SIMPLE ERROR BOUND FOR COUPLED-CHANNEL
SCATTERING CALCULATIONS

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August 12, 1971

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

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by

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ABSTRACT

Since the complete set of rotation-vibration states of a molecule
contains a dissociative continuum, a coupled-channel calculation for
molecular scattering parameters based on an expansion in the set of
discrete molecular states does not give the correct values. Here it
is shown how one can very simply obtain a rigorous bound to the con-
tribution from all internal states — discrete and continuous — which
are omitted in a finite coupled-channel calculation.

I. Introduction

It is apparant that in the next few years there will be an increasing number of coupled-channel scattering calculations of atomic and molecular collision properties.[1] The customary practice is to carry out the calculation with some number of channels, or internal states (the rotation-vibration states of the collision partners) included in the expansion of the total wave function, then to re-do the calculation with more channels included, and so on until the scattering parameters of interest are not significantly changed with the addition of more channels to the expansion.

One obtains the correct result by this procedure, however, only if the complete set of internal states is discrete; i.e., for numerical reasons one must omit any continuous set of internal states, and such an omission causes the coupled-channel expansion to be incomplete. Since all molecules have dissociative continua, all physically realistic[2] systems have a continuous range of internal states, so that one will always be faced with this lack of completeness of the coupled-channel expansion in the discrete internal states.

Ways have been found[3-5] for overcoming this problem, but they are too difficult to be applied routinely. In this Letter we wish to point out a relatively simple method by which one can obtain a rigorous bound to the contribution from all internal states — discrete and continuous — which are not included in the finite coupled-channel expansion.

II. Bounds for the Phase Matrix.

Let R denote the translational coordinate and q all internal coordinates of the collision system (which we assume to be non-reactive); the Hamiltonian is of the form

$$H = T(R) + h(q) + V(q,R) \quad , \tag{1}$$

where T is the center of mass translational kinetic energy operator, h is the internal Hamiltonian, and V is the scattering interaction (the arguments of the operators indicate the variables on which they operate). Carrying out the familiar Feshbach decomposition[6], one finds that the exact Schrödinger equation is equivalent to the following partitioned form:

$$P(H-E)P + P(H-E)Q[Q(E-H)Q]^{-1} Q(H-E)P \ P\Psi = 0 \quad , \tag{2}$$

where E is the total energy and P and Q are projection operators. More specifically, P projects onto the lowest N internal states in the q-space and is identity in R-space.

$$P(R,q) = 1(R) \ p(q) \quad ,$$

where the q-space projector p is

$$p = \sum_{i=1}^{N} |\phi_i> < \phi_i| \quad ,$$

$\phi_i(q)$ being the internal states, i.e., the eigenfunctions of h:

$$h \ \phi_i = \varepsilon_i \ \phi_i \quad ;$$

Q is the complement of P,

$$Q \equiv 1 - P.$$

The N internal states of the P-space must include at least all the energetically accessible states — i.e., $E < \varepsilon_{N+1}$.

The function PΨ in Equation (2) is of the form

$$P\Psi_n = \sum_{i=1}^{N} \phi_i(q) \, f_{i\leftarrow n}(R) \quad , \tag{3}$$

where n denotes the entrance channel (the initial internal state); Equation (2) is a _finite_ set of coupled equations for the radial functions $f_{i\leftarrow n}(R)$. Exact solution of Equation (2) yields the exact scattering results for the system. The second term in Equation (2), the "exact optical potential", however, prevents such an exact (i.e., numerical) solution, for Q projects onto an infinite-dimensional space and the operator $[Q(E-H)Q]^{-1}$ is thus not calculable. Omission of the optical potential gives

$$[P(H-E)P]P\Psi = 0 \quad , \tag{4}$$

which is the operator form of the standard coupled-channel equations; written out explicitly Equation (4) becomes

$$[T(R) - (E - \varepsilon_i)] \, f_{i\leftarrow n}(R) + \sum_{j=1}^{N} V_{i,j}(R) \, f_{j\leftarrow n}(R) = 0, \tag{5}$$

where the potential matrix is

$$V_{i,j}(R) = \int dq \, \phi_i^{*}(q) \, V(q,R) \, \phi_j(q) \quad . \tag{6}$$

Error bounds are obtained by using the fact that the operator QHQ is bounded from below by some number ε. Since the continuous spectrum of QHQ begins at ε_{N+1}, if QHQ has no discrete eigenvalues below this, one may take $\varepsilon = \varepsilon_{N+1}$, the energy of the lowest internal state not included in coupled-channel expansion. If QHQ does have discrete eigenvalues below ε_{N+1}, these will appear (slightly shifted) as resonance energies of metastable states of the composite system; in this case ε must be taken less than or equal to the lowest such discrete eigenvalue of QHQ.

Thus one has the operator inequality

$$Q\varepsilon Q < QHQ \ ,$$

and requiring that $E < \varepsilon$ gives

$$0 < Q(\varepsilon - E)Q < Q(H-E)Q \ ,$$

$$0 < [Q(H-E)Q]^{-1} < Q(\varepsilon - E)^{-1}Q \ ,$$

$$Q(E-\varepsilon)^{-1}Q < [Q(E-H)Q]^{-1} < 0 \ . \tag{7}$$

Upper and lower bounds are obtained, therefore, for the operator $[Q(E-H)Q]^{-1}$, so that the exact optical potential (which is real since Q contains only closed channels) is bounded above and below:

$$(E-\varepsilon)^{-1} PVQVP < PVQ[Q(E-H)Q]^{-1} QVP < 0 \ , \tag{8}$$

where we have used the fact that $Q(H-E)P = QVP$ for a non-reactive system. Replacing Q by $1 - P$, the LHS of Equation (8) becomes

$$(E-\varepsilon)^{-1} PV(1 - P)VP \leqq \Delta V = (E-\varepsilon)^{-1}[PV^2P - PVPVP] \ , \tag{9}$$

or written out explicitly this lower bound to the optical potential matrix is

$$\Delta V_{i,j}(R) = (E-\varepsilon)^{-1}\left[\int dq \ \phi_i^*(q) \ V(q,R)^2 \ \phi_j(q) - \sum_{k=1}^{N} V_{i,k}(R) \ V_{k,j}(R)\right] \ .$$ (10)

Bounds on scattering papameters must refer to some hermitian matrix, for example, the <u>phase</u> <u>matrix</u> $\vec{\eta}$, defined by

$$\vec{S} = \exp(2i\vec{\eta}) \ ,$$

where $\vec{S}$ is the usual S-matrix; $\vec{S}$ and $\vec{\eta}$ are finite matrices whose dimension is the number of open channels. Let $\vec{\eta}_0$ be the phase matrix which results from solution of the standard coupled-channel problem, Equations (4)-(6); this corresponds to replacing the optical potential by 0 which, as seen in Equation (8), is an upper bound to it. $\vec{\eta}_0$ is therefore a lower bound to the exact phase matrix $\vec{\eta}$.[7] Similarly, if $\vec{\eta}_1$ is the phase matrix which results when the optical potential is replaced by the LHS of Equation (8), a lower bound to it, then $\vec{\eta}_1$ is an upper bound to $\vec{\eta}$.

In summary, then, the exact pahse matrix $\vec{\eta}$ is bounded by

$$\vec{\eta}_0 < \vec{\eta} < \vec{\eta}_1 \ ,$$ (11)

where $\vec{\eta}_0$ is the phase matrix which results from the standard coupled-channel calculation with the usual potential matrix $\vec{V}(R)$ defined in Equation (6), and $\vec{\eta}_1$ is the phase matrix which results from the

coupled-channel calculation with the modified potential matrix $\vec{\vec{V}}(R) + \Delta\vec{\vec{V}}(R)$, $\Delta\vec{\vec{V}}(R)$ being defined by Equation (10). As N (the number of channels) is increased, $\vec{\eta}_o$ increases and $\vec{\eta}_1$ decreases — i.e., the bounds become closer — and for any finite N large enough to include at least all the open channels Equation (11) provides a rigorous bound on the contribution from all omitted channels. It is clear, of course, that none of the continuous (i.e., dissociative) channels can be open for this bounding relation to be applicable.

If the potential $\Delta\vec{\vec{V}}(R)$ is small, then evaluation of $\vec{\eta}_1$ to first order in $\Delta\vec{\vec{V}}$ may be sufficiently accurate. This can be accomplished directly, without re-solving the set of coupled equations; it is a form of distorted wave Born approximation in which $\vec{\vec{V}}(R)$ is the distorting potential and $\Delta\vec{\vec{V}}(R)$ is the weak residual interaction. With the radial functions [obtained by solving the coupled equations with $\vec{\vec{V}}(R)$] normalized at large R as

$$f_{i\leftarrow n}(R) \sim k_i^{-\frac{1}{2}} \left[\cos(k_i R)(\sin\vec{\eta}_o)_{i,n} + \sin(k_i R)(\cos\vec{\eta}_o)_{i,n}\right],$$

one has

$$\vec{\eta}_1 = \vec{\eta}_o + \vec{A} ,$$

where

$$A_{i,j} = -(2\mu/\hbar^2) \sum_{k,\ell=1}^{N} \int dR\, f_{k\leftarrow i}(R)\, \Delta V_{k,\ell}(R)\, f_{\ell\leftarrow j}(R) .$$

Since $\Delta\vec{\vec{V}}(R)$ is a negative matrix operator, $\vec{A}$ is a positive matrix, and the bounding relation for the phase matrix [Equation (11)] can be

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written (to first order in $\Delta\vec{V}$) as

$$0 < \vec{\eta} - \vec{\eta}_0 < \vec{A} \quad . \tag{12}$$

The primary additional effort required to apply Equation (11) or (12) is computation of the matrix elements of $V(q,R)^2$ in Equation (10). It would not seem, however, that this should be prohibitively difficult.

ACKNOWLEDGMENTS

REFERENCES

* Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the U.S. Atomic Energy Commission for partial support of this research.

‡ Alfred P. Sloan Fellow

1. There has recently been a great deal of effort and progress in the numerical methods by which one can integrate coupled differential equations. See, for example, (a) B. R. Johnson and D. Secrest, J. Math. Phys., 7, 2187 (1966); (b) W. A. Lester, Jr., and R. B. Bernstein, Chem. Phys. Letters, 1, 207 (1967); (c) S. K. Chan, J. C. Light, and J. L. Lin, J. Chem. Phys., 49, 86 (1968); (d) R. G. Gordon, J. Chem. Phys., 51, 14 (1969); (e) W. N. Sams and D. J. Kouri, J. Chem. Phys., 51, 4809, 4815 (1969).

2. There are some unphysical model systems for which the complete set of internal states is discrete; examples of this are the linear atom-diatom collision system in which the diatom is taken to be a harmonic oscillator, and the atom rigid-rotor system in which the rotor is not allowed to vibrate. Continuous states always correspond to a continuous "vibrational" degree of freedom — i.e., to fragmentation of one of the collision partners.

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