# Mixed Quantum/Classical Approach for Description of Molecular Collisions in Astrophysical Environments

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S *Supporting Information*

ABSTRACT: An efficient and accurate mixed quantum/classical theory approach for computational treatment of inelastic scattering is extended to describe collision of an atom with a general asymmetric-top rotor polyatomic molecule. Quantum mechanics, employed to describe transitions between the internal states of the molecule, and classical mechanics, employed for description of scattering of the atom, are used in a self-consistent manner. Such calculations for rotational excitation of $HCOOCH_3$ in collisions with He produce accurate results at scattering energies above 15 cm^{-1}, although resonances near threshold, below 5 cm^{-1}, cannot be reproduced. Importantly, the method remains computationally affordable at high scattering energies (here up to 1000 cm^{-1}), which enables calculations for larger molecules and at higher collision energies than was possible previously with the standard full-quantum approach. Theoretical prediction of inelastic cross sections for a number of complex organic molecules observed in space becomes feasible using this new computational tool.
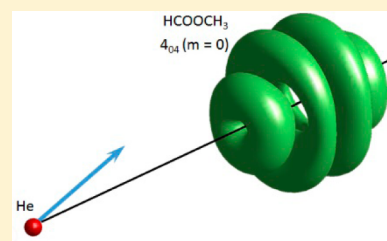
To the present day more than 200 molecular species have been detected in space, including some complex organic molecules and long carbon chains.[1−6] For quantitative interpretation of their observed spectra the inelastic state-to-state transition cross sections for these molecules collided with background gases (H_2 and He in the interstellar medium, or H_2O in cometary environment) are needed, often in a broad range of collision energies. This information, however, is largely missing, and there is no simple way of determining it from experiments. Collisional cross sections could be computed within quantum-mechanical framework[7,8] by numerically solving the Schrödinger equation for nuclear motion of colliding partners, but such brute-force calculations are computationally affordable for only some of the smallest molecules and only at low energies of collision.[1,9] For example, quantum calculations of $H_2O + H_2$ in the required range of collision energies (up to $T = 1500$ K) have been achieved just recently[10] and represent the state-of-the-art in the field. Calculations for $HCOOCH_3$ + He have been attempted[11] but were shown to be computationally affordable only for collision energies below 30 cm^{-1}. Such important process as scattering of $H_2O + H_2O$ in the desired energy range (up to $T \approx 300$ K) is also beyond the reach of theorists. This is quite demonstrative because many astrophysically important molecules are larger than H_2O, for example: CH_3CHO, CH_3OCH_3, C_2H_5CN, C_6H_2, CH_3C_4H, and HC_5N.[1,11−13] One should admit that although a significant progress has been made on inelastic scattering calculations for small molecules and at low collision energies,[1,2] the standard full-quantum approach is basically stuck when the molecules are heavy and the collision energy is large, when molecule−molecule collisions are important, or when in addition to rotation the vibrational motion (torsion, bending) has to be taken into account. Thus, it is desirable to develop an alternative or complementary approach that would

allow circumventing the computational difficulties by employing some kind of approximation.

Recently we developed a mixed quantum/classical theory (MQCT) for inelastic scattering[14,15] where the internal motion of the molecule is still treated quantum mechanically, while the scattering of the atom is described approximately using classical mechanics (Newtonian trajectories), which reduces the computational cost dramatically. We rigorously tested this theory by applying it to CO + He,[16] H_2 + He,[17] N_2 + Na,[18] and H_2O + He,[19] and obtained very good agreement with the standard full-quantum treatment in a broad range of collision energies (computationally affordable for these simpler molecules). We found that MQCT gives a detailed description of the scattering process, even at the level of differential cross sections in the forward scattering quantum regime,[17,18] which is a known unresolved issue for all semiclassical methods.[20] At higher collision energies it reproduces the full-quantum results almost exactly, but even at low collision energies the predictions of MQCT are reasonable.[16−19] The only feature that MQCT does not reproduce is scattering resonances at very low collision energies, near the threshold of the excitation process. In the past decade, a family of closely related theoretical methods has been developed using the quantized Hamiltonian dynamics (QHD) approach.[21−23] They also utilize the mixed quantum/classical ideas based on the Ehrenfest mean-field potential but in a different fashion.

It is interesting that foundations of this theory were laid out by Billing in the 1980s and 90s,[24,25] but then it was largely abandoned without been properly tested. Our recent progress

on diatomics and triatomics was rapid,[14−19] which demonstrated that MQCT can be used as an efficient predictive computational tool for small molecules; however, it is often a challenge to extend an approximate method onto the complex systems. New problems may appear, such as difficulty of accurate representation of the potential energy surface, density of rotational spectrum of a heavy asymmetric-top rotor, and higher costs of numerical calculations, to name just a few. Our goal nowadays is to apply MQCT to several complicated problems, such as small organic molecules of astrophysical importance, which would represents a major step forward.
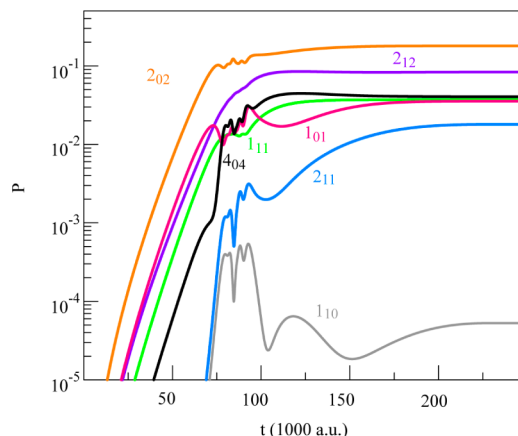
We report MQCT results for rotational excitation of $HCOOCH_3$ (methyl formate) by He in the range of collision energies up to 1000 cm^{-1}, typical for warm star-forming regions. To our best knowledge this is the largest molecule ever considered for the inelastic scattering calculations.[1] The full-quantum scattering results (available for this process at low energy only[11]) serve as a benchmark and demonstrate that our approach is accurate. Our general conclusion is that at medium and higher collision energies, when quantum scattering resonances are not important, MQCT can confidently replace the full-quantum scattering approach. MQCT remains computationally affordable and enables theoretical predictions of inelastic cross sections for larger molecules and at higher collision energies than was possible before, in particular, for the processes of astrochemical importance.

The details of our theory are given in the Supporting Information. In a nutshell, we propagate batches of MQCT trajectories to sample the classical impact parameter for collisions between He and $HCOOCH_3$. Such trajectories are driven by the mean-field potential, averaged over the rotational wave function of the molecule (see the TOC image). Typically, the number of trajectories on order of a hundred is sufficient to capture the dependence of transition probability on the impact parameter, as shown in Figure 1. As trajectory progresses, the evolution of rotational wave function of the molecule is determined by the system of coupled differential equations that includes elements of the transition matrix due to interaction with the atom. In this way, the scattering motion of the atom and the rotational motion of the molecule affect each other, and
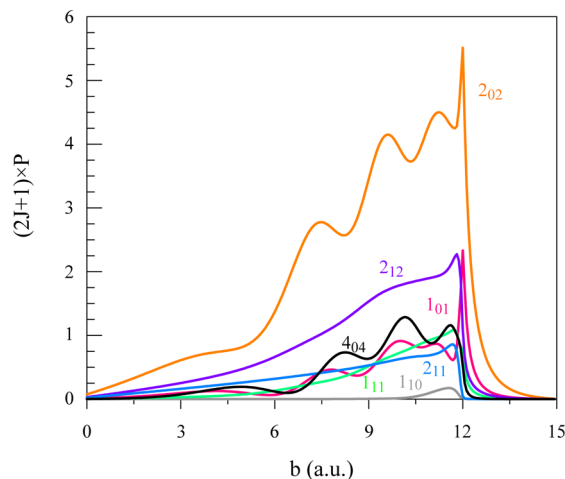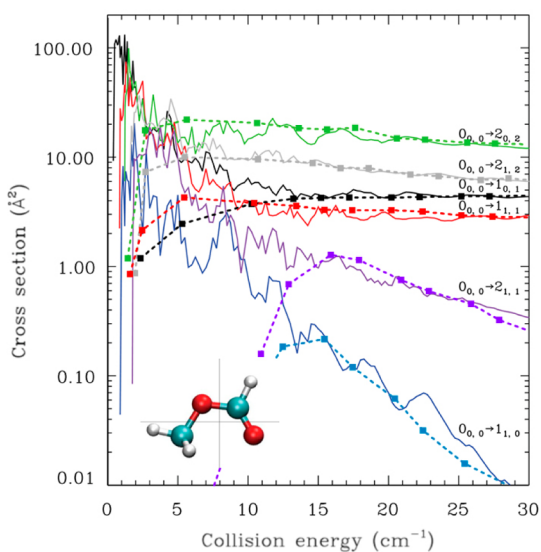
the quantum and classical degrees of freedom are treated self-consistently. The energy is exchanged between translation and rotation, while the total energy is conserved. Figure 2 illustrates

Figure 2. Evolution of state populations in $HCOOCH_3$ along a typical MQCT trajectory that describes its collision with He. The collision energy is 17 cm^{-1}, and the impact parameter is 10.5 a_0. The color of state labels corresponds to the color of curves.

evolution of state populations along a typical MQCT trajectory. In this picture the atom-molecule encounter occurs in the short time interval between $t \approx 70$ and 100×10^3 a.u. Two scenarios of rotational excitations can be identified. For the majority of states the population starts growing exponentially on the precollisional stage and remains almost constant on the post collisional stage. Examples are 2_{02}, 2_{12}, 4_{04}, 1_{11}, and 1_{01}. However, for some states the population starts growing much later, basically during the collision, and continues evolving at the postcollisional stage. Examples are 2_{11} and 1_{10}. This difference comes from the fact that the first group of states is populated by transitions directly from the ground state 0_{00} due to *potential coupling*. The second group of states is populated due to *centrifugal coupling* with other excited states, indirectly, and only after those intermediate states receive enough population. This leads to a later start, longer time evolution, and lower transition probabilities (see Figure 2). As discussed later, such transitions are often neglected by the coupled-states (or centrifugally sudden) approximation, but they are included in MQCT calculations. In either case, the populations of rotational states of the molecule at the end of trajectories are used to compute the state-to-state transition cross sections.[16]

In Figure 3 we compare our MQCT results against the available full-quantum results from ref 11 for rotational excitation of the ground state 0_{00} of $HCOOCH_3$ to several low-lying rotationally excited states using the same potential energy surface. For the most important states (large cross sections) the agreement is excellent: In the energy range 15−30 cm^{-1}, where quantum resonances level off, the typical differences are on the order of only 5%. For the less important state $1_{1,0}$ (small cross section) the difference is somewhat larger near, but it should be stressed that our MQCT results are fully converged with respect to the number of partial waves (J_{max} = 20), while convergence of the full-quantum data from ref 11 for the state $1_{1,0}$ was reported as ∼20% (i.e., not entirely converged, due to high computational cost of better calculations), which explains larger difference obtained for this state. To make comparison meaningful, the rotational basis

Figure 1. Dependence of quantum transition probability on classical impact parameter for excitation (by He collision) of $HCOOCH_3$ from its ground rotational state $0_{0,0}$ into several final rotational states. The collision energy is 17 cm^{-1}. The color of state labels corresponds to the color of curves.
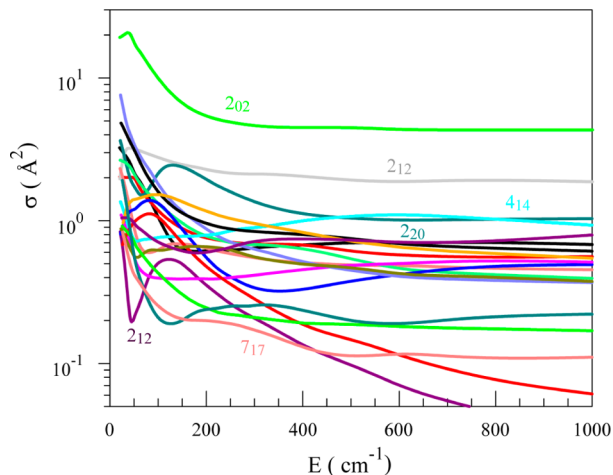
Figure 3. Inelastic cross sections for excitation of several rotationally excited states of HCOOCH$_3$ from its ground state in collisions with He at low scattering energies. Results of the full-quantum calculations from ref 11 are shown by solid lines. Our MQCT results are shown by symbols of the same color (connected by dashed lines for clarity). The inset shows the molecular structure of methyl formate. Reproduced with permission from ref 11. Copyright 2011 AIP Publishing LLC.

Figure 4. Inelastic cross sections for excitation of 20 most important rotationally excited states of HCOOCH$_3$ from its ground state computed by MQCT for a broad range of collision energies. Some of the final states are labeled, and others are listed in the text.

set size in our MQCT calculations was taken the same as in ref 11, namely, $j_{max} = 14$ (225 channels).

In the lower energy range, 5−15 cm^{-1} in Figure 3, the results of MQCT for the most important transitions are still reasonable. The accuracy of MQCT drops significantly only at collision energies below 5 cm^{-1}, where quantum resonances dominate. At these low collision energies many trajectories describe orbiting of the He atom around the molecule, which is classical analogue of quantum resonance. A good recipe for analysis of such trajectories is yet to be found. For now, we simply removed them from consideration, focusing on nonresonant contribution to the process.

Overall, Figure 3 demonstrates that at collision energies near 30 cm^{-1} the MQCT method gives an accurate description of the inelastic HCOOCH$_3$ + He collisions. Our prior experience with MQCT applied to four different systems in a broad energy range[16−19] shows that its accuracy always improves as collision energy is raised. So, based on the results of Figure 3, we can expect that at energies above 30 cm^{-1} (where there are no quantum data available) our MQCT predictions of the inelastic scattering cross sections would be reliable, with errors <5%. In Figure 4 we present the MQCT predictions for excitation of the 20 most important rotational states of HCOOCH$_3$, starting from the ground state 0_{00}, in the collisional energy range expanded by a factor of more than 30, up to 1000 cm^{-1}. These states are 1_{01}, 1_{11}, 2_{02}, 2_{12}, 2_{22}, 2_{21}, 3_{03}, 3_{13}, 3_{21}, 3_{31}, 4_{04}, 4_{14}, 4_{22}, 4_{40}, 5_{05}, 5_{33}, 5_{33}, 5_{41}, 6_{16}, 6_{24}, and 7_{17}. The dependencies in Figure 4 are rather smooth, although some of them are not entirely monotonic and the overall picture is rather complicated. The reason for this is that HCOOCH$_3$ is a heavy rotor and the spectrum of its states is rather dense, with many state-to-state transitions accessible and participating actively in the energy transfer. In these MQCT calculations the number of rotational channels was around 1130, with typical values of J_{max} around 120. This is a very large number of channels. The full-quantum calculations with such number of

channels would not be practical. For all calculations in this paper we used the potential energy surface from ref 11. This surface is based on high-level ab initio electronic structure calculations (CCSD(T)/aug-cc-pVTZ), employs fitting of 476 data points by an analytic function, and is expected to be accurate up to collision energy of 1000 cm^{-1}. Note that we do not employ expansion of the PES over the basis set of spherical harmonics. This procedure, standard for small and simple molecules, does not work well for larger and complicate molecules,[11] such as methyl formate. Elements of the potential coupling matrix were computed numerically, as explained in the Supporting Information.

One known way to make the full-quantum scattering calculations more affordable is the coupled-states (CS) approximation,[26] in which some transitions (between states with different values m of projection of the angular momentum j) are neglected to ease calculations. The CS method is usually employed at higher collision energies. Interestingly, within MQCT one can also formulate the CS approximation and test it by comparing its results against the fully coupled MQCT, which we will now call CC-MQCT.[17] Results of such CS-MQCT calculations are presented in Figure 5. Comparison of these data against CC-MQCT (presented in Figure 3) shows that although the general behavior of energy dependence is similar, the absolute values of CS cross sections are often different (e.g., by a factor of up to ×1.8 for state 2_{20}, by a factor of up to ×2.1 for state 4_{12}, and by a factor of up to ×1.4 for state 2_{02}). For some transitions these differences vanish as collision energy reaches 1000 cm^{-1}, but for several other state-to-state transitions large differences survive even at higher energies. Needless to say, some transitions do not happen at all within the CS approximation (e.g., excitation of states 1_{10} and 2_{11}). One important conclusion is that the CS approximation is not particularly accurate for the HCOOCH$_3$ + He system in the considered energy range. One should not expect that the quantum CS calculations for this molecule will be accurate. Thus, the fully coupled version of MQCT is, perhaps, the only practical way of doing accurate calculations for this and other similar organic molecules of astrophysical relevance.

The numerical cost of our MQCT calculations is represented by Figure 6. The CS version of MQCT is faster than the fully
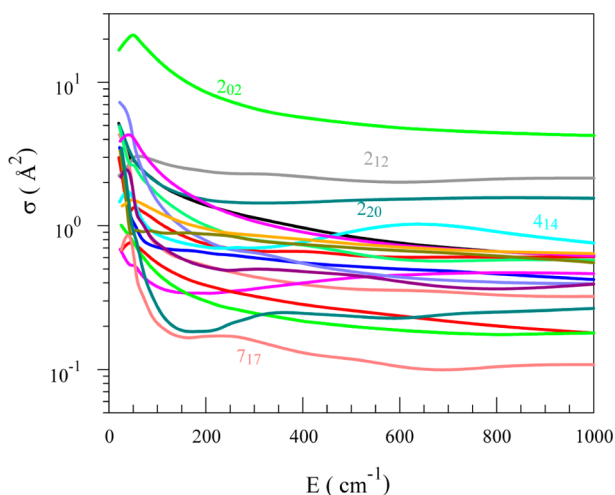
Figure 5. Same as in Figure 4 but computed using CS-approximation within MQCT framework.
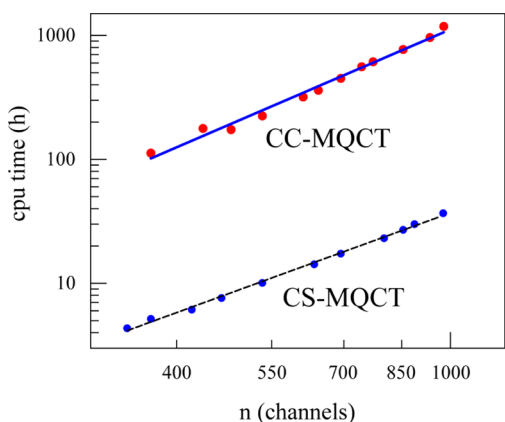
Figure 6. Numerical performance of MQCT, observed for its fully coupled CC version and for the approximate CS version. Logarithmic scale is used for both horizontal and vertical axes. Dashed lines show fits by two different power functions.

coupled MQCT by a factor of roughly 20. The scaling law (computational cost vs number of included channels) is $n^{2.4}$ for the fully coupled MQCT and is n^2 for CS-MQCT. These numbers are taken directly from calculations presented in Figures 3 and 4 and represent a practical measure of the computational cost of the method in a range of collision energies. We also did run an idealized test of performance, when MQCT calculations were done at one representative collision energy, while the number of included channels was varied in a broad range. In such tests the scaling law of the fully coupled MQCT was $n^{2.5}$. For comparison, the full-quantum calculations (e.g., using Hibridon or MOLSCAT)[27,28] are usually said to scale as n^3 with respect to the number of channels, but the cost of converging the quantum calculations with respect to the number of partial waves (which depends on collision energy and the reduced mass) should be added to that, leading, in practice, to the total cost on the order of n^5 or n^6. In contrast, MQCT has no such "overhead" because scattering of the atom is treated classically. Thus, the scaling properties of MQCT are more favorable than those of the full-quantum method, and the advantages are particularly significant for heavier collision partners and at higher collision energies; however, it should also be mentioned that at this point we have only undertaken some basic optimizations of our code. Development of an efficient computer program should reduce the computational costs of MQCT even further.

In conclusion, we carried out the rotationally inelastic scattering calculations for collision of methyl formate with helium atom within the framework of the mixed quantum/classical theory. First, we compared our results against the full-quantum results available at low collision energies and found a very good agreement in the range between 15 and 30 cm^{-1}. Next, we significantly expanded the range of collision energies (by a factor of more than 30, up to 1000 cm^{-1}), covering a practically useful scattering regime. Importantly, the standard full-quantum calculations are computationally unaffordable for such a large molecule in this scattering regime. One can look at MQCT as a method that is complementary to the standard full-quantum method. Namely, at low collision energies one may want to do the full-quantum scattering calculations because they are affordable and because some quantum features, like scattering resonances, may be important; however, at higher collision energies, when the full-quantum calculations become unaffordable (and, in fact, unnecessary) one may want to switch to the mixed quantum/classical theory. It is feasible to apply MQCT to a number of complicated processes of astrophysical relevance, such as collisions of complex organic molecules (CH_3CHO, CH_3OCH_3, C_2H_5CN, and $HCOOCH_3$) or linear carbon chains (C_6H_2, CH_3C_4H, and HC_5N) with He.

It is possible to extend MQCT to the case of two coupled rotors, which would permit inelastic scattering calculations of molecule + molecule collisions. Such developments are in progress. The relevant applications will include excitation/quenching of complex organic molecules and linear carbon chains by H_2 and also collisions between two water molecules (including their isotopomers) and several other triatomic + triatomic systems of astrophysical relevance, which is way too complicated for the full-quantum treatment. Our estimates suggest that calculations for all of these processes are affordable within the framework of MQCT.

Although less relevant to astrophysics, another useful extension of MQCT is toward the high pressure regime, where the multiple collisions of a molecule with bath gas atoms/molecules cannot be treated independently, similar to the falloff regime of recombination kinetics where the three-body collisions are important. The time-dependent formulation of MQCT should allow simulations in which the molecule would interact successively or simultaneously with two or more quenchers along one trajectory. Such theory would have numerous applications in the high-pressure combustion.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Details of our theory. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b00496.

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Notes

The authors declare no competing financial interest.

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