MQCT – A PROGRAM FOR CALCULATIONS OF INELASTIC SCATTERING OF TWO MOLECULES

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We develop theoretical methodology and write a user-ready computer program to cary out the calculations of rotational-vibrational-translational energy transfer in a collision of two molecules, within a framework of the mixed quantum/classical theory (MQCT). In this approach the translational motion of scattering partners is treated classically, while the internal motion of each molecule (rotation, vibration) is described by quantum mechanics [1]. Time-dependent framework is adopted, which includes the propagation of mean-field trajectories for the translational motion (the Ehrenfest approach), and the time-evolution of probability amplitudes for the internal quantum states of the molecules, driven by their collision process. Energy is exchanged between the translational, roattional, and vibartional degrees of freedom but the total energy is concerved (on average).

Within MQCT, both integral and differential cross sections can be computed for transitions between the individual quantum states of collision partners without “binning” of trajectories into any “boxes”, since the probability amplitudes carry all nesessary information about the state-to-state transitions. Moreover, the phases of internal states, introduced in the expansion of MQCT wavefunction, give rise to the relative phase shifts in the equations of motion, and, together with scattering phases (extracted from MQCT trajectories), allow to reproduce a rather complex pattern of *quantum interference* in the differential cross sections, including that for the elastic channel. Recall that neither elastic, nor differential cross section can be reproduced by purely classical trajectories, due to the lack of phase information. However, the MQCT approach has phase information available which permits to capture the quantum interference effects [2,3].

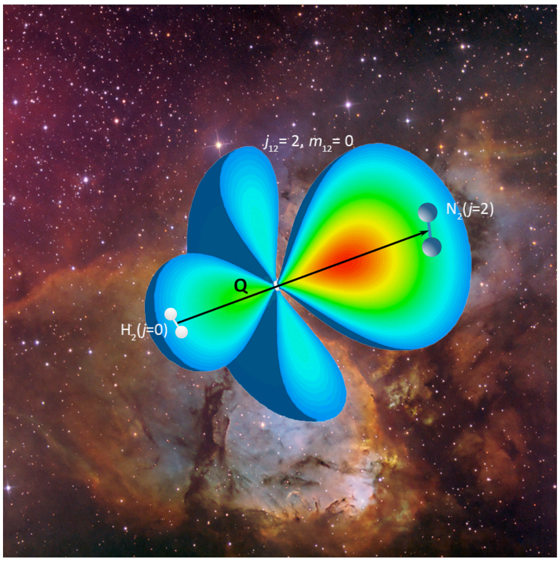

Figure 1: Rotational wave function of N_2 + H_2 system in MQCT calculations, and the molecule-molecule vector treated classically.

Since the translational motion of two collision partners is treated classically, MQCT cannot describe “shape” resonances populated by tunneling, but we found that Feshbach-type resonances, formed by the coupling between open and closed quantum channels, are amenable to the MQCT treatment. Namely, the so-called *orbiting trajectories* in MQCT represent the analogue of quantum Feshbach resonances. They produce a pattern of “spikes” in the energy-dependence of cross sections, very similar to pattern of quantum resonances at low collision energies [2,3].

Another interesting quantum feature, that MQCT allows describing, is the selection rules (allowed vs forbidden transitions) in homonuclear diatomic molecules, such as N_2, and the propensity rules in polyatomic molecules, such as H_2O. Purely classical trajectories do not reproduce these properties, and it is often argued that only the full-quantum methods can reproduce them. Importantly, MQCT has these features, built rigorously into the state-to-state transition matrix. For example, in the case of N_2 only the $\Delta j = \pm 2, \pm 4, \pm 6$, etc., transitions are allowed, others are forbidden, strictly [4]. In the case of H_2O the transitions with $\Delta k = \pm 1$ are

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strongly favored [5]. Another relevant quantum phenomenon is indistinguishability of the identical collision partners, which can also be described within MQCT by appropriate symmetrization of the overall wavefunction, for say $H_2O + H_2O$.

One may think that for MQCT we need a huge number of trajectories (by analogy with a purely classical approach) in order to sample all relative orientations of two collision partners. This is a common misconception, since the rotational motion of both molecules in MQCT is described by wavefunction, so, all relative orientations are captured at once, just like in the full-quantum method. Trajectories are used to sample only the orbital angular momentum ℓ of two collision partners, treated classically (basically, the dependence of opacity function on impact parameter). These dependencies are typically simple, and a few dozens of trajectories is often enough. Including every single value of ℓ is required only for construction of the differential cross section (to reproduce the interference pattern), but for the integral cross section this is not needed, and one can employ an efficient Monte-Carlo sampling technique. Moreover, the sampling of collision energies can be conducted at the same time, to facilitate the calculation of averaged moieties, such as thermal rate coefficients.

The most demanding component of the full-coupled MQCT calculations is calculations of the potential gradient averaged over all quantum states of collision partners (the mean-field potential) at each time step. But recently we proposed a simplified version of MQCT, in which the classical and quantum degrease of freedom can be partially decoupled. This method, named *adiabatic trajectory*, or AT-MQCT, happens to be both efficient and accurate [6,7]. For example, using the existing (preliminary) version of MQCT code we measured the costs of calculations for $H_2O + H_2$ system at collision energy 500 cm^{-1} (see Fig. 2). It shows that for 100-200 quantum channels the CPU cost of AT-MQCT method is almost four orders of magnitude lower than that of full-quantum calculations, and this big advantage is expected to hold for larger number of channels. Figure 2 also shows that in practice the cost of full-quantum calculations scales as N^4 and becomes absurd reaching years for triatomic + triatomic or polyatomic + diatomic systems. In contrast, the total CPU cost of MQCT calculations is expected to remain in the range of few hours. Moreover, the intrinsic parallelism of the method, and a multilevel parallelization implemented in our code, permit to keep the wall-clock time within few minutes (per energy point), making MQCT calculations practical.

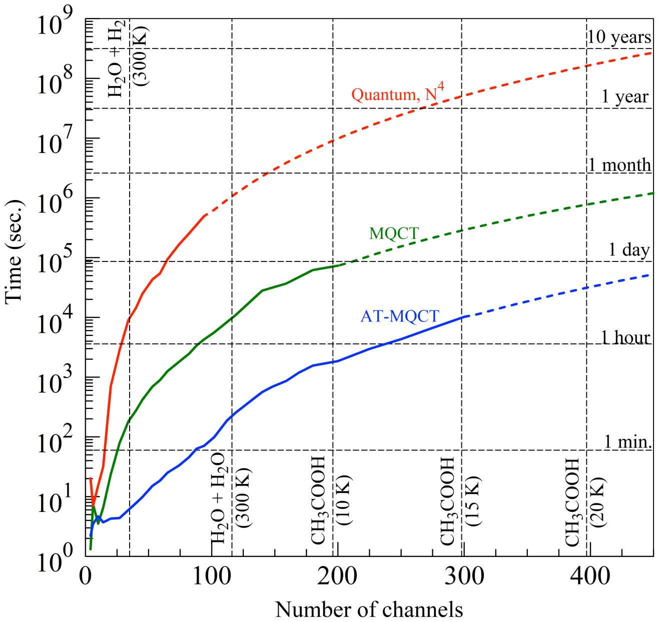

Figure 2: Numerical cost of two versions of MQCT vs full-quantum calculations (MOLSCAT), for molecular systems of increasing complexity (number of channels).

In MQCT program there are ten system types, summarized in Table 1, from the simplest rigid-diatom + atom, to the most general case of two asymmetric-top rotor molecules. For each system, MQCT calculations can be initiated by indicating the rotational and vibrational constants listed in the Table. Those are used by the code to set up and diagonalize Hamiltonian matrix for rotational motion (using the basis set of symmetric-top functions) in order to determine the rotational states of the system (energies and wave-functions). In this version of MQCT the vibartional motion is supported for the diatomic molecules only, but the goal is to introduse vibration for other system types in the future.

Table 1: Ten types of systems handled by MQCT, with required and optional input

SYS_TYPE	**Collision Partners**	**Required Constants**	**Channel Labels**	**Optional Input**
1	rigid diatom + atom	B_e, D_e	j	
2	vibrating diatom + atom	B_e, D_e, ω_e, x_e	j, v	vibrational functions, non-equidistant grid
3	symmetric top + atom	A, C	j, k, ε	
4	asymmetric top + atom	A, B, C	j, k_a, k_c	expansion over symmetric top basis
5	rigid diatom + rigid diatom	B_{e1}, D_{e1}, B_{e2}, D_{e2}	j_1, j_2	
6	vibrating diatom + vibrating diatom	B_{e1}, D_{e1}, ω_{e1}, x_{e1}, B_{e2}, D_{e2}, ω_{e2}, x_{e2}	j_1, v_1, j_2, v_2	vibrational functions, non-equidistant grid
7	symmetric top + rigid diatom	A, C, B_e, D_e	j_1, k_1, ε_1, j_2	
8	asymmetric top + rigid diatom	A, B, C, B_e, D_e	j_1, k_{a1}, k_{c1}, j_2	expansion over symmetric top basis
9	asymmetric top + symmetric top	A_1, B_1, C_1, A_2, C_2	j_1, k_{a1}, k_{c1}, j_2, k_2, ε_2	expansion over symmetric top basis
0	asymmetric top + asymmetric top	A_1, B_1, C_1, A_2, B_2, C_2	j_1, k_{a1}, k_{c1}, j_2, k_{a2}, k_{c2}	expansion over symmetric top basis

The default method in the code is the full-coupled MQCT, named CC-MQCT, but the approximate AT-MQCT calculations (mentioned above) can also be requested as an option. The third option is a well-known coupled-states approximation, named here CS-MQCT, where the Coriolis coupling is neglected.

Two options are available for computation of the potential coupling matrix. One (hystoric) is the traditional expansion of the interaction potential over the basis set of analytic functions (spherical harmonics, Wigner *D*-functions). This option is numerically efficient, but is known to have issues with trancation of the basis set for the cases of more complicate molecules. Therefore, the default in the code is a brute force integration of matrix elements by numerical multidimentional quandrature. In both cases users should supply a PES subroutine expressed using a set of Euler angles for each collision partner, relative to the molecule-molecule reference frame.

A detailed user manual and an example of input file for each system type will be provided with the code.

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