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Iterative Solution in Quantum Scattering Theory

The log Derivative Kohn Approach†

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The log derivative version of the Kohn variational principle is reviewed in the context of a general inelastic molecular collision. Particular emphasis is placed on the possibility of solving the resulting linear equations iteratively for a single initial state column of the scattering matrix, ***S***, and several important practical observations are made in this regard. In particular, it is argued that the discrete variable representation proposed by Light and coworkers leads to an extremely sparse coefficient matrix, and so has distinct advantages over the more obvious variational basis approach. The resulting methodology is applied to the diffractive scattering of a beam of helium atoms from the (001) face of LiF. Here test calculations with up to 2601 coupled channels and 216 translational grid points clearly demonstrate the practical potential of the iterative technique. The implications of these tests for more general scattering problems are also briefly discussed.

1. Introduction

Variational methods have attracted considerable recent attention as a practical approach to quantum reactive scattering. In particular, and largely as a result of several exciting theoretical developments, these methods have already been successfully applied to an interesting variety of atom–diatom reactions.[1–3] These references are, of course, intended to be representative rather than complete: a clear survey of the current situation is given in Dr Connor's keynote paper,[4] which also contains a comprehensive list of references to the recent work in this field.

As has now been discussed several times,[5–7] the computational effort in variational reactive scattering has two main sources. First, one must evaluate costly multi-dimensional matrix elements between basis functions in different chemical arrangements, and then one must solve a large system of linear algebraic equations for the scattering matrix of interest. While the latter of these two tasks is formally the higher order process it is highly vectorisable, and in fact the former often proved to be the rate-determining step in early variational calculations. However, since variational methods have become more established more 'difficult' problems have been addressed, and the solution of the linear equations is already beginning to emerge as the real bottleneck of the approach.[1–3] This is especially true of methods based on the Kohn variational principle,[8,9] in which all[3] (or nearly all[1]) matrix elements are energy independent, and so only have to be evaluated once at the first scattering energy, E.

In this paper we follow Yang and Miller[7,10] in asking whether or not it is possible to speed up the solution of the ***S*** matrix Kohn equations using some sort of iterative technique. Our presentation, and the conclusions of our investigation, are, however, somewhat different from theirs. In particular, we confine our attention almost exclusively to the generic close-coupled equations of inelastic scattering.[11] At first sight this might seem like a strange thing to do, because there are already a number of well known and highly efficient numerical integration methods for solving these close-coupled equations.[12–15] However, there are several reasons why we believe that the present investigation is nevertheless worthwhile.

First, the inelastic scattering equations are simpler to work with, and therefore better known, than their reactive scattering counterparts. This in itself makes them an ideal testing ground for the development of new numerical techniques. Of course if these techniques do readily extend to the reactive problem, which methods based on the Kohn principle most certainly do, then so much the better. Secondly, there are a number of practical simplifications that arise in the inelastic context which may not be equally applicable in the reactive case. Since inelastic scattering problems are important enough in their own right it seems desirable to emphasise and exploit these simplifications when one can. Thirdly, we intend to show that iterative solution of the Kohn equations can, in favourable circumstances, be considerably more efficient than any standard close-coupling technique!

The outline of the paper is as follows. We begin, in section 2, by describing the log derivative version of the Kohn variational principle in the context of a general inelastic molecular collision. Attention is focused primarily on iterative solution of the resulting linear equations for a single initial state column of the scattering matrix, S, and several important practical observations are made in this regard. Then, in section 3, the method is applied to the diffractive scattering of a beam of helium atoms from the (001) face of LiF. (The model we consider here is, in fact, an elastic scattering problem, but it still leads to a system of coupled differential equations with the general inelastic scattering form.[16]) The test calculations reported in section 3 involve up to 2601 coupled channels and 216 translational grid points, and so clearly demonstrate the practical potential of the iterative technique. Finally, in section 4, we conclude by discussing the implications of our results for more general, including reactive, scattering regimes.

2. General Theory for Inelastic Collisions

In this section we review the log derivative version of the Kohn variational principle as it applies to the generic close-coupled equations of inelastic scattering. Particular emphasis is placed on the possibility of solving these close-coupled equations iteratively for a single initial state column of the

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scattering matrix, $\boldsymbol{S}$. In this regard it is argued that the discrete variable representation proposed by Light and coworkers has significant advantages over the more obvious variational basis approach.[17] Not only are the linear equations for $\boldsymbol{S}$ far easier to set up within the discrete representation, but they are also a great deal more sparse. The advantage of sparsity in iterative solution is very well known. Indeed it is probably fair to say that this sparsity, rather than the ease with which matrix elements are evaluated, has been the single most important factor in dynamical applications of the discrete variable representation to date.[18]

2.1 The log Derivative Kohn Principle

The close-coupled equations of inelastic scattering are most conveniently written in matrix notation as[11]

$$\boldsymbol{\Psi}''(r) = \boldsymbol{W}(r)\boldsymbol{\Psi}(r) \tag{2.1}$$

where

$$\boldsymbol{W}(r) = \frac{2\mu}{\hbar^2}\boldsymbol{V}(r) + \frac{\boldsymbol{l}(\boldsymbol{l}+\mathbf{1})}{r^2} - \boldsymbol{k}^2 \tag{2.2}$$

with

$$\boldsymbol{k}^2 = \frac{2\mu}{\hbar^2}(E\mathbf{1} - \boldsymbol{\varepsilon}) \tag{2.3}$$

and the primes denote differentiation with respect to r. In eqn (2.2) μ is the collision reduced mass, $\boldsymbol{V}(r)$ is the real symmetric matrix of the interaction potential, and $\boldsymbol{l}$ is a diagonal matrix of orbital angular momentum quantum numbers. In eqn (2.3), E is the total scattering energy, $\mathbf{1}$ is the unit matrix, and $\boldsymbol{\varepsilon}$ is a diagonal matrix of internal channel energies. We shall assume for simplicity that neither of the collision partners carries a charge, so that all the elements of $\boldsymbol{V}(r)$ vanish faster than r^{-2} as $r \rightarrow \infty$.

In principle the number of coupled equations is infinite, but in practice the expansion can be truncated at some finite value, N. This truncation is equivalent to neglecting all channels that remain strongly classically forbidden throughout the interaction region, and is a valid approximation provided N is sufficiently large. Henceforth all the matrices which appear in eqn (2.1)–(2.3) can therefore be taken to be $(N \times N)$.

The wavefunction $\boldsymbol{\Psi}(r)$ must be regular at the origin, and its asymptotic form defines an augmented scattering matrix, $\boldsymbol{S}$, by means of the relations

$$\boldsymbol{\Psi}(r \rightarrow 0) \sim \mathbf{0} \tag{2.4}$$

$$\boldsymbol{\Psi}(r \rightarrow \infty) \sim \boldsymbol{i}(r) - \boldsymbol{o}(r)\boldsymbol{S} \tag{2.5}$$

where $\boldsymbol{i}(r)$ and $\boldsymbol{o}(r)$ are diagonal matrices of flux-normalised incoming and outgoing waves,

$$\boldsymbol{i}(r) = \boldsymbol{k}^{-(1/2)}\hat{h}_l^{(2)}(\boldsymbol{k}r) \tag{2.6}$$

$$\boldsymbol{o}(r) = \boldsymbol{k}^{-(1/2)}\hat{h}_l^{(1)}(\boldsymbol{k}r) \tag{2.7}$$

and $\hat{h}_n^{(1,2)}(x)$ are the Riccati–Hankel functions defined by Calogero.[19] (It is, of course, perfectly permissible to define transcendental functions of the matrices $\boldsymbol{k}$ and $\boldsymbol{l}$, as we have done in eqn (2.6) and (2.7), simply because both of these matrices are diagonal.) Before leaving these equations it is convenient to define three more diagonal matrix functions of r, all of which are trivially obtained from $\boldsymbol{i}(r)$, $\boldsymbol{o}(r)$ and $\boldsymbol{o}'(r)$:

$$\boldsymbol{a}(r) \equiv \boldsymbol{i}(r)\boldsymbol{o}(r)^{-1} \tag{2.8}$$

$$\boldsymbol{b}(r) \equiv \boldsymbol{o}(r)^{-1} \tag{2.9}$$

$$\boldsymbol{c}(r) \equiv \boldsymbol{o}'(r)\boldsymbol{o}(r)^{-1}. \tag{2.10}$$

These three functions arise quite naturally when scattering boundary conditions are applied in the log derivative Kohn method,[3] and so defining them here will simplify the notation below.

Most variational approaches to eqn (2.1) use a linearly independent translational basis set, $\{u_i(r)\}_1^M$, for the description of the radial motion. The various possibilities which arise then differ only in the choice of the variational functional, and, in the case of the Kohn principle,[8,9] in the boundary conditions satisfied by the basis functions $u_i(r)$. For the log-derivative version of the Kohn principle these boundary conditions are most conveniently specified as[6]

$$u_i(0) = 0 \quad \text{and} \quad u_i(s) = \delta_{iM}. \tag{2.11}$$

Here s is some point in the asymptotic region, so that $\boldsymbol{V}(r \geqslant s) \simeq \mathbf{0}$ and the asymptotic form in eqn (2.5) can be taken to apply. In passing we should perhaps emphasise that the functions $u_i(r)$ are independent of the channel index α. This choice, which corresponds to using a direct product basis of translational and close-coupled internal functions, is certainly not unique. However, it does allow certain useful simplifications, as we shall describe in section 2.2 below.

Having established the boundary conditions on the functions $u_i(r)$ in eqn (2.11) we now define an $(NM \times NM)$ stiffness matrix, $\boldsymbol{K}$, with $(N \times N)$ matrix blocks[6]†

$$\boldsymbol{K}_{ij} = \int_0^s \{u_i'(r)\mathbf{1}u_j'(r) + u_i(r)\boldsymbol{W}(r)u_j(r)\}\,\mathrm{d}r \tag{2.12}$$

for $i,j = 1, 2, \ldots, M$. With this definition the log derivative version of the Kohn variational principle leads to the following remarkably compact expression for the augmented scattering matrix, $\boldsymbol{S}$:

$$\boldsymbol{S} \approx \boldsymbol{a}(s) + 2i\boldsymbol{B}^T[\boldsymbol{K} - \boldsymbol{C}]^{-1}\boldsymbol{B} \tag{2.13}$$

where

$$\boldsymbol{B} = \begin{pmatrix} \mathbf{0} \\ \boldsymbol{b}(s) \end{pmatrix} \tag{2.14}$$

and

$$\boldsymbol{C} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{c}(s) \end{pmatrix}. \tag{2.15}$$

Here the partitioning of $\boldsymbol{C}$ is such that it only contributes non-zero diagonal elements to the bottom right-hand corner (M, M) block of $\boldsymbol{K}$. The partitioning of $\boldsymbol{B}$ is entirely analogous, but in this case only the Mth column block is required.

Eqn (2.13), which was originally derived in the context of a general bimolecular chemical reaction,[3] is the central result of the theory. With the present definitions it is a variationally correct expression for the augmented scattering matrix, $\boldsymbol{S}$, in the direct product (translational × coupled channel) basis described following eqn (2.11). In section 2.2 we shall consider a specific choice for the translational basis functions, $u_i(r)$, which admits a particularly convenient discretisation scheme for the matrix elements of $\boldsymbol{K}$. Then, in section 2.3, we shall consider iterative solution of the linear equations for $\boldsymbol{S}$ in eqn (2.13). However before proceeding with these discussions we should at least give some consideration to 'closed' channels, which have deliberately been ignored until now so as to keep the essential equations of our method clear.

A channel α is said to be 'open' if the corresponding diagonal element k_α^2 of the matrix $\boldsymbol{k}^2$ in eqn (2.3) is positive, and 'closed' if it is negative or zero. The inclusion of a few closed channels in the close-coupled basis is usually necessary before a satisfactory level of convergence is attained, and fortunately this does not affect our results in any significant way. In par-

† The phrase 'stiffness matrix' is borrowed from finite element analysis. See ref. (20).

ticular, the physical scattering matrix, $\hat{\boldsymbol{S}}$, is simply the open channel submatrix of $\boldsymbol{S}$. This matrix is easily, and safely,[3] obtained from eqn (2.13) on contracting both sides to the (open channel × open channel) block. Moreover the form of eqn (2.13) automatically guarantees both the unitarity and the symmetry of our approximation to $\hat{\boldsymbol{S}}$.[3] Physically, the unitarity of $\hat{\boldsymbol{S}}$ ensures that the incoming and outgoing fluxes are equal, or that the total number of particles in the system is conserved.[21] The symmetry of $\hat{\boldsymbol{S}}$ is related to the behaviour of the system under time-reversal, and ensures that the flux scattered from channel α to channel β is equal to that scattered in the reverse direction.[21] Both of these physical properties are clearly desirable, if not essential, features of any approximate (basis set) expression which one might wish to recommend.

2.2 Discrete Variable Representation

In an earlier article[6] we proposed a discrete variable representation (DVR),[17] based on Gauss–Lobatto quadrature,[22] which we advertised as a simple way to speed up the evaluation of the exchange integrals which arise in Miller's formulation of reactive scattering.[23] Unfortunately we have since found that this DVR does not work as well for really large reactive scattering problems as we originally hoped it would.[24] The reason for this is simply that the above exchange integrals have an inherently difficult form. In particular, the integral over the translational coordinate of one arrangement involves the rotational and vibrational basis functions of the other.[23] When projected by the appropriate coordinate transformation these basis functions become highly localised, and in some cases extremely oscillatory, and so pose severe problems for any mechanical quadrature scheme which one might choose to employ. If calculations are required at a large number of energies the DVR, which uses only one grid point per translational function, ultimately becomes less efficient than using a smaller translational basis and doing the integrals exactly.

While we have currently abandoned the DVR for problems which involve exchange (*i.e.* reactive scattering), we still believe that it has distinct advantages for problems with purely local interactions (*i.e.* inelastic scattering). In particular, we have some (as yet unpublished) evidence that the Lobatto DVR works at least as well as exact integration for a variety of inelastic and potential scattering problems. Moreover, the linear equations for the scattering matrix in eqn (2.13) become extremely sparse when the stiffness matrix $\boldsymbol{K}$ is evaluated within the DVR. This has especially important implications with regard to iterative solution, as we shall describe below.

In keeping with the present definitions it is convenient to write the Gauss–Lobatto quadrature rule in the interval $[0, s]$ as[22]

$$\int_0^s f(r)\,\mathrm{d}r \approx \sum_{i=0}^{M} \omega_i f(r_i) \tag{2.16}$$

where $r_0 = 0$, $r_M = s$ and the remaining weights $\{\omega_i\}_0^M$ and nodes $\{r_i\}_1^{M-1}$ are chosen so as to make eqn (2.16) exact for all polynomials of degree $2M - 1$. The corresponding Lobatto shape functions, which are simply Lagrangian interpolating polynomials at the Lobatto quadrature nodes, are then defined as[6]

$$u_i(r) = \prod_{j=0}^{M}{}' \frac{r - r_j}{r_i - r_j}; \quad i = 0, 1, \ldots, M \tag{2.17}$$

where the prime means 'exclude $j = i$' from the product. The properties of these functions are described in some detail in ref. (6). As far as the present work is concerned it suffices to note that the functions $\{u_i(r)\}_1^M$ satisfy the boundary conditions in eqn (2.11), and so provide a complete and natural Mth degree polynomial basis for the description of the radial motion.[6]

Having established this translational basis set we can, of course, simply substitute it into eqn (2.12) and evaluate all integrals over r exactly. This gives, using a second mnemonic devised by Light, Hamilton and Lill,[17] our variational basis representation (VBR) for the stiffness matrix $\boldsymbol{K}$:

$$\boldsymbol{K} = \boldsymbol{T} + \boldsymbol{U} \tag{2.18}$$

where

$$T_{\alpha i,\,\beta j} = \int_0^s u_i'(r)\delta_{\alpha\beta}\,u_j'(r)\,\mathrm{d}r \tag{2.19}$$

and

$$U_{\alpha i,\,\beta j} = \int_0^s u_i(r)W_{\alpha\beta}(r)u_j(r)\,\mathrm{d}r. \tag{2.20}$$

The corresponding discrete variable representation (DVR) is obtained on approximating the integrals for $\boldsymbol{U}$ in eqn (2.20) using the Gauss–Lobatto quadrature formula in eqn (2.16):

$$U_{\alpha i,\,\beta j} \approx \sum_{k=0}^{M} \omega_k u_i(r_k)W_{\alpha\beta}(r_k)u_j(r_k) = \omega_i W_{\alpha\beta}(r_i)\delta_{ij}. \tag{2.21}$$

Here the simplification follows because $u_i(r_j) = \delta_{ij}$, as is immediately apparent from the definition of $u_i(r)$ in eqn (2.17). In passing it is interesting to note that $u_i'(r)$ and $u_j'(r)$ are both polynomials of degree $M - 1$, and so the integrals for $\boldsymbol{T}$ in eqn (2.19) can be evaluated without approximation using exactly the same Gauss–Lobatto rule.

The practical advantages of the DVR should now be clear. First, once the $M(M + 1)/2$ unique non-zero elements of $\boldsymbol{T}$ have been evaluated, using eqn (2.16), (2.17) and (2.19), there are no more quadratures to perform. Secondly, it is immediately apparent from the Kronecker deltas in eqn (2.19) and (2.21) that the discrete representation of $\boldsymbol{K}$ is extremely sparse. In particular, the 'kinetic energy' matrix, $\boldsymbol{T}$, is diagonal in the channel space N, and the 'potential energy' matrix, $\boldsymbol{U}$, is diagonal in the translational space M. Hence there can only ever be a maximum of $N^2M + M^2N$ non-zero elements in $\boldsymbol{K}$. Moreover the term of order N^2M tends to be a fairly conservative upper bound, because it does not account for any sparsity which may be present in $\boldsymbol{W}(r)$. This is certainly the case for the application considered in section 3, in which all but *ca.* $5N$ elements of $\boldsymbol{W}(r)$ vanish identically for all r.

Now it is well known that the operation count for iterative solution, in an ideal situation and with a single right-hand side, scales simply as the number of non-zero elements in the matrix which is solved. In this regard a conservative upper bound of $N^2M + M^2N$ non-zero elements is clearly better than the N^2M^2 non-zero elements which eqn (2.20) seems to suggest. Moreover it is also, and perhaps somewhat surprisingly (since the translational motion is being solved far more accurately for the same value of M), considerably better than the $O(N^3M)$ operations of a standard close-coupling technique!

Finally, since the properties of these functions are central to our formulation of the DVR, and since the indices in eqn (2.16) and (2.17) differ slightly from those we used before,[6] the Lobatto shape functions $\{u_i(r)\}_1^M$ for $M = 7$ and $(r/s) \in [0, 1]$ are plotted again here in fig. 1.

2.3 Iterative Solution

It should be clear from eqn (2.13) that if we only require a single column of the open channel scattering matrix, $\hat{\boldsymbol{S}}$, then

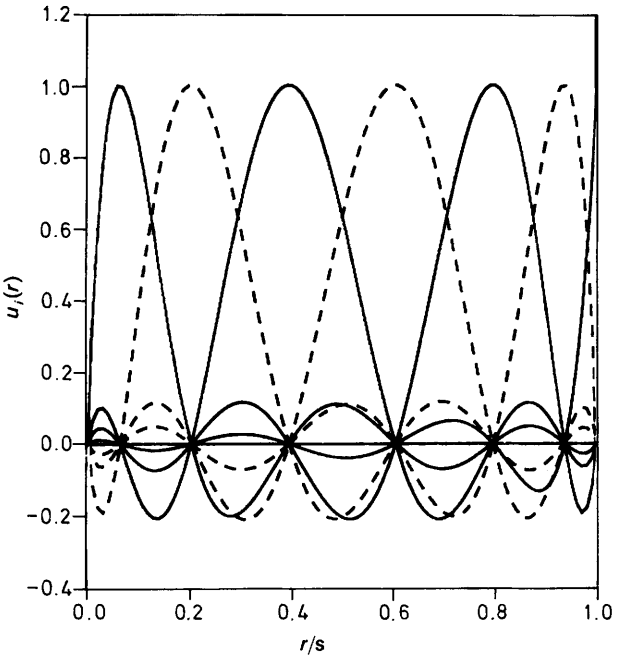

Fig. 1. Lobatto shape functions $u_i(r)$, $i = 1, 2, \ldots, M$, for $M = 7$ and $(r/s) \in [0, 1]$. The shape functions with odd indices ($i = 1, 3, 5, 7$) are plotted as solid lines, and those with even indices ($i = 2, 4, 6$) are dashed.

we only have to solve a single linear system of the form

$$\boldsymbol{A}\boldsymbol{x} = \boldsymbol{b} \tag{2.22}$$

where

$$\boldsymbol{A} \equiv \boldsymbol{K} - \boldsymbol{C} \tag{2.23}$$

is a complex $(n \times n)$ matrix, with $n = NM$, and $\boldsymbol{x}$ and $\boldsymbol{b}$ are vectors. Here we should, of course, mention that since the columns of the scattering matrix correspond to different initial states of the collision system, a single column of $\hat{\boldsymbol{S}}$ is indeed often all that is required.

A variety of iterative methods are now available for solving linear systems like eqn (2.22), and virtually all of these methods readily exploit sparsity in the coefficient matrix $\boldsymbol{A}$.[25] When choosing between the various methods one is guided primarily by the properties of this coefficient matrix, and in this regard we note that our particular $\boldsymbol{A}$ is complex symmetric and therefore non-Hermitian. While this excludes a large number of iterative methods, there are still quite a few possibilities left.[25] Of these possibilities we shall concentrate here on the generalised minimal residual (GMRES) algorithm of Saad and Schultz.[26] This method is known to be fairly robust, and several proceedings of a recent conference on 'practical iterative methods for large scale computations' clearly demonstrate just how well it can be made to work.[27–29] In particular, Duneczky and coworkers have already applied GMRES, with some success, to the (not so sparse) linear equations of reactive scattering which arise in the 'L^2-AD GNVP' formulation of Kouri and Truhlar.[29]

When applied directly to eqn (2.22) the GMRES algorithm begins with an initial approximate solution vector, $\boldsymbol{x}_0$, and the corresponding residual vector, $\boldsymbol{r}_0 = \boldsymbol{b} - \boldsymbol{A}\boldsymbol{x}_0$. The lth iteration of the algorithm then produces a correction, $\boldsymbol{z}_l$, which solves the least-squares problem

$$\min_{\boldsymbol{z}_l} \| \boldsymbol{r}_0 - \boldsymbol{A}\boldsymbol{z}_l \| \tag{2.24}$$

with the Krylov subspace

$$\boldsymbol{z}_l \in \text{span}\{\boldsymbol{r}_0, \boldsymbol{A}\boldsymbol{r}_0, \ldots, \boldsymbol{A}^{l-1}\boldsymbol{r}_0\}. \tag{2.25}$$

In eqn (2.24) $\| \boldsymbol{v} \| \equiv (\boldsymbol{v}\dagger\boldsymbol{v})^{1/2}$ is the usual 2-norm of a vector, and the approximate solution after the lth iteration is simply $\boldsymbol{x}_l = \boldsymbol{x}_0 + \boldsymbol{z}_l$. Since the span of the Krylov subspace increases with each iteration the 2-norm of the residual vector, $\boldsymbol{r}_l = \boldsymbol{b} - \boldsymbol{A}\boldsymbol{x}_l$, is a formally non-increasing function of l. With exact arithmetic the algorithm is also guaranteed to converge to the exact solution of any non-singular $(n \times n)$ linear system in a maximum of n iterations. (For a more detailed description of their algorithm, and a thorough discussion of its implementational details, the reader is referred directly to the original paper by Saad and Schultz.[26])

At this point we note that we have no *a priori* reason to believe that GMRES will converge particularly rapidly when applied directly to the linear system in eqn (2.22) and (2.23), and indeed that some closely related studies already seem to suggest it may not.[7,10] Therefore, in order to obtain a practical iterative method, we may well have to consider a preconditioned version of GMRES.[30] Preconditioned GMRES algorithms have recently been shown to be extremely effective for indefinite linear problems in meteorology[28] and for full potential flow problems in aircraft design.[27] In particular, both of these studies illustrate the advantage of using a preconditioner which is suggested by the physical nature of the problem, and so this approach might be expected to work in the present context as well.

The idea behind preconditioning is quite simple. Rather than applying GMRES directly to the linear system in eqn (2.22), we apply it instead to a 'preconditioned' system

$$(\boldsymbol{P}^{-1}\boldsymbol{A})\boldsymbol{x} = (\boldsymbol{P}^{-1}\boldsymbol{b}) \tag{2.26}$$

where the preconditioner, $\boldsymbol{P}$, is chosen to be both 'close' to $\boldsymbol{A}$, and yet relatively easy to invert using a direct LU factorisation technique. As far as the first of these conditions is concerned we note that as $\boldsymbol{P}$ tends to $\boldsymbol{A}$ the matrix $\boldsymbol{P}^{-1}\boldsymbol{A}$ becomes an identity, and so GMRES applied to eqn (2.26) converges in a single step. The need for the second condition is obvious, because if $\boldsymbol{P}$ were not relatively easy to invert then we could equally well just apply the direct method to $\boldsymbol{A}$, and the whole point of iterative solution is to find a less costly approach!

In practice one never explicitly forms the iteration matrix $\boldsymbol{P}^{-1}\boldsymbol{A}$, but rather develops the preconditioned Krylov subspace *via* a sequence of operations of the form

$$\boldsymbol{s} = \boldsymbol{A}\boldsymbol{r}; \quad \boldsymbol{t} = \boldsymbol{P}^{-1}\boldsymbol{s}. \tag{2.27}$$

For any $\boldsymbol{P} \neq \boldsymbol{1}$ this clearly requires more work per iteration than when GMRES is applied directly to eqn (2.22). However, the advantage is that fewer iterations are usually required as $\boldsymbol{P}$ approaches $\boldsymbol{A}$ and the eigenvalues of $\boldsymbol{P}^{-1}\boldsymbol{A}$ tend to one. Ideally, then, one would like to find a preconditioner which balances the increased work per iteration against the reduced number of iterations in some optimal sort of way. In general, this is quite a difficult thing to do,[30] but, as discussed above, any physical insight into the nature of the problem being solved is likely to provide a good place to start. In the next section we shall simply show that, for one model scattering problem at least, a fairly obvious and simple preconditioner can, in fact, do a remarkably good job.

3. Application to Atom–Surface Scattering

The diffractive scattering of an inert gas atom by a perfectly corrugated solid surface is, in many respects, an ideal application for the method described above. In particular, the compound states of the atom–surface system are characterised by the momentum transfer parallel to the surface on collision.[16] Hence there can only ever be one initial state of physical interest, namely that in which no momentum has initially

been transferred! Moreover atom-corrugated surface interaction potentials typically only have very few significant Fourier components, and most of these are usually very short range. Since this is true of both simple model[16] and more sophisticated[31] potentials, the coupling between the various diffraction channels can quite generally be regarded as being extremely sparse.

3.1 The Wolken He–LiF Problem

Wolken's 1972 study of the diffractive scattering of helium from the (001) face of LiF was the first application of the close-coupling technique to atom–surface scattering.[16] The model problem which he chose to study will be used below as a test case for the iterative method, so we shall now summarise some of its most important features. For a more detailed discussion, which includes a clear derivation of the relevant close-coupled equations, the reader is referred directly to the original paper by Wolken.[16] As far as the present work is concerned it suffices to note that these close-coupled equations have exactly the same form as eqn (2.1), the sole difference being that all the elements of the diagonal orbital angular momentum matrix, l, disappear.

For the interaction between the incident atom and the solid, thermally averaged over the motion of the solid atoms, Wolken assumed a potential of the form

$$V(x, y, z) = V_0(z) + V_1(z)Q(x, y) \tag{3.1}$$

with

$$V_0(z) = D \exp[2\alpha(z_0 - z)] - 2D \exp[\alpha(z_0 - z)] \tag{3.2}$$

$$V_1(z) = -2\beta D \exp[2\alpha(z_0 - z)] \tag{3.3}$$

and

$$Q(x, y) = \cos(2\pi x/a) + \cos(2\pi y/a). \tag{3.4}$$

The coordinates (x, y, z) in this potential define the position of the helium atom relative to a unit cell in the (001) face of LiF, with the z axis lying normal to the surface. (In fact the x axis is taken to be parallel to the 110 direction, as shown in Wolken's fig. 1.) The functional form of eqn (3.1)–(3.4) was first proposed by Lennard-Jones and Devonshire in the 1930s[32,33] and has since been used by several other groups.[34–36]

The laterally averaged potential $V_0(z)$ in eqn (3.2) is a simple Morse potential. The parameters D, α and z_0 in this potential were taken by Wolken to be

$$D = 7.63 \text{ meV};\dagger \quad \alpha = 1.1 \text{ Å}; \quad z_0 = 1.0 \text{ Å} \tag{3.5}$$

and these values will be used again here. (In fact the definition of z_0 is somewhat arbitrary, since it only affects the position of the surface plane. With this particular value, $z_0 = 1.0$, we use the integration range $-2.0 \leqslant z \leqslant 6.0$. The coupling between the diffraction channels is negligible beyond $z = 6.0$, and the remaining elastic distortions are easily solved using standard techniques.) The dimensionless corrugation parameter, β, in eqn (3.3) determines the strength of the coupling between the various diffraction channels. Wolken considered values of β between 0.04 and 0.10, and found some evidence to indicate that a value of β of *ca.* 0.07 was most consistent with the available experimental scattering results.[16] However, in order to provide a more stringent test case for our method, we shall concentrate here on the more strongly coupled problem with $\beta = 0.10$. Finally, the corrugation function $Q(x, y)$ in eqn (3.4) contains the single lattice parameter, $a =$ 2.84 Å, for the (001) face of LiF.

† 1 eV ≈ 1.602 × 10^{-19} J.

Having established this interaction potential we shall now move on to consider the specification of our diffraction channel basis sets.[16] There are, of course, several ways in which such basis sets might be defined, not all of which are equally efficient.[31] However, the goal of the present application is simply to demonstrate various numerical properties of the iterative approach, and in this regard just about any sensible basis set will do. We shall therefore consider only those basis sets containing surface reciprocal lattice vectors, $\boldsymbol{G}_{mn}$, which satisfy

$$-b \leqslant m \leqslant +b \quad \text{and} \quad -b \leqslant n \leqslant +b \tag{3.6}$$

for some input parameter, b. The basis set generated by eqn (3.6) contains a total of $N = (2b + 1)^2$ diffraction channels, and so grows quite rapidly with b. In particular, it can be made sufficiently complete for any incident energy and direction of the atom simply by taking b sufficiently large. Throughout our tests we shall concentrate on the incident direction with polar angle $\theta = 30°$ and azimuthal angle $\phi = 0°$, and shall not bother to symmetrise our basis sets with respect to the $(+n) \leftrightarrow (-n)$ reflection plane which this incident direction preserves. We have stressed this here, along with the simplistic nature of our basis set definition, because we want to emphasise that there are a variety of ways in which our program might still be improved.

3.2 A Physical Choice for $\boldsymbol{P}$

The sole missing ingredient in the general recipe of section 2 is a specific choice for the preconditioner, $\boldsymbol{P}$, which is to be used in conjunction with the GMRES algorithm of Saad and Schultz. In fact we have deliberately not specified this preconditioner until now because, as discussed at the end of Section 2, we would like to base our choice on the physics of the problem being solved. As far as this physics is concerned we now note that the laterally averaged potential, $V_0(z)$, might be expected to provide a reasonable zeroth-order picture of the scattering event. Indeed Lennard-Jones and Devonshire first exploited this observation some 60 years ago.[32,33] Moreover, it turns out to be relatively easy to construct and invert a preconditioner based on $V_0(z)$, as we shall now describe.

Suppose that we define the preconditioner, $\boldsymbol{P}$, as the matrix $\boldsymbol{A} \equiv \boldsymbol{K} - \boldsymbol{C}$ which is obtained when the coupling parameter β is set equal to zero in eqn (3.3). Then since $V_1(z)$ is responsible for all the coupling between the diffraction channels this preconditioner must be diagonal in the channel index, α. It follows that $\boldsymbol{P}$ contains a maximum of M^2N non-zero elements, that its LU factorisation requires $O(M^3N)$ operations, and that the second step in eqn (2.27) requires $O(M^2N)$ operations at each iteration of GMRES. Clearly, then, the LU factorisation of $\boldsymbol{P}$ is the only really 'expensive' step, and even this expense can be reduced.

The key observation is that all the channel-diagonal blocks of $\boldsymbol{P}$ have the same generic form. Assuming that we are working within the DVR of section 2.2, and ignoring for simplicity the effect of the quadrature weights, this form can be written in matrix notation as

$$\boldsymbol{P}_\alpha = \boldsymbol{H}_0 - E_\alpha \boldsymbol{1} - C_\alpha \boldsymbol{\Delta} \tag{3.7}$$

where all matrices are now $(M \times M)$, and $\boldsymbol{\Delta} \equiv \boldsymbol{e}_M \boldsymbol{e}_M^T$ denotes the rank-1 projector onto the final grid point z_M. Notice in particular that the matrix $\boldsymbol{H}_0 \equiv \boldsymbol{T} + \boldsymbol{V}_0$ is independent of the channel index α and that the outgoing-wave correction, C_α, only affects the bottom right-hand corner element of $\boldsymbol{P}_\alpha$. Both of these factors can be exploited to simplify the inversion of $\boldsymbol{P}$. First, we diagonalise $\boldsymbol{H}_0$, once and for all, at the

beginning of the calculation. This only requires $O(M^3)$ operations. Then, at each iteration of GMRES, we 'invert' the first two terms on the right-hand side of eqn (3.7) by (*a*) transforming to the diagonal representation, (*b*) dividing by $\boldsymbol{H}_0 - \boldsymbol{E}$, and (*c*) transforming back to the original representation. With a single right-hand side vector this still requires $O(M^2N)$ operations, and so is only slightly more expensive than working with the LU factorisation of $\boldsymbol{P}$. Finally, the corrections C_α are applied to the resulting solution vector using the well known Sherman–Morrison rule.[37] This last step only requires $O(MN)$ operations, and so becomes insignificant compared with the inversion of $\boldsymbol{H}_0 - \boldsymbol{E}$.

While the above discussion may seem a little complicated, the resulting algorithm is in fact quite simple. It turns out to be easy to program, and dramatically reduces both the core memory and cpu time required. However, it does exploit several unique features of the atom–surface problem, and so may not be equally applicable in a more general inelastic scattering regime. (For example, if all the orbital angular momentum quantum numbers were not zero then one would have to repeat the diagonalisation step for each unique diagonal element of l.) Precisely because of this we shall not bother to describe the algorithm in any more detail here. Instead we shall move on to discuss several numerical experiments which we have performed on the Wolken He–LiF problem, and which we feel clearly demonstrate the practical potential of the iterative approach.

3.3 Numerical Experiments

First we shall consider the effect of the above preconditioner, $\boldsymbol{P}$, on the GMRES algorithm of Saad and Schultz. For this purpose a suitable test case is provided by the incident energy, $E = 20$ meV, which was studied most extensively by Wolken.[16] Table 1 compares what we believe to be accurate diffraction probabilities for this energy with those given in Wolken's table 2. While several of his low-order diffraction spots agree very well with ours, Wolken's results become increasingly unreliable for the higher diffraction orders. We believe that this is because he was forced to use a comparatively small basis set, with only 41 diffraction channels, by the limited computational resources of his time. The present calculations, which were performed with the preconditioned version of GMRES, used the 121 diffraction channels that are generated on setting $b = 5$ in eqn (3.6).

Table 1. Comparison of diffraction probabilities for the Wolken ^{4}He–LiF problem ($E_i = 20$ meV, $\theta_i = 30°$, $\phi_i = 0°$)

	intensity	
diffraction spot	Wolken[a]	present
(0, 0)	0.025	0.025
(−1, 0)	0.013	0.011
(1, 0)	0.029	0.028
(0, ±1)	0.024	0.020
(−2, 0)	0.035	0.029
(0, ±2)	0.021	0.022
(1, ±1)	0.100	0.101
(−1, ±1)	0.085	0.077
(−2, ±1)	0.093	0.083
(−1, ±2)	0.045	0.054
(−3, 0)	0.023	0.020
(−2, ±2)	0.035	0.048
(−3, ±1)	0.029	0.029
(−4, 0)	0.001	0.002
(−3, ±2)	0.004	0.008
(−4, ±1)	0.001	0.001

[a] Ref. (16).

Fig. 2 plots the log of the error as a function of the number of GMRES iterations, with and without preconditioning, for this 20 meV test problem. Here the 'error' is defined as the normalised residual

$$R_l = \frac{\| \boldsymbol{r}_l \|}{\| \boldsymbol{r}_0 \|} \tag{3.8}$$

and the initial approximation is given in both cases by $\boldsymbol{x}_0 = \boldsymbol{0}$. It is clear from the figure that the GMRES algorithm converges much more rapidly with preconditioning than without. However, some care should be taken when interpreting this result, because the definition of R_l is itself sensitive to whether or not preconditioning is used. To eliminate this remaining doubt we examined the sum of the diffraction probabilities generated after 50 iterations of each method. (Since the log derivative Kohn principle automatically guarantees unitarity, the departure of this sum from one furnishes an internal check on the accuracy with which the linear equations have been solved.) We found that while the preconditioned results were unitary to twelve significant figures the results obtained without preconditioning were not even unitary to two. This seems to indicate quite strongly that fig. 2 does indeed provide a realistic picture of events. Throughout the remainder of our tests we shall therefore concentrate exclusively on the preconditioned version of GMRES.

The 20 meV test case considered above is not a particularly 'difficult' problem by modern standards, and could easily have been solved using any standard close-coupling technique.[12–15] We shall now move on to consider scattering at progressively higher incident energies, eventually to reach a regime ($E = 500$ meV) in which no existing close-coupling algorithm could possibly compete.

As the incident energy of the atom increases so do both the number of open diffraction channels and the z component of the incident momentum. Therefore, in order to obtain converged results, one has simultaneously to increase both N and M. In our tests we increased these two parameters at

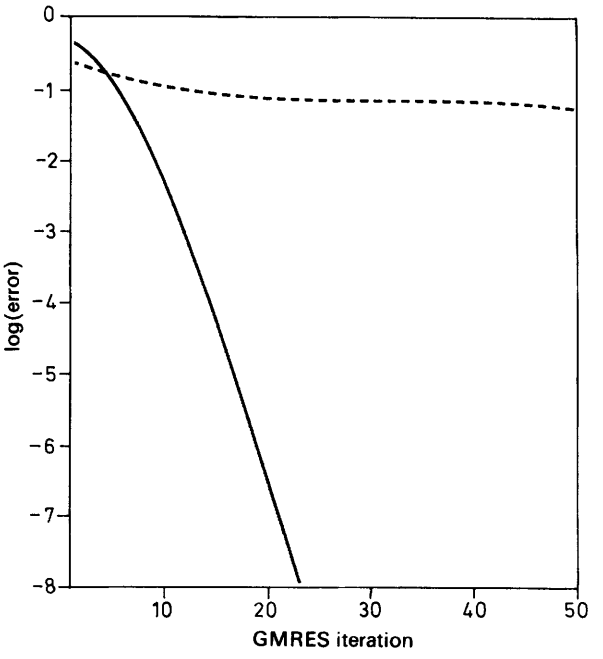

Fig. 2. The effect of preconditioning on the GMRES algorithm of Saad and Schultz. The definition of the 'error', and the specific form of the block diagonal preconditioner, are discussed in the text. Wolken ^{4}He–LiF problem, $E_i = 20$ meV, $\theta_i = 30°$, $\phi_i = 0°$. (– – – –) No preconditioner, (———) block diagonal preconditioner.

each incident energy E until the computed diffraction probabilities stopped changing in the fourth decimal place. The preconditioned GMRES algorithm was then terminated automatically at each energy using a convergence test of the form $R_l < \varepsilon$. After some trial and error we found $\varepsilon = 10^{-6}$ sufficient to give diffraction probabilities accurate to four decimal places at all the energies considered. (Since this is already consistent with the quality of our basis-set representation there seems to be little point in iterating more.) Table 2 shows how the computational effort increases with incident energy when the parameters are determined in this way.

Several interesting results are immediately apparent from this table. First, it is clear that N increases much more rapidly than M as a function of E. This is to be expected, because N is the number of basis functions in two degrees of freedom (x and y), while M is the number in only one (z). Secondly, the number of preconditioned GMRES iterations required for a given accuracy increases only very slowly with E. This is an extremely important result, and clearly demonstrates the potential of the iterative approach for high-energy scattering. Thirdly, the computer time required by the program also increases quite slowly with E. This becomes all the more exciting when one recalls that the computer time for a standard close-coupling technique scales as N^3M, and that N is itself a fairly rapid function of E.

For the sake of completeness we have listed the results of the 500 meV calculation in table 3. These results are presented as intensities scattered into various diffraction orders, where the kth diffraction order includes all diffraction channels (m, n) with $|m| + |n| = k$ (so that, for example, the second diffraction order contains the eight channels specified by (± 2, 0), (0, ± 2) and (± 1, ± 1), with all possible combinations of the $\pm$ taken as read). As discussed above, we believe that these results are accurate to all four decimal places shown. They might, therefore, be of interest to anyone who wishes to test their program in a high-energy atom–surface scattering regime.

There is yet another interesting result buried in table 2 which we have not yet had a chance to discuss. This concerns the way in which the number of GMRES iterations required for a given accuracy fluctuates as a function of E. For example, the iteration count at $E = 250$ meV is slightly larger than that at 275 meV, despite the general trend towards more iterations at higher energies. We believe that these mild fluctuations are due to the presence of bound-state (selective adsorption) resonances near certain of the energies in the list.[16,31,36] These resonances are one of the most interesting features in atom–surface scattering, so it now seems prudent to assess the performance of the iterative method in a highly resonant regime.

With this end in mind fig. 3 shows how the specular intensity varies with incident energy in the range $0 \leqslant E \leqslant 15$ meV. These calculations were performed on a very tight energy grid ($\delta E = 0.05$ meV), with 81 diffraction channels ($b = 4$) and 45 Lobatto grid points used in each run. The top panel of the figure shows the specular intensity, the centre panel the predicted zeroth-order positions of all possible bound-state resonances, and the bottom panel the number of GMRES iterations required to achieve $R_l < 10^{-6}$. The zeroth-order resonance positions are based on the three bound-state energies of ^{4}He under the influence of the laterally averaged potential $V_0(z)$. These three energies are listed by Wolken,[16]

Table 2. Computational effort as a function of the incident energy of the atom ($\theta_i = 30°$, $\phi_i = 0°$)

	GMRES[a]			
E_i/meV	N	M	L	cpu time/s
25	169	54	22	1
50	225	72	21	2
75	289	87	21	4
100	361	99	21	6
125	441	110	24	9
150	529	120	22	12
175	625	129	23	16
200	729	138	24	22
225	841	146	25	28
250	961	153	29	41
275	1089	161	26	45
300	1225	168	27	56
325	1369	174	28	68
350	1521	181	29	84
375	1681	187	29	98
400	1849	193	30	118
425	2025	199	30	136
450	2209	205	30	156
475	2401	210	31	183
500	2601	216	33	221

[a] Preconditioned GMRES algorithm with $\varepsilon = 10^{-6}$. N is the number of channels, M is the number of Lobatto grid points, and L is the number of GMRES iterations. All calculations were performed on the Univeristy of Texas Cray X-MP/24.

Table 3. Computed diffraction probabilities for the Wolken ^{4}He–LiF problem ($E_i = 500$ meV, $\theta_i = 30°$, $\phi_i = 0°$)

diffraction order	intensity
0	0.0029
1	0.0248
2	0.0348
3	0.0858
4	0.1177
5	0.1240
6	0.1600
7	0.1332
8	0.1135
9	0.0938
10	0.0610
11	0.0309
12	0.0124
13	0.0040
14	0.0010
15	0.0002
Σ	1.0000

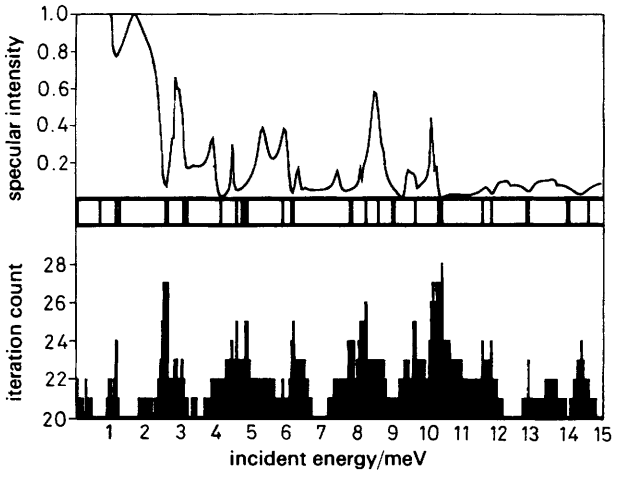

Fig. 3. The effect of bound-state (selective adsorption) resonances on the iteration count for preconditioned GMRES. The top panel shows the specular (0, 0) intensity, the centre panel the predicted zeroth order positions of all possible bound-state resonances, and the bottom panel the number of GMRES iterations required to achieve a specified accuracy. Wolken ^{4}He–LiF problem, $\theta_i = 30°$, $\phi_i = 0°$.

who also shows how the corresponding resonance positions may be obtained.

It can be seen from fig. 3 that there is indeed a significant correlation between the location of bound-state resonances and the number of iterations required by GMRES. In this regard it is important to notice, however, that in not one of the 300 separate calculations does the iteration count increase beyond 28. Since the minimum iteration count is 20 we can reasonably conclude that fluctuations in the iteration count due to resonances are unlikely to be a particularly serious drawback of the iterative approach.

4. Conclusions

The log derivative version of the Kohn variational principle has been reviewed in the context of a general inelastic molecular collision. This formulation leads, in common with several other variational methods,[1–3] to a system of linear algebraic equations which can be solved iteratively for a single initial state column of the scattering matrix, $\boldsymbol{S}$. It is therefore potentially far more efficient for certain problems than standard close-coupling techniques,[12–15] which by necessity require that one calculate transitions from all possible initial states at the same time. As a preliminary test of the iterative method we have solved the He–LiF atom–surface diffractive scattering problem described by Wolken.[16] The results of this test, which are summarised in section 3, are clearly very encouraging. However, atom–surface diffractive scattering is in many respects an ideal application for the iterative approach. We shall therefore end with two brief comments about more general scattering regimes.

First, for inelastic scattering problems, we believe that the discrete variable representation proposed by Light and coworkers is quite generally to be preferred over the more conventional variational basis approach.[17,18] In particular, the linear equations for the scattering matrix become extremely sparse when the Hamiltonian is evaluated within the DVR, and the advantage of sparsity in iterative solution is very well known. Unfortunately, however, one cannot extend this conclusion directly to any of the usual variational treatments of reactive scattering.[1–3] The reason for this is simply that these treatments all share in the adoption of Miller's 1969 formulation.[23] The exchange integrals which arise in this formulation have a much more complicated structure than the integrals for $\boldsymbol{K}$ in eqn (2.12), and while the DVR can be used to facilitate their evaluation the resulting Hamiltonian and overlap matrices are no longer so particularly sparse.[6]

Finally, our tests seem to suggest that preconditioning will quite generally be crucial to the practical success of any Krylov subspace method for solving the Kohn equations. In this regard a physically based preconditioner is clearly desirable, and fortunately such preconditioners are relatively easy to find. For an atom–diatom reaction one might, for example, include all the translational and rotational coupling in the preconditioner, leaving the vibrational and arrangement coupling to be solved by the iterative technique. In fact, Duneczky and coworkers have already used a similar scheme,[29] albeit with a rotationally inelastic reference Hamiltonian rather than an explicit preconditioner, to solve the 'L^2-AD GNVP' reactive scattering equations of Kouri and Truhlar.[2] Since the results of the present paper are so particularly encouraging we intend to pursue these ideas in more detail elsewhere.

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