IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Unitarization of complex symmetric matrices

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys. A: Math. Gen. 27 2923

(http://iopscience.iop.org/0305-4470/27/8/028)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 171.66.16.68
The article was downloaded on 01/06/2010 at 23:30

Please note that terms and conditions apply.

J. Phys. A: Math. Gen. 27 (1994) 2923–2933. Printed in the UK

Unitarization of complex symmetric matrices

G J N Brown† and D S F Crothers†‡

† Theoretical and Computational Physics Research Division, Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland, UK

‡ Institute for Theoretical Atomic and Molecular Physics, Havard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA*

Received 13 July 1993

Abstract. Given any complex symmetric non-singular $(n \times n)$ matrix **S** we show that it is always possible to find a $(2n-1) \times (2n-1)$ matrix **X** which is complex symmetric *and* unitary, and which contains **S** as its leading minor. We also prove that, of the set of all complex symmetric unitary matrices which contain **S** as their leading minor, **X** is the smallest such matrix. We apply this result to the scattering matrix of atomic collision theory to correct a loss of unitarity due to the use of a finite basis set in the solution of a collision problem.

1. Introduction: a problematic

In atomic collision theory one is often concerned with setting up a scattering matrix **S** where the element S_{ij} of **S** represents the transition probability form state i to state j. From this scattering matrix one can then extract the physical observables for the colliding system under investigation, for example, total and differential cross sections, collision strengths, resonance widths, etc. The scattering matrix ought in theory to be unitarity. This has the physical interpretation of conservation of probability, that is, the sum of the probabilities of all the various possible outcomes of the collision is one. In practice, however, this is not always the case. For any real atomic system there is an infinitely numerable number of bound states and an infinitely denumerable number of continuum states, all of which would be included in an exact calculation, and whose inclusion would lead to an exactly unitary scattering matrix. Such an infinite basis set is obviously not practical. Often, however, one can surmount this difficulty by using a variational formulation so that, even with a finite basis set, unitarity of the scattering matrix is guaranteed, though the success of the calculation is obviously still limited by the finite size of the basis set.

Recently, a new theory of electron capture by a fast, heavy, fully stripped projectile ion from a one-electron target ion, called phase-integral halfway-house variational continuum distorted wave (PIVCDW) theory, was introduced (Crothers 1987) and implemented (Brown and Crothers 1991) for the case of protons impinging on atomic hydrogen in the ground state. In this theory the scattering matrix **S** is given by

$$\mathbf{S} = \mathbf{U}^*(-\infty)\mathbf{N}^{-+}(0)\mathbf{U}^\dagger(-\infty)\,.$$

The evolution matrix $\mathbf{U}^*(-\infty)$, derived variationally, represents the motion of the heavy particles from $t = -\infty$ to $t = 0_-$. Similarly the evolution matrix $\mathbf{U}^\dagger(-\infty)$, also derived

* Permanent address.

0305-4470/94/082923+11$19.50 © 1994 IOP Publishing Ltd

variationally, represents the motion of the heavy particles from $t = 0_+$ to $t = +\infty$. The matching matrix $\mathbf{N}^{-+}(0)$ matches the two solutions at $t = 0$, so that, although at this point there is a local discontinuity of the wavefunction, the probability density is made to be continuous. The matrix $\mathbf{N}^{-+}$ (and therefore the matrix $\mathbf{S}$) is symmetric. The evolution matrices are unitary. The problem is that the matching matrix $\mathbf{N}^{-+}$ is not unitary because in a practical application of the theory we include only a finite number of bound states in our basis set. This lack of unitarity manifests itself in the total cross sections, which are generally too low due to the large amount of probability flux lost in the matching matrix. The question this paper seeks to address is, whether it is possible to correct this loss of unitarity in the scattering matrix without including more states in the basis and therefore considerably complicating and lengthening the calculation. In the next section we prove a theorem which shows this is indeed possible.

2. A theorem and its proof

Theorem. If $\mathbf{S}$ is a complex symmetric non-singular $(n \times n)$ matrix then a complex symmetric unitary $(2n-1) \times (2n-1)$ matrix $\mathbf{X}$ which contains $\mathbf{S}$ as its leading minor is given by

$$\mathbf{X} = \frac{1}{\sqrt{\lambda_n}} \begin{pmatrix} \mathbf{S} & \mathbf{A} \\ \mathbf{A}^{\mathrm{T}} & \mathbf{Z} \end{pmatrix}$$

where $\mathbf{A}$ is the $n \times (n-1)$ matrix

$$\mathbf{A} = \left(\alpha_1 \, e^{i\theta_1} \mathbf{U}^{(1)} \;\; \alpha_2 \, e^{i\theta_2} \mathbf{U}^{(2)} \ldots \;\; \alpha_{n-1} \, e^{i\theta_{n-1}} \mathbf{U}^{(n-1)}\right)$$

and $\mathbf{Z}$ is the diagonal matrix

$$\mathbf{Z} = \mathrm{diag}\left(\sqrt{\lambda_1}\, e^{i\phi_1}, \sqrt{\lambda_2}\, e^{i\phi_2}, \ldots, \sqrt{\lambda_{n-1}}\, e^{i\phi_{n-1}}\right)$$

where $\mathbf{U}^{(i)}$, $i = 1, 2, \ldots, n-1$, are the eigenvectors of the Hermitian matrix $\mathbf{S}\mathbf{S}^{\dagger}$ corresponding to the $(n-1)$ *smallest* eigenvalues λ_i, $i = 1, 2, \ldots, n-1$, and where the real constants α_i, θ_i and ϕ_i, $i = 1, 2, \ldots, n-1$, are given by

$$\alpha_i = \sqrt{\lambda_n - \lambda_i} \qquad \phi_i = \pi - \arg\left(\mathbf{U}^{(i)\dagger} \mathbf{S}\, \mathbf{U}^{(i)*}\right) - 2\theta_i$$

that is, $\mathbf{X}$ contains $n-1$ arbitrary constants.

A corollary to the theorem. Of the set of matrices that are complex, symmetric and unitary, and which contain the matrix $\mathbf{S}$ as the leading minor, the matrix $\mathbf{X}$ is the smallest such matrix (that is, the one containing the least number of elements).

Proof of theorem and corollary. Let $\mathbf{X}$ be given by

$$\mathbf{X} = \begin{pmatrix} \mathbf{S} & \mathbf{A} \\ \mathbf{A}^{\mathrm{T}} & \mathbf{Z} \end{pmatrix} \tag{1}$$

where the superscript T denotes transposition. $\mathbf{A}$ is a rectangular $(n \times r)$ matrix and $\mathbf{Z}$ a square $(r \times r)$ matrix, where r is to be determined. Assume for the moment that $\mathbf{Z}$ is not symmetric. The requirement that $\mathbf{X}$ be unitary gives four matrix equations, namely

$$\mathbf{S}\mathbf{S}^{\dagger} + \mathbf{A}\mathbf{A}^{\dagger} = \mathbf{I} \tag{2}$$

$$\mathbf{S}\mathbf{A}^{*} + \mathbf{A}\mathbf{Z}^{\dagger} = \mathbf{0} \tag{3}$$

$$\mathbf{A}^{\mathrm{T}}\mathbf{S}^{\dagger} + \mathbf{Z}\mathbf{A}^{\dagger} = \mathbf{0} \tag{4}$$

$$\mathbf{A}^{\mathrm{T}}\mathbf{A}^{*} + \mathbf{Z}\mathbf{Z}^{\dagger} = \mathbf{I} \tag{5}$$

We note that (3) and (4) are Hermitian conjugates of each other.

The crux of the problem is to find the matrices **A** and **Z** such that $\mathbf{XX}^\dagger$ is a *diagonal* matrix. It is then always possible to find another (without loss of generality) real diagonal matrix **D** such that $\mathbf{X} \to \mathbf{DX}$ and **DX** is unitary.

In order to solve the equations (2)–(5) we proceed as follows.
Pre-multiplying (2) by **A** and taking the complex conjugate of (5), we find

$$\mathbf{SS}^\dagger\mathbf{A} + \mathbf{A}(\mathbf{A}^\dagger\mathbf{A}) = \mathbf{A} \tag{6}$$

$$\mathbf{A}^\dagger\mathbf{A} + \mathbf{Z}^*\mathbf{Z}^\mathrm{T} = \mathbf{I}. \tag{7}$$

Substituting for $\mathbf{A}^\dagger\mathbf{A}$ and rearranging, one then finds

$$\mathbf{SS}^\dagger\mathbf{A} = \mathbf{AZ}^*\mathbf{Z}^\mathrm{T}. \tag{8}$$

In order to see how (3) fits in with (8) if we take the conjugate of (3) and post-multiply by **S** we find that

$$\mathbf{SS}^*\mathbf{A} + \mathbf{SA}^*\mathbf{Z}^\mathrm{T} = \mathbf{0}. \tag{9}$$

Using the fact that **S** is symmetric we can substitute for $\mathbf{SS}^*\mathbf{A}$ from (8) to get

$$(\mathbf{SA}^* + \mathbf{AZ}^*)\mathbf{Z}^\mathrm{T} = \mathbf{0}. \tag{10}$$

Finally, using (3) we have

$$\mathbf{A}^*(\mathbf{Z} - \mathbf{Z}^\mathrm{T})\mathbf{Z}^\dagger = \mathbf{0}. \tag{11}$$

Thus it is clear that if **Z** is symmetric then (3) is consistent with (2) and (5).

In order to solve (8) for **A**, let

$$\mathbf{H} = \mathbf{SS}^\dagger \tag{12}$$

$$\mathbf{h} = \mathbf{Z}^*\mathbf{Z}^\mathrm{T}. \tag{13}$$

Clearly **H** and **h** are Hermitian, therefore there exist unitary matrices **M** and **N** which diagonalize **H** and **h** respectively to **D** and **E** respectively, that is

$$\mathbf{M}^\dagger\mathbf{HM} = \mathbf{D} = \mathrm{diag}(\lambda_1, \lambda_2, \ldots, \lambda_n)$$

$$\mathbf{N}^\dagger\mathbf{hN} = \mathbf{E} = \mathrm{diag}(\mu_1, \mu_2, \ldots, \mu_r)$$

where

$$\mathbf{MM}^\dagger = \mathbf{M}^\dagger\mathbf{M} = \mathbf{I} \qquad \mathbf{NN}^\dagger = \mathbf{N}^\dagger\mathbf{N} = \mathbf{I}.$$

The matrices **M** and **N** contain the orthonormal eigenvectors of **H** and **h**, respectively, in *columns* corresponding to the respective eigenvalues placed in *ascending* order, that is, $\lambda_1 < \lambda_2 < \cdots < \lambda_n$, $\mu_1 < \mu_2 < \cdots < \mu_r$. Substituting for **H** and **h** in (8), pre-multiplying by $\mathbf{M}^\dagger$ and post-multiplying by **N**, we have

$$\mathbf{D}\hat{\mathbf{A}} = \hat{\mathbf{A}}\mathbf{E} \tag{14}$$

where

$$\mathbf{A} = \mathbf{M}\,\hat{\mathbf{A}}\,\mathbf{N}^\dagger. \tag{15}$$

Without loss of generality we may take the solution of (14) to be

$$\begin{cases} (\hat{\mathbf{A}})_{ij} = \alpha_i\, e^{i\theta_i}\delta_{ij} & i, j = 1, 2, \ldots, n \\ (\hat{\mathbf{A}})_{ij} = 0 & i, j > n \\ (\mathbf{E})_{ij} = \lambda_i\delta_{ij} & i, j = 1, 2, \ldots, n \\ (\mathbf{E})_{ij} = 0 & i, j > n \end{cases} \tag{16}$$

where $\alpha_i e^{i\theta_i}$ (α_i, θ_i real) are a set of complex constants to be determined. In other words we may choose $\mathbf{E} = \mathbf{D}$, and $\hat{\mathbf{A}}$ to be a diagonal ($n \times n$) matrix (that is, $r = n$). If we now re-write (2) and (5) in terms of $\mathbf{M}$, $\mathbf{N}$ and $\hat{\mathbf{A}}$ we find

$$\left(\mathbf{D} + \hat{\mathbf{A}}\hat{\mathbf{A}}^\dagger\right)_{ij} = 0 \qquad i \neq j$$

$$\left(\mathbf{E} + \hat{\mathbf{A}}^\dagger\hat{\mathbf{A}}\right)_{ij} = 0 \qquad i \neq j$$

as required.

In order to find the matrix $\mathbf{A}$ from (15) we try $\mathbf{N} = \mathbf{I}$ as a possible solution and take $\mathbf{Z}$ to be

$$\mathbf{Z} = \mathrm{diag}\left(\sqrt{\lambda_1}\, e^{i\phi_1}, \sqrt{\lambda_2}\, e^{i\phi_2}, \ldots, \sqrt{\lambda_n}\, e^{i\phi_n}\right) \tag{17}$$

for real ϕ_i. We note that, since the $\lambda_i \geqslant 0$, it is always possible to do this and keep the ϕ_i completely arbitrary. We now find from (15) that $\mathbf{A} = \mathbf{M}\hat{\mathbf{A}}$, that is, the matrix $\mathbf{A}$ contains the n eigenvectors of $\mathbf{H}$, each eigenvector being indeterminate with respect to a complex constant. In other words the columns of $\mathbf{A}$ are othogonal and normalized to α_i^2. The problem now contains $3n$ constants to be determined: α_i, θ_i and ϕ_i, $i = 1, 2, \ldots, n$.

We determine the *real* constants α_i in the following way. We note that (2) is independent of θ_i and gives a set of $2\,{}^nC_2$ simultaneous linear equations for the n α_i. To show that this set of equations only has rank n, i.e. a unique solution, we adopt the following notation: Let

$$\mathbf{M} = \left(\mathbf{U}^{(1)}\ \mathbf{U}^{(2)} \ldots\ \mathbf{U}^{(n)}\right)$$

$$\mathbf{A} = \left(\alpha_1 e^{i\theta_1}\mathbf{U}^{(1)}\ \alpha_2 e^{i\theta_2}\mathbf{U}^{(2)} \ldots\ \alpha_n e^{i\theta_n}\mathbf{U}^{(n)}\right)$$

where

$$\mathbf{U}^{(i)} = \begin{pmatrix} U_1^{(i)} \\ U_2^{(i)} \\ \cdot \\ \cdot \\ \cdot \\ U_n^{(i)} \end{pmatrix}$$

is the ith eigenvector of $\mathbf{H}$ corresponding the the eigenvalue λ_i. From (2) we require

$$H_{ij} + \sum_{k=1}^{n} \alpha_k^2 U_i^{(k)} U_j^{(k)*} = 0 \qquad i \neq j\,. \tag{18}$$

But

$$\mathbf{M}\,\mathbf{M}^\dagger = \mathbf{I} \qquad \Rightarrow \sum_{k=1}^{n} U_i^{(k)} U_j^{(k)*} = \delta_{ij}$$

and

$$\mathbf{M}\,\mathbf{D}\,\mathbf{M}^\dagger = \mathbf{H} \qquad \Rightarrow \sum_{k=1}^{n} \lambda_k U_i^{(k)} U_j^{(k)*} = H_{ij}\,.$$

Rearranging these last two we find

$$H_{ij} + \sum_{k=1}^{n} (\lambda_n - \lambda_k) U_i^{(k)} U_j^{(k)*} = \lambda_n \delta_{ij}\,.$$

Finally, equating coefficients with (18), we have the two important results

$$\alpha_k = \sqrt{\lambda_n - \lambda_k} k = 1, 2, \ldots, n \tag{19}$$

$$H_{ii} + \sum_{k=1}^{n} \alpha_k^2 \left| U_i^{(k)} \right|^2 = \lambda_n . \tag{20}$$

The following is now clear: the rank of the set of simultaneous equations given by (2) is n with the nth solution always being $\alpha_n = 0$. For the problem at hand this means that, without loss of generality, we may take the matrix $\mathbf{A}$ to be $n \times (n-1)$, since the last column will otherwise contain only zeros. This means that $\mathbf{Z}$ is an $(n-1) \times (n-1)$ diagonal matrix containing the $n-1$ *smallest* eigenvalues of $\mathbf{H}$. This also proves the corollary that the matrix $\mathbf{X}$ must be of order $(2n-1)$ at least.

We now determine θ_i and ϕ_i $(i = 1, 2, \ldots, n-1)$. We observe that the nature of $\mathbf{A}$ and $\mathbf{Z}$, and the fact that (3) is a homogeneous equation, allows us to write (3) in the alternative forms

$$\mathbf{S}\mathbf{U}^{(i)*} + \sqrt{\lambda_i}\mathbf{U}^{(i)} e^{2i\theta_i - i\phi_i} = \mathbf{0} \tag{21}$$

$$\mathbf{S}\hat{\mathbf{M}}^* + \hat{\mathbf{M}}\hat{\mathbf{Z}}^\dagger = \mathbf{0} \tag{22}$$

where $\hat{\mathbf{M}}$ is an $n \times n$ matrix of the eigenvectors of $\mathbf{H}$ with the ith column multiplied by $e^{i\theta_i}$, and $\hat{\mathbf{Z}}$ is the $n \times n$ matrix

$$\hat{\mathbf{Z}} = \begin{pmatrix} \mathbf{Z} & 0 \\ 0 & \sqrt{\lambda_n} e^{i\phi_n} \end{pmatrix} .$$

We note from (22) that

$$\mathbf{S} = -\hat{\mathbf{M}}\,\hat{\mathbf{Z}}\,\hat{\mathbf{M}}^{\mathrm{T}}$$

which is consistent with the fact that $\mathbf{S}$ is symmetric. In matrix terminology this means that the matrix $i\mathbf{M}$ is congruent to $\mathbf{S}$ (Gantmacher 1959). We can now see that one of the parameters θ_i, ϕ_i is arbitrary. Using (21) we can solve for the ϕ_i in terms of the θ_i. Hence

$$\phi_i = \pi - \arg\left(\mathbf{U}^{(i)\dagger}\mathbf{S}\,\mathbf{U}^{(i)*}\right) - 2\theta_i . \tag{23}$$

We have now virtually solved the problem, in that $\mathbf{X}\mathbf{X}^\dagger$ is diagonal†. It is clear from (20) and the fact that the eigenvectors are normalized to α_i^2 that $\mathbf{X}\mathbf{X}^\dagger = \lambda_n \delta_{ij}$, so that, in the notation above we let $\mathbf{X} \to \lambda_n^{-1/2}\mathbf{X}$ so that now $\mathbf{X}\mathbf{X}^\dagger = \mathbf{I}$. This proves the theorem.

3. A numerical example

Let $\mathbf{S}$ be

$$\mathbf{S} = \begin{pmatrix} \frac{\sqrt{3}}{2} e^{i\pi/4} & 0 & 1 \\ 0 & i & \frac{1}{2} e^{i\pi/24} \\ 1 & \frac{1}{2} e^{i\pi/24} & i e^{i\pi/12} \end{pmatrix}$$

† The constants α_i ensure (2) holds and the phases θ_i that (3) holds. The othogonality of the eigenvectors and the fact that $\mathbf{Z}$ is diagonal means that the equality of (5) is also assured.

so that

$$\mathbf{H} = \mathbf{S}\mathbf{S}^{\dagger} = \begin{pmatrix} \frac{7}{4} & \frac{1}{2}\,e^{-i\pi/24} & \frac{1}{2}\,e^{-i\pi/4} \\ \frac{1}{2}\,e^{i\pi/24} & \frac{5}{4} & 0 \\ \frac{1}{2}\,e^{i\pi/4} & 0 & \frac{9}{4} \end{pmatrix}.$$

The diagonalizing matrix $\mathbf{M}$ turns out to be

$$\mathbf{M} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ -\frac{\sqrt{3}+1}{2}\,e^{i\pi/24} & e^{i\pi/24} & \frac{\sqrt{3}-1}{2}\,e^{i\pi/24} \\ -\frac{\sqrt{3}-1}{2}\,e^{i\pi/4} & -e^{i\pi/4} & \frac{\sqrt{3}+1}{2}\,e^{i\pi/4} \end{pmatrix}$$

with the diagonal matrix $\mathbf{D}$ given by

$$\mathbf{D} = \begin{pmatrix} \frac{7}{4} - \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & \frac{7}{4} & 0 \\ 0 & 0 & \frac{7}{4} + \frac{\sqrt{3}}{2} \end{pmatrix}.$$

Hence one finds that

$$\alpha_1^2 = \sqrt{3} \qquad \alpha_2^2 = \frac{\sqrt{3}}{2}$$

$$\phi_1 = 2\theta_1 + \tan^{-1}\left(\frac{3+\sqrt{3}}{2}\right) - \frac{3}{4}\pi \qquad \phi_2 = 2\theta_2 + \tan^{-1}\left(\frac{\sqrt{3}}{2}\right) - \frac{3}{4}\pi$$

so that the result is

$$\mathbf{X} = \frac{2}{\sqrt{7+2\sqrt{3}}} \times \begin{pmatrix} \frac{\sqrt{3}}{2}\,e^{i\pi/4} & 0 & 1 & \frac{\alpha_1}{\sqrt{3}} & \frac{\alpha_2}{\sqrt{3}} \\ 0 & i & \frac{1}{2}\,e^{i\pi/24} & -\frac{\alpha_1(\sqrt{3}+1)}{2\sqrt{3}}\,e^{i\pi/24} & \frac{\alpha_2}{\sqrt{3}}\,e^{i\pi/24} \\ 1 & \frac{1}{2}\,e^{i\pi/24} & i\,e^{i\pi/12} & -\frac{\alpha_1(\sqrt{3}-1)}{2\sqrt{2}}\,e^{i\pi/4} & -\frac{\alpha_2}{\sqrt{3}}\,e^{i\pi/4} \\ \frac{\alpha_1}{\sqrt{3}} & -\frac{\alpha_1(\sqrt{3}+1)}{2\sqrt{3}}\,e^{i\pi/24} & -\frac{\alpha_1(\sqrt{3}-1)}{2\sqrt{3}}\,e^{i\pi/4} & \sqrt{\frac{7}{4} - \frac{\sqrt{3}}{2}}\,e^{i\phi_1} & 0 \\ \frac{\alpha_2}{\sqrt{3}} & \frac{\alpha_2}{\sqrt{3}}\,e^{i\pi/24} & -\frac{\alpha_2}{\sqrt{3}}\,e^{i\pi/4} & 0 & \sqrt{\frac{7}{4}}\,e^{i\phi_2} \end{pmatrix}$$

where we have chosen $\theta_1 = \theta_2 = 0$. One now easily finds that $\mathbf{X}\mathbf{X}^{\dagger} = \mathbf{I}$.

4. An application

As described in the introduction, the scattering matrix $\mathbf{S}$ of PIVCDW is given by

$$\mathbf{S} = \mathbf{U}^{*}(-\infty)\mathbf{N}^{-+}(0)\mathbf{U}^{\dagger}(-\infty)$$

where, due to the inclusion of only a finite basis set, the matrix $\mathbf{N}^{-+}$ (and therefore $\mathbf{S}$) is no longer unitary. We now show how to correct this lack of unitarity using the theroem proven above. We shall concentrate on the simplest case, that is, a two-state basis set for which much of the unitarization procedure is analytic. We have also, however, investigated the convergence of the cross sections by performing a four-state calculation.

We take for our example an undistorted travelling atomic orbital (UTAO) model of charge transfer between protons and atomic hydrogen (McCarroll 1961), in which we deliberately break the symmetry of the basis set at $t = 0$. This will allow us to concentrate on the essential features of the unitarization procedure without unduly complicating the mathematics. Although a simplification of the more refined PIVCDW approach, this approach mimics well the PIVCDW result. In what follows, the quantities v and b are measures of the impact velocity and the impact parameter, respectively, of the collision.

In the two-state model for the total wavefunction we take

$$\Psi^{\pm} = c_0^{\mp}(t)\psi_i^{\pm}(r,t) + c_1^{\mp}(t)\psi_f^{\pm}(r,t)$$

where the $+(-)$ indicates a out-going (in-coming) wavefunction, and

$$\psi_i^{\pm}(r,t) = \Phi_i(r,t)\mathrm{D}_{-v}^{\pm}(r_p)$$
$$\psi_f^{\pm}(r,t) = \Phi_f(r,t)\mathrm{D}_{v}^{\pm}(r_T)$$

with

$$\mathrm{D}_v^{\pm}(r) = \mathrm{e}^{\pm \mathrm{i}\delta(vr - v\cdot r)}.$$

Here the Φ's are the travelling atomic orbitals and δ is a time-independent function of v and b chosen in such a way as to mimic PIVCDW. The detailed form of δ is not important, but physically it should 'switch off' for large v and b. We chose

$$\delta = \frac{1 - (1 + q + \frac{1}{2}q^2)\mathrm{e}^{-q}}{v^2 q^2} \qquad q = vb.$$

We now find that the elements of the matrix $\mathbf{U}$ are given by

$$U_{11} = U_{22} = \cos(Q) \qquad U_{12} = U_{21} = -\mathrm{i}\sin(Q)$$

where

$$Q = \int_{-\infty}^{0} \left(\frac{k - sh}{1 - s^2}\right) \mathrm{d}t$$

where s, k and h are, respectively, the usual overlap, transition and polarization matrix elements (McCarroll 1961). The matrix elements of $\mathbf{N}^{-+}$, i.e. $N_{11}^{-+} = N_{22}^{-+} = \alpha$ and $N_{12}^{-+} = N_{21}^{-+} = \beta$, are easily calculated by standard methods. A measure of the total cross section (in arbitrary units) for the inelastic process is given by

$$\sigma = 2\int_0^{\infty} \mathrm{d}b\, b\, |S_{12}(b)|^2 \tag{24}$$

with

$$|S_{12}(b)|^2 = \alpha^2 \sin^2(2Q) + \beta^2 \cos^2(2Q). \tag{25}$$

In order to correct the unitarity of the scattering matrix we correct the unitarity of the matching matrix $\mathbf{N}^{-+}$ in the manner described above. This means of course augmenting the evolution matrix by adding extra rows and columns in such a way as to leave its unitarity unaltered. Thus for the two-state model we have

$$\mathbf{U}_{\mathrm{aug}} = \begin{pmatrix} \mathbf{U} & \mathbf{0} \\ \mathbf{0} & 1 \end{pmatrix}$$

$$\mathbf{N}^{-+}_{\text{aug}} = \begin{pmatrix} \mathbf{N}^{-+} & \mathbf{A} \\ \mathbf{A}^{\mathrm{T}} & \mathbf{Z} \end{pmatrix}$$

and

$$\mathbf{S}_{\text{aug}} = \begin{pmatrix} \mathbf{U}^{*}\mathbf{N}^{-+}\mathbf{U}^{\dagger} & \mathbf{U}^{*}\mathbf{A} \\ \mathbf{A}^{\mathrm{T}}\mathbf{U}^{\dagger} & \mathbf{Z} \end{pmatrix}. \tag{26}$$

Using the theorem above we find that

$$\mathbf{A} = \begin{pmatrix} \sqrt{2\alpha\beta} \\ -\sqrt{2\alpha\beta} \end{pmatrix}$$

and

$$Z = \beta - \alpha$$

that is,

$$\mathbf{N}^{-+}_{\text{aug}} = \frac{1}{\alpha+\beta} \begin{pmatrix} \alpha & \beta & \sqrt{2\alpha\beta} \\ \beta & \alpha & -\sqrt{2\alpha\beta} \\ \sqrt{2\alpha\beta} & -\sqrt{2\alpha\beta} & \beta-\alpha \end{pmatrix} \tag{27}$$

where once again without loss of generality we have taken $\theta_1 = 0$ since its value does not alter the total cross section, which in view of (26) and (27) is now given by

$$\sigma_{\text{aug}} = 2\int_0^{\infty} \mathrm{d}b\, b \left| \frac{S_{12}(b)}{\alpha+\beta} \right|^2 \tag{28}$$

where $S_{12}(b)$ is still given by (25). Figures 1 and 2 show the quantities H_{11} and H_{12} as a function of b for several different v values, where $\mathbf{H} = \mathbf{N}^{-+}\mathbf{N}^{-+\dagger}$. Thus these figures show the lack of unitarity of the matching matrix $\mathbf{N}^{-+}$. Clearly $\mathbf{N}^{-+}$ is less unitary for small v but much closer to unitarity at larger v. The broken lines on the figures are the asymptotic values of H_{11} and H_{12}, i.e. their values in the limit $v \to \infty$. This behaviour of H_{11} and H_{12} is explained by the fact that the excited levels of the target play a more important role at lower energies, therefore their exclusion causes a relatively greater error at these energies than at higher energies.

Figure 3 shows the quantity $(\alpha+\beta)^{-2}$ as a function of b for the same values of v as figures 1 and 2. As can be seen from (28) it is this quantity which, if it is bigger than one, raises the cross section. As the loss of unitarity is greatest for small values of v, as might be expected $(\alpha+\beta)^{-2}$ is also greatest for these values. The broken line once again represents the asymptote $v \to \infty$.

Finally table 1 shows the values of σ and σ_{aug} calculated from (24) and (28), respectively. As expected, the cross section is raised for small values of v but virtually unaltered for larger values of v.

In order to investigate the convergence of the cross sections we have performed a four-state calculation, that is, we are now including the first excited state of each ion. The values of the four-state cross sections and the augmented cross sections are also shown in table 1. For the unitarization procedure to make sense, we require that, as the basis set becomes more complete, the scattering matrix becomes more unitary and $\sigma \to \sigma_{\text{aug}}$. We can show formally that this is indeed the case by the following argument. If the basis set is complete

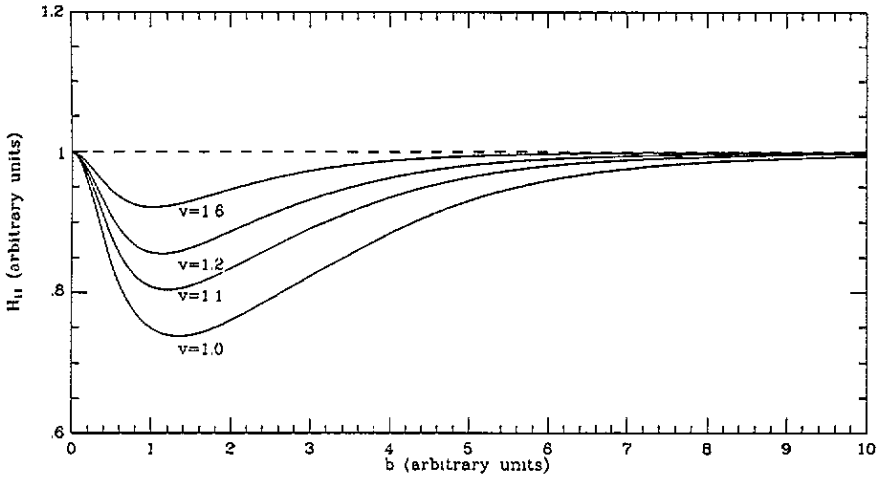

Figure 1. The diagonal matrix element H_{11} (see text) shown as a function of 'impact parameter', b, for a range of 'impact velocities', v. The deviation of H_{11} from 1 represents a loss of unitarity of the scattering matrix. The broken line represents the asymptote $v \to \infty$.

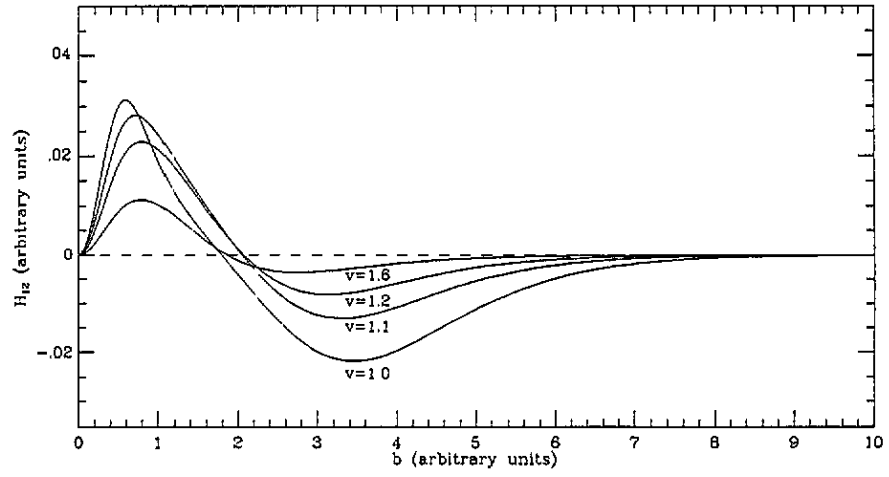

Figure 2. The off-diagonal matrix element H_{12} (see text) shown as a function of 'impact parameter', b, for a range of 'impact velocities', v. The deviation of H_{12} from 0 represents a loss of unitarity of the scattering matrix. The broken line represents the asymptote $v \to \infty$.

then

$$\begin{aligned}
\mathbf{H} &= \mathbf{N}^{-+}\mathbf{N}^{-+\dagger} \\
&= \mathbf{N}^{-+}\mathbf{N}^{+-} \\
&= \langle \psi^- \mid \psi^+ \rangle \langle \psi^+ \mid \psi^- \rangle \\
&= \langle \psi^- \mid \psi^- \rangle \qquad \text{(closure)} \\
&= \mathbf{I} \qquad \text{(orthonormality)}
\end{aligned}$$

where the ψ's represent the (orthonormalized) basis set (Crothers 1987). All the eigenvalues of $\mathbf{H}$ are 1 and therefore $\sigma = \sigma_{\text{aug}}$. Clearly it is the property of closure that is affected by the

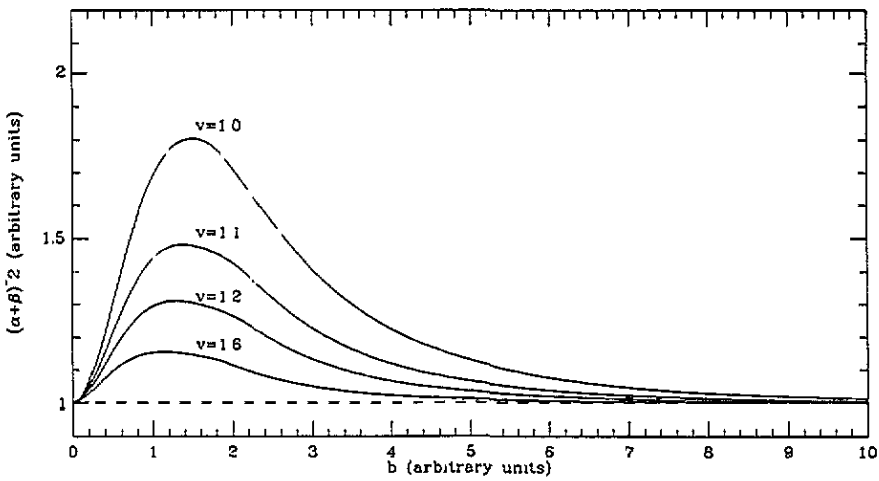

Figure 3. The quantity $(\alpha + \beta)^{-2}$ (see text) shown as a function of 'impact parameter', b, for a range of 'impact velocities', v. The broken line represents the asymptote $v \to \infty$.

Table 1. Cross sections σ and augmented cross sections σ_{aug} (arbitrary units) for a two-state (columns 2–4) and a four-state (columns 5–7) calculation by 'impact velocity' v (arbitrary units). Columns 4 and 7 represent the factor by which the unitarization technique raises the cross sections in the two-state and four-state cases, respectively. The numbers in parentheses are exponents.

	2-state			4-state		
v	σ	σ_{aug}	σ_{aug}/σ	σ	σ_{aug}	σ_{aug}/σ
1.0	0.992(+0)	0.156(+1)	1.568	0.119(+1)	0.144(+1)	1.213
1.1	0.824(+0)	0.111(+1)	1.346	0.957(+0)	0.110(+1)	1.154
1.2	0.670(+0)	0.819(+0)	1.223	0.775(+0)	0.960(+0)	1.109
1.3	0.534(+0)	0.615(+0)	1.152	0.617(+0)	0.665(+0)	1.078
1.4	0.418(+0)	0.463(+0)	1.109	0.480(+0)	0.508(+0)	1.057
1.5	0.323(+0)	0.349(+0)	1.080	0.369(+0)	0.384(+0)	1.042
1.6	0.248(+0)	0.263(+0)	1.061	0.281(+0)	0.290(+0)	1.032
1.7	0.189(+0)	0.198(+0)	1.048	0.213(+0)	0.218(+0)	1.024
1.8	0.144(+0)	0.149(+0)	1.037	0.161(+0)	0.164(+0)	1.019
1.9	0.109(+0)	0.113(+0)	1.029	0.122(+0)	0.124(+0)	1.014
2.0	0.831(−1)	0.851(−1)	1.023	0.925(−1)	0.936(−1)	1.011
2.5	0.198(−1)	0.199(−1)	1.009	0.219(−1)	0.220(−1)	1.004
3.0	0.538(−2)	0.540(−2)	1.004	0.593(−2)	0.594(−2)	1.002
3.5	0.158(−2)	0.159(−2)	1.002	0.175(−2)	0.175(−2)	1.000
4.0	0.504(−3)	0.504(−3)	1.001	0.556(−3)	0.556(−3)	1.000

number of basis states, so that the more complete the basis set the better the approximation of $|\psi^+\rangle\langle\psi^+|$ by $\mathbf{I}$. Our four-state results bear this out, in that the unitarization procedure makes a relatively smaller correction in this case than in the four-state case.

It is also clear that, except at the lowest recorded velocities ($v \leqslant 1.2$), the two-state augmented cross sections are a better approximation to the four-state results. This shows that the method is of use in correcting cross sections for a loss of unitarity in the scattering matrix. Indeed our unitarization procedure is analogous in this heavy-particle scattering

example to the so-called 'Buttle correction' (Buttle 1967) of R-matrix theory for light-particle scattering (Burke and Robb 1975), which corrects for a loss of unitarity due to a matching procedure at the R-matrix boundary. For the lowest velocities we find that the augmented two-state result tends to over-estimate either of the four-state results. The reason for this is that scattering matrix at these velocities if far from unitarity (see figures 1 and 2) so that our approximation of the scattering matrix is likely to be less accurate. However, observation of the ratio of σ_{aug} to σ at these velocities would lead us to conclude that the cross section had not converged and a new calculation was necessary. In this way the unitarization procedure may act as a diagnostic for convergence by indicating whether or not it is necessary to include more states in the calculation.

5. Conclusions

We have proved a theorem and corollary which show how to unitarize a complex symmetric matrix. We have illustrated this by giving a simple numerical example. As an application we have shown that the technique may be used in a straightforward and simple manner to correct for a loss of unitarity in the scattering matrix of a heavy-particle rearrangement collision. We have illustrated this in an example where the basis set contains two states. We have also shown by performing a four-state calculation, that the unitarization procedure gives consistent results and has the ability to indicate whether or not the cross sections have converged. The method is obviously generalizable to any size of basis set. All one actually has to do in practise is to find the largest eigenvalue of the matrix $\mathbf{H}$ of (12) and divide the probability amplitudes by this number. Subroutines which find the eigenvalues of Hermitian matrices are readily available and very fast on modern computers.

Acknowledgement

One of us (DSFC) acknowledges partial support by the National Science Foundation through a grant for a short-term visiting-scientist fellowship at the Institute for Atomic and Molecular Physics at Harvard University and Smithsonian Astrophysical Observatory. This research was performed under the auspices of the UK-SERC, under grant GR/H 59862.

References

Brown G J N and Crothers D S F 1991 *J. Phys. B: At. Mol. Phys.* **24** 195
Burke P G and Robb W D 1975 *Advances in Atomic and Molecular Physics* vol II (New York: Academic) pp 143
Buttle J P A 1967 *Phys. Rev.* **160** 719
Crothers D S F 1987 *Nucl. Inst. Meth.* B **27** 555
Gantmacher F R 1959 *Matrix Theory* vol I and II (New York: Chelsea)
McCarroll R 1961 *Proc. R. Soc.* A **264** 547