Lawrence Berkeley National Laboratory

Recent Work

Title

CLASSICAL TRAJECTORY STUDY OF ROTATIONAL EXCITATION IN LOW ENERGY He - CO AND He - H₂ COLLISIONS

Permalink

<https://escholarship.org/uc/item/83g2415d>

Authors

Augustin, Stuart D.
Miller, William H.

Publication Date

1974-05-01

CLASSICAL TRAJECTORY STUDY OF ROTATIONAL EXCITATION IN
LOW ENERGY He - CO AND He - H₂ COLLISIONS

Stuart D. Augustin and William H. Miller

May 1974

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

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

CLASSICAL TRAJECTORY STUDY OF ROTATIONAL EXCITATION IN

LOW ENERGY He - CO AND He - H₂ COLLISIONS^{*}

Stuart D. Augustin and William H. Miller[†]

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

ABSTRACT

Classical trajectory calculations for the rotational excitation of CO and H₂ by collision with He have been carried out and compared to the accurate quantum mechanical calculations of other workers. The agreement is reasonably encouraging, although some inherent limitations of this strictly classical approach are observed and discussed.

I. INTRODUCTION

Rotational excitation in molecular collision systems is typically a strong, or "classically allowed"¹ process, meaning simply that there exists classical trajectories along which the requisite amount of rotational excitation takes place. As a function of initial collision energy, for example, a rotational excitation cross section usually rises from zero sharply at its energetic threshold. This is in contrast to vibrationally inelastic transitions which are typically weak, "classically forbidden"¹ processes; it often requires collision energies significantly above the energetic threshold for these transitions to have a sizeable cross section.

The most important quantum effects in classically allowed processes are of an interference nature.² Often, however, the averaging over impact parameter, m-components of rotational states, etc., quench this interference structure so that a completely classical treatment becomes adequate. The rule of thumb, therefore, is that a completely classical treatment (eg. a quasi-classical trajectory calculation) is adequate to describe integral cross sections for inelastic collision processes that are classically allowed.

It is important to test the validity of the above "rule of thumb" by comparison of classical calculations with accurate quantum mechanical results whenever the latter are available. La Budde and Bernstein³ have made such a comparison for the $0 \rightarrow 2$ rotational excitation of H_2 by collision with Li^+ . Even though

only a few quantum states are involved in this process, they nevertheless find quite good agreement between their quasi-classical trajectory calculation³ and the accurate coupled channel quantum mechanical calculations of Lester and Schaefer.⁴

Green and Thaddeus⁵ have recently carried out accurate quantum mechanical coupled channel calculations for rotational excitation of CO by He, and this has motivated us to generate the classical trajectory results to provide another comparison of dynamically exact classical mechanics with dynamically exact quantum mechanics. To provide an even more stringent test of the classical approach we have carried out a similar calculation for the $0 \rightarrow 2$ rotational excitation of H_2 by He, comparing with Shafer and Gordon's⁶ and Green's⁷ accurate coupled channel calculations. The He - H_2 system should be the weakest rotational transition of any atom-diatom collision system and the one for which the purely classical treatment is thus most questionable.

II. METHODOLOGY

The He - CO and He - H₂ collision systems are both treated as rigid rotor-atom system, the potentials being the same as those used for the quantum calculations.^{5,6} The classical calculations were carried out in a way which is equivalent to the now standard quasi-classical trajectory procedure.⁸

The rotational quantum number j is defined by

$$E_{\text{rot}} = B \left(j + \frac{1}{2} \right)^2 \quad (2.1)$$

where E_{rot} is the classical rotational energy of the rotor and B the rotational constant ($B_{\text{H}_2} = 60.99 \text{ cm}^{-1}$, $B_{\text{CO}} = 1.9226 \text{ cm}^{-1}$). Trajectories were all begun with $j = 0$, and after collision the final rotational quantum number was determined by first solving for the final non-integral value of j from equation (2.1) and then assigning the closest integer (the closest even integer for H₂). The cross section for the $0 \rightarrow j$ transition is then given by

$$\sigma_{j \rightarrow 0} = \pi b_{\text{max}}^2 (N_j / N_{\text{tot}}) \quad (2.2)$$

where b_{max} is the maximum impact parameter which defines the usual impact parameter sampling⁸ (i.e., $b = b_{\text{max}} \sqrt{\xi}$, where ξ is a random number), N_{tot} is the total number of trajectories run, and N_j is the number of these for which the final rotational quantum number is j .

III. RESULTS

Figure 1 shows the results of the trajectory calculations for the $0 \rightarrow 2$ rotational excitation of H_2 by He, compared with the quantum mechanical results of Shafer and Gordon⁶ and Green⁷; this comparison is entirely analogous to that made by La Budde and Bernstein³ for $Li^+ + H_2$. The agreement of the classical and quantum results in Figure 1 is not as good as that for the $Li^+ + H_2$ case,³ but this is expected since the cross section for He - H_2 is much smaller and for $Li^+ - H_2$. Given the fact that the He - H_2 system should be as weak a rotational excitation as for any molecular collision system, the agreement in Figure 1 is encouraging.

Cross sections for the $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, and $0 \rightarrow 4$ excitations of CO by He are shown in Figure 2 as a function of initial translational energy, along with the quantum mechanical results of Green and Thaddeus.⁵ The overall agreement is quite reasonable, probably typical of what one should expect of a quasi-classical trajectory calculation.

A more interesting comparison, which reveals some of the inherent limitations of a purely classical theory, is shown in Figure 3; here the cross section for the $0 \rightarrow j$ excitation is plotted as a function of j for a fixed initial translational energy. (The comparison is similar for other values of E .) The quantum mechanical results⁵ show an oscillatory structure which the classical values do not reproduce; this is the reason that the classical cross sections for the $0 \rightarrow 2$ and $0 \rightarrow 3$

transitions in Figure 2 are consistently too small and too large, respectively.

This interference effect seen in Figure 3 can be understood as the remnant of the $\Delta j = 2$ selection rule that would exist if CO were a homonuclear molecule; i.e., if CO were homonuclear the $0 \rightarrow j$ cross sections would be identically 0 for odd j , rather than simply diminished. This means that the P_2 term in the He - CO potential is somewhat stronger than the P_1 term. (For the homonuclear case P_1 term is completely absent.)

Classical S-matrix theory^{1,2}--a semiclassical approach which uses classical trajectories but which also incorporates the superposition principle of quantum mechanics--is able to account for the $\Delta j = 2$ selection rule for the homonuclear case quite naturally: classical trajectories with odd Δj exist in the homonuclear case, but the addition of the appropriate amplitudes results in totally destructive interference and thus a net amplitude of zero for these transitions. For the "almost homonuclear" case there will still be this type of interference which diminishes--but does not completely annihilate--the odd Δj transitions. It is clear, therefore, that a classical S-matrix calculation would produce the interference structure seen in Figure 3; such a calculation, however, is more difficult to carry out than the present purely classical ones.

IV. CONCLUDING REMARKS

This paper has presented two more comparisons of exact classical and exact quantum mechanics for a three dimensional atom-diatom collision. The results tend to support the thesis that a purely classical approach is quite useful for describing inelastic collision processes that are classically allowed. It has also been noted that rotational excitation is almost always a classically allowed process, even for perhaps the weakest of all possible cases, the excitation of H_2 by He. Purely classical approaches cannot, of course, produce quantum interference effects, such as those seen in Figure 3; if it is necessary to describe these effects correctly, then a more sophisticated theory will be required, eg. a purely quantum treatment, or an approach such as classical S-matrix theory.

Finally, we have not addressed the question of which approach--coupled channel or classical trajectory--is easier computationally, i.e., takes less computer time. The quantum calculations become easier the lower the collision energy because fewer channels are required in the coupled channel expansion. The classical calculations, on the other hand, become easier with increasing energy because the trajectories run faster. (A typical He - CO trajectory took 1.0 and 0.4 seconds at an energy of 10 and 150 cm^{-1} , respectively, on a CDC 7600; a He - H_2 trajectory required 0.08 - 0.09 seconds for the entire energy range 600-5000 cm^{-1} .) At what energy the computational advantage switches from the quantum to the classical approach is not clear, and it will of course depend on the particular system

under study. The important point is that there seems to be a broad overlap of the regions for which the quantum and the classical calculations can both be carried out with reasonable effort and for which the classical treatment is moderately reliable.

ACKNOWLEDGMENT

This work was stimulated by the coupled channel calculations carried out by Green and Thaddeus, and we would like to thank them for making their results available to us prior to publication. We would also like to thank Dr. S. Green for carrying out the coupled channel calculations for He - H₂ at energies above 900 cm⁻¹ and communicating his results to us.

REFERENCES

- * Supported in part by the U. S. Atomic Energy Commission,
and by the National Science Foundation under grants GP-34199X
and 41509X.
- † Camille and Henry Dreyfus Teacher-Scholar.
1. For a more precise discussion of the terms "classically
allowed" and "classically forbidden" in the sense that
we use them, see for example, W. H. Miller, J. Chem.
Phys. 53, 3578 (1970). See also ref. 2.
 2. For a review, see W. H. Miller, Adv. Chem. Phys. 25,
63 (1974); pp. 112-114 discuss the semiclassical origin
of selection rules.
 3. R. A. La Budde and R. B. Bernstein, J. Chem. Phys. 59,
3687 (1973).
 4. W. A. Lester and J. Schaefer, J. Chem. Phys. 59, 3676
(1973).
 5. S. Green and P. Thaddeus, to be published.
 6. R. Shafer and R. G. Gordon, J. Chem. Phys. 58, 5422
(1973).
 7. S. Green, private communication.
 8. See, for example, M. Karplus, R. N. Porter, and R. D.
Sharma, J. Chem. Phys. 43, 3259 (1965). For a recent
review, see D. L. Bunker, Methods in Comp. Phys. 10,
287 (1971).

FIGURE CAPTIONS

Figure 1. The cross section for the $0 \rightarrow 2$ rotational excitation of H_2 by He, as a function of initial translational energy. The solid curve shows the accurate quantum mechanical calculations of Shafer and Gordon⁶ and Green,⁷ and the dashed curve the classical trajectory results.

Figure 2. The cross section for the $0 \rightarrow j$, $j = 1 - 4$, rotational excitation of CO by He, as a function of initial translational energy. The solid curve is the accurate quantum mechanical result of Green and Thaddeus,⁵ and the dashed curve the results of the classical trajectory calculation.

Figure 3. The same quantity as in Figure 2 (solid line = quantum, dashed line = classical) but shown as a function of final rotational quantum number j for a given initial translational energy $E = 100 \text{ cm}^{-1}$.

Fig. 1

Fig. 2

XBL 745-6291

Fig. 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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