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*Perspective*

# Perspective on "Molecular collisions. VIII"

## Curtiss CF (1968) J Chem Phys 49:1952–1957

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**Abstract.** We present an overview of the influence of C.F. Curtiss on the theory of molecular collisions, as exemplified by the title paper. Both authors were graduate students of Curtiss and, as such, were strongly influenced by his ideas and approaches to theoretical chemistry. This resulted in a subsequent collaboration that provided the rigorous basis for understanding the success of the so-called centrifugal sudden and energy sudden approximations (the two combined being the "infinite order sudden" approximation).

**Key words:** Centrifugal sudden approximation – Infinite order sudden approximation – Sudden approximations – Inelastic collisions – Rotationally inelastic collisions

## 1 Background

A fundamental approach, now routinely employed in essentially all quantal treatments of molecular collisions (both inelastic and reactive), is to use rotating coordinate systems which are generalizations of those commonly used to describe rigid-body dynamics. Additionally, the most accurate and widely used quantal approximations for rotationally inelastic molecular collisions are those based on the so-called "sudden assumption" (essentially a time-scale criterion in which an internal degree of freedom is assumed to be slow compared to the time scale or suddenness of the collision). We give a brief summary of these ideas, focussing on Curtiss' role both in his research and as a mentor. We conclude with a summary of subsequent developments which show the success of Curtiss' research and mentoring.

The paper "Molecular collisions. VIII" is a landmark in the theory of inelastic scattering of molecules because it was the first to bring together two of the most useful and powerful techniques in the field: the use of body-fixed or rotating frames and the sudden approximation as applied to internal and/or orbital angular momentum operators. Unfortunately, for reasons we discuss later, Curtiss' work has not received the acclaim that it deserves. This is in large measure due to the rather formal, mathematical style that typifies all of Curtiss' research papers, and the fact that computational demonstrations of the power and accuracy of the methods were first given by others. (In fact, these individuals all have connections to Curtiss and to the Theoretical Chemistry Institute at the University of Wisconsin!) The recognition of the accuracy of these approximate methods was also delayed because of the unavailability of numerically converged quantal results to serve as "gold standards".

To appreciate the beauty of this paper (and the monumental series of papers in which it appeared), we begin by noting that the idea of using rotating or body-fixed frames arose very early in the history of quantum mechanics. The earliest work of which we are aware is that of Eckart [1, 2], but his main focus was on describing the bound rotational–vibrational states of polyatomic molecules. As far as we are aware, the first ones to consider the possibility of rotating frames with the ultimate goal of treating collisions (which involve large separations of particles not relevant for the bound molecular states considered by Eckart) were Hirschfelder and Wigner [3]. It is no coincidence that Curtiss acquired an interest in body-frame approaches to molecular collisions, since his Ph. D. thesis advisor was Hirschfelder. Indeed, the first papers published by Curtiss on this subject were joint ones with Hirschfelder [4, 5]; however, subsequently Curtiss went on to make the body-frame approach his own specialty with the initial papers of his long running Molecular collisions series [6]. The present authors were graduate students under Curtiss in the early 1960s, with Kouri doing research in atom–atom collisions using a rotating-frame description, and in numerical approaches to solving the Schrödinger equation for scattering. Hoffman's research with Curtiss was in classical and quantal nonequilibrium statistical mechanics (in addition, he gained further exposure to the

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kinetic theory of nonspherical molecular fluids and gases while a postdoctoral fellow with John Dahler, another student of Hirschfelder's).[1]

Because of the necessity of evaluating collision integrals as a part of a kinetic theory of gases and liquids, Curtiss maintained research efforts in both fields. It is particularly significant that much of the more analytical work in kinetic theory involved the use of simple molecular models (e.g., rigid ellipsoids of revolution) interacting through a hard core potential. Except for the possible "chattering" collisions, such classical scattering dynamics satisfies, to the best degree possible, the condition that the collision is sudden compared to internal and/or relative orbital rotation. Much of Curtiss' computational effort in scattering focussed on classical and semiclassical treatments of the dynamics, and he did very little on numerically converged quantum approaches, with the exception of Kouri's thesis research [7]. However, the preceding discussion indicates why Curtiss was destined to have a particularly important impact on inelastic scattering. Of course, there were other researchers exploring the use of rotating frames for collision processes [8–11], but it was the "Wisconsin school" led by Curtiss and Hirschfelder that ultimately provided the decisive research that remains at the core of our understanding of inelastic molecular collisions, and which has also been of great importance in the treatment of quantum reactive scattering.

The first accurate quantum scattering results for molecular collisions were obtained by Allison and Dalgarno, and independently by Lester and Bernstein (at Wisconsin!) using an approach due to Arthurs and Dalgarno [12–14]. Both treatments used a total angular momentum representation but quantized along a space-fixed, center-of-mass $z$-axis. It is to some degree ironic that results obtained by this "space-fixed" formalism ultimately provided the standard used to establish the body-frame approximate results as highly accurate for appropriate interactions, and in the process showed that the body-frame approaches were more efficient even for converged full quantal calculations. We now turn to a description of Curtiss' landmark paper.

## 2 Curtiss' body-frame/sudden approximation ideas

In this section, we outline the basic ingredients of Curtiss' paper. Rather than go through detailed derivations, we concentrate on the key ideas and simply refer to the specific equations in "Molecular collisions. VIII" that resulted. First, we note that Curtiss virtually always preferred to treat diatom–diatom scattering as his "lowest level" system, pointing out that the atom–diatom and atom–atom scattering cases resulted simply by assigning appropriate limiting values to the various internal angular momentum quantum numbers. As a result, the first major difficulty one has in reading the "Molecular collisions" series of papers is notational. In the case of "Molecular collisions. VIII", this is further compounded by his use of the diagrammatic treatment of angular momentum coupling [15], which was (and still is, for the most part) unfamiliar to theoretical chemists. The second stumbling block facing the reader attempting to understand this paper is the introduction of numerous new functions (defined for mathematical convenience, but seldom, if ever, accompanied by motivation). The starting equation is Eq. (VIII.5), which is written as an integral equation using Green's functions.[2] This further contributed to a certain opacity of Curtiss' papers on scattering because he was one of the few theoretical chemists to use this mathematical tool. The equation cited is one of a set of coupled equations in which a very compact notation is used for representing the various quantum numbers needed to characterize the system. Note that barred quantum numbers are precollision and unbarred ones are postcollision. The asymptotic form of the exact scattering solution is given in Eq. (VIII.6). The second section of the paper deals with the diagonalization of the potential matrix: the eigenvalues are found to be simply the potential in the body-frame coordinate representation. This is followed by a section that introduces auxilliary sets of scattering-type infinite order sudden (IOS) functions that are used formally to solve the full scattering problem. This is done by applying the diagonalizing transformation for the potential to the exact equation, written in differential-equation form. The IOS Hamiltonian is essentially used to define a reference Green's function having a well-defined orbital rotational energy. In particular, Eq. (VIII.30) defines a function $\psi(\bar{l}S_\mathrm{a}S_\mathrm{b})$, which is identical to the so-called initial-$l$-, initial-$k$-labeled IOS approximation wavefunction satisfying standing-wave boundary conditions. Note that the use of the eigenvalue form of the centrifugal energy operator corresponds to a "centrifugal sudden" or "coupled states" (CS) approximation. The use of an effective radial kinetic energy eigenvalue corresponds to the "energy sudden" approximation. The exact differential equation describing the scattering is Eq. (VIII.29), and Curtiss expresses its exact solution in terms of the IOS functions, obtaining Eq. (VIII.37). Here, he has made use of the eigenstates of the potential matrix and IOS-type scattering functions to construct a Green's function by using the linear independence of the causal and anticausal IOS states. This procedure for constructing Green's functions may be found in the "bible" of mathematical physics written by Morse and Feshbach [17]. A crucial feature of this equation is the appearance of an infinite ranged perturbation, $V(\bar{l}l, r)$, given explicitly in Eq. (VIII.36). Thus, analysis of higher-order

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[1] It is perhaps worth our pointing out that graduate students of Curtiss all had the same major hurdle to surmount in order to do a Ph.D. thesis under his direction. It was not passing the usual courses or Candidacy Exams, but rather a consequence of the fact that Curtiss' research program was very strongly integrated so that each of his research projects built in some way on his previous work. Thus, the major difficulty was to read and understand one of the previous papers in Curtiss' publication list. The project you ended up working on depended on which paper it was that you finally understood

[2] We follow the convention that equations quoted from Molecular collisions. VIII are denoted by their equation number in that paper, but preceeded by the Roman numeral VIII

contributions to the scattering requires the use of singular or boundary perturbation theory, but this can be carried out.[3] The rest of this section deals with how one obtains asymptotically correct behavior for the exact solutions, and is not needed for the usual IOS level of treatment. Finally, in the last section of the paper, Curtiss presents a careful asymptotic analysis, with the main result being obtained for the situation where the change in the internal rotational energies is small. The most readily recognized equations are the expression for the IOS **S** matrix, Eq. (VIII.53), the expression for the IOS **T** matrix, Eq. (VIII.56), and the IOS approximation for the moments of the cross sections, Eq. (VIII.58). The essential feature of the **S**- or **T**-matrix expressions is that they are given as averages over the rotational states of the **S**-matrix, which depends on orientation-dependent scattering phase shifts. It is especially interesting to note that Curtiss' approach automatically ensured that the basic nature of the quantum numbers is preserved, and so orbital angular momentum quantum numbers are not approximated by the total angular momentum quantum number. Thus, Curtiss' results do not suffer from basic difficulties resulting from the use of "$J$-labeling" as opposed to "$l$-labeling" [18, 23]. In Sect. 3 we describe what we believe to be the best way of understanding physically why the approximations are, in fact, so useful. This will necessitate a brief summary of work done by not only the present authors, but by other researchers. The remarkable aspect we wish to stress is that these other studies are dominated by students of either Curtiss or Hirschfelder!

## 3 Exact quantum scattering and the propensity to conserve the $z$ component of internal angular momentum

The advances of the next few years after the appearance of "Molecular collisions. VIII" are summarized in a chapter in a book edited by Bernstein (also at Wisconsin and a collaborator with Curtiss) [23]. The next major impetus to this approach to molecular collisions came in the period 1973–74 with the publication of two papers [18, 19] dealing especially with the CS approximation. One paper is by a former student of Hirschfelder and the other involves one of the present authors. The relationship between these two papers can best be seen by a brief consideration of how each treated the orbital rotational kinetic energy operator. Both papers used rotating-frame ideas and the Hamiltonian written either in the form

$$H = T_\mathrm{R} + T_\mathrm{r} + \frac{\mathbf{j}^2}{2\mu r^2} + \frac{(\mathbf{J}-\mathbf{j})^2}{2MR^2} \quad , \tag{1}$$

or in the form

$$H = T_\mathrm{R} + T_\mathrm{r} + \frac{\mathbf{j}^2}{2\mu r^2} + \frac{\mathbf{l}^2}{2MR^2} \quad . \tag{2}$$

Equation (1) is the form used in Pack's approach while McGuire and Kouri (MK) actually refer to both forms. As noted in both papers, the evaluation of the cross term, $\mathbf{J} \cdot \mathbf{j}$, by raising and lowering operators leads to coupling in the magnetic states of the diatom rotation, which physically are the Coriolis effects. Pack suggested approximating the centrifugal energy operator by the eigenvalue of the total angular momentum, $J(J+1)\hbar^2/2MR^2$. MK instead replaced it by the centrifugal energy eigenvalue form $l(l+1)\hbar^2/2MR^2$. It is clear that the latter is in the exact same spirit as Curtiss' treatment, but both are sudden approximations. MK [18] also included detailed calculations of complete degeneracy-averaged differential and integral state-to-state cross sections for the scattering of He off $H_2$, and the accuracy of the results was unprecedented! Of course, the converged close-coupling results used to establish the accuracy of the CS approximation were not available when Curtiss' paper was published. Once the accuracy of the approach was proven, there was great activity in the field focussed on its implementation and further testing. MK also discussed conditions under which the method could be expected to perform well. In particular, they pointed out that strongly backscattered systems should be well described, which translates to scattering dominated by a repulsive core potential; however, they also pointed out that for systems satisfying an approximate total cross section conservation rule, the optical theorem implies that the elastic forward scattering ought also to be treated accurately.

The next major advance in understanding came with a paper by Secrest [24], another student of Hirschfelder. This work follows even more closely the approach used by Curtiss, in that it essentially involves the approximate diagonalization of the rotational part of the Hamiltonian using the transformation that diagonalizes the potential matrix. However, unlike Curtiss, there was no attempt to write the exact solution in terms of the approximate ones, so there was no systematic way to compute corrections to the sudden approximations. However, Secrest's paper was much more accessible to the general audience and thus increased interest and activity in the methods.

It should be pointed out that the CS approximation was soon shown not to be a general solution to inelastic rotational scattering in another paper by Kouri and McGuire [25]. The system studied was the scattering of $Li^+ + H_2$. In this system, one has a very long ranged, attractive anisotropy and the scattering is no longer dominated by the short-range repulsive interaction. This, of course, was in agreement with the ideas proposed by MK. At about this same time, numerous other groups tried to extend the CS and IOS approximations to treat other kinds of cross sections than the degeneracy-averaged differential and integral cross sections. The results were confusing because extremely large errors were found in calculations done for line-broadening and other phase-sensitive cross sections [23]. The first clarification came in a study by Goldflam, Kouri and coworkers [26, 27]. They showed that if such generalized relaxation cross sections were computed using the MK expression for the differential scattering amplitude

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[3] Such an analysis has been carried out by V. Khare and D.J. Kouri but is unpublished

(which clearly depended strongly on subtle phase relationships), then the same high accuracy was also obtained for these phenomena. (This was true for almost all the generalized cross sections except for those that are associated with the effects of external magnetic field gradients on transport coefficients. These turn out to depend on the very small differences between large opacity-like sums, and the CS and IOS approximations failed miserably in these cases!) The way to understand this was arrived at independently, and at about the same time by Shimoni and Kouri [20] (see also Ref [28]) and by Parker and Pack [21]. The result essentially was that the most consistent treatment of the basic CS and IOS $T$-matrix requires that the approximate solutions be superposed so that the correct incident plane wave and angular momentum coupling of the rotor and orbital angular momenta is satisfied. When this is done, one finds that the CS and IOS amplitudes must be multiplied by Clebsch–Gordan coefficients, and summed over the effective orbital angular momentum quantum number. When this is done, it is seen that although the equations determining the CS and IOS wavefunctions are diagonal in the rotor magnetic quantum number, magnetic transitions are predicted in all other quantization frames. The degeneracy-averaged cross sections were shown to be identical whether one used the "$l$-initial" or "$l$-final" choice of approximate orbital angular momentum quantum number. Pfeffer and Secrest [29] suggested using the arithmetic average of the initial and final orbital angular momentum quantum numbers for determining the centrifugal potential in the CS and/or IOS calculations, but they did not analyze the implications of this choice. In fact, the fundamental question became "is there any quantization frame for which there is a true strong propensity to conserve $\mathbf{j_z}$?". Closely related to this issue was another raised by Stolte and Reuss [30] and by Dickinson and Richards [31]. They were able to prove that either an initial-$l$- or final-$l$-labeled CS approximation predicts qualitatively incorrect behavior in the near-forward elastic ($\Delta j = 0$) scattering, particularly in the diffraction–oscillation region. In a series of papers by Khare and Kouri and coworkers [32], it was shown that such difficulties could be removed by use of the $l_{\text{av}} = \frac{1}{2}(l_{\text{initial}} + l_{\text{final}})$ choice of CS parameter. This brings us to the final, ultimate resolution of the physical basis of the sudden approximations. During a trip by Hoffman to Houston, he, Kouri and Khare discussed the possibility of collaborating on the explication of the physical basis of the angular sudden approximations. Drawing on his experience with the classical kinetic theory of gases, Hoffman suggested that the way to attack the problem was in terms of quantization along the apse vector. In scattering by a spherical potential, the apse vector is directed along the difference between the initial and final relative linear momenta. When there is inelasticity (as in a nonspherical interaction between an atom and a diatom), the apse direction is dependent on the initial and final internal states of the diatom. Consequently, in collisions of nonspherical molecules, there is a different apse direction for each $\Delta j$ transition; however, in the case of the IOS approximation all rotor states are considered degenerate and one again has a single apse vector for all transitions. First Khare, Kouri and Hoffman (KKH) [33] were able to show explicitly that this "geometric-apse" quantization was the natural result of using the $l_{\text{av}}$ CS parameter. Thus, when one parameterizes the CS in terms of $l_{\text{av}}$, $\mathbf{j_z}$ is rigorously conserved along the geometric apse! However, of even greater interest was the fact that Hoffman showed that if the true, state-dependent "kinematic-apse" is used as the quantization axis, $\mathbf{j_z}$ is exactly conserved for the classical collision of a rigid, non-spherical molecule with an atom! The proof is exceptionally simple and is reproduced here. The total classical angular momentum for such a collision is given exactly by

$$\mathbf{J} = \mathbf{r_a} \times \mathbf{p_a} + \mathbf{r_m} \times \mathbf{p_m} + \mathbf{j} \ , \tag{3}$$

where the subscripts **a** and **m** denote the atom and the molecule, respectively. Then the first two terms in Eq. (3) give the orbital angular momentum of the atom and molecule, and the last term is the intrinsic angular momentum of the molecule. However, the total angular momentum is conserved in the absense of external torques, so one requires that

$$\Delta\mathbf{J} \equiv 0 \tag{4}$$

for the overall collision. Therefore,

$$0 = \Delta(\mathbf{R} \times \mathbf{P}) + \Delta\mathbf{j} \ , \tag{5}$$

where **R** is the usual scattering vector, **P** is the linear momentum for the relative motion of the atom and diatom, and $\Delta\mathbf{j}$ is the change in the diatom's angular momentum. Now for an exactly impulsive (hard core) collision, the collision time is zero (if chattering collisions are ignored) and there is no change in the collision geometry. This requires that $\Delta\mathbf{R}$ vanishes identically. Then Eq. (5) implies that

$$\Delta\mathbf{j} = -(\mathbf{R} \times \Delta\mathbf{P}) \ . \tag{6}$$

This result shows that $\Delta\mathbf{j}$ must be orthogonal to the apse vector, since the apse is defined to be along the vector $\Delta\mathbf{P}$! The final step in establishing that this is indeed the correct physical basis of the sudden approximations is to carry out numerically converged fully quantal calculations of polarization transition cross sections for a number of systems and see if there is such a propensity to conserve the component of **j** along the apse. In fact, such studies were carried out by KKH [34], in which they tested converged close-coupling cross sections for polarization transitions using four different choices of quantization: namely, the standard space-fixed axes, the helicity axes (where the initial states are quantized relative to the incident relative linear momentum and the final states are quantized along the final relative linear momentum), the geometric apse (GA), and the kinematic apse (KA). The first results [34] were for the polarization-state-resolved integral cross sections for He − CO, Ne − HD and He − $H_2$. It was only for the GA and KA quantization schemes that a completely systematic propensity to preserve $j_z$ was found. Finally, KKH [35] reported a detailed study of numerically exact quantum differential state-to-state scattering cross sections for the He + CO and He + HCl systems. Again, they showed that only for the KA and GA choices of quantization was there a systematic propensity to conserve $j_z$. Furthermore, it was found in both the integral and differential cross sections that the KA was the best in terms of the extent of the $j_z$-preserving propensity. A comparison of these two choices of quantization showed that they agreed well except in the extreme forward scattering direction (angles smaller than about 15°). Since the integral cross section involves a Jacobian weight that vanishes in the exact forward direction, it is clear that the GA and KA will agree very well. This is borne out in Ref. [34]. Another very interesting result obtained in Ref. [35] is the fact that one can obtain reasonably good results for the differential cross section quantized in the space-fixed scheme by transforming only the $\Delta j_z = 0$ KA amplitude and neglecting all other KA amplitudes for a given $j_\mathrm{i} \rightarrow j_\mathrm{f}$ rotational transition. This completes the story regarding the physical basis of the angular-sudden approximations. There is much more to tell in the area of reactive scattering.[4] There still remains a need for research into the best way to implement such approximations for this problem. Certainly the issue has been studied but that would lead us into another mass of literature. Suffice it to say that even though Curtiss never considered the problem, his and Hirschfelder's mentoring influence has been strong.

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