Surjan *et al* (1998), Angeli *et al* (2000), Maniero *et al* (2002), Angeli and Cimraglia (2002) and Wind *et al* (2002). Goodson (2000) applied rational and algebraic Padé approximants in order to obtain good estimates of the full configuration interaction results for several molecules from low-order MP perturbation theory results.

The full configuration interaction result, of course, plays the role of the ‘exact’ one in the context of matrix calculations with a large basis set (whatever the ‘true’ chemical accuracy obtained). The question of practical interest is whether the use of wave operator or perturbation techniques, allied with Padé or other extrapolation methods, will simplify the treatment of low-energy states and so avoid the direct diagonalization of the very large matrices involved.

The MP and EN perturbation approaches are two different ways of partitioning the Hamiltonian matrix of an atom or molecule when calculating the correlation energy correction due to the inter-electron repulsion, starting from a Hartree–Fock or similar approximate wavefunction. Some of the modern developments in the theory, although not based on a wave operator approach, nevertheless involve some useful general principles and so are briefly sketched here. The case of a state which can be represented by a single Hartree–Fock determinant is taken, to simplify the discussion. The determinant contains optimised orbitals found by solving the Hartree–Fock equations. However, from a matrix diagonalization point of view the orbitals have the property that the perturbing Hamiltonian (i.e., the residual inter-electron repulsion) has zero matrix elements between the determinant and any single excitation determinant obtained from it. This is the essence of Brillouin’s theorem but can be seen to be simply a necessary criterion for the energy of the determinant to be stationary with respect to a variation of the orbitals within it. However, the exact groundstate eigenfunction would have no matrix elements with *every* function which is orthogonal to it; the single excitation states are just a very simple subset of these orthogonal functions. Kutzelnigg and Mukherjee (2000) adopted an approach which tries to extend this line of thought, by applying the criterion

that the exact wavefunction (which cannot, of course, remain a single determinant) should have no double (then triple, etc) excitation matrix elements. They had to use the second quantization approach to handle the problem and produced a hierarchy of equations which must be satisfied by the wavefunction. They showed that this approach via a generalization of Brillouin's theorem naturally led to the use of cumulants in the calculation of various energy expectation values and led to a more direct understanding of how such cumulants arose in the work of Mazziotti (1998), which studied reduced density matrices and in that of Valdemoro *et al* (2001) on the contracted Schrödinger equation approach, which also led to reduced density matrices by studying the contracted Schrödinger equation obtained by integrating over the variables of (in the simple case) $N - 2$ electrons in an N electron system.

Silverman (1983) pointed out that many of the common approaches to RS perturbation theory use the intermediate normalization convention and so use an energy correction formula which is linear, in the sense that the N th order energy correction appears to depend on the N th order perturbed eigenvector, whereas a variational approach to the theory would indicate that knowledge of the N th order wavefunction should be able to give the energy up to the $(2N + 1)$ th order. He rearranged the RS matrix perturbation formalism to take advantage of this fact. It should be noted, however, that a more direct way to proceed is to calculate the expectation value of the Hamiltonian for the full perturbed wavefunction up to a given order. In the topics covered by the present review the relationship between perturbation and variational methods is exploited both in the calculations with the energy-dependent effective Hamiltonian HL and in the distinction made between effective Hamiltonians such as HB and HBV . The RS formalism used to carry out the test matrix calculations reported above was, as explained, chosen as the most effective out of several which had been proposed in the literature. A further variant of this chosen method was also tried, in which the SCM was used to diagonalize $H(AA)$ at the start. Thus $H(AA)$ was rendered diagonal and the $H(AB)$ and $H(BA)$ parts of the matrix had to be recomputed to allow for the change in the basis functions in the A space. At first sight it might appear that this approach would lead to better results but it turned out that for the reported test calculations this preliminary diagonalization had little effect on the performance of the RS calculation; in particular it did not avoid the need to use the Wynn epsilon algorithm in those cases for which it had been necessary in the original calculations.

Although the test examples given in the present paper all involve numerical calculations based on simple algorithms, it would in principle be possible to follow through the steps of the algorithm to obtain algebraic expressions for the results at each step. This would lead to the typical sum over states expressions which appear in many formal works on low-order perturbation theory. Another way to obtain algebraic perturbation series is to perform an expansion in powers of V of the roots of the secular determinant which arises from the matrix eigenvalue problem for the operator $H_0 + V$. This approach has a long history (e.g., Sasakawa 1964, Chan 1966) and has been applied more recently by Chen *et al* (2002) to obtain perturbation series for the energy of a state in the context of the one-state-at-a-time approach to multi-reference perturbation theory.

5.2. Brillouin–Wigner Gauss–Seidel methods

In a discussion of perturbation methods it should be noted that many of the relaxation methods which have been used to find matrix eigenvalues are essentially modified versions of Brillouin–Wigner (BW) perturbation theory for the special case of a one-dimensional model space. Although such methods have a close resemblance to the iterative methods which use the

energy-dependent effective Hamiltonian HL , it is still worth giving an outline of some particular aspects of the relaxation methods. The usual approach in such calculations is to set the coefficient $A(I)$ of the I th basis function in the desired eigenfunction equal to 1; this corresponds to the intermediate normalization convention in perturbation theory. The initial E value can be taken to be $H(I, I)$ or can be chosen at will. Each other coefficient $A(J)$ is then calculated by re-arranging the J th row of the standard eigenvalue equation into a form which expresses $A(J)$ in terms of the other $A(K)$. In assignment statement form this gives

$$(J \neq I) \quad B(J) := [E - H(J, J)]^{-1} \sum_{K \neq J} H(J, K)A(K). \quad (5.6)$$

In this equation the new value of $A(J)$ has not been used to overwrite the old value but has been put into a separate B array. At the end of a full cycle through the J indices the $B(J)$ are copied into the $A(J)$, which are then used in the next cycle over the J indices. The iterative process used is thus what is called the Jacobi process, in which the old values of $A(J)$ are held fixed while all of the new $A(J)$ values are worked out. At the end of the cycle number N a running total $F(E)$ is augmented as follows:

$$T(N) := \sum_J H(I, J)A(J) : F(E) := F(E) + T(N). \quad (5.7)$$

The initial value of $F(E)$ before the first cycle is set as $H(I, I)$. If the cycles are followed through algebraically it can be seen that the running total $F(E)$ is actually the numerical value of the traditional sum of terms of increasing order which appears on the right of the usual implicit equation $E = F(E)$ for the eigenvalue of state number I in the traditional BW perturbation theory. Similarly, the running total of the $A(J)$ values from each cycle gives the J component of the eigenvector in BW theory. In a numerical calculation the important point of interest is whether the sequence of $F(E)$ values can produce a well-defined numerical function of E as N increases. Even when the sequence of values of $F(E)$ diverges it turns out that the sequence can often be made to yield a very precise numerical result by applying the epsilon algorithm. This particular effectiveness of the Padé approximant approach or of equivalent continued fraction methods within BW perturbation theory has been noted and exploited by many workers (Young *et al* 1957, Goscinski 1967, Brandas and Goscinski 1970, Bartlett and Brandas 1972).

The discussion which has been given above of the relaxation approach has presented it in the form of a BW matrix perturbation theory which is appropriate to the context of this section of the review. However, this ‘pure’ form of the method has been used only rarely in the literature: the majority of workers use Gauss–Seidel iterations rather than Jacobi ones and also update the value of E on every cycle rather than trying to evaluate $F(E)$ for a fixed E . The resulting calculation is a hybrid one in which different orders of BW theory are mixed together. This approach can be described by replacing the assignment statement (5.6) by the pair of assignment statements

$$(I \neq J) \quad T := [E - H(J, J)]^{-1} \sum_{K \neq J} H(J, K)A(K) \\ A(J) := A(J) + RC[T - A(J)] \quad (5.8)$$

and the assignment statements (5.7) by the assignment statements

$$T := \sum_J H(I, J)A(J) : E := E + RE[T - E] : TS := TS + T. \quad (5.9)$$

The introduction of the relaxation parameters RC and RE helps to constrain the iterates to the vicinity of a desired solution, whereas the standard method with $RC = RE = 1$ has a

tendency to fall to the lowest eigenvalue unless the H matrix is diagonally dominant. If RE is set equal to 0 and RC is set equal to 1 then E is held fixed and a sequence of TS values is produced, leading (possibly after treatment by the Wynn algorithm) to a numerical function which turns out to have the same numerical value as the function $F(E)$ of the 'pure' BW version of the calculation, even though the Gauss–Seidel iterations mix up successive orders of the traditional BW perturbation theory. In the numerical calculations reported here the method was applied to the full H matrix rather than to the HB matrix, with RC and RE being initially set at 1 and then reduced if any convergence problems were encountered, particularly for excited states. The sequence of values of E was itself subjected to the Wynn algorithm and this proved to be very effective in speeding up convergence or even in producing it in some case in which the sequence does not converge. Finding the Rayleigh quotient for the approximate eigencolumn at each step would also be another way to convert the linearly convergent iterative process into a quadratically convergent one. In their multireference perturbation calculations Cave and Davidson (1988b) used an iterative method which is virtually the same as the BWGS one and devised another method to convert the linear convergence into quadratic convergence. The paper by Castano *et al* (1985) presented a method very similar to BWGS, except that it did not assume intermediate normalization but included extra steps to normalize the perturbed eigencolumn. Rather than making direct numerical calculations Castano *et al* traced through the iterations algebraically, producing sum over states expressions for the energy and eigencolumn elements in a variety of perturbation expansions and then using those expansions themselves in their numerical test calculations.

The BWGS method described above was applied to some of the test matrices, with the simple ($RC = RE = 1$) method being tried first. For test matrix 1 with $x = 0.08$ and for test matrix 2 with $x = 0.1$ the simple method gives all the eigenvalues as the index I is varied. For test matrix 3 the eigenvalues 1, 5 and 6 are obtained directly by keeping the parameters RC and RE sufficiently small to control the convergence and by varying I . For the cases of eigenvalues 2, 3 and 7 the sequence of varying E values does not converge or even behave well with the Wynn algorithm. However, setting $RE = 0$ and $RC = 1$ produces a sequence of $F(E)$ estimates which, although divergent, yields an accurate $F(E)$ value when treated by the Wynn algorithm. Varying E so as to make $E = F(E)$ then gives a good eigenvalue (although it involves a more tedious calculation!). For the case of test matrix 3 it is, of course, important to avoid using the numerical value 1 as the initial eigenvalue estimate, since the first five diagonal elements all equal 1 and so would lead to a division by zero. For test matrices 5 and 6 the direct method works. For test matrix 5 it gives eigenvalues 1 and 2 successfully and for test matrix 6 it gives the eigenvalues 1 to 5. For test matrix 4, which involves a near-zero eigenvalue in the midst of a spectrum, the best that the method appears capable of doing is to give a rough estimate of around $-0.000\ 56$ for the eigenvalue.

It is clear that the difficult cases in the test calculations were mainly those for which the exact eigencolumn did not have one single dominant component $A(I)$ which could be taken to be the component held at the value 1 during the calculation. Since the equations which are used in the calculations do not exploit any symmetry properties of the matrix, the relaxation method as described here would be applicable to matrices such as HB which are not Hermitian but which have real eigenvalues. The linear equation (5.9) used to find the eigenvalue is a generally valid one which appears in the intermediate normalization form of perturbation theory, rather than one based on a Rayleigh quotient. Although most works using the relaxation technique described above have treated the standard eigenvalue problem there have been a few applications to the generalized eigenvalue problem. Arias de Saavedra and Buendia (1990) used the method for a double well problem for which basis states in different wells are not orthogonal. It seems probable that a similar application would be possible for

the generalized eigenvalue problem associated with the Kato effective Hamiltonian HK for those cases in which the F matrix has small elements, so that the matrix $I + F^\dagger F$ is not far from the unit matrix I .

5.3. Calculations of second order

In the test calculations of the present work an iterative calculation of second order was used for the calculations involving HL , since the Hermiticity of the matrices involved made it possible to exploit the properties of the Rayleigh quotient. For the other calculations, however, first-order iterative processes were used, with relaxation parameters to control convergence and with Padé approximant analysis either to control divergence or to produce second-order convergence from the sequence of results produced by a first order iterative process. Durand *et al* (1994) and Durand and Paidarova (1996) looked at a more general theory of second-order iterative processes to calculate the wave operator, even for cases in which the matrices concerned are not symmetric or even real. In the general case of a multi-dimensional model space they needed a superoperator formalism to express their results and they also introduced a partition of their operators into perturbed and unperturbed parts so as to produce iterative methods within the specific RS and BW forms of perturbation theory. For the benefit of general readers the present section sets out some of the basic notions of their approach while sticking to the simple matrix eigenvalue problem in the form which has been used in the preceding sections. The essential aim of this simple illustrative example is to use an A space of only one dimension and to repeat the calculation of section 2.2 from another point of view. If the column element $A(I)$ is kept fixed with the value 1 then the matrix eigenvalue problem can be written in the form

$$\text{row } I \quad E = H(I, I) + \sum_{J \neq I} H(I, J)A(J) \quad (5.10)$$

$$(J \neq I) H(J, J)A(J) + \sum_{K \neq J} H(J, K)A(K) = EA(J). \quad (5.11)$$

Solving the second equation for $E(J)$ by moving the first term to the right of the equation produces an expression for $A(J)$ which involves a division by $(E - H(J, J))$. If E is then replaced by the right-hand side of the first equation then the result is an implicit equation for the elements of the column A , which for this simple case can be seen to be the elements of the reduced wave operator as defined in the preceding discussions. The equation is quickly found to be

$$A(J) = [D(J)]^{-1} \sum_{K \neq J} H(J, K)A(K) \quad (5.12)$$

with

$$D(J) = H(I, I) - H(J, J) + \sum_{K \neq I} H(I, K)A(K). \quad (5.13)$$

This is a vector form of the common scalar problem of the type $x = f(x)$ which arises in ordinary algebra. To treat this scalar problem by means of a Newton–Raphson iterative approach with second-order convergence it is convenient to regard it as simply requiring that the functions $F(x) = [x - f(x)]$ shall be zero. Applying the usual Newton–Raphson approach to $F(x)$ leads to a formula which can be expressed in several different ways. Perhaps the most simple form is the incremental one which can be expressed in the assignment statement form

$$x := x + [1 - G]^{-1}[f(x) - x] \quad (5.14)$$

where G should be precisely df/dx to give an exact second-order Newton–Raphson process. However, it is clear that a stationary state will be attained when $x = f(x)$ even if g is only a very rough approximation to the exact derivative of f . In the case of the vector equation above for the vector A the role of the derivative of f is taken by the square matrix of partial derivatives of the function $f(J)$ on the right of equation (5.12). Denoting by $G(J, K)$ the partial derivative of $f(J)$ with respect to $A(K)$ the result obtained can be written in the form

$$G(J, K) = [D(J)]^{-1}[H(J, K) - H(I, K)f(J)]. \quad (5.15)$$

In principle this would permit a Newton–Raphson process for the calculation of the column A , with the $G(J, K)$ matrix being worked out at each cycle, somewhat in the spirit of the Jacobi iteration process. However this would involve a considerable amount of calculation at each step because of the matrix $[I - G]^{-1}$ appearing in equation (5.14). To render the process computationally feasible it is necessary to seek for reasonable approximations to the inverse, perhaps as a polynomial in G or as a fixed approximation worked out at an early stage of the iterations. The result of such approximations is to lose the exact second-order nature of the iterative process. Durand and co-workers, in the works cited above, tried several approximations to the derivative operator in an attempt to obtain ‘nearly’ second-order processes.

5.4. A deflation method

Several deflation techniques exist for removing a specified eigenvalue from the spectrum of a matrix (Wilkinson 1965). In the test calculations of the present work the problem which sometimes arises is that if a matrix is not diagonally dominant then an iterative method such as the BWGS one might only be able to give the lowest eigenvalue with any speed or reliability. In such cases the most appropriate way to find several low eigenvalues is to remove each lowest eigenvalue as it is found, thus exposing a new lowest eigenvalue to be calculated. For an Hermitian matrix with initial elements $H(J, K)$ this can be done by adding to $H(J, K)$ a sum of terms of form $e(N)Y(J, N)Y^T(K, N)$, one for each lowest eigenvalue which has already been found. Here the Y elements are those of the normalized eigencolumn and $e(N)$ is the artificial eigenvalue which has been assigned to move the N th eigenvalue upwards to a position far above the original true eigenvalue. In Dirac notation the term $E(N)|N\rangle\langle N|$ in the spectral decomposition of H has been changed by replacing the true eigenvalue $E(N)$ by the new number $e(N)$. In actual calculations the H matrix is left unchanged and the appropriate extra terms are constructed during the formation of products such as $H(J, K)X(K)$. Thus only the elements $Y(J)$ are stored rather than the square matrix which they would produce. If the matrix H is sparse or banded this type of deflation slows down the calculations since it formally renders the matrix full, even though the modification only appears during the actual formation of matrix products (and in the term $H(J, J)$ in the $[E - H(J, J)]$ denominators). However, the test matrices 3 and 6 are themselves full matrices and so the penalty incurred is not so great. To render test problem 6 impossible for the simple BWGS approach the off-diagonal element was increased from 1 to 5. Finding the lowest eigenvalues one at a time by the direct relaxation approach with $RC = RE = 1$ and moving each calculated eigenvalue up to $e = 50$ then produced the eigenvalue sequence $-3.580\ 289\ 372\ 3$, $-1.502\ 808\ 228\ 3$, $0.550\ 591\ 494\ 5$, $2.593\ 891\ 278\ 1$, $4.631\ 565\ 266\ 0$ and so on. For test matrix 3 this deflation method easily gives sequentially the lowest seven eigenstates. Convergence to the new lowest state rather than to another state was found to be best ensured by setting the I index for which $A(I) = 1$ equal to the sequence of values 1, 2, 3 as the calculation progressed.

If the matrix being treated is real, with real eigenvalues, but is not symmetric, then the term $e(N)Y(J, N)Y^T(K, N)$ used in the deflation process would have to be replaced by $e(N)Y(J, N)Z^T(J, N)$, where the set Y and Z together give a biorthogonal set of functions. Rather than finding the set of Z in terms of the Y by some collective calculation it is possible to find the Z as the (suitably scaled) right eigenvectors of the transpose of the matrix for which the Y are the right eigenvectors.

The deflation method described here is just one of the many ways in which it is possible to exploit the reliability of the BWGS for the lowest eigenstate. Another possibility would be to treat individually each one of the M states with the smallest M diagonal elements, using the relaxation method with the other $M - 1$ states omitted. Each calculation would become that for the lowest level of a truncated matrix and would lead to a function which included the coupling to the higher states. The resulting set of M orthogonal functions could then be used as a basis in the M -dimensional subspace, producing an $M \times M$ eigenvalue problem which gives upper bounds to the lowest M levels. To obtain M levels of high accuracy would be likely to need a subspace of more than M of the ‘enriched’ basis functions produced by this procedure, although for a small subspace the solution of a generalized eigenvalue problem rather than an ordinary eigenvalue problem would not cause any difficulty.

5.5. An adjustable BW calculation

The energy-dependent effective Hamiltonian

$$HL(AA) = H(AA) + H(AB)[eI(BB) - H(BB)]^{-1}H(BA) \quad (5.16)$$

can be formally expanded as a series in the perturbation V if it is supposed that $H = H_o + V$ for some unperturbed Hamiltonian H_o . In the present discussion using matrix models it will be assumed (as in the previous RS calculations) that H_o is composed solely of diagonal elements, so that for brevity its A and B space portions can be labelled $D(AA)$ and $D(BB)$. The perturbation V is then taken to be all the rest of the matrix and is allowed to have diagonal as well as off-diagonal elements. With the notation $H(BB) = D(BB) + V(BB)$ it is clear that the action of the operator $[e - H(BB)]^{-1}$ on $H(BA)$ (which is also $V(BA)$) can be written in terms of an operator geometric series. If the notation $R(e)$ is used to denote the diagonal matrix $[e - D(BB)]^{-1}$ then the first term of $[e - H(BB)]^{-1}H(BA)$ is $R(e)H(BA)$ and each later term is calculated by multiplying the previous one by $R(e)V(BB)$. These terms are just those in the expansion of the energy-dependent reduced wave operator $F(BA)$. As the N th term is found (by matrix multiplication from the preceding one) the product of that term with $H(AB)$ is formed and the total so far is stored in an array labelled so that $T(N, J, K)$ holds the total so far of the contributions to the element (J, K) of $HL(AA)$ for the given e value. The sequences will often diverge but the use of the Wynn algorithm can be effective in producing a well-defined HL from the sequence.

Since the BW approach requires a state by state self-consistent approach even for a multi-dimensional model space, it is necessary that the calculation, if necessary with the aid of the Wynn algorithm, should give an accurate $HL(e)$ for a wide range of e values. The method allows the choice of H_o and V to be varied at will in order to improve the accuracy or rate of convergence of the numerical results. In principle, when the B space has finite dimension the use of the Wynn algorithm should produce an exact $HL(e)$ in a finite number of steps, if exact arithmetic is used. In actual single or double precision calculations, however, varying the choice of the V part of the matrix has a visible effect on the accuracy obtained when the B space is of large dimension. The most simple way to proceed is to use the off-diagonal part of the H matrix as the perturbation V . For the small test matrices 1, 2 and 5 this method with an

A space of dimension 2 gives highly accurate $EL(e)$ elements. For the test matrices 3 and 6, however, several digits of accuracy are lost and the results are much worse than those which are obtained using the RS perturbation theory.

The next most simple stage of complication is to adjust the choice of V so as to render the unperturbed A or B space Hamiltonians degenerate. Several calculations were tried for some of the test matrices with the B space unperturbed diagonals all being set equal to a fixed number $E(B)$ and with the diagonal part of V being adjusted to leave the full H matrix invariant. Perhaps the most extreme choice is to use an A space of one dimension and to take the unperturbed matrix to be simply a null matrix except for the element $H(AA)$, so that the Brillouin–Wigner energy series has powers of E in its denominators and moments of the full Hamiltonian matrix in its denominators. This choice was made in the work of Brandas and Bartlett (1971) and Bartlett and Brandas (1972, 1973) and was studied by Surjan and Szabados (2002a, 2002b). It leads to a strongly divergent sequence for $HL(e)$ but the action of the Wynn algorithm then produces numerical results which are reasonably accurate for the test matrices 1, 2 and 5. If the B matrix is strongly diagonally dominant then another rough approximation would be to ignore the off-diagonal elements of B , which for the present calculation would remove the terms beyond second order in the perturbation. This approximation has been used in some calculations on molecules and is called the B_K approximation. It has been explained in terms of partitioned matrix theory by Nitzsche and Davidson (1978). In some of the traditional discussions of the convergence of the BW perturbation theory a clear distinction has not always been made between the convergence of the partial sums for the function $F(e)$ at a fixed e and the convergence of the sequence of eigenvalues $E(N)$ which are found by the more complicated process of solving the equation $E = F(E)$ iteratively using the N th order sum for $F(e)$. Bhattacharyya (1982) gave a careful study of the different quantities appearing in BW theory and of their treatment in the previous literature.

While the vast majority of matrix perturbation calculations use a diagonal matrix as the unperturbed matrix, thus making the calculation of the inverse easy, some workers have explored the possibility of using an unperturbed matrix of a tridiagonal or even more general form. Znojil (1987) and Bishop *et al* (1989) discussed this more general theory. The direct use of the partial sums of the perturbation series for energies or wavefunctions naturally leads to a study of convergence properties, summation techniques, etc. An alternative approach, which goes back as least as far as the work of Dalgarno and Stewart (1961) is to regard the perturbed wavefunctions of successive orders as functions which have been correctly ‘shaped’ by the perturbation and thus should make suitable non-orthogonal basis functions to be used in a Rayleigh–Ritz calculation. This approach was applied by Allen (1983) and a similar idea was also used in one of the techniques discussed by Certain and Hirschfelder (1970). Cederbaum and Schonhammer (1975) described a highly flexible way of using perturbed wavefunctions in a matrix variational calculation and discussed the relationship of their approach to that of previous workers within the context of BW and RS perturbation theory and continued fraction methods. The method of forming an ‘enriched’ basis which is mentioned at the end of the BWGS section of the present review is based on the same approach of using information from a perturbation calculation to improve the performance of a matrix generalized eigenvalue calculation. The early work of Lennard-Jones (1931) had the interesting feature (from the point of view adopted in this review) that it derived what is essentially BW perturbation theory from a study of a partitioning of the Hamiltonian matrix. Later workers such as Feenberg (1948, 1958), Feshbach (1948), Goldhammer and Feenberg (1956) and Barr (1971) sought to improve the results obtainable at a given order of BW perturbation theory by including extra adjustable parameters in the theory. Leinaas and Kuo (1978) studied the convergence properties of BW theory by using an operator which is the HL effective Hamiltonian of the

present work. Lain and Torre (1987) gave an elementary way of unifying the derivations of RS and BW perturbation series. Works which have given efficient approaches to the BW series within the context of applications to atomic or molecular problems include those of Grimaldi (1969) and Lindgren (1984).

Several authors have chosen the unperturbed Hamiltonian matrix to be $PHP + QHQ$ (in the notation of this review), with $PHQ + QHP$ as the perturbation. This approach was described by Adams (1966) and is sometimes called Löwdin–Adams perturbation theory. It can be shown that obtaining the first-order perturbed wavefunction suffices to find the energy up to fifth order, with all odd-order perturbed energies being zero. If the A space is taken to be a single approximate eigenfunction of the Hamiltonian then in principle the B space can be regarded as the rest of Hilbert space. The first-order perturbed wavefunction cannot be found exactly but can be found with high accuracy by using a variational principle with trial functions which are suitably chosen to allow for correlation effects. The method has been applied to two-electron atoms by Devine and Stewart (1972), using a Hartree–Fock function as the A space function, and by Chong *et al* (1973), using a split-shell function as the A space function. Both choices sufficed to obtain the He atom groundstate energy to within 0.0001 atomic units using just the variationally determined first-order perturbed wavefunction.

6. Conclusion

Part 1 of this review has given an historical survey of the use of the time-independent wave operator concept in several branches of applied quantum mechanics and has presented the basic theory in the context of matrix algebra, both to make it more accessible to general readers who are familiar with matrix techniques and to present an alternative approach to specialists who are mainly familiar with the projection operator formalism which tends to dominate some parts of the research literature. As the writing of the review progressed and the various test calculations were performed it soon became apparent that a closed and definitive account of the field could not be achieved. Each new method of calculation which succeeded would suggest a possible combination with an earlier method and each point of dispute in the literature would call for a more lengthy analysis of the fundamental theory. Thus the longer the review became the more distant became the hypothetical endpoint of the work, as the parts of the assembled material began to combine to produce an increasing progeny of ideas and possibilities. Faced with this ‘effet du lapin’, the authors have left scattered throughout the text a variety of conjectures about theoretical points and possible computational methods; these will demonstrate to the general reader that the subject is still far from closed and will give specialists in the field some material and ideas for further work. Of the several techniques which have been introduced and tested during the writing of the review it is perhaps the simple matrix square root algorithm 1, based on Higham’s work, and the versatile SCM algorithm which will be of the most general use to both general readers and to specialists. At several points throughout the text it has been pointed out that, despite its widespread application to Hermitian (usually real symmetric) matrices, the wave operator formalism is applicable in a wider context. In part 2 of the review the power of the formalism will become even more apparent when its modern time-dependent version is described. When the Hamiltonian begins to vary with time it is clear that the fixed F transformation which has been used in part 1 will have to be replaced by some time-dependent entity. As might be anticipated on intuitive grounds, the quantity which is zero for a fixed F (the function $f(F, H)$ of part 1) plays the role of a driving term in an equation of motion which can be constructed for a time-dependent counterpart of F which appears in the dynamical version of the theory. The appendix gives a foretaste of this behaviour using a simple case which is understandable within the formalism

of the present part of the review. Despite the increased complication associated with the theory of the time-dependent wave operator it will emerge that some of the tools developed in the simple test calculations of part 1 will also be of value when tackling the time-dependent wave operator calculations described in part 2. As a consequence of the new time-dependence of the variables appearing in the theory the methods of part 1 will often be called upon to handle complex (rather than real) matrices and so will be able to show their full capabilities. Like the Sundance Kid, they are even better when they move!

Dedication

Gert Due Billing made many original contributions to molecular theory and for more than a decade was a much-valued colleague of the authors. Illness prevented him from joining the authors in Besançon during the writing of the present review. We wish to dedicate this work to his memory.

Appendix

The present part 1 deals with the more traditional time-independent aspects of Bloch wave operator theory. Even so it is possible to get a preliminary idea of the dynamical theory of part 2 by looking at the simple case in which the A subspace is taken to be one dimensional. If a fixed basis is used then it is the coefficients $C(J)$ in the column describing the wavefunction which will vary. $C(1)$ will vary in some way and so will the ratios $F(J) = C(J)/C(1)$ which correspond to the elements of the reduced wave operator as defined in this review. Taking the column C to vary in accord with the time-dependent Schrödinger equation

$$i\hbar \frac{dC}{dt} = HC \quad (\text{A.1})$$

the varying column C can be written in the form of a product

$$C = (I + F)C(1)e(1) \quad (\text{A.2})$$

where I and F are in full matrix square form and $e(1)$ is the traditional unit column. F only contains non-zero elements in column 1 and has a zero first element. The representation (2) is still perfectly general. By recalling the matrix multiplication properties summarized in section 2.4 the reader will quickly establish the results.

$$F = 0 \quad : \quad F \, dF/dt = 0 \quad : \quad (I + F)^{-1} = I - F \quad (\text{A.3})$$

since dF/dt is also a matrix with its non-zero elements in column 1. Substituting (A.2) into (A.1) and working out the left- and right-hand sides leads to the result

$$i\hbar \left[\frac{dC}{dt} + \frac{dF}{dt}C(1) \right] e(1) = (I - F)H(I + F)C(1)e(1). \quad (\text{A.4})$$

Multiplying this equation on the left with the transpose first of $e(J)$ for $J \neq 1$ and then with the transpose of $e(1)$ gives, after cancelling those terms which are zero by virtue of equations (A.3), two equations which can be written in component form as follows (note that the full matrix forms are involved):

$$i\hbar \frac{dF(J, 1)}{dt} = [(I - F)H(I + F)](J, 1) \quad (\text{A.5})$$

$$\begin{aligned} i\hbar \frac{dA(1)}{dt} &= [(I - F)H(I + F)](1, 1)C(1) \\ &= [H(I + F)](1, 1) \end{aligned} \quad (\text{A.6})$$

where the third member of (A.6) follows on removing the formally zero terms from the second member. The results above are (for this simple case) the promised generalizations of equation (2.28) of the text, with terms which are zero in the time-independent case acting as driving terms in the equations of motion of the time-dependent case. When applications of the equations above are made it becomes important to know whether the use of a finite basis can suffice to describe a particular dynamical process which in principle requires a complete basis; this is analogous to the simpler problem of choosing a finite basis to simulate a Hilbert space calculation in the Rayleigh–Ritz approach. The most obvious problems, of course, are those of finding integration methods for the family of nonlinear equations of motion arising above and of seeing what happens in the case of a selected A space with more than one component. Part 2 of this review (which is now being completed) will deal with the relatively modern and ongoing set of ideas and calculational methods which have been and currently are being developed to deal with a dynamical extension of the traditional Bloch wave operator concept.

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