

Use of approximate scattering theories as interpolation guides

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Use of approximate scattering theories as interpolation guides

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A simple method is given for using a fast but not necessarily accurate scattering approximation to interpolate the results of an exact calculation. The goal is to minimize the number of points where the expensive, exact calculation must be done. The approximate theory is used to remove the rapidly varying parts of the exact S -matrix to obtain a slowly varying correction matrix which can then be interpolated over a large interval in energy or angular momentum. After the interpolation, the rapidly varying approximate parts are put back in to give an accurate S -matrix. The method preserves the phase of the S -matrix. It is demonstrated for the cases of symmetric molecular charge exchange and for rotationally inelastic scattering.

I. INTRODUCTION

The accurate numerical solution of the Schrödinger equation for inelastic and reactive scattering is notoriously difficult.^{1,2} It involves the solution of a large number of coupled differential equations, one for each quantum state included in the calculation. Because most scattering calculations fall near the classical limit, the wave functions oscillate rapidly as functions of R , and the usual numerical methods require very small step sizes, and this makes them too slow to be practical. Furthermore, the calculation is usually repeated at many values of the orbital or total angular momentum and/or the energy. The computer time generally scales as N^3 for N states; a modest increase in the energy or in the complexity of the problem then requires an enormous increase in computer time. It is no surprise that the literature abounds with a variety of approximate solutions which give results in much less time than the exact calculations.³⁻⁹ In many cases, however, these are either not accurate enough or not reliable enough to do the job. Being greedy, we would like a method which has the speed of the approximate method but has the accuracy of the exact calculation.

We describe here a method of combining the two. An approximate method is used as an interpolation guide for the exact result so that we can achieve high accuracy while doing the exact calculation at only a few selected points. The output of both theories is the scattering or S -matrix which relates the wave function after the collision to the wave function before the collision. The S -matrix is unitary so that flux is conserved, and it is symmetric so that microscopic reversibility is observed. Unfortunately, it is usually a rapidly varying function of the energy and the various quantum numbers. Some experiments, such as the differential cross section, depend on the phase of the S -matrix, while others such as the integral cross section depend only on its magnitude. We would like a method which preserves the phase so that we can use it more generally. Since the phase is the part that generally varies the most as energy and angular momentum is changed, the method may be more useful here.

The interpolation procedure begins by using the ap-

proximate theory to remove the rapidly varying parts of the S -matrix, resulting in a more slowly varying correction matrix. The simplest approximation is that of elastic scattering from some spherically averaged potential. Here,

$$S = \exp[2i\eta^{(0)}], \quad (1)$$

where $\eta^{(0)}$ is the diagonal matrix of phase shifts. These can be rapidly calculated by using the Wentzel-Kramers-Brillouin (WKB) approximation.³ We can remove the elastic scattering by using

$$S^{(1)} = \exp[-i\eta^{(0)}] S \exp[-i\eta^{(0)}]. \quad (2)$$

Indeed, for many problems $\eta^{(0)}$ can range from a few radians to tens or hundred of radians and can vary rapidly as a function of energy and angular momentum. $S^{(1)}$ is therefore a more slowly varying quantity than S .

Many approximate theories can be cast in the form⁶⁻⁹

$$S = \exp[i\eta^{(0)}] \exp[2i\Delta\eta^{(1)}] \exp[i\eta^{(0)}], \quad (3)$$

where $\Delta\eta^{(1)}$ is some sort of correction matrix which includes some or all of the inelastic scattering. We can then remove this piece as well,

$$S^{(2)} = \exp[-i\Delta\eta^{(1)}] \exp[-i\eta^{(0)}] S \exp[-i\eta^{(0)}] \\ \times \exp[-i\Delta\eta^{(1)}]. \quad (4)$$

If Eq. (3) is accurate, then $S^{(2)}$ will be slowly varying. If Eq. (3) is exact, then $S^{(2)}$ is the unit matrix.

The method is demonstrated in two systems. The first is an adiabatic, exponential perturbation theory for the symmetric charge exchange in O_2 .⁷ The second is a modified infinite-order sudden (IOS) treatment of the rotationally inelastic scattering in $Ar+N_2$.^{8,9} The next sections describe these two cases. The discussion section mentions other possible ways to apply the method.

II. ADIABATIC TREATMENT OF MOLECULAR CHARGE EXCHANGE

The basic theory of symmetric, molecular charge transfer has been given previously and will only be sketched here.^{7,10} The first accurate numerical calculations

were done by Becker¹⁰ for the system $O_2^+ + O_2$. The exact results used here were done using the program MOLSCAT, kindly provided by Dr. Sheldon Green. The calculations include two degenerate electronic states, D corresponding to the arrangement $O_2^+ + O_2$ and X corresponding to $O_2 + O_2^+$. Each electronic state has several vibrational levels. To make the exact calculation tractable, the potential was assumed to be spherically symmetric so that changes in rotational and orbital angular momentum are zero. Rotation is therefore ignored. Because of the symmetry, we can transform to a symmetric and an antisymmetric basis set,

$$|\pm mn\rangle = 2^{-1/2} [|Dmn\rangle \pm |Xmn\rangle], \quad (5)$$

where n is the vibrational quantum number of the neutral and m the vibrational quantum number of the ion. The coupled differential equations are given by,^{7,10}

$$\left[\frac{d^2}{dR^2} + k_{m'n'}^2 - \frac{l(l+1)}{R^2} - \frac{2\mu}{\hbar^2} V_0(R) \right] u_{\pm m'n'}(R) \mp \frac{2\mu}{\hbar^2} \sum_{mn} \Delta V(R) \langle m'n' | nm \rangle u_{\pm mn}(R) = 0. \quad (6)$$

Here, μ is the reduced mass, l is the orbital angular momentum quantum number, $u(R)$ is the radial wave function, and

$$k_{mn}^2 = (2\mu/\hbar^2)(E_{\text{tot}} - E_m - E_n). \quad (7)$$

There is then no coupling between the $+$ and the $-$ functions, and the calculation breaks up into two independent parts. This feature results in a savings in computer time of approximately a factor of 4 since each block requires roughly an eighth the amount of computer time. It also serves as an interesting test case for the interpolation theory, since the final scattering probabilities (in the D and X representations) require the correct phases of the S -matrices for the symmetric and antisymmetric halves of the problem. The two parts of the potential are independent of the vibrational coordinate, but the coupling term ΔV is multiplied by the vibrational overlap between the neutral and ionic vibrational functions.

The approximate treatment⁷ uses an adiabatic vibrational basis, obtained by diagonalizing the potential at each R . Since the transformation is R -dependent, the kinetic energy term in the Hamiltonian now contains off-diagonal elements. If these are neglected, we obtain the elastic phase shift used in Eq. (2). These can be as high as hundreds of radians, and the differences between the elastic phase shifts for the symmetric and antisymmetric combinations can be a few radians. The theory then removes the elastic scattering and treats the remaining part of the problem using a first-order perturbation theory. The result of the perturbation is the matrix $\Delta\eta^{(1)}$ used in Eq. (4). $\Delta\eta^{(1)}$ is calculated by integrating the perturbation over the classical trajectory given by $V_0(R)$. Figures 1 and 2 show the probabilities ($|S|^2$) for the direct scattering and for the charge exchange. The perturbation theory is good, but the deviations from the exact result are obvious. Using Eq. (4) at selected values of l , we obtain the exact $S^{(2)}$. $S^{(2)}$ is then interpolated and the approximate $\Delta\eta^{(1)}$ and $\eta^{(0)}$ are put back in

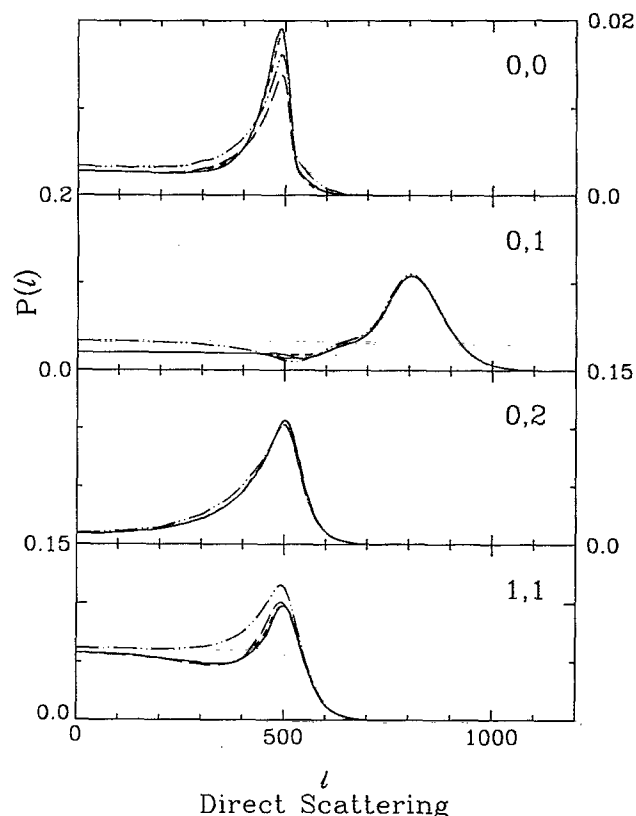


FIG. 1. The curves show the probabilities, $P = |S^2|$ vs the orbital angular momentum quantum number l for the direct scattering for $O_2^+(v=1) + O_2(v=0) \rightarrow O_2^+(v=m) + O_2(v=n)$ for several combinations (m,n) . The kinetic energy is 8.0 eV. The curves are —, exact result; ---, approximate result; ···, interpolation for $\Delta l=100$; ····, interpolation for $\Delta l=200$.

to generate the full S -matrix. The results of the interpolated calculation are shown in Figs. 1 and 2. The points for the exact and approximate curves are calculated for $\Delta l=20$. In one calculation the interpolation used points spaced at $\Delta l=100$. The resulting curves are virtually indistinguishable from the exact curve except for a small region around $l=500$. The largest deviation in any curve is $<7\%$ of the maximum in the curve. Since some of the features have a width of ~ 100 , it is obvious that this interpolation is very considerably more accurate than simply interpolating the final probabilities. A second calculation was done using an interpolation interval of $\Delta l=200$. The agreement is poorer but still very much better than the adiabatic results. The biggest deviation is in the $(0,0)$ curve for the direct process. The interpolation seriously underestimates the intensity of the peak. The interpolation uses the points at $l=400$ and 600 , both of which are outside the peak. A straight interpolation of the probabilities would completely miss the peak.

In practice, we can do the calculation in stages. We would first do the approximate calculations, and then we might decide to do the exact calculations at $l=0, 200, 400, 600$, and 800 . Since the approximation is a perturbation theory, we would hope that it is very accurate at large l . A plot of the interpolated and approximate results would

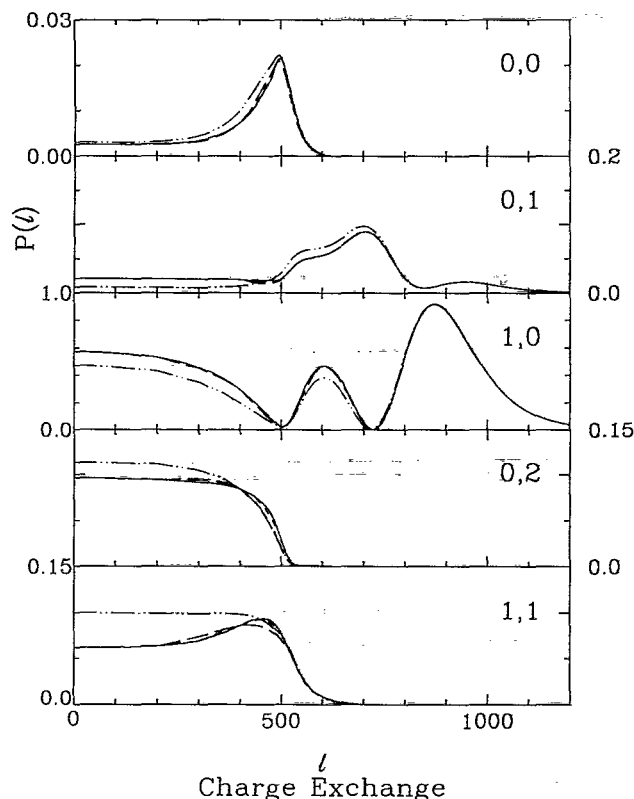


FIG. 2. The probabilities for charge exchange, $O_2^+(v=1)+O_2(v=0) \rightarrow O_2(v=n)+O_2^+(v=m)$. See the caption of Fig. 1 for details.

show that this is indeed the case. We would also note a large deviation between the two at $l=500$. The accuracy of an interpolation depends largely on the derivatives of the function being interpolated and not on its value, and the derivatives are clearly large near $l=500$. We would then do an exact calculation at $l=500$ and perhaps at $l=300$. The result would be very good agreement with the exact curve using only seven points!

A second interpolation method was also tried. Using the matrix $S^{(2)}$ we can define a corresponding phase shift matrix,

$$S^{(2)} = \exp[2i\Delta\eta^{(2)}], \quad (8)$$

where $\Delta\eta^{(2)}$ is calculated by diagonalizing $S^{(2)}$, obtaining the eigenvalues of $\Delta\eta^{(2)}$, and then transforming $\Delta\eta^{(2)}$ back to the original representation. The idea was that $\Delta\eta^{(2)}$ might be more slowly varying than $S^{(2)}$ and therefore the interpolation would be more accurate. The two methods gave almost identical results so that the extra work in calculating $\Delta\eta^{(2)}$ is clearly not worth it.

III. ROTATIONALLY INELASTIC SCATTERING

Ever since its inception in 1970 the IOS approximation⁶ has enjoyed a love-hate relationship with dynamacists. To its detractors the basic assumptions are at best numerically inaccurate and at worst physically unrealistic. Yet its basic simplicity allows it to be used where no other

theory works and makes it useful for a qualitative understanding of diverse scattering phenomena. It is fitting therefore that we use it as our second example of the interpolation technique. We consider the rotationally inelastic scattering of $Ar+N_2$ at an energy of 0.0103 eV (300 K). Because N_2 is homonuclear, the potential couples only even or only odd rotational levels. We consider only the even states. At this energy the states $j=0, 2, 4, 6$, and 8 are open. The coupled differential equations are,¹

$$\left[\frac{d^2}{dR^2} + k_j^2 - \frac{l'(l'+1)}{R^2} - \frac{2\mu}{\hbar^2} V_0(R) \right] u_{Jj'l'}(R) - \sum_{j'l'} \frac{2\mu}{\hbar^2} \langle Jj'l' | \Delta V(R) | Jjl \rangle u_{Jjl}(R). \quad (9)$$

In the space-fixed (SF) coordinate system the four quantum numbers are J, j, l , and M , where j and l give the rotational angular momentum and the orbital angular momentum, respectively. J and M are the magnitude and projection quantum numbers for the total angular momentum. The coupling matrix is diagonal in J and M and is independent of M . We can further decouple the equations into a block of even parity and a block of odd parity which are uncoupled to each other.¹ The potential has been arbitrarily divided into a spherically symmetric part $V_0(R)$ and the remainder which contains the inelastic coupling terms. We use the Patingill potential¹¹ for the system. $V_0(R)$ is a spherically symmetric Lennard-Jones (6-12) potential; $\Delta V(R, \gamma)$ is a modified Lennard-Jones potential multiplied by $P_2(\cos \gamma)$, where γ is the angle between R and the internuclear axis of N_2 . The "exact" calculations were done with Molscat.

The IOS uses the sudden approximation on both the orbital angular momentum and on the rotational energies. First, we transform Eq. (9) to the body-fixed (BF) coordinate system, a rotating coordinate system whose z -axis lies along R . The transformation is given by,¹²

$$|Jj\nu\rangle = \sum_l \{ [l]/[J] \}^{1/2} C(ljJ; 0\nu\nu) (-1)^l - j |Jjl\rangle, \quad (10)$$

where $[l] = (2l+1)$, and C is a Clebsch-Gordan coefficient. The quantum number ν is the projection of j along the z -axis (R). The corresponding projection quantum number for l is, of course, 0. If we use the parity symmetry, we break this into two parts by taking the sums and differences of the positive and negative ν 's. We then multiply Eq. (10) by $2^{-1/2}$ for all nonzero ν . The transformation greatly simplifies the matrix element for $\Delta V(R)$, but it introduces off-diagonal terms in the orbital angular momentum term in the kinetic energy. In the orbital sudden approximation these are neglected. The effect is to replace $l(l+1)$ in Eq. (9) by $l_{\text{eff}}(l_{\text{eff}}+1)$, where l_{eff} is some constant, effective l . There has been much discussion over the proper choice of l_{eff} ,⁵ but, as we shall see below, in our modified IOS approximation, this makes little difference.

Next, we transform the coupled equations to a position representation. There are several ways to do this, but the simplest and most elegant is the discrete-variable representation (DVR) of Light and co-workers.¹³ The rotational

wave functions (spherical harmonics) can be written in terms of a set of orthogonal polynomials (related to the associated Legendre functions). Each matrix element of the potential is then expressed as a Gaussian quadrature. With a small amount of rearrangement, the quadrature becomes a unitary transformation from the BF basis set $|Jjv\rangle$ to the DVR basis set $|Jiv\rangle$, where i labels a fixed orientation of the molecule. If we have N j 's, we get N i 's which are the N positions for an N -point Gaussian quadrature. In the DVR the potential matrix is diagonal. Because k^2 depends on j , the kinetic energy is not diagonal. The energy sudden approximation consists in replacing k_j^2 with some averaged k_{eff}^2 . With these approximations the entire problem is diagonal and can be solved trivially by using the WKB approximation.

Because we are using a coordinate system which rotates with \mathbf{R} , the IOS assumes that the angle γ remains fixed during the collision. Except for the case of the head-on collision of a light atom with a heavy diatom, this is simply not true. Quantum mechanically, one might expect to be able to transform the true S -matrix into the DVR and find it to be nearly diagonal. It is not even close.¹⁴ The reasons for this are obvious. The phase shifts $\eta^{(0)}$ corresponding to the spherically average potential are large and depend strongly on both l and k . Since $\eta^{(0)}$ is diagonal in the SF representation, it is strongly nondiagonal in the DVR.

We can easily fix this problem. First, we remove the elastic scattering as shown in Eq. (2) using for $\eta^{(0)}$ the elastic phase shift at the correct k and l for each state in the SF representation. We then transform $S^{(1)}$ to the DVR. It turns out that $S^{(1)}$ is nearly diagonal in the DVR. We can now calculate $\Delta\eta^{(1)}$ using the IOS,

$$\langle Jiv | \Delta\eta^{(1)} | Jiv \rangle = \eta^{(s)}(\gamma_{im}, k_{\text{eff}}, l_{\text{eff}}) - \eta^{(0)}(k_{\text{eff}}, l_{\text{eff}}), \quad (11)$$

where $\eta^{(s)}$ is calculated using the full potential (including ΔV) at the γ appropriate to the particular DVR point and using the averaged, effective k and l . We then subtract off the elastic phase shift using the same effective k and l . The resulting $S^{(2)}$ is now roughly equal to the unit matrix. We can then interpolate $S^{(2)}$ and put back in $\Delta\eta^{(1)}$ and $\eta^{(0)}$ to generate the full S -matrix.

The scattering probabilities are shown in Fig. 3. The modified IOS results are in fair agreement with the exact results except for the transition $0 \rightarrow 8$ where they are off by a factor of 3. This is not surprising since $k_0/k_8 = 1.8$. The exact and approximate curves were calculated at intervals of $\Delta J = 1$. The interpolated curves correspond to $\Delta J = 20$. They show good agreement with the exact curves. The largest deviation in any of the curves is $< 4\%$ of the maximum in the curve. As in the case of charge transfer, a reasonable approach would be to do the approximate calculation and the exact calculation over a coarse grid of points. Regions of discrepancy can then be readily spotted, and the exact data can be filled in for those regions.

The largest deviation is in the $0 \rightarrow 8$ curve where the exact curve shows distinct structure. This structure is due to interactions with closed channels. It is completely absent if $j_{\text{max}} = 8$. It is present, but much larger and in the

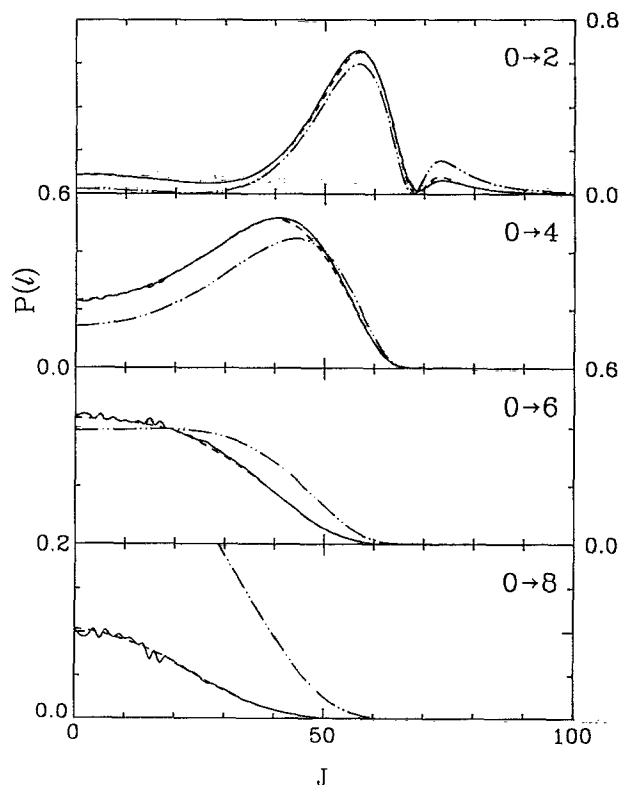


FIG. 3. The probabilities for rotationally inelastic scattering for $\text{Ar} + \text{N}_2$ at an energy of 300 K. J is the total angular momentum. The curves are —, exact result; ---, approximate result; - · -, interpolation for $\Delta J = 20$.

wrong position for $j_{\text{max}} = 10$; $j_{\text{max}} = 12$ and 14 both give identical results as shown in Fig. 3. The approximate theory does not include the closed channels and therefore misses the structure.

The IOS data were calculated using $l_{\text{eff}} = J$ and $k_{\text{eff}} = k_0$. We found that using a smaller k_{eff} corresponding to an average k gave good answers except near $J = 50$, where the probabilities fall off rapidly. Here the IOS probability falls off at a smaller J than the exact results, and the interpolation becomes less accurate. This can be corrected by including an extra point or two in the exact calculation.

It is possible to go one step beyond the IOS. One can remove from the exact equations both the elastic scattering and the IOS, as we have done here. Then one can solve the resulting coupled differential equations using perturbation theory to get $\Delta\eta^{(2)}$; this is, in effect, a double perturbation which goes to zero in either the elastic limit or in the IOS limit.⁹ This $\Delta\eta^{(2)}$ can then be removed from the S -matrix as well, and the resulting correction matrix $S^{(3)}$ should be even closer to the unit matrix and so give a better interpolation. In view of the high accuracy of the IOS-based interpolation and of the increased complexities of this procedure, it was not tried here. There may be other systems, however, where it can be useful.

There was one small difficulty in the calculation not described above. For $J > j_{\text{max}}$ the S -matrix has a constant size. However, for $J < j_{\text{max}}$ states with certain values of l must be excluded in order to conserve angular momentum.

At small J , then, the size of the S -matrix decreases. Furthermore, at $J=0$, there is no odd-parity block. For small J the calculation proceeded as described above to give an $S^{(2)}$ of reduced size. This was then mapped onto a matrix of the full size, and the missing elements were filled in with the unit matrix. The interpolation could then be done in a straightforward way.

IV. DISCUSSION

We have presented here a simple method to use an approximate calculation as a means of interpolating the results of a long and costly exact calculation. The goal, of course, is to minimize the computing cost by calculating only the minimum number of points with the exact calculation. The procedure starts by removing the approximate results from the exact S -matrix to obtain a correction matrix. If the approximate treatment is reasonably accurate, then the correction matrix is approximately the unit matrix and does not vary much as a function of energy and angular momentum. It can therefore be interpolated accurately over a much large interval than the original S -matrix can. The examples given here are interpolated over the orbital or total angular momentum, however the method can be used equally well in an interpolation over energy.

The examples described here work well for a semiclassical approximation where the result comes out as a phase shift. What happens if the approximate solution is given as a full S -matrix rather than as a set of phase shift matrices? This situation arises in the coupled-states (CS) approximation.³⁻⁵ An elegant solution to this problem has been given by Sisak and Secrest for a related problem.¹⁵ Let the approximate S -matrix be S_{appr} . We then define the correction matrix

$$S^{(1)} = S_{\text{appr}}^{-1/2} S_{\text{exact}} S_{\text{appr}}^{-1/2}. \quad (12)$$

The square root of S_{appr} is taken by diagonalizing the matrix, taking the square root of the eigenvalues, and then transforming back to the original representation.

A second use of this type of interpolation would be to use, as the approximate S -matrix, the results of a calculation with a smaller basis set. For example, one often includes closed channels in a good calculation. The approximate calculation could be done using only the open channels. The approximate calculation may be done using a smaller number of open channels. In this case the matrix would have to be augmented to make it as large as the

exact S -matrix. This could be done by putting ones along the diagonal for the missing states in the approximate S -matrix. The interpolation would then not be accurate for the states not included in the approximate calculation or those strongly coupled to these states, but it may be accurate for those states only weakly coupled to the added states.

ACKNOWLEDGMENTS

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