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INELASTIC MOLECULAR COLLISIONS - APPLICATION OF THEORETICAL METHODS
TO PROBLEMS RELEVANT TO LASER OPERATION

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Herschel Rabitz

Herschel Rabitz
Principal Investigator

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SUMMARY

The basic goals of this research are to develop and evaluate various techniques for the calculation of rotational and vibrational inelastic molecular collisions. Our aim is to achieve a better understanding of these processes, particularly as related to gas-phase relaxation phenomena (e.g., in laser kinetic studies). Research is under way primarily in the areas of effective Hamiltonian theory and decomposition methods for calculating collisional information. Significant progress was made in these various areas during the past year. In addition to the original research plans, we were also able to extend the decomposition procedure to chemically reactive situations. This research was a collaborative effort under this contract and with Professor R. Conn, University of Wisconsin, under contract AT(11-1)-2555. Much of the material outlined below has already been made available to ERDA in preprint form (items indicated by * in the references).

I. Decomposition Theory of Molecular Collisions

(a) Non-Reactive Scattering

The operator decomposition method developed by Conn and Rabitz¹ provides a family of approximations to the K and T matrices from which the transition probabilities and scattering cross sections for inelastic molecular collisions may be calculated. The decomposition methods have much of the computational simplicity of low-order perturbation theory but can be applied to stronger interactions not adequately handled by perturbation theory.

Some of the features of the decomposition method are illustrated by the following simplified analysis. It is assumed the Hamiltonian can be expressed in the form

$$H = H_0 + V \quad (1)$$

where H_0 represents the unperturbed motion and V is the interaction potential. The Lippmann-Schwinger equation for T is

$$T = V + VG_0^+ T \quad (2)$$

where G_0^+ is the unperturbed Green's function $(E - H_0 + i\epsilon)^{-1}$. An analogous result can be written for K by using G_0^P the unperturbed principle-valued Green's function $\frac{P}{E + H_0}$. Perturbation theory assumes Eq.(2) can be solved by iteration, resulting in the (Born) series.

$$T = V + VG_0^+ V + VG_0^+ VG_0^+ V + \dots \quad (3)$$

The exact formal solution of Eq.(2) can be written as

$$T = V(V - VG_0^+ V)^{-1}V \quad (4)$$

The decomposition methods may be thought of as the matrix analog of Eq.(4).

In the simplest form the decomposition expression for the T matrix is

$$\underline{T}^J = \underline{V}^J (\underline{V}^J - \underline{T}_2^J)^{-1} \underline{V}^J \quad (5)$$

where $\underline{V}^J$ and $\underline{T}_2^J$ are first and second Born matrices in the partial wave or total angular momentum representation.¹

Although only first and second Born information is required by the decomposition methods, they have the character of the summed series, Eq.(3), and yield higher order non-perturbative results. Also, the approximations are rational in the potential strength which suggests that their range of validity should extend beyond the radius of convergence of the Born series.

The indices of the matrices above are the molecular states. The matrices entering Eq.(5) are the same size as the matrices that enter close coupling calculations, but Eq.(5) requires only one matrix inversion and two matrix multiplications to yield the entire T matrix. On the other hand, these operations must be performed many times in close coupling calculations.

Typically one works in a partial wave representation where the uncoupled internal states are $n_1 n_2 j_1 j_2 j_{12} l J$, where n_1 and n_2 represent vibration of the two molecules, j_1 and j_2 are the rotational states, $\vec{j}_{12} = \vec{j}_1 + \vec{j}_2$, l is the orbital angular momentum, and J is the total angular momentum. The latter quantity is conserved leading to a decoupling of the matrices in J .

In order to prepare for the eventual application to large vibration-rotation-translation (V-R-T) problems, a matrix indexing scheme based on a partial wave representation has been devised to handle the most general molecule-molecule non-reactive collision problem. In this scheme, j_1 and j_2 are restricted to a range $0 \leq (j_1 \text{ and } j_2) \leq j^*$. An index algorithm has been written for ordering combinations of $j_1 j_2 j_{12} \ell$ within their respective ranges to yield an arbitrary total angular momentum J . The dimensionality of the problem is further cut in half by splitting the matrices into sets of even and odd parity, defined as $(-1)^{j_1+j_2+\ell+J}$. Additional dimensionality reduction will be made by application of effective Hamiltonian methods as the need arises. The programming required to manipulate and invert the complex matrices has been completed and is presently being used on a test problem to described below. A subroutine to numerically evaluate second Born matrix elements (which are input to the various decomposition procedures) has also been developed to efficiently handle problems in which the radial dependence of the interaction potential consists of terms of the form a_n/r^n .

Although our primary interest is in three-dimensional V-R-T problems, a simple collinear atom-diatom collision problem has been selected as a first case. It will allow us to evaluate the decomposition method itself together with various approximations and subroutines while keeping the overall labor required to a minimum. The diatomic molecule is assumed to be a harmonic oscillator and the interaction potential is an exponential repulsion between the atom and the closest member of the molecules. Because of the exponential nature of the potential, a distorted wave treatment is employed to evaluate the required input matrix elements. The second Born integrals are evaluated numerically. This particular collinear collision problem is particularly useful for testing new methods. The model has been heavily favored in the

literature,^{2,3} and there is a wealth of results available,⁴ including essentially exact quantum mechanical solutions.⁵ This should allow us to compare the accuracy of various decomposition methods with other approximate techniques and the exact results.

We are presently using the model to investigate the trade-offs between a more laborious (and accurate) fully off-shell decomposition calculation and the half-off-shell or fully on-shell treatments that are possible.¹ We are also investigating various simplified techniques for evaluating second Born integrals such as using only the delta-function part of the unperturbed Green's function. The collinear problem should conveniently yield some useful physical insight which will be valuable when we apply the decomposition to realistic three-dimensional problems.

(b) Reactive Scattering

Reactive scattering introduces the possibility of the chemical constituents changing upon collision. This formally results in the addition of a new quantum number α to label the channels (reactants and/or products). In addition, all of the usual features of inelastic scattering are still present. The inclusion of reactive channels leads to new mathematical considerations. It is generally desirable and sometimes necessary to include all of the reactive channels in the calculation simultaneously. This may be expressed in terms of coupled sets of equations for the transition operators $T_{\alpha\beta}$ between channels α and β .⁶

$$\begin{aligned} T_{\alpha\beta} &= V_{\alpha} + V_{\alpha} G_{\beta} T_{\beta\beta} \\ &= V_{\alpha} + T_{\alpha\beta} G_{\beta} V_{\beta}, \quad \text{for all } \alpha, \beta \end{aligned} \quad (6)$$

It is strictly necessary to calculate $T_{\alpha\beta}$ for all α and β simultaneously since the collision process is not separable (i.e., channels α and β "know" about the presence of channel γ during the collision). Therefore, a theoretical framework is needed that retains this coupling but is still viable for practical calculations. The nature of this reactive problem makes it amenable to the same type of decomposition approach developed earlier for non-reactive processes.¹ In particular the desire to retain channel couplings is exactly analogous to our original goal of retaining multi-channel non-reactive couplings. Indeed both can now be treated in a unified theory. Details of this are presently being prepared for publication,⁷ and a summary is provided below.

The form of the Lippmann-Schwinger equation (2) allows for the derivation of a convenient variational function for T in the non-reactive case.⁸

$$I(T) = 2T - TV^{-1}T + TG_0T \quad (7)$$

Upon substitution of an appropriate trial form for T into Eq.(7), we were able to variationally derive the non-reactive result in Eq.(5).¹ In the reactive case it is not at first obvious that this is possible since Eq.(6) is not of the simple Lippmann-Schwinger type. However, the introduction of a channel ordering array $\underline{W}$ where $\sum_i W_{ij} = 1$ does allow for such a development⁹

$$\underline{T} = \underline{V}\underline{W} + \underline{V}\underline{W}\underline{G}_0\underline{T} \quad (8)$$

where $\underline{T}$ is now a matrix of operators with elements $T_{\alpha\beta}$. Using Eq.(8) a variational functional analogous to Eq.(7) may be derived. It is then

possible to follow through in a fashion similar to the non-reactive procedures and obtain the reactive analogue of Eq.(4) in the total angular momentum representation

$$\underline{\underline{T}}^J = \underline{\underline{V}}^J \underline{\underline{W}} \left[\underline{\underline{V}}^J \underline{\underline{W}} - \underline{\underline{V}}^J \underline{\underline{W}} \underline{\underline{G}}_0 \underline{\underline{V}}^J \underline{\underline{W}} \right]^{-1} \underline{\underline{V}}^J \underline{\underline{W}} \quad (9)$$

This form readily reduces to the earlier non-reactive expression upon suppression of the channel quantum numbers α . Importantly a full unitary scattering matrix may be generated this way utilizing the $\underline{\underline{K}}$ matrix rather than $\underline{\underline{T}}$. This is not possible by conventional procedures that do not couple the channels properly. Equation (9) requires only first- and second-order input information, but the full expression may be identified as an approximate summation of the entire perturbation series. Application and further development of this approach will be undertaken in the coming year.

II. Effective Hamiltonian Theory

The basic theoretical problem of calculating molecular collision phenomena can be cast in the form of solving sets of coupled differential equations (or related integral equations)

$$\sum_j H_{ij} \psi_j = E \psi_i$$

where j labels the free target states of the colliding molecules. The Hamiltonian matrix is still a differential operator on the translational coordinates. A prime source of difficulty here has been associated with the large number N of coupled equations involved. This is particularly important since the expense in solving the equations grows as $\sim N^3$. Since

our initial effective Hamiltonian work on this problem,¹⁰ several related approaches have been taken.¹¹ They all have in common the desire to reduce the number of coupled equations to $N^{\text{eff}} < N$, where the reduction is achieved by controlling certain aspects of the rotational portion of the problem. These approaches have proved to be valuable aids in performing practical vibrational and rotational inelastic collision studies. During the past year the following research was accomplished in this area under the ERDA contract.

- (i) A comprehensive review of the subject was drawn together to make the techniques more accessible to the field.¹² All of the procedures (effective potential, body-fixed decoupling, and space-fixed decoupling) were extended to the general case of two colliding vibrating-rotating molecules. The body-fixed and space-fixed procedures were shown to be special cases of general projection operator techniques. This work provides for a better understanding of the basic theory and also allows for further practical computational studies.
- (ii) The various effective Hamiltonian procedures were compared on their ability to reduce the computational effort for both atom-molecule and molecule-molecule calculations.¹³ It was shown that the computational expense can be controlled to span the range of a normal full close-coupling calculation down to a minimum size effective potential calculation. In general the number of effective equations N^{eff} can be chosen on the range $\sqrt{N} \leq N^{\text{eff}} \leq N$, with N being the original full number of equations. Flexible choices for N^{eff} can now be made to suit the desired applications. Various symmetry related aspects of the body-fixed equations were also discussed in this paper.

(iii) All of our collision calculations ultimately have the purpose of correlating, better understanding, and hopefully predicting measurable relaxation phenomena. Laser kinetic modeling falls into this category along with a wide variety of other areas. These diverse phenomena are connected with collision theory through appropriate generalized collision cross sections. As a natural extension of effective Hamiltonian theory, we formulated the relaxation cross sections in these terms with particular emphasis on collisional line broadening effects.¹⁴ Partial wave decomposition was used along with a generalized impact parameter treatment.

(iv) In order to gain added physical insight into the body-fixed effective Hamiltonian approach,¹¹ a detailed set of rotational calculations was performed on Ar-HCl.¹⁵ In addition to quantum calculations a series of analogous classical effective Hamiltonian trajectory studies was carried out. Particular attention was devoted to examining whether the body-fixed projection quantum number Ω is conserved during the collision. Contrary to the commonly accepted assumption, the projection was not conserved during the quantum or classical collisions. Detailed analysis of this matter gave a better physical description of the approximations involved. Two different approaches to the calculation of differential cross sections were also examined in this study. Certain practical computational conclusions were drawn in this regard. Further effective Hamiltonian developments will be explored in the continuing research.

III. Calculation of Intermolecular Potentials

In the original proposal we pointed to the importance of determining appropriate intermolecular potentials in order to perform detailed dynamics calculations on specific molecular systems. Given such potentials, it would then be possible to calculate the cross sections needed to analyze these systems. This is of particular importance in our planned studies of laser collision kinetics. We have now completed a study¹⁶ using the Gordon and Kim electron gas model¹⁷ to determine the interaction potential for the He-HF and Ar-HF systems. Since our interest is in rotational and vibrational inelastic collisions, the potentials V were calculated as a function of interatomic distance, angle, and vibrational coordinate. In addition, the results for He-HF were compared to SCF calculations by Lischka¹⁸ and the agreement is very good when correlation corrections are included with the SCF results. It appears that the calculated potentials will be acceptable for the scattering calculations, and these will be carried out during the coming year. Samples of the potential calculation results are shown in Figures 1, 2, and 3, and complete details are given in the original publication.¹⁶

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Fig. (1)

INTERMOLECULAR POTENTIAL

Fig. (2)

Fig. (3)