

Role of direct and resonant (compound state) processes and of their interferences in the quantum dynamics of the collinear $\text{H} + \text{H}_2$ exchange reaction*

George C. Schatz[†] and Aron Kuppermann
 Arthur Amos Noyes Laboratory of Chemical Physics,[‡]
 California Institute of Technology, Pasadena, California 91109
 (Received 25 April 1973)

The question of the relative importance of compound state (i. e., activated complex) and direct reaction mechanisms has been of central importance for the dynamical foundations of chemical kinetics.^{1,2} The studies here reported indicate that in the quantum dynamics of the historically important collinear $\text{H} + \text{H}_2$ exchange reaction not only do both

such mechanisms contribute but also that their interference plays a central role in determining the pronounced quantum oscillations of the reaction probability as a function of energy.³ This accounts not only for the absence of such oscillations in quasiclassical calculations,⁴ but also for the inability of the present semiclassical formalism⁵ to produce them.⁶

We have used the close-coupling propagation method of Kuppermann⁷ to obtain accurate values for the elements of the scattering matrix \mathbf{S} as a function of the total energy E for the collinear collision $\text{H} + \text{H}_2$, using the same surface as previously.³ From these elements, we calculated the reaction probabilities $P_{ij}^R(E)$, phases $\delta_{ij}^R(E)$, and time delays $\tau_{ij}^R(E) = \hbar d\delta_{ij}^R(E)/dE$ corresponding to the vibrational states i and j of the reagent and product H_2 , respectively.

Figure 1 shows $P_{00}^R(E)$, $\delta_{00}^R(E)$, and $\tau_{00}^R(E)$ in the energy ranges 0.80–1.00 eV and 1.20–1.35 eV. $\delta_{00}^R(E)$ and $\tau_{00}^R(E)$ are reasonably smooth monotonic functions except near $E = 0.90$ and 1.276 eV.⁸ In the regions of relatively smooth behavior, the direct processes dominate the reaction mechanism. The more rapid variations in $\delta_{00}^R(E)$ and $\tau_{00}^R(E)$ near 0.90 and 1.276 eV result from the presence of internal excitation (Feshbach) resonances⁹ at these energies.^{10,11} The resonant component of the scattering matrix element S_{00}^R has essentially a Breit-Wigner energy dependence¹² while the direct component is characterized, in our case, by a slowly varying amplitude and a monotonically decreasing phase.¹³ We find that these direct and resonant components have amplitudes within an order of magnitude or less of one another at the resonance energies and that their interferences determine the over-all shapes of the curves in Fig. 1. The widths of the resonances at 0.90 and 1.276 eV are about 0.05 and 0.008 eV, respectively. An additional resonance of intermediate width has been found at $E = 1.67$ eV.¹⁴ From the resonant contribution to S_{00}^R , we have computed the corresponding resonance state delay times $(\tau_{00}^R)_{\text{res}}$ and displayed them as the solid curves of Fig. 1(c). The maxi-

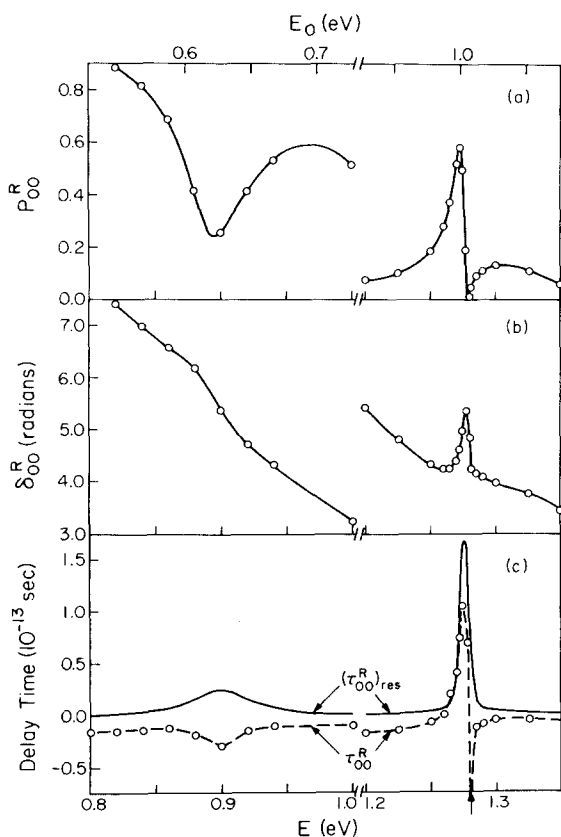


FIG. 1. Reaction probability P_{00}^R , phase δ_{00}^R of the scattering matrix element, time delay τ_{00}^R , and resonant component of the time delay $(\tau_{00}^R)_{\text{res}}$ for the collinear $\text{H} + \text{H}_2$ reaction as a function of the total energy E and the relative translational energy E_0 . The arrow in the abscissa indicates the opening of the $j=2$ vibrational state of H_2 (at 1.280 eV). For display purposes, the phases in the 1.20–1.35 eV range have been increased by 2π with respect to those in the 0.80–1.00 eV range.

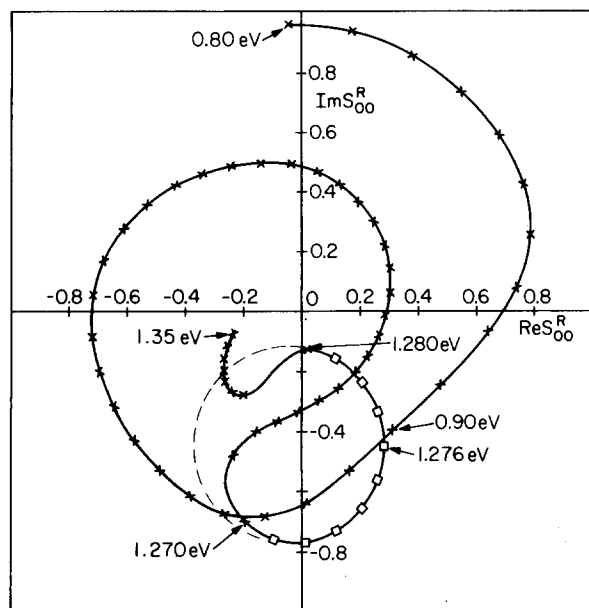


FIG. 2. Argand diagram of $\text{Im } S_{00}^R$ versus $\text{Re } S_{00}^R$ with the energy E as a parameter. The crosses are placed at intervals of 0.01 eV. The squares near the 1.276 eV resonance are at 0.001 eV intervals and indicate that the resonance component of the phase is increasing rapidly near this energy [although the over-all phase varies in a manner indicated in Fig. 1(b)]. The dashed circle calls attention to the existence of a resonance circle in the energy region near 1.276 eV.

imum delay time at the 1.276 eV resonance is about an order of magnitude greater than the vibrational period of 1.66×10^{-14} sec for the symmetric stretch of H_3 at the saddle point, indicating a long-lived state.

The interference effects are most clearly revealed by the Argand plot¹⁵ of $\text{Im } S_{00}^R$ versus $\text{Re } S_{00}^R$ with E as a parameter, as shown in Fig. 2. Near 1.276 eV, a characteristic counterclockwise resonance circle¹⁵ is traced out while elsewhere the plot tends to circle the origin clockwise as E increases. The resonance at 0.90 eV is too broad to show a well-formed resonance circle but its affect on the Argand diagram is quite apparent. Despite this broadness, the interference effects between the resonant and direct interactions at each of the resonances result in the very significant oscillations in the reaction probability plot [Fig. 1(a)] and are to a large extent responsible for the differences between these exact quantum calculations and the corresponding quasiclassical and

semiclassical results.

We are presently investigating the importance of such resonances and interferences for other reactions, such as $\text{F} + \text{H}_2 \rightarrow \text{FH} + \text{H}$.¹⁶

*Research supported in part by the U. S. Atomic Energy Commission, Report Code Number CALT-767P4-115.

†National Science Foundation predoctoral fellow. Work performed in partial fulfillment of the requirements for the Ph.D. in Chemistry at the California Institute of Technology.

‡Contribution Number 4679.

¹S. Glasstone, K. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941), Chap. 3, 4.

²M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.* **43**, 3259 (1965).

³(a) D. G. Truhlar and Aron Kuppermann, *J. Chem. Phys.* **52**, 3841 (1970); (b) **56**, 2232 (1972).

⁴J. M. Bowman and Aron Kuppermann, *Chem. Phys. Lett.* **12**, 1 (1971).

⁵W. H. Miller, *J. Chem. Phys.* **53**, 1949 (1970); **53**, 3578 (1970); **54**, 5386 (1971).

⁶J. M. Bowman and Aron Kuppermann, *Chem. Phys. Lett.* **19**, 166 (1973).

⁷Aron Kuppermann, *Potential Energy Surfaces in Chemistry*, edited by W. Lester, (University of California at Santa Cruz, 1970), p. 121-129; *Electronic and Atomic Collisions*, VII International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers (North-Holland, Amsterdam, 1971), p. 3.

⁸The results presented near 1.276 eV in Ref. 3(b) (the dashed portions of the curves in their Figs. 3-6, 11-13) were inaccurate because an insufficient number of closed channels was used, whereas the present results are fully converged.

⁹H. Feshbach, *Ann. Phys. (N. Y.)* **5**, 357 (1958); **19**, 287 (1962).

¹⁰G. C. Schatz and Aron Kuppermann, VIII International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, July 1973.

¹¹Related resonances were studied by R. D. Levine and S.-F. Wu, *Chem. Phys. Lett.* **11**, 557 (1971); S.-F. Wu and R. D. Levine, *Mol. Phys.* **22**, 881 (1971).

¹²G. Breit and E. Wigner, *Phys. Rev.* **49**, 519 (1936).

¹³The partitioning of the scattering matrix into resonant and direct components is discussed by Feshbach.⁹

¹⁴G. C. Schatz and Aron Kuppermann (unpublished results).

¹⁵R. K. Adair, *Phys. Rev.* **113**, 338 (1959); R. H. Dalitz, *Ann. Rev. Nucl. Sci.* **13**, 346 (1964); J. Macek and P. G. Burke, *Proc. Phys. Soc. (Lond.)* **92**, 351 (1967); R. G. Moorhouse, *Ann. Rev. Nucl. Sci.* **19**, 301 (1969); R. D. Levine, M. Shapiro and B. R. Johnson, *J. Chem. Phys.* **52**, 1755 (1970).

¹⁶G. C. Schatz, J. M. Bowman, and Aron Kuppermann, *J. Chem. Phys.* **58**, 4023 (1973).