

Marquette University
e-Publications@Marquette

Chemistry Faculty Research and Publications

Chemistry, Department of

1-1-2016

Inelastic Scattering of Identical Molecules within Framework of the Mixed Quantum/Classical Theory: Application to Rotational Excitations in $\text{H}_2 + \text{H}_2$

Alexander Semenov
Marquette University

Dmitri Babikov
Marquette University, dmitri.babikov@marquette.edu

Accepted version. *Journal of Physical Chemistry A*, Vol. 120, No. 22 (2016): 3861-3866. [DOI](#).

This document is the Accepted Manuscript version of a Published Work that appeared in final form in *Journal of Physical Chemistry A*, copyright © American Chemical Society after peer review and technical editing by the publisher.

Inelastic Scattering of Identical Molecules within Framework of the Mixed Quantum/Classical Theory: Application to Rotational Excitations in $\text{H}_2 + \text{H}_2$

Alexander Semenov

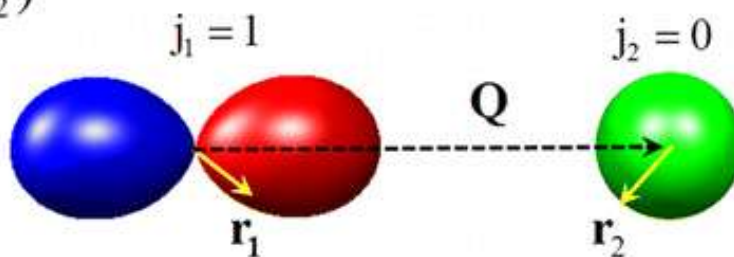
*Chemistry Department, Marquette University,
Milwaukee, WI*

Dmitri Babikov

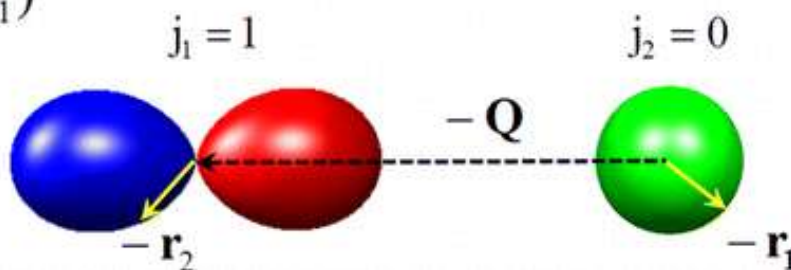
*Chemistry Department, Marquette University,
Milwaukee, WI*

Abstract

$$\Psi_{j_1 j_2 j m}(\mathbf{r}_1, \mathbf{r}_2)$$



$$\tilde{\Psi}_{j_1 j_2 j m}(\mathbf{r}_2, \mathbf{r}_1)$$



Theoretical foundation is laid out for description of permutation symmetry in the inelastic scattering processes that involve collisions of two identical molecules, within the framework of the mixed quantum/classical theory (MQCT). In this approach, the rotational (and vibrational) states of two molecules are treated quantum-mechanically, whereas their translational motion (responsible for scattering) is treated classically. This theory is applied to $\text{H}_2 + \text{H}_2$ system, and the state-to-state transition cross sections are compared versus those obtained from the full-quantum calculations and experimental results from the literature. Good agreement is found in all cases. It is also found that results of MQCT, where the Coriolis coupling is included classically, are somewhat closer to exact full-quantum results than results of the other approximate quantum methods, where those coupling terms are neglected. These new developments allow applications of MQCT to a broad variety of molecular systems and processes.

I Introduction

In the feature article published in *JPC A* a few months ago,¹ we outlined the history of and recent advances in the development and

applications of the mixed quantum-classical theory (MQCT) for inelastic scattering. In this method for description of molecular collisions the internal (rotational, vibrational) states of collision partners are treated using time-dependent Schrodinger equation, while their relative (translational) motion is treated using classical trajectories.²⁻⁸ Energy is exchanged between vibrational, rotational, and translational degrees of freedom, but the total energy is conserved.⁹⁻¹³ The corresponding theory for all relevant cases, starting with the simplest *diatomic + atom*, and going to the most general *molecule + molecule* case, including collision of two *asymmetric-top* rotors, has been recently developed. Careful benchmark studies have also been carried out for several diatomic molecules, such as CO + He,¹³ N₂ + Na,⁴ and H₂ + He,⁵ triatomic H₂O + He,⁶ tetra-atomic CH₃ + He,¹ and polyatomic molecule⁷ HCOOCH₃ + He (all collided with an atom) and also for one molecule + molecule system, N₂ + H₂.⁸ These calculations included collisions of light and heavy collision partners, at low and high collision energies (in a broad range from 1 to 10⁴ cm⁻¹), near threshold for excitation and for the quenching processes that have no threshold, for both rotational and vibrational transitions of total and differential scattering cross sections (including forward scattering), at low levels of rotational excitation and for highly excited cases (e.g., *j* = 22), running the fully coupled MQCT calculations and a simplified (coupled-states) version of MQCT.

It was found that at high collision energies this method is accurate, often giving results *identical* to those of accurate full-quantum close-coupling calculations. At moderate collision energies (typical of room temperature and below) differences on the order of 10% have been observed for some of the systems listed above. At low collision energies predictions of MQCT are often less accurate, particularly near threshold energy, but even there they remain reasonable (within 30%; see figures 10 and 11 in ref 1). It is still not clear whether the MQCT approach is suitable for the description of individual scattering resonances, but we saw that when resonances are multiple and narrow^{4,8} MQCT describes well the nonresonant "background" value of scattering cross section, while when the resonances are broad and overlapping^{6,8} MQCT gives an averaged over resonances behavior.

Importantly, the computational cost of MQCT is much lower compared with the cost of full-quantum coupled-channel scattering calculations, and it scales more favorably with increasing complexity of the problem (collision energy, number of internal states, maximum value of total angular momentum J_{\max}).^{1,6-8} This allows treating collisions of more complicated molecular systems than was previously possible, including small organic molecules, such as HCOOCH₃ and triatomic + triatomic systems. Demands for such inelastic scattering calculations are significant nowadays due to the needs of astrochemical community¹⁴⁻²¹ and also in other fields such as atmospheric chemistry^{9-11,22,23} and combustion.^{24,25}

To enable broad and general applications of MQCT to the important problems in various fields, we still have to demonstrate that this method is able to reproduce (with sufficient accuracy) several quantum phenomena important in scattering. As we outlined in the recent feature article,¹ one of these remaining challenges was the description of identical particle scattering. Indistinguishability of collision partners imposes symmetry constraints onto the wave function of the system, which is important in all scattering regimes (low and high collision energy), for all systems (light and heavy), and for all state-to-state transitions and manifests in all kinds of observables. Thus, incorporation of the exchange symmetry into MQCT is very much needed. Examples of the systems where this feature is essential include H₂ + H₂,²⁶ CO + CO,²⁷ NH + NH²⁸ and many other diatomic molecules and also triatomic molecules, such as H₂O + H₂O²⁹ or HCN + HCN,³⁰ to name just a few. Theoretical prediction of cross sections for rotational excitation and quenching of these (and many other) molecules is needed, for example, for interpretation of spectra emitted by various kinds of astrochemical objects, such as cold molecular clouds, prestellar cores, and cometary comas.¹⁴⁻¹⁹

We propose how this symmetry can be built into MQCT calculations, and we demonstrate that it works really well for the case of H₂ + H₂, which is the lightest and most quantum (rather than classical) system. To our best knowledge this has never been done in the past.

II Theory

Probability distribution is an observable moiety, and it should not change under swap of two identical particles. This means that wave function of the system should either remain the same or change its sign under this operation. In MQCT this wave function depends on quantum degrees of freedom that include, in the case of rotationally inelastic scattering, the angles needed to describe individual orientations of colliding molecules. For a diatomic + diatomic system, those are $\mathbf{r}_1 = (r_1, \theta_1, \varphi_1)$ and $\mathbf{r}_2 = (r_2, \theta_2, \varphi_2)$ or using a composite notation $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2)$. The TOC graphic illustrates that these quantum degrees of freedom are defined in the so-called body-fixed (BF) reference frame, tied to the molecule–molecule vector \mathbf{Q} , the evolution of which is treated classically in the space-fixed (SF) reference frame. Note that, although here we focus on rotational transitions only, we still include, for generality, the bond length of each molecule because this allows describing vibrational states and, in the future, will permit us to study ro-vibrational transitions. The total time-dependent wave function of the system is expressed in MQCT as follows (in atomic units)

$$\psi(\mathbf{r}, t) = \sum_{nm} a_{nm}(t) \Psi_{nm}(\mathbf{r}) e^{-iE_n t} \quad (1)$$

where a_{nm} are time-dependent expansion coefficients, Ψ_{nm} is the basis set of rotational eigenstates of the system, and E_n is their corresponding energy eigenvalue. Index n is a composite index that labels states, and its meaning depends on the system. For a diatomic + diatomic case $n \equiv \{j_1 j_2 j\}$, where j_1 and j_2 are angular momenta of individual molecules, while j represents the total angular momentum of two molecules, $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$, which is also quantized in MQCT: $|j_1 - j_2| \leq j \leq j_1 + j_2$. The meaning of m is projection of \mathbf{j} onto the molecule–molecule vector \mathbf{Q} , which plays the role of the z axis in the BF reference frame (see TOC image). Energy E_n of an eigenstate depends on n only and does not depend on m .

The rotational eigenstates $\Psi_{nm}(\mathbf{r}) \equiv \Psi_{j_1 j_2 j m}(\mathbf{r}_1, \mathbf{r}_2)$ are analytic for diatomic + diatomic systems and are expressed through spherical harmonics of two molecules using Clebsch–Gordan coefficients.³¹ In the case of nonidentical molecules, say AB + CD, we use⁸

$$\Psi_{j_1 j_2 j m}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{m_1 m_2} (j_1 m_1 j_2 m_2 | j m) Y_{j_1 m_1}(\mathbf{r}_1) Y_{j_2 m_2}(\mathbf{r}_2) \quad (2)$$

In the case of identical molecules, say AB + AB, under swap of the molecules 1 and 2, this expression transforms as follows

$$\begin{aligned} \tilde{\Psi}_{j_1 j_2 j m}(\mathbf{r}_2, \mathbf{r}_1) &= \sum_{m_1 m_2} (j_2 m_2 j_1 m_1 | j m) Y_{j_1 m_1}(-\mathbf{r}_2) Y_{j_2 m_2}(-\mathbf{r}_1) \\ &= \sum_{m_1 m_2} (-1)^{j_1 + j_2 + j} (j_1 m_1 j_2 m_2 | j m) (-1)^{j_1} Y_{j_2 m_2}(\mathbf{r}_1) (-1)^{j_2} Y_{j_1 m_1}(\mathbf{r}_2) \\ &= (-1)^j \sum_{m_1 m_2} (j_1 m_1 j_2 m_2 | j m) Y_{j_2 m_2}(\mathbf{r}_1) Y_{j_1 m_1}(\mathbf{r}_2) \\ &= (-1)^j \Psi_{j_2 j_1 j m}(\mathbf{r}_1, \mathbf{r}_2) \end{aligned} \quad (3)$$

Note that here we replaced \mathbf{r}_1 by $-\mathbf{r}_1$, and \mathbf{r}_2 by $-\mathbf{r}_2$, because under this swap the direction of the molecule-molecule vector \mathbf{Q} in the SF reference frame also changes, $(X, Y, Z) \rightarrow (-X, -Y, -Z)$, and thus orientation of the entire BF reference frame changes with respect to the SF reference frame (see TOC image). Using this transformed version, the symmetrized wave function of given parity can be written as

$$\begin{aligned} \Psi_{j_1 j_2 j m}^{(\pm)} &= \frac{1}{\sqrt{2(1 + \delta_{j_1 j_2})}} [\Psi_{j_1 j_2 j m}(\mathbf{r}_1, \mathbf{r}_2) \pm \tilde{\Psi}_{j_1 j_2 j m}(\mathbf{r}_2, \mathbf{r}_1)] \\ &= \frac{1}{\sqrt{2(1 + \delta_{j_1 j_2})}} [\Psi_{j_1 j_2 j m}(\mathbf{r}_1, \mathbf{r}_2) \pm (-1)^j \Psi_{j_2 j_1 j m}(\mathbf{r}_1, \mathbf{r}_2)] \end{aligned} \quad (4)$$

Symmetrized states of positive and negative parity are degenerate if the set of quantum numbers $n = \{j_1 j_2 j\}$ is the same. Using these states in the expansion of eq 1, substituting this expansion into the time-dependent Schrodinger equation, and using the Ehrenfest theorem leads to a set of coupled differential equations for time evolution of probability amplitudes a_{nm} , which are exactly equivalent to the MQCT equations previously reported,^{1,2,5,8} except that now the state-to-state transition matrix is different, as explained next.

Consider the transition from the initial state $n = \{j_1 j_2 j\}$ to the final state $n' = \{j_1' j_2' j'\}$. For the case of nonidentical collision partners

the corresponding state-to-state transition matrix elements $M_{n',n}$ for diatomic + diatomic system were derived in our recent paper (see equation 16 in ref 8). Using those, the matrix elements of given parity $M_{n',n}^{(\pm)}$ for collision of identical molecules can be conveniently expressed as follows

$$\begin{aligned} M_{n'}^{n(\pm)} &= \frac{1}{2\sqrt{(1+\delta_{j_1j_2})(1+\delta_{j_1'j_2'})}} [M_{n'}^n \pm (-1)^{j'} M_{\tilde{n}'}^n \pm (-1)^j M_{n'}^{\tilde{n}} + (-1)^{j+j'} M_{\tilde{n}'}^{\tilde{n}}] \\ &= \frac{1}{\sqrt{(1+\delta_{j_1j_2})(1+\delta_{j_1'j_2'})}} [M_{n'}^n \pm (-1)^{j'} M_{\tilde{n}'}^n] \end{aligned} \quad (5)$$

where $\tilde{n} = \{j_2j_1j\}$ is obtained from n by permutation of j_1 with j_2 . From eq 4 it follows that $\Psi^{\pm}_{\tilde{n}m}$ is different from Ψ^{\pm}_{nm} just by an overall sign change; that is, they are practically equivalent. Thus, the basis set size in eq 1 can be effectively reduced by a factor of roughly two (compared with the case of nonidentical molecules) to include only the states with $j_1 > j_2$; however, two independent sets of MQCT calculations are needed, with basis sets of each parity. Still, the reduction of matrix size has a dominant effect, which makes MQCT calculations for identical molecules less expensive, compared with the case of nonidentical molecules. The states with $j_1 = j_2$ are all special because they require only one set of calculations, with either even or odd parity basis functions, depending on the value of total j . This is because the second of those wave functions vanishes, according to eq 4.

Classical-like equations for evolution of the molecule–molecule vector in the SF reference frame also remain identical to those that we recently published,^{1,2,5,8} except the form of state-to-state transition matrix (as explained above) and its gradients. Note that the relative (orbital) angular momentum l of two collision partners and the total angular momentum of the system J are classical moieties within MQCT framework. They are sampled continuously, uniformly, and randomly through the ranges $0 \leq J \leq J_{\max}$ and $|J - j| \leq l \leq J + j$ and are not quantized.^{1,2,5,8} In contrast, in the full-quantum calculations l is quantized, and, in the case of identical-particle scattering, its value affects the symmetry of the total wave function. Namely, instead of the factor of $(-1)^j$ in eq 4 of MQCT, the full-quantum version of this formula contains a factor of $(-1)^{l+j_1+j_2}$, where l is included (see, for

example, equation 14 in ref [31](#)). Because of this, the full-quantum calculations for identical-particle scattering are done with basis functions of different parities for even and odd values of l (depending on the value of $j_1 + j_2 + j$ in a given state). To mimic this effect within MQCT framework we see two options. One option, similar to "binning" used in the classical trajectory simulations, would be to include 50% of MQCT trajectories (say, with l closer to even integers) in the calculations for one parity and the remaining 50% of MQCT trajectories (say, with l closer to odd integers) in the calculations for the other parity. Alternatively, one could sample l continuously in exactly the same way for two independent MQCT calculations of both parities (without pretending that l is quantized) but, at the end, to divide the resultant transition probabilities by two. In the classical scattering limit $l \gg 1$ the two options should give similar results if properly converged. The first option may be closer to quantum interpretation in the case of small l . We employed the second option because the idea of binning seemed to be less general.

Initial conditions for MQCT calculations are set up by specifying $a_{nm} = 1$ for the initial state, where $n = \{j_1 j_2 j\}$. The values of probability amplitudes $a_{n'm'}$, where $n' = \{j_1' j_2' j'\}$, at the final moment of time (after the collision) are used to compute the corresponding state-to-state transition cross sections as follows

$$\sigma_{j_1 j_2}^{j_1' j_2'} = \frac{\pi(1 + \delta_{j_1 j_2})(1 + \delta_{j_1' j_2'})}{k^2(2j_1 + 1)(2j_2 + 1)} \times \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^j \left(\frac{1}{2N} \sum_i \left(\sum_{j'=|j_1'-j_2'|}^{j_1'+j_2'} \sum_{m'=-j'}^{j'} (2J^{(i)} + 1) |a_{j_1' j_2' m'}^{(\pm, i)}|^2 \right) \right) \quad (6)$$

In short, the inner parentheses in this equation contain a sum of transition probabilities over the final degenerate states m' of each final state j' varied in the range $|j_1' - j_2'| \leq j' \leq j_1' + j_2'$ for a given pair of the final j_1' and j_2' . Those are averaged, by two outermost sums in [eq 6](#), over the degenerate initial states. There are $2j + 1$ of such initial m states for each initial j , with j taking values in the range $|j_1 - j_2| \leq j \leq j_1 + j_2$, which results in $(2j_1 + 1)(2j_2 + 1)$ degenerate initial states total for a given pair of the initial j_1 and j_2 , which shows up in the denominator of [eq 6](#) for the overall average.

Sampling of the initial classical conditions for MQCT trajectories has already been discussed in our previous publications.^{[1,2,5,8](#)} Index i in

eq 6 labels N collision trajectories in a batch, and MQCT cross section is averaged over those as well. This is done by the sum in the middle of eq 6, which replaces summation over l in the corresponding full-quantum expression for cross section. The factor of 1/2 in front of the sum symbol appears only in the case of identical-molecule scattering, as we discussed above. Equation 6 is used to compute $\sigma_{j_1 j_2^{j_1' j_2'^{(+)$ and $\sigma_{j_1 j_2^{j_1' j_2'^{-)$ in two sets of independent calculations, then $\sigma_{j_1 j_2^{j_1' j_2' = \sigma_{j_1 j_2^{j_1' j_2'^{(+)} + \sigma_{j_1 j_2^{j_1' j_2'^{-)$.

It should also be mentioned that the internal symmetry of each collision partner is fully incorporated into MQCT in a straightforward way through the elements of state-to-state transition matrix $M_{n'n}$. Some elements of this matrix vanish (due to integration of the product of symmetric and antisymmetric functions), naturally leading to forbidden transitions. This is entirely equivalent to the full-quantum theory. For example, in homonuclear diatomic molecules only the transitions with $\Delta j = \pm 2$ are allowed.^{4,5,8} Here we consider *para*-H₂ in the initial state $j = 0$. So, the allowed final states will have even values of the angular momentum quantum number, such as $j = 2, 4, 6$, etc. Allowed versus forbidden transitions have also been discussed for triatomic⁶ and tetra-atomic¹ molecules with identical atoms, all within MQCT framework.

III Results and Discussion

As one can see, incorporation of permutation symmetry into MQCT is possible, and it does not require any additional numerical effort. In this study we considered the case of H₂ + H₂ and employed the potential energy surface (PES) of Boothroyd et al.³² In the past, full-quantum calculations of H₂ + H₂ rotationally inelastic scattering have been done on this surface by three different groups,³³⁻³⁶ and those references are used here as a benchmark. Figure 1 reports cross sections for excitation of the ground rotational state $(j_1 j_2) = (0 0)$ into several excited rotational states: $(j_1' j_2') = (2 0), (2 2), (4 0)$ and $(4 2)$, in a broad range of collision energies (note that in the case when the initial state is the ground rotational state only one set of calculations, that of positive parity, is needed: $\sigma_{j_1 j_2^{j_1' j_2' = \sigma_{j_1 j_2^{j_1' j_2'^{(+)$). Dependencies of cross sections on collision energy presented exhibit threshold at low energies and tend to plateau at higher energies (see Figure 1). Full-

quantum results of Lee et al.^{33,34} are shown by dashed line, and our MQCT results are shown by green symbols. We see that comparison is very good through the entire range of collision energies and for all transitions. At higher collision energies the differences on the order of $\sim 10\%$ are observed for excitation of state (4 0) and some larger deviations for state (4 4). Usually, MQCT is more accurate at higher energies, so some nonvanishing deviations in that regime signal about possible differences in representation of the potential energy surface.

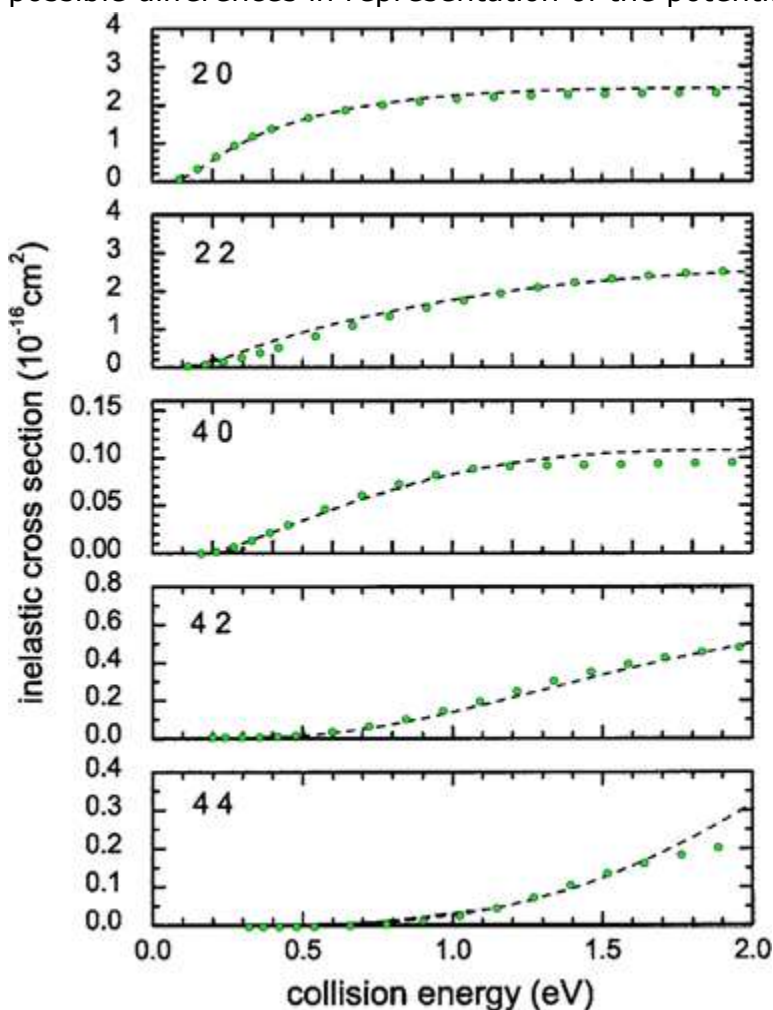


Figure 1. Inelastic cross section, as a function of energy in a broad range, for transitions into five lowest excited rotational states in $\text{H}_2 + \text{H}_2$ system, starting from the ground rotational state (0 0). Final state is indicated in the upper left corner of each frame. Full-quantum results of Lee et al.³³ are shown by dashed line, and our MQCT results are shown by green symbols. Reproduced with permission from ref 33. Copyright 2006 AIP Publishing LLC.

For these calculations we expanded the PES of ref 32 over a symmetrized basis set of spherical harmonics, just as Lee et al.³³ did.

But we noticed that for convergence of numerical quadrature we needed more points than were used by Lee et al.³³ (25 in our calculations vs 10 points in their). So, our R -dependent coefficients were slightly different from those presented in figure 2 of ref 33. Also, we noticed that eq 12 of Lee et al.³³ (or the same PES expansion of Diep et al.³⁷) was different from the original formula of Green (see equation 4 in ref 31), which is how the PES should be fed into the MOLSCAT³⁸ code. So, it looks like the differences observed in [Figure 1](#) at high energies for transitions into (4 0) and (4 4) are, most probably, due to some differences in PES representation.

[Figure 2](#) focuses on the low-energy regime for excitation of states $(j_1'j_2') = (2\ 0)$, $(2\ 2)$ and $(4\ 0)$, starting from the ground state $(j_1j_2) = (0\ 0)$. Three sets of the full-quantum calculations are presented. Solid line represents results of time-independent coupled-channel calculations of Lee et al.³³ (same data as in [Figure 1](#)), and these data may be regarded as "exact". The dashed line represents results of Gatti et al.,³⁵ obtained using the time-dependent wave packet technique that, in principle, is also expected to be very accurate. The dotted line represents older results of Lin and Guo³⁶ obtained using an approximate method, with Coriolis coupling term neglected. One can see that out of three approximate methods our results (green dots) are closest to the "exact" results of Lee et al.³³ This underlines the importance of inclusion of the Coriolis coupling terms, which is done in MQCT in the mixed quantum/classical fashion but appears to work really well even for the lightest, most nonclassical molecule + molecule system, $H_2 + H_2$. For heavier molecules MQCT is expected to work even better.

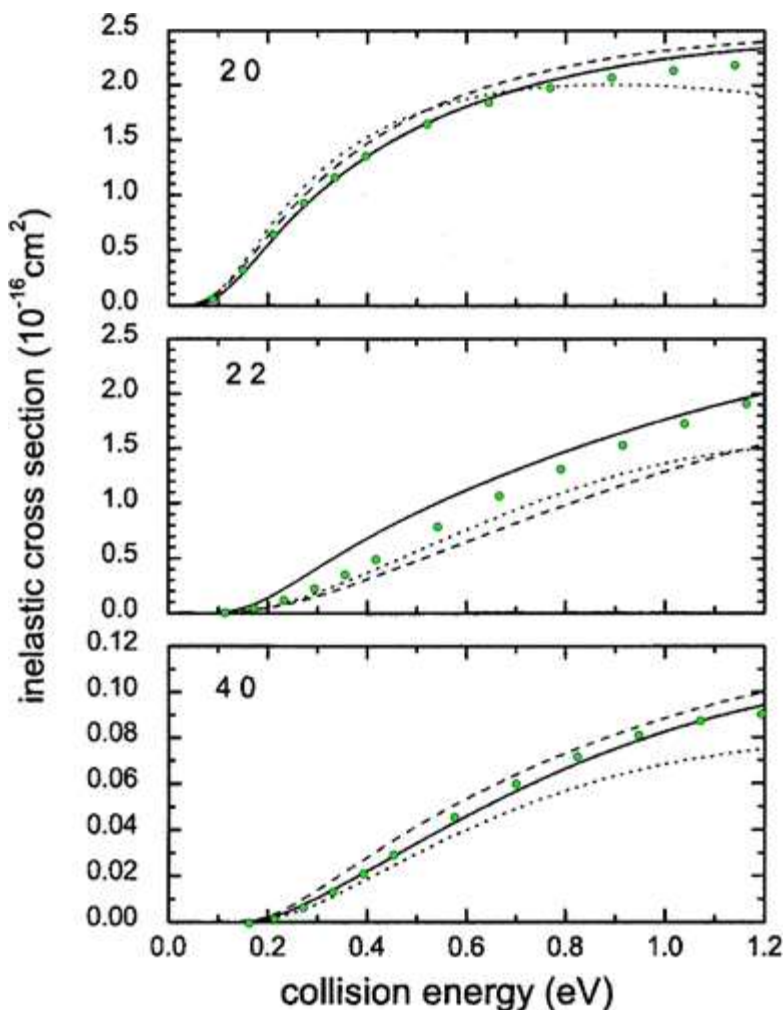


Figure 2. Inelastic cross section as a function of energy, with low-energy range emphasized, for excitation of three rotational states of $\text{H}_2 + \text{H}_2$ system, starting from the ground rotational state (0 0). Final state is indicated in the upper left corner of each frame. Full-quantum results of Lee et al.³⁴ are shown by solid line, and our MQCT results are shown by green symbols (same data as in Figure 1). Results of Gatti et al.³⁵ (dashed line) and of Lin and Guo³⁶ (dotted line) are also included. Reproduced with permission from ref 34. Copyright 2007 AIP Publishing LLC.

Figure 3 compares results of several theoretical methods against experimental data of Bauer et al.³⁹ (large symbols with error bars) for the elastic scattering channel, $(j_1 j_2) = (j_1' j_2') = (0 0)$. All theoretical data show good agreement with experiment, but some show more oscillations than observed in the experiment, where the dependence is rather smooth. MQCT results are certainly closer to experimental data than some of the previous results and are comparable to more recent theoretical data presented in Figure 3.

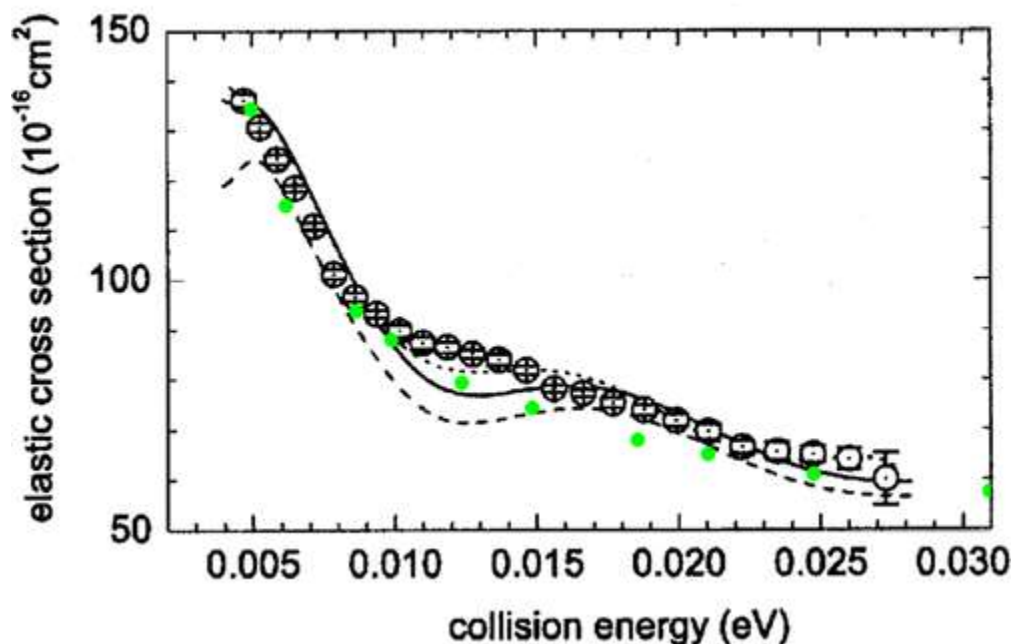


Figure 3. Elastic scattering cross section as a function of energy for the ground rotational state (00) of $\text{H}_2 + \text{H}_2$ system. Our MQCT results are shown by green symbols; experimental data of Bauer et al.³⁹ are shown by large symbols with error bars. Solid, dashed, and dotted lines represent results of calculations using different quantum methods and potential energy surfaces, as discussed by Lee et al.³³ Reproduced with permission from ref 33. Copyright 2006 AIP Publishing LLC.

It should be noted that some experimental data, at lower collision energies, are also available for the inelastic transition (00) \rightarrow (20) in $\text{H}_2 + \text{H}_2$, from the work of Mate et al.⁴⁰ It was shown, however, that the BMKP PES of Boothroyd et al.³² (employed here for benchmark purposes) disagrees with these experimental data. Another PES for $\text{H}_2 + \text{H}_2$ called DJ³⁷ is known to agree well with experimental data of Maté et al.,⁴⁰ but the range of validity of that PES is limited to collision energies below 3000 cm^{-1} . For this reason, the BMKP surface was chosen for the broad-range benchmark studies of this work, up to 2 eV, or $\sim 16000 \text{ cm}^{-1}$.

IV Conclusions

Without the proper treatment of exchange symmetry, developed and tested in this article, the level of agreement that we see in [Figures 1–3](#) between MQCT and the full-quantum calculations or experiments would be impossible. This development permits us to carry out in the near future the calculations of rotationally inelastic scattering in such

complex systems as $\text{H}_2\text{O} + \text{H}_2\text{O}$ and calculations of ro-vibrationally inelastic scattering in many diatomic + diatomic systems, which carries both fundamental and applied importance. Moreover, comparisons presented in [Figure 2](#) indicate that results of the fully coupled MQCT (with Coriolis coupling included) are superior to results of the approximate quantum coupled-states calculations, where the corresponding coupling terms are omitted to reduce numerical cost. It is a very important conclusion that it is better to include this type of interaction classically within MQCT framework rather than neglect it completely. This finding has rather broad applications as well, in various subfields of the chemical reaction dynamics, beyond the rotationally inelastic scattering.

The authors declare no competing financial interest.

Acknowledgment

This research was partially supported by NASA, through the grant NNX15AL29G. We used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-5CH11231. A.S. acknowledges support of the Raynor Fellowship at Marquette.

References

- ¹Babikov, D.; Semenov, A. Recent Advances in Development and Applications of Mixed Quantum/Classical Theory for Inelastic Scattering *J. Phys. Chem. A* 2016, 120, 319– 331. feature article (cover art), DOI: 10.1021/acs.jpca.5b09569
- ²Semenov, A.; Babikov, D. Mixed Quantum/Classical Theory of Rotationally and Vibrationally Inelastic Scattering in Space-fixed and Body-fixed Reference Frames *J. Chem. Phys.* 2013, 139, 174108, DOI: 10.1063/1.4827256
- ³Ivanov, M. V.; Dubernet, M.-L.; Babikov, D. Rotational Quenching of H_2O by He: Mixed Quantum/Classical Theory and Comparison with Quantum Results *J. Chem. Phys.* 2014, 140, 134301, DOI: 10.1063/1.4868715
- ⁴Semenov, A.; Babikov, D. Accurate Calculations of Rotationally Inelastic Scattering Cross Sections Using Mixed Quantum/Classical Theory *J. Phys. Chem. Lett.* 2014, 5, 275– 278, DOI: 10.1021/jz402542w
- ⁵Semenov, A.; Babikov, D. Mixed Quantum/Classical Calculations of Total and Differential Elastic and Rotationally Inelastic Scattering Cross Sections

- for Light and Heavy Reduced Masses in a Broad Range of Collision Energies *J. Chem. Phys.* 2014, 140, 044306, DOI: 10.1063/1.4862409
- ⁶Semenov, A.; Dubernet, M.-L.; Babikov, D. Mixed Quantum/Classical Theory for Inelastic Scattering of Asymmetric-Top-Rotor + Atom in the Body-Fixed Reference Frame and Application to the H₂O + He System *J. Chem. Phys.* 2014, 141, 114304, DOI: 10.1063/1.4895607
- ⁷Semenov, A.; Babikov, D. Mixed Quantum/Classical Approach for Description of Molecular Collisions in Astrophysical Environments *J. Phys. Chem. Lett.* 2015, 6, 1854– 1858, DOI: 10.1021/acs.jpcllett.5b00496
- ⁸Semenov, A.; Babikov, D. Mixed Quantum/Classical Theory for Molecule-Molecule Inelastic Scattering: Derivations of Equations and Application to N₂ + H₂ System *J. Phys. Chem. A* 2015, 119, 12329– 12338, DOI: 10.1021/acs.jpca.5b06812
- ⁹Ivanov, M. V.; Babikov, D. Mixed Quantum-Classical Theory for the Collisional Energy Transfer and the Ro-Vibrational Energy Flow: Application to Ozone Stabilization *J. Chem. Phys.* 2011, 134, 144107, DOI: 10.1063/1.3576103
- ¹⁰Ivanov, M. V.; Babikov, D. Efficient Quantum-Classical Method for Computing Thermal Rate Constant of Recombination: Application to Ozone Formation *J. Chem. Phys.* 2012, 136, 184304, DOI: 10.1063/1.4711760
- ¹¹Ivanov, M. V.; Babikov, D. On Molecular Origin of Mass-Independent Fractionation of Oxygen Isotopes in the Ozone Forming Recombination Reaction *Proc. Natl. Acad. Sci. U. S. A.* 2013, 110, 17708, DOI: 10.1073/pnas.1215464110
- ¹²Semenov, A.; Babikov, D. Equivalence of the Ehrenfest Theorem and the Fluid-Rotor Model for Mixed Quantum/Classical Theory of Collisional Energy Transfer *J. Chem. Phys.* 2013, 138, 164110, DOI: 10.1063/1.4801430
- ¹³Semenov, A.; Ivanov, M. V.; Babikov, D. Ro-vibrational Quenching of CO ($v = 1$) by He Impact in a Broad Range of Temperatures: A Benchmark Study Using Mixed Quantum/Classical Inelastic Scattering Theory *J. Chem. Phys.* 2013, 139, 074306, DOI: 10.1063/1.4818488
- ¹⁴Roueff, E.; Lique, F. Molecular Excitation in the Interstellar Medium: Recent Advances in Collisional, Radiative, and Chemical Processes *Chem. Rev.* 2013, 113, 8906– 8938, DOI: 10.1021/cr400145a
- ¹⁵Yang, B.; Nagao, M.; Satomi, W.; Kimura, M.; Stancil, P. C. Rotational Quenching of Rotationally Excited H₂O in Collisions with He *Astrophys. J.* 2013, 765, 77, DOI: 10.1088/0004-637X/765/2/77
- ¹⁶Wernli, M.; Wiesenfeld, L.; Faure, A.; Valiron, P. Rotational Excitation of HC₃N by H₂ and He at Low Temperatures *Astron. Astrophys.* 2007, 464, 1147– 1154, DOI: 10.1051/0004-6361:20066112

- ¹⁷Troscompt, N.; Faure, A.; Wiesenfeld, L.; Ceccarelli, C.; Valiron, P. Rotational Excitation of Formaldehyde by Hydrogen Molecules: Ortho-H₂CO at Low Temperature *Astron. Astrophys.* 2009, 493, 687–696, DOI: 10.1051/0004-6361:200810712
- ¹⁸Rabli, D.; Flower, D. R. The Rotational Excitation of Methanol by Molecular Hydrogen *Mon. Not. R. Astron. Soc.* 2010, 406, 95–110, DOI: 10.1111/j.1365-2966.2010.16671.x
- ¹⁹Faure, A.; Josselin, E. Collisional Excitation of Water in Warm Astrophysical Media: I. Rate Coefficients for Ro-Vibrationally Excited States *Astron. Astrophys.* 2008, 492, 257–264, DOI: 10.1051/0004-6361:200810717
- ²⁰Daniel, F.; Dubernet, M.-L.; Grosjean, A. Rotational Excitation of 45 Levels of Ortho/Para-H₂O by Excited Ortho/Para-H₂ from 5 to 1500 K: State-to-State, Effective, and Thermalized Rate Coefficients *Astron. Astrophys.* 2011, A76, 536–546, DOI: 10.1051/0004-6361/201118049
- ²¹Faure, A.; Wiesenfeld, L.; Scribano, Y.; Ceccarelli, C. Rotational Excitation of Mono- and Doubly-Deuterated Water by Hydrogen Molecules *Mon. Not. R. Astron. Soc.* 2012, 420, 699–704, DOI: 10.1111/j.1365-2966.2011.20081.x
- ²²Kirste, M.; Wang, X.; Schewe, H. C.; Meijer, G.; Liu, K.; van der Avoird, A.; Janssen, L. M.; Gubbels, K. B.; Groenenboom, G. C.; van de Meerakker, S. Y. Quantum-State Resolved Bimolecular Collisions of Velocity-Controlled OH with NO Radicals *Science* 2012, 338, 1060–1063, DOI: 10.1126/science.1229549
- ²³Schewe, H. C.; Ma, Q.; Vanhaecke, N.; Wang, X.; Kłos, J.; Alexander, M. H.; van de Meerakker, S. Y. T.; Meijer, G.; van der Avoird, A.; Dagdigian, P. J. Rotationally Inelastic Scattering of OH by Molecular Hydrogen: Theory and Experiment *J. Chem. Phys.* 2015, 142, 204310, DOI: 10.1063/1.4921562
- ²⁴Dagdigian, P.; Alexander, M. H. Theoretical Investigation of Rotationally Inelastic Collisions of the Methyl Radical with Helium *J. Chem. Phys.* 2011, 135, 064306, DOI: 10.1063/1.3624525
- ²⁵Tkáč, O.; Ma, Q.; Rusher, C. A.; Greaves, S. J.; Orr-Ewing, A. J.; Dagdigian, P. J. Differential and Integral Cross Sections for the Rotationally Inelastic Scattering of Methyl Radicals With H₂ And D₂ *J. Chem. Phys.* 2014, 140, 204318, DOI: 10.1063/1.4879618
- ²⁶dos Santos, F. S.; Balakrishnan, N.; Forrey, R. C.; Stancil, P. C. Vibration-Vibration and Vibration-Translation Energy Transfer in H₂-H₂ Collisions: a Critical Test of Experiment with Full-Dimensional Quantum Dynamics *J. Chem. Phys.* 2013, 138, 104302, DOI: 10.1063/1.4793472
- ²⁷Ndengue, S. A.; Dawes, R.; Gatti, F. Rotational Excitations in CO-CO Collisions at Low Temperature: Time Independent and

- Multiconfigurational Time Dependent Hartree Calculations *J. Phys. Chem. A* 2015, 119, 7712– 7723, DOI: 10.1021/acs.jpca.5b01022
- ²⁸Janssen, L. M. C.; van der Avoird, A.; Groenenboom, G. C. Quantum Reactive Scattering of Ultracold $\text{NH}(X, ^3\Sigma^-)$ Radicals in a Magnetic Trap *Phys. Rev. Lett.* 2013, 110, 063201/1– 063201/5, DOI: 10.1103/PhysRevLett.110.063201
- ²⁹Agg, P. J.; Clary, D. C. Infinite Order Sudden Calculation of Raman Q-Branch Linewidths for $\text{H}_2\text{O} + \text{H}_2\text{O}$ *J. Chem. Phys.* 1991, 95, 1037– 1048, DOI: 10.1063/1.461131
- ³⁰Hernández Vera, M.; Kalugina, Y.; Denis-Alpizar, O.; Stoecklin, T.; Lique, F. Rotational Excitation of HCN by Para- and Ortho- H_2 *J. Chem. Phys.* 2014, 140, 224302, DOI: 10.1063/1.4880499
- ³¹Green, S. Rotational Excitation in $\text{H}_2 + \text{H}_2$ Collisions: Close-Coupling Calculations *J. Chem. Phys.* 1975, 62, 2271– 2277, DOI: 10.1063/1.430752
- ³²Boothroyd, A. I.; Martin, P. G.; Keogh, W. J.; Peterson, M. J. An Accurate Analytic H_4 Potential Energy Surface *J. Chem. Phys.* 2002, 116, 666– 689, DOI: 10.1063/1.1405008
- ³³Lee, T.-G.; Balakrishnan, N.; Forrey, R. C.; Stancil, P. C.; Schultz, D. R.; Ferland, G. J. State-to-State Rotational Transitions in $\text{H}_2 + \text{H}_2$ Collisions at Low Temperatures *J. Chem. Phys.* 2006, 125, 114302, DOI: 10.1063/1.2338319
- ³⁴Lee, T.-G.; Balakrishnan, N.; Forrey, R. C.; Stancil, P. C.; Schultz, D. R.; Ferland, G. J. Erratum: "State-to-State Rotational Transitions in $\text{H}_2 + \text{H}_2$ Collisions at Low Temperatures *J. Chem. Phys.* 2007, 126, 179901, DOI: 10.1063/1.2730820
- ³⁵Gatti, F.; Otto, F.; Sukiasyan, S.; Meyer, H.-D. Rotational Excitation Cross Sections of Para- $\text{H}_2 + \text{Para-}\text{H}_2$ Collisions. A Full-Dimensional Wave-Packet Propagation Study Using an Exact Form of the Kinetic Energy *J. Chem. Phys.* 2005, 123, 174311, DOI: 10.1063/1.2085167
- ³⁶Lin, S. Y.; Guo, H. Full-Dimensional Quantum Wave Packet Study of Rotationally Inelastic Transitions in $\text{H}_2 + \text{H}_2$ Collision *J. Chem. Phys.* 2002, 117, 5183– 5191, DOI: 10.1063/1.1500731
- ³⁷Diep, P.; Johnson, J. K. An Accurate $\text{H}_2 - \text{H}_2$ Interaction Potential from First Principles *J. Chem. Phys.* 2000, 112, 4465– 4473, DOI: 10.1063/1.481009
- ³⁸Hutson, J. M.; Green, S. *MOLSCAT Computer Code, version 14; 1994. Distributed by Collaborative Computational Project No. 6 of the Engineering and Physical Sciences Research Council, Swindon, U.K.*
- ³⁹Bauer, W.; Lantsch, B.; Tonnie, J. P.; Walaschewski, K. Observation of Symmetry Undulations in the Integral Cross Section of Para-Hydrogen ($j = 0$) + Para-Hydrogen ($j = 0$), and the Determination of the

NOT THE PUBLISHED VERSION; this is the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation at the bottom of the page.

Attractive Potential *Chem. Phys.* 1976, 17, 19– 26, DOI:
10.1016/0301-0104(76)85003-3

⁴⁰Maté, B.; Thibault, F.; Tejada, G.; Fernández, J. M.; Montero, S. Inelastic Collisions in Para-H₂: Translation-Rotation State-to-State Rate Coefficients and Cross Sections at Low Temperature and Energy *J. Chem. Phys.* 2005, 122, 064313, DOI: 10.1063/1.1850464