

Adiabatic Trajectory Approximation: A New General Method in the Toolbox of Mixed Quantum/Classical Theory for Collisional Energy Transfer

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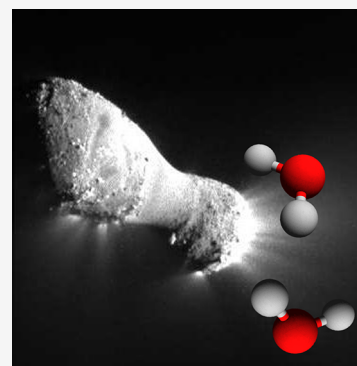


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ABSTRACT: A new version of the MQCT program is presented, which includes an important addition, adiabatic trajectory approximation (AT-MQCT), in which the equations of motion for the classical and quantum parts of the system are decoupled. This method is much faster, which permits calculations for larger molecular systems and at higher collision energies than was possible before. AT-MQCT is general and can be applied to any molecule + molecule inelastic scattering problem. A benchmark study is presented for $\text{H}_2\text{O} + \text{H}_2\text{O}$ rotational energy transfer, an important asymmetric-top rotor + asymmetric-top rotor collision process, a very difficult problem unamenable to the treatment by other codes that exist in the community. Our results indicate that AT-MQCT represents a reliable computational tool for prediction of collisional energy transfer between the individual rotational states of two molecules, and this is valid for all combinations of state symmetries (such as *para* and *ortho* states of each collision partner).



Energy transfer among translational, rotational, and vibrational degrees of freedom during an encounter between two molecules is a fundamentally important process in physical chemistry. Two theoretical methods, known for decades and most frequently used for the description of collisional energy transfer, are the classical trajectory method,^{1–4} often called a quasi-classical trajectory, and the full-quantum time-independent inelastic scattering approach,^{5–7} called the coupled-channel formalism. Both have their pros and cons. For example, the classical method permits the treatment of large molecular systems^{8–12} but has several fundamental flaws such as zero-point energy leakage and violation of microscopic reversibility and lacks many essential features, such as quantization of the internal molecular states, selection rules for state-to-state transitions, quantum interference, and symmetry effects. All of these are present in the full-quantum approach, but the penalty for quantum treatment of scattering is its significant computational cost. In practice, the full-quantum description of collisional energy transfer is feasible only for simple collision partners in the low-energy scattering regime, such as in the coldest parts of interstellar media or in ultracold physics experiments.^{13–18} Newer time-dependent quantum methods, such as MCTDH,^{19,20} offer a somewhat better scaling (compared to the traditional time-independent coupled-channel formalism) and thus are being actively developed.^{21,22} Still, the numerical effort required for the full-quantum treatment of scattering is expected to remain high.

A recently proposed quantum statistical approach^{23,24} is one way to avoid the cost of scattering calculations. Another practical alternative, which falls between the standard classical

and full-quantum methods, is a recently developed mixed quantum/classical theory (MQCT) approach.^{25–31} In this method, the time-dependent Schrödinger equation is used to describe the internal degrees of freedom of molecules (their rotation and vibration), while the mean-field trajectories are used to describe the relative translational motion of two collision partners. In recent years, this approach has been applied to many molecular systems, including diatomic, triatomic, tetra-atomic, and polyatomic molecules colliding with an atom,^{23,32–35} and to molecule + molecule collisions, including diatom + diatom^{36,37} and asymmetric-top rotor + diatom^{24,27,38} collisions, and the most general case of collision between two asymmetric-top rotor molecules.^{39,40} It was found, by comparison against the full-quantum calculations, that MQCT is reasonably accurate and much less computationally expensive. It enables calculations for larger molecules and higher collision energies than was possible before. A user-ready general computer code MQCT was released a few years ago.³⁸

It is now well established that at high collision energies the results of MQCT are very close to the full-quantum results.^{27,31,35,38,41} At lower collision energies, dominated by

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Feshbach resonances, MQCT is less accurate but still gives a qualitatively correct description of the collision process.⁵¹ One phenomenon that MQCT cannot describe in principle is quantum tunneling that is important for the formation of “shape” resonances, but this effect is expected to be less relevant for larger and heavier collision partners. In the work done so far, MQCT was applied mostly to the rotational transitions and to the simplest vibrational transitions in diatomic molecules.^{42,43} More work is certainly needed to expand MQCT to the vibrational transitions in triatomic molecules and to the coupled rotational–vibrational transition processes.

Importantly, mixed quantum/classical theory represents a general framework that permits the development and testing of new computational methodologies for the description of collisional energy transfer. For example, a very efficient decoupling scheme was recently proposed,²⁷ which permits to run approximate MQCT calculations for a fraction of the numerical cost of the fully coupled MQCT. This method, named adiabatic trajectory approximation (AT-MQCT), was found to be reliable for H₂O + H₂ rotational energy transfer (including excitation and quenching of both collision partners) and for C₆H₆ + He rotational excitation and quenching in a broad range of rotational excitations and collision energies.⁴¹ One goal of this paper is to expand AT-MQCT to the most general and complex case of asymmetric top + asymmetric top, required for the treatment of molecule + molecule collisions, such as H₂O + H₂O collisions. It should be stressed that no full-quantum scattering results are available for this case, and no quantum codes can handle it, to the best of our knowledge. Therefore, we present a comparison of AT-MQCT versus the fully coupled CC-MQCT method for H₂O + H₂O collisions. Collisional energy transfer in this molecular system is important, in particular, for interpretation of astrophysical observations of molecular species in cometary comae⁴⁴ and in atmospheres of icy planets such as Jupiter’s moons.⁴⁵ Another goal of this paper is to add AT-MQCT to the suite of MQCT_2022 codes (for all 10 system types), to offer a general approach and an efficient computer code for the treatment of rotational transitions in any molecule + molecule system, for potential users in the fields of astrochemistry, atmospheric chemistry, and chemical kinetics in general. Being a time-dependent method, MQCT can provide very useful physical insight into the dynamics of collisional energy transfer in a variety of molecular systems and processes. For this, we present a performance study of AT-MQCT versus CC-MQCT and versus the full-quantum MOLSCAT calculations. Moreover, this paper can also be used as a brief user’s guide for the potential users of the MQCT_2022 code. A full version of the user manual is provided in the [Supporting Information](#).

For the sake of completeness, we outline the MQCT equations of motion for classical and quantum degrees of freedom. Rigorous derivation of these formula can be found in the recent literature.^{25–35,39,40} A laboratory-fixed reference frame is employed to describe classically the relative motion of two collision partners. Vector \vec{R} connects centers of mass of two collision partners and is described by its length R and azimuthal angle Φ that determines the scattering angle in the equatorial plane (the polar angle is not needed because MQCT trajectories are restricted to one plane due to the cylindrical symmetry of the mean-field potential). R and Φ are classical degrees of freedom, and their evolution is driven by the following classical-like equations of motion (where P_R and P_Φ

are generalized momenta associated with R and Φ , respectively):^{28,29}

$$\dot{R} = \frac{P_R}{\mu} \quad (1)$$

$$\dot{\Phi} = \frac{P_\Phi}{\mu R^2} \quad (2)$$

$$\dot{P}_R = -\sum_{n'} \sum_{n''} e^{ie_{n''}t} \sum_m \frac{\partial M_{n''}^n}{\partial R} a_{mn''}^* a_{mn'} + \frac{P_\Phi^2}{\mu R^3} \quad (3)$$

$$\begin{aligned} \dot{P}_\Phi = & -i \sum_{n'} \sum_{n''} e^{ie_{n''}t} \sum_m M_{n''}^n \\ & \times \left[a_{m-1,n''}^* a_{mn''} \sqrt{j''(j''+1) - m(m-1)} \right. \\ & + a_{m+1,n''}^* a_{mn''} \sqrt{j''(j''+1) - m(m+1)} \\ & - a_{mn''}^* a_{m-1,n'} \sqrt{j'(j'+1) - m(m-1)} \\ & \left. - a_{mn''}^* a_{m+1,n'} \sqrt{j'(j'+1) - m(m+1)} \right] / 2 \quad (4) \end{aligned}$$

Multiple sums in eqs 3 and 4 go over all quantum states of the system. $e_{n''}^n$ terms correspond to energy differences between the initial (lower index) and final (upper index) internal states of the system, say rotational or ro-vibrational states with energies $E_{n''}$ and $E_{n''}$. Index m labels projections of molecular angular momentum j onto molecule–molecule axis \vec{R} (which is used as quantization axis z in the body-fixed reference frame). Time evolution of quantum states is described in the so-called body-fixed reference frame, the rotating frame tied to molecule–molecule vector \vec{R} . Probability amplitudes $a_{mn}(t)$ for molecular quantum states (rotational and ro-vibrational) evolve according to the following quantum-like system of coupled equations:^{28,29}

$$\begin{aligned} \dot{a}_{mn''} = & -i \sum_{n'} a_{mn''} M_{n''}^n e^{ie_{n''}t} \\ & - \dot{\Phi} \left[a_{m-1,n''} \sqrt{j''(j''+1) - m(m-1)} \right. \\ & \left. + a_{m+1,n''} \sqrt{j''(j''+1) - m(m+1)} \right] / 2 \quad (5) \end{aligned}$$

Summation in the first term of this equation includes quantum state-to-state transitions, within given m , driven by potential coupling matrix $M_{n''}^n$ that depends parametrically on R (omitted for the sake of clarity). This matrix is real-valued, time-independent, and diagonal in m (also omitted for the sake of clarity):

$$M_{n''}^n(R) = \langle \Psi_{n''}(\Lambda_1, \Lambda_2) | V(R, \Lambda_1, \Lambda_2) | \Psi_n(\Lambda_1, \Lambda_2) \rangle \quad (6)$$

Wave functions $\Psi_n(\Lambda_1, \Lambda_2)$ and $\Psi_{n''}(\Lambda_1, \Lambda_2)$ correspond to the initial and final states, respectively. They describe rotations of two collision partners relative to the molecule–molecule axis \vec{R} using a set of Euler angles $\Lambda_1 = \{\alpha_1, \beta_1, \gamma_1\}$ and $\Lambda_2 = \{\alpha_2, \beta_2, \gamma_2\}$ for molecules 1 and 2, respectively. Potential energy surface $V(R, \Lambda_1, \Lambda_2)$ is expressed through the same variables. The second term in eq 5 describes transitions between the rotational states with $\Delta m = \pm 1$, driven by classical orbital angular velocity $\dot{\Phi}$, which is the Coriolis coupling effect.

To conduct a meaningful test of the cost of MQCT calculations in comparison with the cost of full-quantum calculations, we picked the $\text{H}_2\text{O} + \text{H}_2$ system, because the full-quantum CC calculations can be carried out for this system type using the standard code MOLSCAT^{46,47} and because it was shown that CC-MQCT and AT-MQCT give reliable results for these collision partners.²⁷ Thus, for the $\text{H}_2\text{O} + \text{H}_2$ system, we carried out MOLSCAT calculations at a total energy of 500 cm^{-1} with a fixed total angular momentum J_{TOT} of 100 but increased the number of rotational states included in the basis. The largest MOLSCAT calculations we finished had 140 states of the $\text{H}_2\text{O} + \text{H}_2$ system with the following maximum values: $j_1 = 13$ (for water) and $j_2 = 4$ (for hydrogen) and $E_{\text{max}} = 2000 \text{ cm}^{-1}$ (energy of the upper state in the basis). A set of close to 20 independent runs was performed. The serial version of MOLSCAT was used (very long runs using one processor), and the NERSC Cori Haswell computer system was employed (2.3 GHz Intel Xeon Processor, 128 GB of memory). MQCT calculations were done in parallel using 10 processors of the same computer system at the same collision energy and with the same J_{TOT} (which corresponds to the maximum impact parameter of ~ 25 Bohr and requires 101 MQCT trajectories). Again, the number of rotational states in the basis set was varied, reaching 200 states as the maximum for CC-MQCT and 300 states as the maximum for AT-MQCT calculations. This was sufficient to see the trends.

It is important to stress that the state-to-state transition matrix $\mathbf{M}_n^{n'}$ in MQCT formalism does not depend on orbital angular momentum l . MQCT trajectories with different values of l are propagated independently and use the same matrix, for any choice of l_{max} . This is different from the full-quantum method, in which the size of the matrix depends on J_{TOT} . The only common physical indicator, present in both MQCT and MOLSCAT calculations, is the number of states in the system. Therefore, the comparison of performance in Figure 1 is presented as a function of the number of rotational states. From Figure 1, we can see that when the number of states

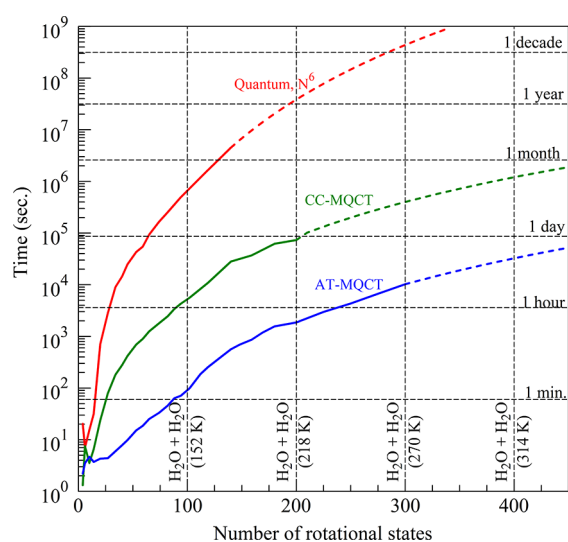


Figure 1. Numerical cost of two versions of MQCT calculations vs full-quantum calculations (MOLSCAT), for molecular systems of increasing complexity (number of rotational states). Calculations are done using the $\text{H}_2\text{O} + \text{H}_2$ system, and a projection for the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system is made.

exceeds 100, the cost of full-quantum calculations increases as N^6 , where N is the number of rotational states. In the range of $N \sim 150$, the cost of full-quantum calculations is 4 orders of magnitude higher than the cost of AT-MQCT. It should also be emphasized that MQCT calculations are intrinsically parallel and can be carried out using ≤ 1000 processors with minimal communication overhead, which reduced the wall-clock time by an additional 3 orders of magnitude. In contrast, the full-quantum calculations are hard to parallelize. While custom versions of parallel MOLSCAT exist among users, the standard version we used was serial.

In the range of $N \sim 300$ states, the cost of AT-MQCT increases as N^3 , which is a much more favorable scaling law compared to that of the full-quantum calculations (see Figure 1). For example, for the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system, we found that AT-MQCT calculations with $N > 1000$ states remain feasible. In Figure 1, we also projected the cost of calculations for the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system at various temperatures, assuming that the basis set size should be on the order of $4kT$, or $E_N = 4kT$, where E_N is energy of rotational state number N in the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system (see below).

Next, we conducted a test of the accuracy of the approximate AT-MQCT method by comparing its results against the results of the fully coupled CC-MQCT method. For these calculations, we included 12 states of the “target” water molecule up to $j_1 = 3$ (six *para* states and six *ortho* states) combined with 28 states of the “quencher” water molecule up to $j_2 = 6$ (14 *para* states and 14 *ortho* states). Due to symmetry considerations, four independent calculations can be carried out in this case for the *p*-target + *p*-quencher, *p*-target + *o*-quencher, *o*-target + *p*-quencher, and *o*-target + *o*-quencher combinations [84 channels of the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system formed in each case (six states of the target combined with 14 states of the quencher)], with a total rotational energy of $\lesssim 620 \text{ cm}^{-1}$. This rotational basis set is not that large, considering the well depth of the $\text{H}_2\text{O} + \text{H}_2\text{O}$ PES (on the order of 1800 cm^{-1}), but is sufficient to compare two versions of MQCT. Convergence of cross sections with respect to the basis set size is within 40% on average.

For the water + water system, we used the CCpol-8sf[2014] PES from refs 48 and 49. This PES was expanded over the basis set of analytic functions listed in Table 8 of the user manual (see the Supporting Information) for $\text{SYS_TYPE} = 0$ and using the keyword $\text{IDENTICAL_PES} = \text{YES}$ (see page 21 of the user manual) to take advantage of the PES symmetry imposed by two identical collision partners. We retained 28 symmetrized expansion terms ($\lambda_1, \mu_1, \lambda_2, \mu_2, \lambda$) that contain 84 individual functions included in the expression for $\text{SYS_TYPE} = 0$ in Table 8 of the user manual. For example, a symmetrized expansion term with $\mu_1 = 4$ and $\mu_2 = 2$ contains four individual functions expressed through the products of D-functions for collision partners one (1) and two (2): with $\mu(1) = +4$ and $\mu(2) = +2$, with $\mu(1) = -4$ and $\mu(2) = -2$, with $\mu(1) = +4$ and $\mu(2) = -2$, and finally with $\mu(1) = -4$ and $\mu(2) = +2$. This expansion has 23 unique coefficients listed in Table 1 and includes a majority of the dipole and quadrupole interaction terms (λ_1 and λ_2 up to 2) as well as some higher-order interaction terms (λ_1 and λ_2 up to 4). The largest value of the total λ included was 6. The definition of D-functions is given on page 5 of the user manual (see the Supporting Information).

The dependencies of 23 expansion coefficients on the molecule–molecule distance $v_{\lambda_1, \mu_1, \lambda_2, \mu_2, \lambda}(R)$ are plotted in Figure

Table 1. Values of the Expansion Coefficients for the PES of the H₂O + H₂O System at $R = 8.09$ Bohr^a

	$(\lambda_1, \mu_1, \lambda_2, \mu_2, \lambda)$	$v_{\lambda_1\mu_1\lambda_2\mu_2\lambda}$ (cm ⁻¹)
$\lambda_1 = 0$	(0, 0, 0, 0, 0)	-4774.19
$\lambda_1 = 1$	(1, 0, 0, 0, 1)	544.31
	(1, 0, 1, 0, 0)	-131.69
$\lambda_1 = 2$	(1, 0, 1, 0, 2)	-14250.92
	(2, 0, 1, 0, 3)	-342.14
	(2, 2, 1, 0, 3)	4548.47
	(2, 2, 2, ± 2 , 4)	1953.05
$\lambda_1 = 3$	(2, 2, 2, 0, 4)	-128.63
	(3, 0, 0, 0, 3)	-68.52
	(3, 0, 1, 0, 4)	839.36
	(3, 0, 2, 2, 5)	407.71
	(3, 0, 3, 0, 6)	-107.84
	(3, 2, 0, 0, 3)	137.84
	(3, 2, 1, 0, 4)	-1112.08
	(3, 2, 2, ± 2 , 5)	-540.28
	(3, 2, 3, ± 2 , 6)	-188.47
	(3, 2, 3, 0, 6)	142.53
$\lambda_1 = 4$	(4, 0, 1, 0, 5)	-232.47
	(4, 0, 2, 2, 6)	-147.79
	(4, 2, 1, 0, 5)	206.02
	(4, 2, 2, ± 2 , 6)	130.58
	(4, 4, 1, 0, 5)	175.29
	(4, 4, 2, ± 2 , 6)	108.51

^aThe normalization of expansion functions is given in Table 8 on page 22 of the user manual (see the Supporting Information).

2. Isotropic term $v_{00000}(R)$ has a minimum near $R = 6.6$ Bohr and a well depth of $\sim 10\,000$ cm⁻¹. Interestingly, the dipole–dipole interaction term $v_{10102}(R)$ is approximately 3 times

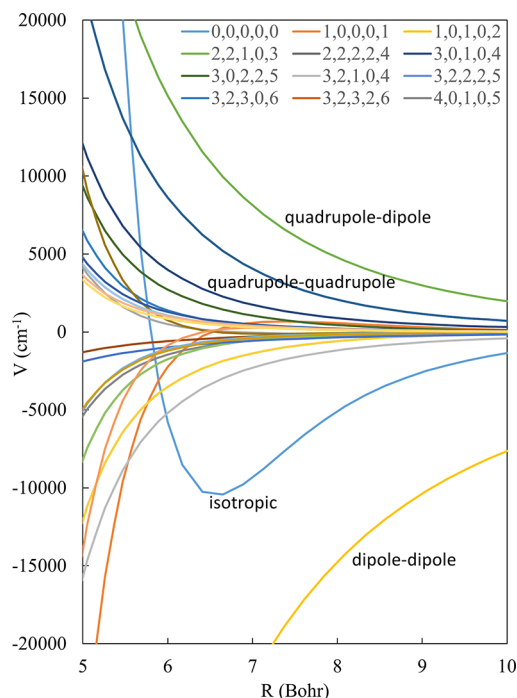


Figure 2. Radial dependence of 23 expansion coefficients $v_{\lambda_1\mu_1\lambda_2\mu_2\lambda}(R)$ for the H₂O + H₂O interaction potential. The four most important expansion terms are labeled, and the largest 12 are labeled by $\lambda_1\mu_1\lambda_2\mu_2\lambda$.

larger. The next most important term is $v_{22103}(R)$ that corresponds to the quadrupole–dipole interaction, and the next $v_{22224}(R)$ corresponds to the quadrupole–quadrupole interaction. Their magnitudes are roughly 3 and 6 times smaller, respectively, than the dipole–dipole term but are still comparable to the isotropic interaction term. The next most significant is hexapole–dipole term $v_{32104}(R)$, followed by the group of $v_{30104}(R)$, $v_{32225}(R)$, $v_{30225}(R)$, and $v_{42105}(R)$ terms that include interactions up to the octupole. These are ~ 1 order of magnitude smaller than the dipole–dipole term. All 23 dependencies $v_{\lambda_1\mu_1\lambda_2\mu_2\lambda}(R)$ are shown in Figure 2, and the 12 largest terms are labeled. The values of expansion coefficients near $R = 8$ Bohr are listed in Table 1. One can see that the magnitude of the largest term (dipole–dipole) is close to $14\,251$ cm⁻¹, while that for the smallest included term is only ~ 68.5 cm⁻¹.

To quantify the accuracy of PES expansion, we computed by direct numerical integration the values of matrix elements for a small subset of states ($0_{00}0_{00}$, $0_{00}1_{11}$, $0_{00}2_{02}$, $1_{11}0_{00}$, $1_{11}1_{11}$, $1_{11}2_{02}$, $2_{02}0_{00}$, $2_{02}1_{11}$, and $2_{02}2_{02}$) at two molecule–molecule distances (near $R = 6$ and 8 Bohr). Direct integration is numerically expensive and is impractical for calculations of the entire matrix for the H₂O + H₂O system, but it can be employed to obtain a set of benchmark data for a smaller subset of transitions. In Figure 3, we plot a comparison of

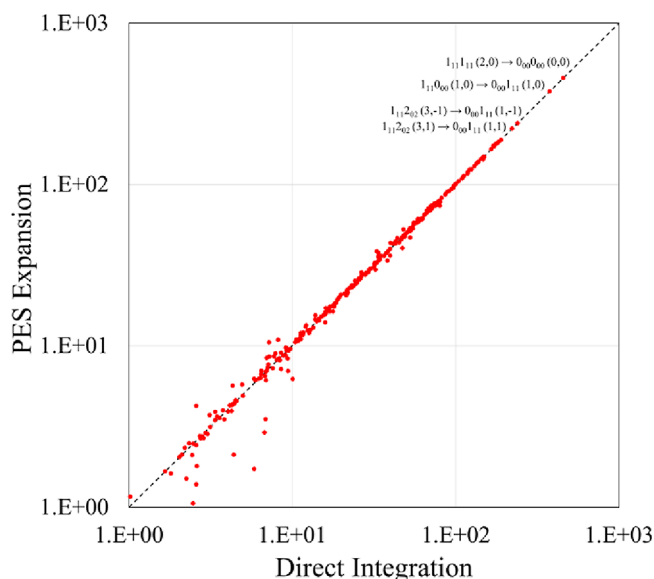


Figure 3. Comparison of matrix elements for the H₂O + H₂O system computed analytically (using PES expansion) vs those computed by direct numerical integration. State-to-state transitions that correspond to the four largest matrix elements are labeled. The numbers in parentheses correspond to the initial and final values of the overall (j , m).

matrix elements obtained by direct integration versus those computed analytically using PES expansion. We can see that the magnitudes of the larger matrix elements exceed 500 cm⁻¹ and those are computed very accurately. Many matrix elements fall in the range between 10 and 200 cm⁻¹, and for those, the PES expansion also works reasonably well. However, smaller matrix elements (<10 cm⁻¹) indicate visible errors due to truncation of the PES expansion. One option is to recompute these elements with a larger PES expansion (which can be numerically challenging), and another option is to neglect

MQCT, the adaptive step size procedure specific to this method was enabled using the keyword `AT_ADAPTOL = 0.0005` (see page 12 of the user manual). This resulted in an acceleration of AT-MQCT calculations by a factor of 76 compared to CC-MQCT calculations. The results of the two calculations are presented in Figure 5. We see that the two sets

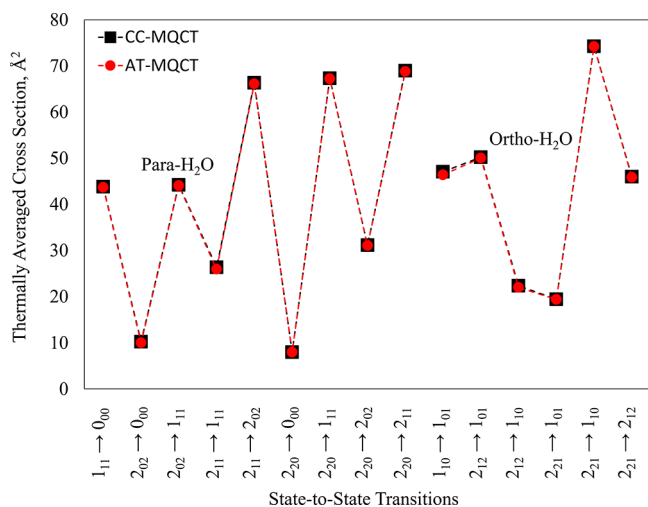


Figure 5. Comparison of thermally averaged cross sections computed by the fully coupled CC-MQCT method (black squares) and the approximate AT-MQCT method (red circles) for several state-to-state transitions in *para* and *ortho* water.

of data are barely distinguishable. The differences we saw in the individual state-to-state transitions in Figure 4 are largely washed out by thermal averaging in Figure 5, where the largest deviation is just slightly more than 1% of the cross section value. One conclusion is that AT-MQCT is particularly well suited for the calculations of thermally averaged cross sections. The second observation is that even in the thermally averaged cross sections the quantum propensity rules remain important. Namely, from Figure 5, one can notice that all transitions with odd values of Δk_a and Δk_c exhibit systematically larger cross sections, compared to transitions with even values of Δk_a and Δk_c that are always smaller, and this is valid for the *para* and *ortho* states of water.

In this paper, we present a new version of the MQCT program that includes an important addition, an adiabatic trajectory method or AT-MQCT, in which the propagations of the equations of motion for classical and quantum parts of the system are decoupled. This approximate method is much faster, which enables calculations for larger molecular systems and at higher collision energies than was possible before. Because the method is general, it can be applied to any molecule + molecule inelastic scattering problem. In MQCT_2022, an adiabatic trajectory approximation is implemented for all system types up to the most general case of an asymmetric-top rotor + asymmetric-top rotor system.

The results presented here for the $\text{H}_2\text{O} + \text{H}_2\text{O}$ system, which is one example of an asymmetric-top + asymmetric-top system, indicate that AT-MQCT is rather accurate for prediction of state-to-state transition cross sections between the individual rotational states of two collision partners, and this is valid for all combinations of state symmetries (such as the *para* and *ortho* states of each collision partner). Moreover,

thermally averaged cross sections obtained by AT-MQCT are nearly identical to those obtained by the fully coupled MQCT method (CC-MQCT). The calculations of a database of thermally averaged cross sections for $\text{H}_2\text{O} + \text{H}_2\text{O}$ collisional energy transfer, very much in demand in the astrochemistry community, are ongoing, in which we use the rotational basis set of 1064 states of the water + water system that includes 28 states of the target molecule up to $j_1 = 8$ combined with 38 states of the quencher up to $j_2 = 10$, in each of the four independent calculations for the *ortho* and *para* combination. The results will be reported elsewhere.

A summary of MQCT_2022 code capabilities is presented herein, and a detailed user manual, including the list of all keywords for the expert-level calculations, is provided in the Supporting Information. In addition to AT-MQCT, the new version of the MQCT package includes many fixes (found in the previous version of the code) and several major improvements for efficiency and portability. See the user manual for further information. At present, the code is available from authors by reasonable request. In the near future, the code will be made available to the community through GitHub.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.2c03328>.

Complete and updated user manual for MQCT_2022, which includes a description of all system types available in the MQCT_2022 program, a list of all required and optional keywords, suggested strategies for the efficient use of the code, a procedure for connecting the external PES, and a summary of equations used to compute matrix elements (PDF)

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Notes

The authors declare no competing financial interest.

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