**Title**

MODIFIED CLASSICAL S-MATRIX FOR TUNNELING IN THE COLLINEAR H + H2 REACTION

**Permalink**

https://escholarship.org/uc/item/4tj4g8qk

**Authors**

Hornstein, Steven M.
Miller, William H.

**Publication Date**

1974-03-01

Submitted to The Journal of
Chemical Physics

LBL-2595 c.2
Preprint

# MODIFIED CLASSICAL S-MATRIX FOR TUNNELING IN THE COLLINEAR H + $H_2$ REACTION

Steven M. Hornstein and William H. Miller

March 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

25

# DISCLAIMER

# Modified Classical S-Matrix for Tunneling in the Collinear $H + H_2$ Reaction*

Steven M. Hornstein and William H. Miller‡

Department of Chemistry and Inorganic
Materials Research Division, Lawrence
Berkeley Laboratory; University of California,
Berkeley, California 94720

One of the most interesting, and potentially quite useful, aspects of the recently developed "classical S-matrix"[1] description of molecular collisions is the ability to treat "classically forbidden" processes--i.e. those which do not take place by ordinary classical dynamics--by classical trajectory methods. Such processes are characterized by analytically continued, complex-valued classical trajectories, and the resulting transition probabilities are exponentially damped; classically forbidden processes are thus a generalized kind of tunneling.

George and Miller[2] carried out such calculations for the collinear $H + H_2$ reaction (on the Porter-Karplus surface[3]) in the energy region just below the classical threshold for reaction (this being the most important region for determining the thermally averaged rate constant), but at the time there were no definitive quantum mechanical calculations in this energy region (for this potential surface) by which to judge the absolute accuracy of the semiclassical theory. Since then, however, two groups of workers[4,5], using different computational methods, have carried out such quantum calculations, and agreeing well with each other, these are presumably the correct quantum mechanical values. Figure 1 shows the comparison of the semiclassical values[2] with these quantum mechanical results[4,5] for an energy just below the classical threshold down to where the transition probability has dropped to below $10^{-10}$. The agreement over this range of ten orders of magnitude in reaction probability, for a process which is normally thought of as highly quantum-like, is impressive. The relative error in the semiclassical values (35-50%), however, is greater than that for non-reactive collinear examples that have been studied[6,7], and we have sought to understand its origin in order, perhaps, to mend it. Such is the purpose of this Note.[8]

George and Miller[2] found only one complex-valued classical trajectory corresponding to the ground state to ground state reaction probability of $H + H_2 \rightarrow H_2 + H$, and the semiclassical transition probability is thus given by

$$P_{n_2, n_1} = [2\pi \, |n_2'(q_1)| \,]^{-1} \exp \, [-2 \, \mathrm{Im} \, \Phi \, (E)/\hbar] \, . \qquad (1)$$

An obvious modification of these semiclassical results would arise if other complex-valued trajectories could be found. We have conducted a much more thorough search for such trajectories, and unable to find any, conclude that this is probably <u>not</u> the source of the error. By analyzing one dimensional WKB tunneling expressions for known model problems, we also conclude that "intrinsic" quantum effects are probably not the explanation; i.e. the paramater $\alpha(2\mu V_o)^{1/2}/\hbar$, where $V_o$ is the barrier height and $\alpha$ a length paramater characterizing the size of the barrier, is still fairly large even for the $H + H_2$ system.

The reasoning which seems to explain the situation best is to regard the two factors in Eq. (1) separately: the exponential factor is the tunneling probability, and the pre-exponential Jacobian factor is the distribution of final vibrational states given the fact that tunneling has occurred. Since only the ground vibrational state is energetically allowable at these energies, this pre-exponential factor should clearly be unity; it is well known[6,7], however, that this "primitive" semiclassical distribution can be an error when there are not many final states accessible. The implication of this reasoning, therefore, is that a better result should be obtained if the pre-exponential factor in Eq. (1) is replaced by unity. The dotted lines in Figures 1 and 2 are the result of this modification, and it shows a marked improvement in agreement with the quantum mechanical values, particularly in the important region just below the classical threshold (Figure 2).

# References

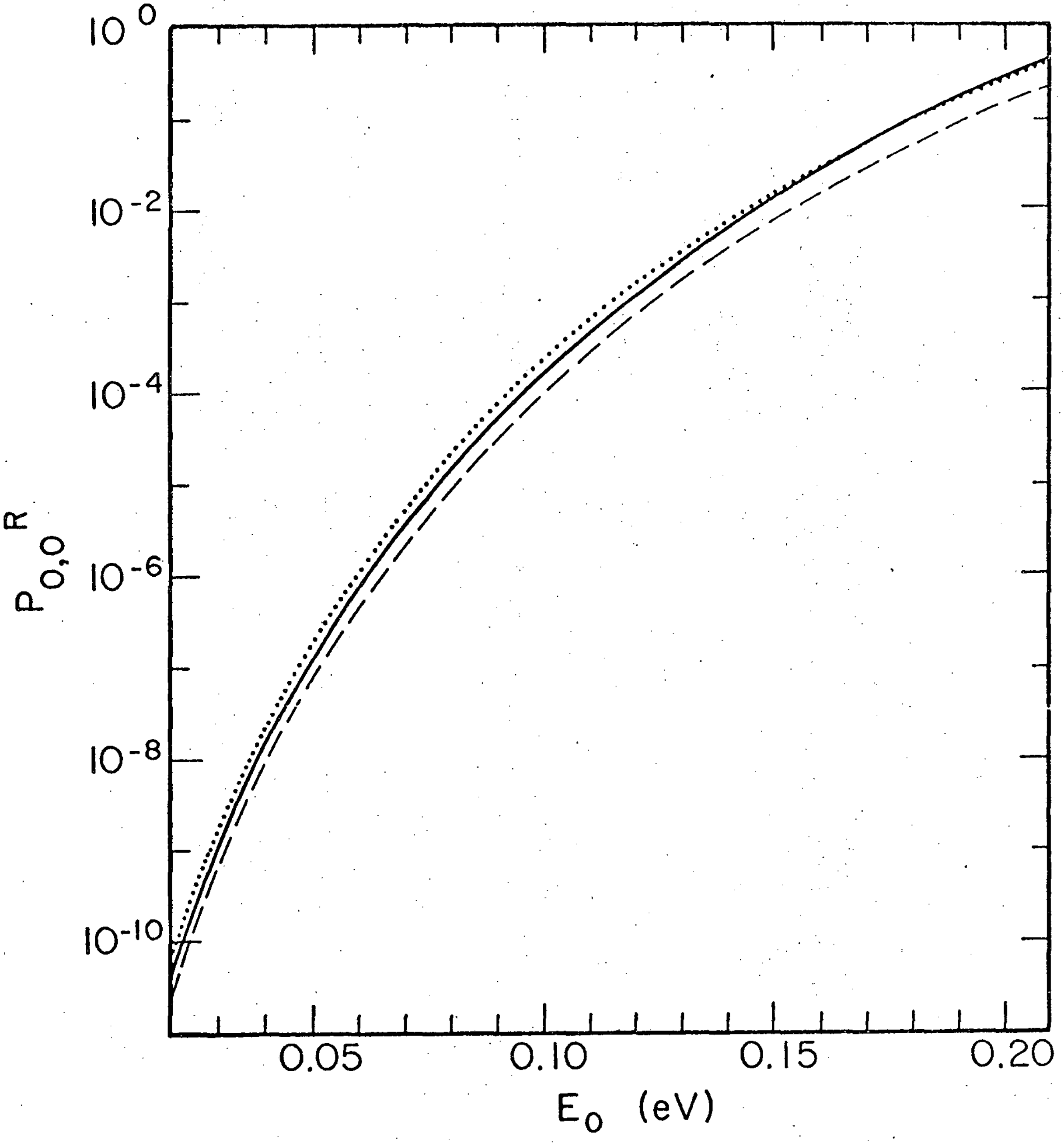
* Supported in part by the U.S. Atomic Energy Commission, and by the National Science Foundation under grant GP-34199X.

‡ Camille and Henry Dreyfus Teacher-Scholar.

1. For a review, see W.H. Miller, *Adv. Chem. Phys.* **25**, 63 (1974).
2. T.F. George and W.H. Miller, *J. Chem. Phys.* **56**, 5722 (1972); *ibid.* **57**, 2458 (1972).
3. R.N. Porter and M. Karplus, *J. Chem. Phys.* **40**, 1105 (1964).
4. G.C. Schatz and A. Kuppermann, private communication.
5. J.W. Duff and D.G. Truhlar, *Chem. Phys. Lett.* **23**, 327 (1973).
6. W.H. Miller, *J. Chem. Phys.* **53**, 3578 (1970); W.H. Miller and T.F. George, *J. Chem. Phys.* **56**, 5668 (1972).
7. W.H. Wong and R.A. Marcus, *J. Chem. Phys.* **55**, 5663 (1971); J. Stine and R.A. Marcus, *Chem. Phys. Lett.* **15**, 536 (1972).
8. Several groups of workers [J.M. Bowman and A. Kuppermann, *J. Chem. Phys.* **59**, 6524 (1973), and J.W. Duff and D.G. Truhlar, *Chem. Phys.*, to be published] have also seen that the semiclassical theory does not work well for collinear H + $H_2$ in the energy region *above* the classical threshold. This is well understood, however: the quantum number function $n_2(q_1)$ is too structured for the Airy function expression to be the appropriate uniform asymptotic approximation.

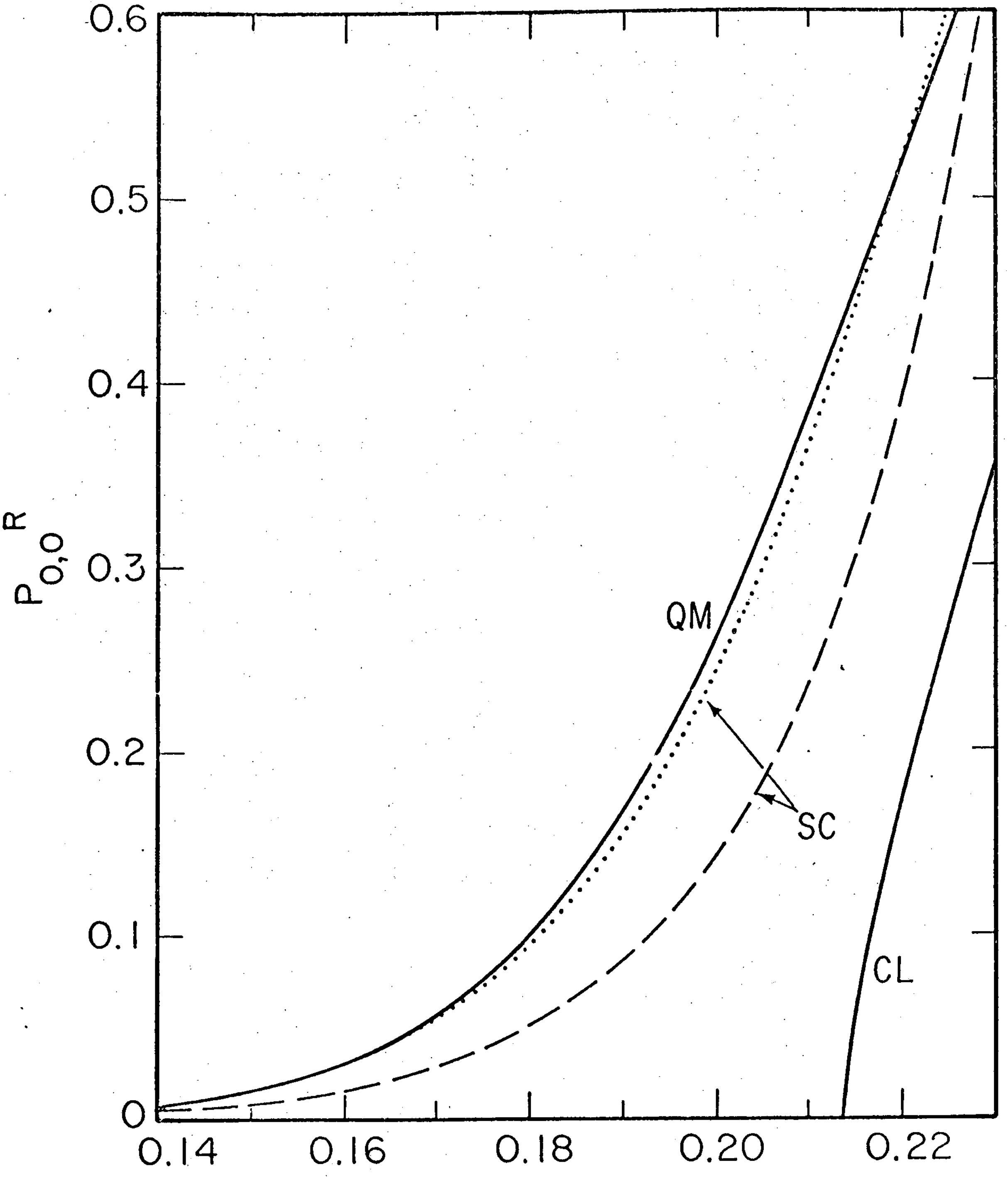
## Figure Captions

1. The solid line is the accurate quantum mechanical ground state to ground state reaction probability (refs. 4 and 5) for the collinear $H + H_2$ reaction on the Porter-Karplus potential surface (ref. 3). The dashed line is the original semiclassical result (ref. 2), and the dotted line is the result of the modification suggested in this paper.
2. Same as Figure 1, except the abscissa is shown here on a linear scale. The classical curve (CL) is the completely classical Monte Carlo result [D.J. Diestler and M. Karplus, J. Chem. Phys. **55**, 5832 (1971)].



XBL 741-5412

Fig. 1



XBL 741-5413

Fig. 2

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720