1Bp02

ON THE DETERMINATION OF CAUSTICS AND THE INCORPORATION OF TUNNELING EFFECTS INTO CLASSICAL TRAJECTORY SIMULATIONS.

(GUAS, IMS) **O** P. Oloyede, G.V. Mil'nikov, H. Nakamura

Classical and semiclassical methods are known to be effective tools in treating chemical reaction dynamics. However these methods cannot take into account purely-quantum effects such as tunneling. All the approaches which have been suggested to remedy this drawback depend importantly on being able to accurately specify the boundary between the classically-allowed and classically-forbidden region (**caustics**)[1].

Generally, the caustics are to be found as singularities of Jacobi matrix dP/dQ which satisfies a certain differential equation [2] with initial condition appropriate for a specified reaction process (initial quantum number). However, as opposed to the case of finding the focal point from the monodromy matrix, these singularities of dP/dQ prevent the successful propagation through the caustic. We avoid this problem by formulating a mathematical recipe, which transforms this Jacobi matrix into a form amenable to smooth propagation through the singularity. This transformation is completely general such that it ensures successful propagation even through regions of multiple singularities (i.e. caustics occurring in more than one direction). Thus, we are able to determine accurately the caustics for a family of trajectories for a given reactive process.

As a demonstration, we apply our method to a model tri-atomic system with total zero angular momentum, (**J = 0)**, using the conventional classical trajectory simulation but with the added refinement of including tunneling effects.

The recipe is conceptually simple, easy to implement and has no limitation imposed by dimensionality.

References

[1] K. Takatsuka, H. Ushiyama and A. Inoue-Ushiyama, Phys. Rep. 322, 5 (1999)
[2] G.V Mil'nikov and H. Nakamura, J. Chem. Phys. 115,6881 (2001).