Section 17.4:Continuous Surface Switching: Refinements and Extensions*

This model contains two adjustable parameters, V_0 and η. The guiding principle for a suitable choice of V_0 is to prevent any spurious mixing of the contributing electronic states as the system approaches the interaction zone. If the value V_0 is too low, the simulation will move too close to the Ehrenfest extreme, implying the possibility of state coupling beyond the nonadiabatic regime. Correspondingly, choosing V_0 too high will suppress physical mixing effects. As outlined in [45], a strategy that involves monitoring the first significant extremum of the population variable n_1 or n_2 as a function of time can be applied to obtain the desired compromise value for V_0.

The parameter η made explicit by relation (17.79) allows for further improvement of the method. From the definition of W, it follows that the choice $\eta = 0$ will asymptotically populate the state that is more strongly occupied as the system leaves the interaction zone. If the order of n_1 and n_2 reflects that of the quantum mechanical populations, this procedure can be expected to yield realistic results. It is, however, more accurate to determine η in a self-consistent fashion. For this purpose, one may start by evaluating the average asymptotic population difference $\Delta n = \lim_{t\to\infty}\langle n_2 - n_1\rangle$ for a set of trajectories run in the Ehrenfest limit, i.e. for small or vanishing Q. For a subsequently computed batch of trajectories, Q is treated in accordance with Eq.(17.82), and η provides the initial guess for the quantity Δn. This will lead to a new average of $n_2 - n_1$ etc. The iteration may be terminated when the fraction of trajectories that end in state 2 is equal to $\langle n_2\rangle$, the average of the population variable for this state.

The outlined model gives one example for a generalized nonadiabatic trajectory scheme that allows to shift back and forth between complementary approximations, according to their respective domains of validity. More refined approaches have been suggested. Thus, a *generalized continuous surface switching* (GCSS) procedure [48] has been introduced that implements the same methodological idea as the CSS model but utilizes a more realistic parametrization of the weight functions w_k which are designed to satisfy conditions not automatically fulfilled by the CSS formalism. Among these criteria is the constraint that w_k has to reduce to zero or one for all k. Further, it holds that $w_k = 1$ if $n_k = 1$, and that the coefficients that determine V_c (see Eq.(17.74)), equated in the CSS approach to $\rho_{kk'} = \sqrt{n_k n'_k}\cos(q_k - q'_k)$, $k \neq k'$, vanish if $w_k = 1$ or $w_k = 0$. Extensive test calculations have been carried out, involving reaction and quenching processes of the form [48]:

$$M^* + HX(v,k) \to H + MX(v',j') \tag{1}$$

$$M^* + HX(v,k) \to M + HX(v'',j''), \tag{2}$$

with M as a model metal atom and X as a pseudohalogen. The labels v and j denote vibrational and rotational quantum numbers, respectively. Various quantities characteristic of the considered processes, among them reaction and quenching probabilities, were obtained by fully quantal computations, as well as

a variety of approximations to the quantal treatment, such as trajectory surface hopping in the fewest switches version (Sect.11.2), Ehrenfest dynamics, and the CSS and GCSS models. This assessment demonstrated the latter method to be superior to both the CSS and the Ehrenfest method, and to perform at least as successfully as the fewest switches procedure.

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