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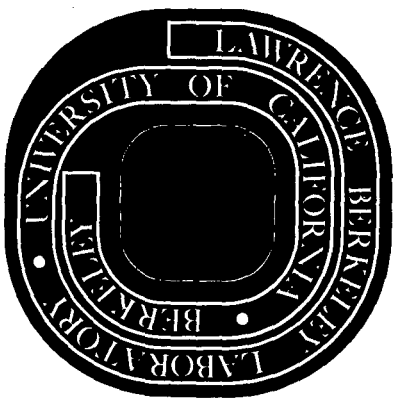

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Direct Integration of the Classical Equations of Motion for Classically Forbidden Collision Processes*

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There has been much interest and progress recently in semiclassical formulations of molecular scattering that permit one to use numerically computed classical trajectories to construct classical-limit approximations to quantum mechanical S-matrix elements for transitions between individual quantum states.[1,2]

One of the situations in which this "classical S-matrix" theory seems likely to be most useful is that of weak, or "classically forbidden" transitions. In previous work[1c] classically forbidden processes have been described by numerical analytic continuation of the appropriate classical trajectory functions, and here we report success in direct numerical integration of the classical equations of motion through classically inaccessible regions of coordinate and momentum space. This way of describing classically forbidden processes is more general and potentially much more powerful than that of numerical analytic continuation; e.g., reactive tunneling and non-adiabatic electronic transitions can be treated by direct integration of the equations of motion, but not by numerical analytic continuation. (When the two approaches can both be applied then, of course, they give precisely the same results since they are different ways of analytically continuing the same expressions.)

The physical system investigated initially is the linear non-reactive A + BC collision (vibrational excitation) as studied quantum mechanically by Secrest and Johnson.[3] The semiclassical formulation of the problem is precisely as before, and the reader should consult reference 1b for these details. In constructing

the 0→1 vibrational transition probability, for example, the primary task is to find the classical trajectory (or trajectories) for which the vibrational quantum number (more precisely, the action variable of the vibrational degree of freedom) is 0 initially and 1 finally. To do this one considers the classical trajectory function $n_2(q_1,n_1)$, the final vibrational quantum number that is determined by the classical trajectory with initial values n_1 and q_1 for the vibrational quantum number and its conjugate angle variable.[4] The 0→1 transition, therefore, is constructed from those trajectories that satisfy the equation $n_2(q_1,0) = 1$.

The 0→1 transition is classically forbidden if there are no real values of q_1 for which $n_2(q_1,0) = 1$; there will, however, be complex roots of this equation. An earlier attempt[1c] was made at finding these complex roots by allowing q_1 to take on complex values and integrating the equations of motion in the usual manner (with appropriate COMPLEX statements inserted in the computer routines). This was not successful, however, for the following reason: with q_1 complex, $n_2(q_1,0)$ is in general complex (until the "right" value of q_1 is found), and trajectories for which n_2 is complex are <u>divergent</u>. This is easy to see by noting that the solution for $q(t)$ in the final asymptotic region is $q(t) = \varepsilon'(n_2)t$ + constant, where $\varepsilon(n)$ is the vibrational eigenvalue function. If n_2 is complex, the imaginary part of q thus increases with t, so that the physical vibrational coordinate $r \equiv (2n+1)^{1/2} \cos q$ becomes infinite.

The situation, therefore, is that the trajectory is well-behaved if q_1 is the particular complex value for which $n_2(q_1,0) = 1$, but it diverges if q_1 is only slightly different from this value. The way out of this unstable state of affairs is simple (in retrospect): one begins the trajectory at <u>both ends</u> with the initial values $n_1 = 0$ and q_1, and final values $n_2 = 1$ and q_2, and integrates both branches toward the interaction region; the initial and final angle variables q_1 and q_2 are adjusted iteratively so that all the coordinates and momenta are equal at some intermediate point (see below). Since the two quantum numbers are real in their respective asymptotic regions, the trajectories are perfectly well-behaved.

For such trajectories all the coordinates and momenta, and the time also, must be allowed to be complex. This causes no inconsistencies, however, since the scattering boundary conditions require only that n(t) and R(t) be real in the initial and final asymptotic regions; as a consequence of energy conservation, P(t) is also real asymptotically, but the angle variable q is completely unrestricted.[5] Likewise, the path in the complex time plane along which the trajectory is integrated need not be the real time axis, but is restricted only in that $\mathrm{Re}(t_2-t_1) \to +\infty$, $\mathrm{Im}(t_2-t_1) =$ finite.

More specifically, the initial branch of the trajectory is assigned initial conditions (for the 0→1 transition, for example) $n_1 = 0$, q_1, $R_1 =$ large, $P_1 = -\sqrt{2\mu[E-\varepsilon(n_1)]}$, and the final branch has final values $n_2 = 1$, q_2, $R_2 =$ large, $P_2 = +\sqrt{2\mu[E-\varepsilon(n_2)]}$. The initial branch of the trajectory is integrated[6] forward in

time to that (complex) time at which P = 0, and the final branch is similarly integrated backward in time to the (complex) time at which P = 0. The quantities Δn and Δq are the differences of n and q on the two branches at this intermediate point; considering them as functions of q_1 and q_2, one must thus solve the two simultaneous equations $\Delta n(q_2,q_1) = 0$, $\Delta q(q_2,q_1) = 0$. With these particular values of q_1 and q_2 it is clear that the two branches have the same values of n, q, and P at this intermediate point, and by energy conservation it follows that they must also have the same value of R; i.e., all the coordinates and momenta match at this intermediate point, so that the two branches form one complete trajectory for which $n_1 = 0$ and $n_2 = 1$. From the classical action along this trajectory and the Jacobian associated with it, it is then a simple matter to construct the 0→1 transition probability.[1c]

Application of this procedure has given extremely encouraging results; all of the classically forbidden transitions reported in reference 1c, and others not accessible by the method described there, are calculable by this procedure (and, of course, give the same numerical values). In other applications, such as reactive tunneling, the matching criteria in the intermediate region will have to be re-designed, but should otherwise proceed in a similar manner. The important feature that has been learned is the unstable character of "classically forbidden trajectories" and that it can be circumvented by integrating inward from both ends of the trajectory. More details will be reported subsequently.

References

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2. (a) R.A. Marcus, J. Chem. Phys. 54, 3965 (1971); (b) J.N.L. Connor and R.A. Marcus, ibid. 55, 5636 (1971); (c) R.A. Marcus, ibid. 56, 311 (1972).
3. D. Secrest and B.R. Johnson, J. Chem. Phys. 45, 4556 (1966).
4. Initial values for the translational coordinate and momentum R and P are R_1 = large, $P_1 = -\{2\mu[E-\varepsilon(n_1)]\}^{1/2}$.
5. A vibrational quantum state is characterized semiclassically by a specific (integer) value of the action variable n, so that the Uncertainty Principle implies that the conjugate angle variable q is completely unspecified and thus may be complex. The fact that the physical vibrational coordinate and momentum r and p may be complex is irrelevant, for they are not the observables (n is).
6. Since the time increments Δt for the numerical integration are allowed to be complex, and therefore unequal in various parts of the trajectory, we have devised a numerical integrater that is analogous to a fifth-order Adams-Moulton routine but for which the time increments may be different at each step.

Since the routine automatically picks an optimal step-size at each step, we have found incidentally that this "variable step-size Adams-Moulton" integrater is more efficient for ordinary classical trajectories than the conventional Adams-Moulton integrater.

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