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Mixed quantum/classical theory of rotationally and vibrationally inelastic scattering in space-fixed and body-fixed reference frames

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We formulated the mixed quantum/classical theory for rotationally and vibrationally inelastic scattering process in the diatomic molecule + atom system. Two versions of theory are presented, first in the space-fixed and second in the body-fixed reference frame. First version is easy to derive and the resultant equations of motion are transparent, but the state-to-state transition matrix is complex-valued and dense. Such calculations may be computationally demanding for heavier molecules and/or higher temperatures, when the number of accessible channels becomes large. In contrast, the second version of theory requires some tedious derivations and the final equations of motion are rather complicated (not particularly intuitive). However, the state-to-state transitions are driven by real-valued sparse matrixes of much smaller size. Thus, this formulation is the method of choice from the computational point of view, while the space-fixed formulation can serve as a test of the body-fixed equations of motion, and the code. Rigorous numerical tests were carried out for a model system to ensure that all equations, matrixes, and computer codes in both formulations are correct. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4827256]

I. INTRODUCTION

Theoretical predictions of inelastic scattering cross sections for ro-vibrationally excited molecules become increasingly important for quantitative interpretation of molecular spectra observed in a wide variety of astrophysical objects, such as pre-stellar cores and proto-stellar environments, interstellar media, and surcumstellar envelopes.[1–11] The range of relevant temperatures is very broad, from 5 K up to 2500 K, and the role of scattering partner (quencher) is played by the interstellar background gasses, mostly He and H_2, but also by H_2O in cometary comas. Usually, calculations of inelastic cross sections[12] are carried out using quantum scattering codes such as MOLSCAT.[13] These calculations are not trivial,[14–20] but recently a significant progress has been achieved in the rotational quenching of H_2O by H_2.[21–25] Another outstanding example of such calculations is rotational quenching of methyl formate, $HCOOCH_3$ (astrophysically relevant small organic molecule, SOM) by He with collision energy $E < 30$ cm^{-1}.[26]

One should admit, however, that quantum mechanics, indispensable (and affordable) at low temperatures and for the low-mass collision partners, becomes prohibitively demanding at higher temperatures and/or for larger molecules and quenchers. Computational time increases with kinetic energy of collision (more partial waves should be included) and with the number of internal quantum levels (e.g., $j \geq 50$ becomes prohibitive). Today it is possible to do 6D diatom-diatom inelastic scattering calculations using exact quantum

mechanics, in a broad range of collision energies and without resorting to any decoupling approximation. Beyond that the calculations become prohibitive. For example, quantum inelastic scattering calculations of H_2O + H_2O and their deuterated forms are not yet computationally affordable, same as quenching calculations for several important SOMs (e.g., methanol, acetaldehyde, dimethyl ether) in the temperature range of interest.

It is also a question whether the exact full-quantum framework is really needed in those cases. *Can we switch from full-quantum mechanics to a simpler and more affordable theory in the temperature range where this theory becomes accurate? And what theory is suitable for this purpose?* If the answer to the first question is positive and the answer to the second question is found, many of the astrophysically relevant inelastic scattering calculations could become possible.

It is probably true to say that at $T > 10$ K the translational motion (scattering) can be described classically for most collision partners except the lightest, such as H + H_2. An attractive method for dynamics emerges if the classical trajectory treatment of scattering is interfaced with quantum treatment of internal (rotational and/or vibrational) states in a self-consistent way, which allows energy exchange between collisional and internal degrees of freedom, but keeps total energy conserved. The idea of such mixed quantum/classical approach is not entirely new, but it has never been fully developed to the level of a predictive computational tool.

Foundations of the quantum/classical theory were laid by Gert Billing in 1980s and 1990s and published in several journal articles,[27–29] one large paper[30] and one book.[31] He also did calculations for a number of systems to support his theory. In recent years we tried to revive this

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quantum/classical approach, and took a closer look at the ranges of its validity. Sometimes it is argued that two Delos criteria must be satisfied:[32] (1) the de Broglie wavelength should be very small, $(\lambda/a_0)^{1/2} \ll 1$, and (2) the translation energy of reduced mass should be much larger than energy of transition $E_t \gg |\Delta\varepsilon_{if}|$. With respect to the second criterion, a distinction should be made between vibrationally and rotationally inelastic transitions. The vibrational quanta are particularly large and, formally, it looks like this property limits significantly the range of applicability of the mixed quantum/classical approach, to high-energy collisions only. Recently, we carried out the mixed quantum/classical calculations of vibrational quenching of $CO(v = 1)$ by He impact in a broad range of collision energies using the method where only vibrations of CO are treated quantum mechanically, while rotation of CO and scattering of He are both treated classically.[33,34] Excellent agreement with full quantum calculations has been obtained at collision energies down to 100 cm^{-1}, despite the fact that vibrational quantum of CO is rather large, 2140 cm^{-1}. Similar mixed quantum/classical method was also very useful for description of collisional energy transfer in the recombination reaction that forms ozone, O_3.[35–38] Finally, our recent calculations of rotationally inelastic transitions in $N_2 + Na$[39] show that for excitation cross sections the mixed quantum/classical approach becomes accurate at energies roughly equal to $\frac{1}{4}$ of rotational quantum above the channel threshold, while the quenching cross sections are described accurately down to very low energies (few wavenumbers, consistent with first Delos criterion, rather than second). This is very encouraging and, probably, means that the mixed quantum/classical approach for ro-vibrational transitions remains accurate at energies much smaller than those indicated by the second Delos criterion.

In this paper we focus on the mixed quantum/classical treatment of purely rotational quenching, where the vibrational motion is not important, rotational motion is treated quantum mechanically, and only the scattering is treated classically. It appears that such theory is very easy to formulate in the space-fixed (SF) reference frame, but the corresponding state-to-state transition matrix may be hard-to-handle numerically. Much simpler transition matrix is obtained in the body-fixed (BF) reference frame, but the underlying derivations are notably difficult and the resultant equations of motion are rather complicated. Gert Billing published some of the final equations[31] but not all of them, and did not provide enough details about their derivation. So, one purpose of this paper it to present a complete and detailed mixed quantum/classical theory (MQCT) of rotationally inelastic scattering in the BF reference frame. The second goal is to present an equivalent theory in the SF reference frame, which Billing did not do, and compare numerical results of two theories for a model system in order to ensure that final equations of both theories are correct. Finally, it appears that Billing carried out his MQCT calculations only within framework of the coupled-states (CS) approximation, where transitions between different m-states, within the same rotational energy level j, are neglected.[31] In this paper, we go well beyond this assumption by formulating and numerically testing the fully coupled version of MQCT.

II. THEORETICAL FRAMEWORK

Here we present MQCT method for treatment of inelastic diatomic molecule + atom scattering:

$$AB^* + M \rightarrow AB + M,$$
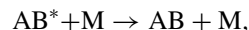
where the rotational and vibrational (internal) motions of the molecule are treated quantum mechanically, while the translational motion of both particles (scattering) is treated classically. So, the molecule is AB and the quencher atom is M.

A. The Ehrenfest approach in general case

Consider a system characterized by a set of variables treated classically (some of coordinates and their conjugate momenta) and another set of variables described by quantum mechanics (the remaining coordinates). In this situation wave function of the system depends *explicitly* on classical variables. This dependence can be written as $\Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P})$, where $\mathbf{q}$ denotes all quantum variables, while $(\mathbf{Q}, \mathbf{P})$ denotes a set of classical generalized coordinates and their conjugate momenta. Our goal is to derive equations for evolution of such quantum/classical system.

Quantum part of the Hamiltonian operator $\hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P})$ and its classical part $H_c(\mathbf{Q}, \mathbf{P})$ are used to set up the full Hamiltonian for evolution of the classical sub-system, according to the Ehrenfest theorem:[40]

$$H(\mathbf{Q}, \mathbf{P}) = H_c(\mathbf{Q}, \mathbf{P}) + \langle \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) \rangle. \tag{1}$$

The Hamilton's equations of motion are then obtained as

$$\dot{\mathbf{Q}} = \frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial \mathbf{P}}, \quad \dot{\mathbf{P}} = -\frac{\partial H(\mathbf{Q}, \mathbf{P})}{\partial \mathbf{Q}}. \tag{2}$$

Substitution of (2) into (1) and differentiation using the chain-rule give

$$\dot{\mathbf{Q}} = \frac{\partial H_c(\mathbf{Q}, \mathbf{P})}{\partial \mathbf{P}} + \langle \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \frac{\partial \hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P})}{\partial \mathbf{P}} | \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) \rangle$$
$$+ 2\text{Re}\langle \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \frac{\partial \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P})}{\partial \mathbf{P}} \rangle, \tag{3a}$$

$$\dot{\mathbf{P}} = -\frac{\partial H_c(\mathbf{Q}, \mathbf{P})}{\partial \mathbf{Q}} - \langle \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \frac{\partial \hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P})}{\partial \mathbf{Q}} | \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) \rangle$$
$$- 2\text{Re}\langle \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P}) | \frac{\partial \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P})}{\partial \mathbf{Q}} \rangle. \tag{3b}$$

For evolution of quantum part of the system we should solve the time-dependent Schrodinger equation (TDSE):

$$\hat{H}_q(\mathbf{q}; \mathbf{Q}, \mathbf{P})\Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P}) = i\hbar \frac{\partial \Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P})}{\partial t}. \tag{4}$$

The system of Eqs. (3) and (4) completely describes behavior and time evolution of any quantum-classical system.

It is important to note several points. The wave function evolves (depends on time) but we also have to differentiate it
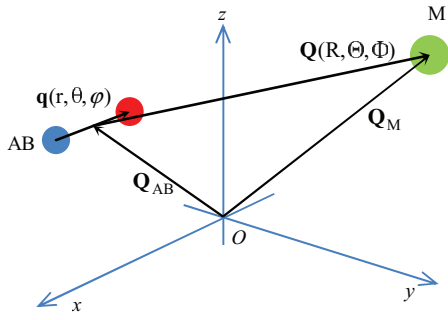
FIG. 1. Space-fixed (SF) reference frame. Cartesian coordinates x, y, and z are introduced for convenience.

with respect to classical variables, since it depends on them too. These classical coordinates also evolve. It is just a formal mathematical rule which has very important physical consequence: without the last term in Eqs. (3a) and (3b) we will not satisfy the energy conservation law. In what follows we will see that in the SF reference frame only the second term in Eqs. (3a) and (3b) is important, while in the BF reference frame only the third term matters.

B. MQCT in the SF reference frame

Figure 1 is used to define coordinates of the system. The quantum Hamiltonian is

$$\hat{H}_q = \hat{H}_{\text{vib}} + \frac{\hat{\mathbf{j}}^2}{2\mu_{\text{AB}}r^2} + V(R, \Theta, \Phi, r, \theta, \varphi), \quad (5)$$

where μ_{AB} is the reduced mass of the molecule, $\mathbf{Q} = \mathbf{Q}_M - \mathbf{Q}_{\text{AB}} = (R, \Theta, \Phi)$ describes the relative position of quencher and center of mass of the diatomic molecule, angles (θ, φ) describe molecular orientation, and r is the interatomic distance in the molecule. The vibrational Hamiltonian contains potential of the diatomic only: $\hat{H}_{\text{vib}} = \hat{T}_{\text{vib}} + V_{\text{AB}}(r)$, while the potential V in Eq. (5) has everything but this term:

$$V(R, \Theta, \Phi, r, \theta, \varphi) = V_{\text{ABM}}(R, \Theta, \Phi, r, \theta, \varphi) - V_{\text{AB}}(r). \quad (6)$$

The PES of the entire system V_{ABM} does not have to be separable.

For convenience we will switch to the radial wave function ψ defined as $\Psi = \psi(r, \theta, \varphi)/r$, with corresponding vibrational kinetic energy operator:

$$\hat{T}_{\text{vib}} = -\frac{\hbar^2}{2\mu_{\text{AB}}} \frac{\partial^2}{\partial r^2}. \quad (7)$$

For solution of TDSE we will use expansion over the basis set of ro-vibrational eigenstates with time-dependent coefficients:

$$\psi(r, \theta, \varphi, t) = \sum a_{njm}(t)\phi_{nj}(r)Y_{jm}(\theta, \varphi) \exp\{-iE_{nj}t/\hbar\}. \quad (8)$$

To simplify notations we will leave out the time dependence: $a_{njm} = a_{njm}(t)$. Substituting Eqs. (5)–(8) into TDSE (4) and projecting out eigenstates in a standard way, we obtain the

system of coupled equations:

$$i\hbar \frac{\partial a_{njm}}{\partial t}$$
$$= \sum_{n'j'm'} a_{n'j'm'} \exp\{i(E_{nj} - E_{n'j'})t/\hbar\} M_{njm}^{n'j'm'}(R, \Theta, \Phi), \quad (9)$$

where

$$M_{njm}^{n'j'm'}(R, \Theta, \Phi)$$
$$= \langle \phi_{n'j'}(r)Y_{j'm'}(\theta, \varphi)|V(R, \Theta, \Phi, r, \theta, \varphi)|\phi_{nj}(r)Y_{jm}(\theta, \varphi)\rangle$$
$$= A_{j'm'jm} \int_0^{2\pi} e^{i(m-m')\varphi} \int_0^{\pi} P_{j'm'}(\cos\theta)P_{jm}(\cos\theta)$$
$$\times \int_0^{\infty} \phi_{n'j'}(r)\phi_{nj}(r)V(R, \Theta, \Phi, r, \theta, \varphi)dr \sin\theta d\theta d\varphi. \quad (10)$$

Here

$$A_{j'm'jm} = \frac{1}{4\pi}\sqrt{\frac{(2j+1)(2j'+1)(j-m)!(j'-m')!}{(j+m)!(j'+m')!}}$$

is a constant factor that comes from normalization coefficients. The Jacobian with respect to r is just dr. Notice that $M_{njm}^{n'j'm'}$ is a function of variables (R, Θ, Φ). Summation in Eq. (10) goes over all quantum states, including the diagonal element njm. In general the matrix elements of $M_{njm}^{n'j'm'}$ are complex-valued and non-zero for $m \neq m'$, because wave functions depend on φ.

So, the quantum coordinates here are $\mathbf{q} = (r, \theta, \varphi)$, while classical coordinates are $\mathbf{Q} = (R, \Theta, \Phi)$. The wave function $\Psi(\mathbf{q})$ depends on quantum coordinates only, which is the simplest case, no explicit $\Psi(\mathbf{q}; \mathbf{Q}, \mathbf{P})$ dependence. The classical equations of motion can be derived either in the reference frame associated with center-of-mass of the entire ABM system using spherical polar coordinates, or in the reference frame where AB is initially at rest using Cartesian coordinates. In the first case, according to Eq. (1):

$$H = \frac{P_R^2}{2\mu} + \frac{P_\Theta^2}{2\mu R^2} + \frac{P_\Phi^2}{2\mu R^2 \sin^2\Theta} + H_0 + \tilde{V}(R, \Theta, \Phi), \quad (11)$$

where μ is the reduced mass of AB + M, and we introduced

$$H_0 = \langle \psi(r, \theta, \varphi)|\hat{T}_q + V_{\text{AB}}(r)|\psi(r, \theta, \varphi)\rangle$$
$$= \sum_{nj}\sum_m |a_{njm}|^2 E_{nj} \quad (12)$$

and

$$\tilde{V}(R, \Theta, \Phi) = \langle \psi(r, \theta, \varphi)|V(R, \Theta, \Phi, r, \theta, \varphi)|\psi(r, \theta, \varphi)\rangle$$
$$= \sum_{n'j'm'}\sum_{njm} a^*_{n'j'm'}a_{njm} \exp\{i(E_{n'j'} - E_{nj})t/\hbar\}$$
$$\times M_{njm}^{n'j'm'}(R, \Theta, \Phi). \quad (13)$$

This average potential is a real number (for detailed prove see Appendix C), which means that all forces produced by partial

derivatives with respect to classical variables (R, Θ, Φ) are also real. The equations of motion, from Eq. (3), are

$$\dot{R} = \frac{P_R}{\mu}, \tag{14a}$$

$$\dot{\Theta} = \frac{P_\Theta}{\mu R^2}, \tag{14b}$$

$$\dot{\Phi} = \frac{P_\Phi}{\mu R^2 \sin^2 \Theta}, \tag{14c}$$

$$\dot{P}_R = -\frac{\partial \tilde{V}(R, \Theta, \Phi)}{\partial R} + \frac{P_\Theta^2}{\mu R^3} + \frac{P_\Phi^2}{\mu R^3 \sin^2 \Theta}, \tag{14d}$$

$$\dot{P}_\Theta = -\frac{\partial \tilde{V}(R, \Theta, \Phi)}{\partial \Theta} + \frac{P_\Phi^2 \cos \Theta}{\mu R^2 \sin^3 \Theta}, \tag{14e}$$

$$\dot{P}_\Phi = -\frac{\partial \tilde{V}(R, \Theta, \Phi)}{\partial \Phi}. \tag{14f}$$

Alternatively, using six Cartesian coordinates, the Hamiltonian is

$$H = \frac{P_{X_M}^2}{2m_M} + \frac{P_{Y_M}^2}{2m_M} + \frac{P_{Z_M}^2}{2m_M} + \frac{P_{X_{AB}}^2}{2m_{AB}} + \frac{P_{Y_{AB}}^2}{2m_{AB}} + \frac{P_{Z_{AB}}^2}{2m_{AB}}$$
$$+ \tilde{V}(X_M - X_{AB}, Y_M - Y_{AB}, Z_M - Z_{AB}). \tag{15}$$

The equations of motion are simply:

$$\dot{Q}_i = \frac{P_i}{m_i}, \quad \dot{P}_i = -\frac{\partial \tilde{V}}{\partial Q_i}. \tag{16}$$

C. MQCT in the BF reference frame

The body-fixed frame is an inertial reference frame. Its origin is placed into the center-of-mass of the entire ABM system. The same classical variables $\mathbf{Q} = (R, \Theta, \Phi)$ are used,[41] but the quantum degrees of freedom are described by Jacobi coordinates $\mathbf{q} = (r, \gamma, \varphi')$, as shown in Fig. 2. The potential does not depend on classical angles and angle φ' due to symmetry, so $V = V(R, r, \gamma)$. In these new coordinates the basis function $Y_{jm'}(\gamma, \varphi')$ can be re-expressed through the SF basis
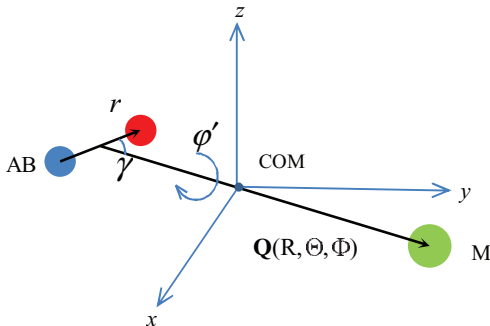

FIG. 2. Body-fixed (BF) reference frame. Origin of Cartesian coordinates is in the center of mass (COM) of the entire AB + M system.

functions $Y_{jm}(\theta, \varphi)$ and the Wigner rotation functions[42, 43] (see Appendix A):

$$Y_{jm'}(\gamma, \varphi') = \sum_m D_{mm'}^j(\Phi, \Theta, 0) Y_{jm}(\theta, \varphi). \tag{17}$$

Note that in this section, and in Appendix A, we use unprimed index m to label spherical harmonics of angle φ in the SF reference frame, while we use primed index m' (and later m'') to label spherical harmonics of angle φ' in the BF reference frame. (In contrast, indexes j and n are the same in both SF and BF reference frames and we will use j, j', and j'' below as needed, without association with SF or BF.)

The wave function $\psi(r, \gamma, \varphi')$ is, again, expanded in a basis set:

$$\psi(r, \gamma, \varphi', t) = \sum_{n\,j\,m'} a_{njm'}(t) \phi_{nj}(r) Y_{jm'}(\gamma, \varphi') \exp\{-i E_{nj} t / \hbar\}. \tag{18}$$

It is important to note that in the BF the quantum angles (γ, φ') depend on classical variables (Θ, Φ) that change over time as collision progresses, and now the wave function depends on classical variables explicitly: $\psi = \psi(r, \gamma, \varphi'; \Theta, \Phi)$. To be more specific, this dependence is through spherical harmonics $Y_{jm'}(\gamma, \varphi'; \Theta, \Phi)$ that, in turn, depend on $D_{mm'}^j(\Phi, \Theta, 0)$. The angles (Θ, Φ) depend on time, so, the time derivative in the TDSE should be computed as

$$\frac{\partial \psi}{\partial t} = \sum_{n\,j\,m'} \exp\{-i E_{nj} t / \hbar\} \phi_{nj}(r)$$
$$\times \left(\frac{\partial a_{njm'}}{\partial t} Y_{jm'}(\gamma, \varphi') - a_{njm'} \frac{i E_{nj}}{\hbar} Y_{jm'}(\gamma, \varphi') \right.$$
$$\left. + a_{njm'} \sum_m \frac{\partial D_{mm'}^j(\Phi, \Theta, 0)}{\partial t} Y_{jm}(\theta, \varphi) \right). \tag{19}$$

Analytic expression for time derivative of the Wigner function is derived in Appendix B:

$$\frac{\partial D_{mm'}^j(\Phi, \Theta, 0)}{\partial t}$$
$$= \frac{\partial D_{mm'}^j}{\partial \Theta} \dot{\Theta} + \frac{\partial D_{mm'}^j}{\partial \Phi} \dot{\Phi}$$
$$= \frac{1}{2}[\sqrt{j(j+1) - m'(m'-1)} D_{mm'-1}^j(\Phi, \Theta, 0)$$
$$- \sqrt{j(j+1) - m'(m'+1)} D_{mm'+1}^j(\Phi, \Theta, 0)]\dot{\Theta}$$
$$+ \sin \Theta \frac{1}{2}[\sqrt{j(j+1) - m'(m'-1)} D_{mm'-1}^j(\Phi, \Theta, 0)$$
$$+ \sqrt{j(j+1) - m'(m'+1)} D_{mm'+1}^j(\Phi, \Theta, 0)]\dot{\Phi}$$
$$- i m' \cos \Theta D_{mm'}^j(\Phi, \Theta, 0)\dot{\Phi}. \tag{20}$$

Using (20) in (19), substituting (19) into the TDSE and projecting out eigenstates, we obtain

$$i\hbar \frac{\partial a_{njm'}}{\partial t} = \sum_{n'\,j'} a_{n'j'm'} \exp\{i(E_{nj} - E_{n'j'})t/\hbar\} M_{nj}^{n'j'}(R)$$
$$- i\hbar \sum_{m''} a_{njm''} W_{m'}^{m''}. \tag{21}$$

Here we introduced for every m' the state-to-state transition matrix:

$$M_{n\,j}^{n'j'}(R) = A_{j'm'\,j\,m'}$$
$$\times \langle \phi_{nj}(r)P_{jm'}(\cos\gamma)|V(R,r,\gamma)|\phi_{n'j'}(r)P_{j'm'}(\cos\gamma)\rangle \quad (22)$$

and for every j the state-to-state matrix:

$$W_{m'}^{m''} = \frac{1}{2}[\sqrt{j(j+1)-m''(m''-1)}\delta_{m',m''-1}$$
$$-\sqrt{j(j+1)-m''(m''+1)}\delta_{m',m''+1}]\dot{\Theta}$$
$$+i\bigg(\sin\Theta\frac{1}{2}[\sqrt{j(j+1)-m''(m''-1)}\delta_{m',m''-1}$$
$$+\sqrt{j(j+1)-m''(m''+1)}\delta_{m',m''+1}]$$
$$-m''\cos\Theta\delta_{m',m''}\bigg)\dot{\Phi}. \quad (23)$$

The structure of coupled equations (21) is such that the matrix $M_{nj}^{n'j'}(R)$ describes only transitions from (nj) to $(n'j')$, within the same value of m'. It is computed for every m', separately, because its elements depend on m' through Legendre polynomials and the constant factor in Eq. (22). Each such matrix is symmetric, $M_{nj}^{n'j'}(R) = M_{n'j'}^{nj}(R)$, and its elements are real (see Appendix C). Each element is a function of R only. This matrix does not depend on time; it is computed once.

In contrast, the matrix $W_{m'}^{m''}$ is not a constant matrix, due to time evolution of classical entities $\Theta(t)$, $\dot{\Theta}(t)$, and $\dot{\Phi}(t)$. It describes transitions between m' and $m'' = m' \pm 1$, within the same energy level (nj). This matrix is computed for every j, separately, because its elements depend on j. In Appendix C we also show that this matrix is anti-Hermitian: $(W_{m'}^{m''})^* = -W_{m''}^{m'}$. The last imaginary term in $W_{m'}^{m''}$ is diagonal. It corresponds to the non-intermultiplet transition. Simply speaking, it is responsible for the change of wave function's phase, $im\Phi$, during rotation by angle Φ. The coupled-states (CS) approximation is easily formulated by setting $W_{m'}^{m''} = 0$.

For future reference it is convenient to introduce two simpler real-valued matrixes:

$$U_{m'}^{m''} = \frac{1}{2}[\sqrt{j(j+1)-m''(m''-1)}\delta_{m',m''-1}$$
$$-\sqrt{j(j+1)-m''(m''+1)}\delta_{m',m''+1}] \quad (24a)$$

and

$$V_{m'}^{m''} = \frac{1}{2}[\sqrt{j(j+1)-m''(m''-1)}\delta_{m',m''-1}$$
$$+\sqrt{j(j+1)-m''(m''+1)}\delta_{m',m''+1}], \quad (24b)$$

so that we can express

$$W_{m'}^{m''} = U_{m'}^{m''}\dot{\Theta} + i\big(\sin\Theta V_{m'}^{m''} - m''\cos\Theta\delta_{m',m''}\big)\dot{\Phi}. \quad (25)$$

Matrixes $U_{m'}^{m''}$ and $V_{m'}^{m''}$ are time-independent and should be computed only once.

As for classical degrees of freedom, the equations of motion for $\dot{R}$, $\dot{\Theta}$, $\dot{\Phi}$, and $\dot{P}_R$ are exactly the same as in the SF reference frame, Eqs. (14a)–(14d), with one difference that in

the BF the average potential $\tilde{V}$ depends on R only:

$$\tilde{V}(R) = \langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\psi(r,\gamma,\varphi')\rangle. \quad (26)$$

However, equations for $\dot{P}_\Theta$ and $\dot{P}_\Phi$ are more complicated in the BF reference frame, because they use the last term in Eqs. (3a) and (3b). Namely, instead of Eqs. (16e) and 16(f) in the SF, we have in the BF:

$$\dot{P}_\Theta = -2\text{Re}\langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial\psi(r,\gamma,\varphi')}{\partial\Theta}\rangle$$
$$+\frac{P_\Phi^2\cos\Theta}{\mu R^2\sin^3\Theta}, \quad (27a)$$

$$\dot{P}_\Phi = -2\text{Re}\langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial\psi(r,\gamma,\varphi')}{\partial\Phi}\rangle. \quad (27b)$$

Analytic expressions for these matrix elements are derived in Appendix B. They can be conveniently expressed through the commutator matrixes $[\mathbf{M}, \mathbf{U}]$ and $[\mathbf{M}, \mathbf{V}]$. The final expressions are

$$\dot{P}_\Theta = \sum_{n''j''m''}\sum_{n'j'm'} a_{n''j''m''}^* a_{n'j'm'}\exp\{i(E_{n''j''}-E_{n'j'})t/\hbar\}$$
$$\times [\mathbf{M},\mathbf{U}]_{n'j'm'}^{n''j''m''} + \frac{P_\Phi^2\cos\Theta}{\mu R^2\sin^3\Theta} \quad (28a)$$

and

$$\dot{P}_\Phi = -i\sum_{n''j''m''}\sum_{n'j'm'} a_{n''j''m''}^* a_{n'j'm'}\exp\{i(E_{n''j''}-E_{n'j'})/\hbar\}$$
$$\times \sin\Theta[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}. \quad (28b)$$

These formulas look rather complicated but, in fact, each commutator is a time-independent matrix computed once (since $\mathbf{M}$, $\mathbf{U}$, and $\mathbf{V}$ are all time independent). In the case of CS-approximation these equations reduce to much simpler formula:

$$\dot{P}_\Theta = \frac{P_\Phi^2\cos\Theta}{\mu R^2\sin^3\Theta}, \quad (29a)$$

$$\dot{P}_\Phi = 0. \quad (29b)$$

Before finalizing this section we want to stress again the difference between SF and BF formulations. In the SF reference frame the third term of Eqs. (3a) and (3b) is zero, and only the second term makes contribution to the equations of motion. This term involves gradients of potential. In contrast, in the BF reference frame the second term of Eqs. (3a) and (3b) is zero, and only the third term makes contribution, which has no gradients of potential. Instead, it involves derivatives of wave functions. Indeed, in the BF reference frame the potential does not depend on (classical) angles Θ and Φ, but the basis functions do!

III. NUMERICAL RESULTS

Without the purpose of computing converged quenching cross sections for any real system, but in order to test the cor-

rectness of our theory (in particular, the equivalence of SF and BF formulations) we conducted some numerical calculations using the model PES of the rigid rotor:

$$V(R, \gamma) = D((\exp\{-(R - R_e)/a\} - 1)^2 - 1)\left(1 + \frac{\cos\gamma}{2}\right).$$

(30)

The Morse parameters were as follows: $D = 50\,\text{cm}^{-1}$, $R_e = 5\,a_0$, and $a = \sqrt{2D/\mu}\,/\,\omega$, where $\omega = D$. The values of reduced mass and equilibrium inter-nuclear distance $r_e = 2.79\,a_0$ in the molecule correspond to He + SO system.[44] Equations (14a)–(14e) and (28a) and (28b) are propagated using 4th-order Runge-Kutta method. Energies of rotational levels were computed analytically, $E_j = j(j + 1)B$, where $B = 1/(2\mu_{SO}r_e^2)$. In order to compute analytic gradients of this potential with respect to Θ and Φ for equations of motion in the SF reference frame we used:

$$\cos\gamma = \cos\theta\cos\Theta + \cos\varphi\sin\theta\cos\Phi\sin\Theta$$
$$+ \sin\varphi\sin\theta\sin\Phi\sin\Theta.$$

(31)

This expression is obtained from the scalar product of two unit vectors: $\mathbf{n_q}(\theta, \varphi)$ and $\mathbf{n_Q}(\Theta, \Phi)$, with γ being the angle between them. The minimal rotational basis set of $j = 0, 1$ and $m = 0, \pm 1$ was used (four states). In the following two tests we took the rotationally excited state $j = 1$ and computed probability of its stabilization into $j = 0$ in several different ways. In each case the impact parameter was $b = 3\,a_0$ and the collision energy was $E_Q = 300\,\text{cm}^{-1}$. The initial relative orientation (and the trajectory of collision) was physically equivalent in each calculation, but it was intentionally made different mathematically, in order to check the equations of motion, as explained below.

A. Testing BF equations

Namely, in the BF reference frame we launched three different trajectories. For one of them the vector of initial velocity was placed in the $\Phi = 0$ plane. This situation corresponds to $\dot{P}_\Phi = 0$ and $\dot{\Phi} = 0$. Such trajectory stays in the polar plane, $\Phi = const$. In practice, the equation of motion (28b) for $\dot{P}_\Phi$ can be ignored. All we have to do is to propagate Eq. (28a) for $\dot{P}_\Theta$ and Eq. (14b) for $\dot{\Theta}$, since the value of Θ changes along such trajectory.

For the second trajectory the vector of initial velocity was placed in the $\Theta = \pi/2$ plane. This situation corresponds to $\dot{P}_\Theta = 0$ and $\dot{\Theta} = 0$. Such trajectory stays in the equatorial plane, $\Theta = const$. Now the equation of motion (28a) for $\dot{P}_\Theta$ can be ignored. All we have to do is to propagate Eq. (28b) for $\dot{P}_\Phi$ and Eq. (14c) for $\dot{\Phi}$, since the value of Φ changes along such trajectory.

For the third (most general) trajectory the vector of initial velocity was placed arbitrarily. The trajectory is still planar, but both angles Θ and Φ evolve and we have to propagate

both Eqs. (28a) and (28b) for $\dot{P}_\Theta$ and $\dot{P}_\Phi$, and both Eqs. (14b) and (14c) for $\dot{\Theta}$ and $\dot{\Phi}$.

In all these cases the initial state was $j = 1$, $m' = 0$ and we looked at the probability of its quenching into $j = 0$, $m' = 0$.

B. Testing BF *vs.* SF equations

In the SF reference frame we launched two more trajectories. One was launched from the point on z-axis towards the $j = 1$, $m = 0$ state (with some arbitrary value of Φ). Such trajectory stays in the $\Phi = const$ plane. The second trajectory was launched from the point on the x-axis, towards the superposition state $(m^+ - m^-)/\sqrt{2}$ of $j = 1$ (with an arbitrarily directed velocity vector). In these two cases we looked at the probability of quenching into $j = 0$, $m = 0$.

Note that in all these (five) trajectories the relative orientation of the velocity vector and the wave function of the system at the initial moment of time were physically equivalent. We propagated all five and found that the quenching probability at the end of trajectory, as well as population of the ground state $j = 0$ during the course of trajectory, were all identical (within small numerical errors). Population of the (final) ground state, as a function of time, is shown in Fig. 3. All five curves coincide, which means that all five trajectories are identical.

One practical result of these tests is that in the BF reference frame we do not really need the classical equations of motion for both Θ and Φ. The trajectory is planar (exception is discussed below), so that without the loss of generality we can restrict our calculations to $\Phi = 0$ plane, where $\dot{\Phi} = 0$ and $\dot{P}_\Phi = 0$. In most situations we only have to propagate Eqs. (14b) and (28a) for $\dot{\Theta}$ and $\dot{P}_\Theta$.

Still, the value of Eqs. (14c) and (28b) for $\dot{\Phi}$ and $\dot{P}_\Phi$ in the BF reference frame is clear. First of all, they allow testing the theory and the computer code. Second, they become important if the initial state of the system is a superposition of rotational eigenstates (see below) that has no cylindrical
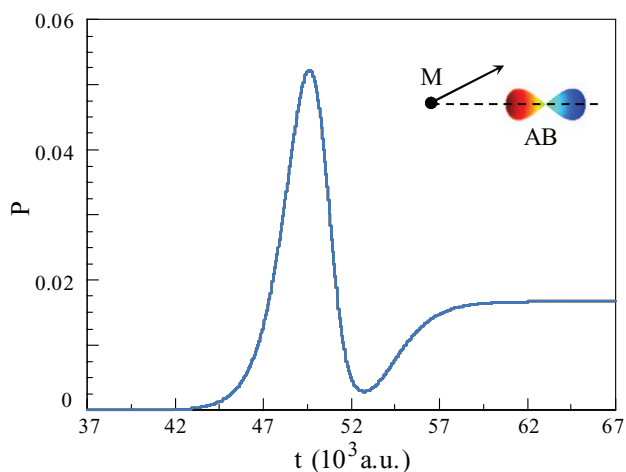

FIG. 3. Time evolution of population in the ground rotational state $j = 0$ during the process of quenching of the excited state $j = 1$ for a typical trajectory. Initial orientation of the velocity vector of M with respect to the wave function of AB is shown schematically on the insert. See text for details.

symmetry around the vector $\mathbf{Q} = (R, \Theta, \Phi)$. In such cases the trajectory is not planar, which may be important for some applications.

C. Testing BF to SF projection

In this test we took the $j = 1$, $m = +1$ eigenstate as initial state in the SF calculations. In order to start the equivalent BF calculations from this very state, we projected this m-state onto the m' eigenstates of the BF at the initial moment of time and for the initial position of the quencher (to determine the expansion coefficients). Then, as initial state in the BF calculations, we took the corresponding superposition of m' states (with coefficients determined by projection). Wave function of such initial state has no cylindrical symmetry around the vector $\mathbf{Q} = (R, \Theta, \Phi)$, so, in the BF calculations we had to propagate classical equations of motion for both Θ and Φ.

The impact parameter was $b = 5.4a_0$, the initial position of quencher M was on x-axis, but the initial velocity vector was directed arbitrarily. As trajectory progressed, we determined populations of the m-states along the trajectory directly from the SF calculations, and indirectly from the BF calculations, by projecting the BF wave function (superposition of m' states) onto m-states in the SF reference frame after each time step.

Results are presented in Fig. 4. For this trajectory the most notable process is a transfer of $\sim 10\%$ of population from the excited initial state (red) to the ground state $j = 0$ (green). This transition occurs within a short time interval of the molecule-atom encounter around $t \sim 5500$ a.u., which is seen in both the SF (Fig. 4(a)) and BF (Fig. 4(b)) calculations. However, transitions within the multiplet states of $j = 1$ occur very differently in the SF and BF calculations. In the SF calculations transitions from $m = +1$ to $m = 0$ and $m = -1$ states also occur only during the short time-interval of the molecule-atom encounter (blue in Fig. 4(a), probabilities are 1.09% and 0.41%, respectively). In contrast, in the BF calculations at the initial moment of time the population is distributed between different m'-states, and the transitions between them occur *continuously* (Fig. 4(b)). When the molecule and the atom are close these transitions are more intense (due to geometric considerations) but, strictly speaking, they never end. Nor the populations of $m' = \pm 1$ states reach any asymptotic values. However, if the corresponding BF wave functions are used to obtain the populations of m states in the SF (dashed black lines in Fig. 4(a)), the results of direct SF calculations are accurately reproduced.

From these three tests we can conclude that all our equations for calculations in the SF and BF reference frames are correct.

D. Testing matrixes U and V

In this test (BF only) we artificially switched off the molecule-quencher interaction potential. This makes matrix **M** null, so that time-evolution includes only transitions between different m'-states, within the initial constant value of $j = 1$, due to action of matrixes **U** and **V**. Initial conditions were
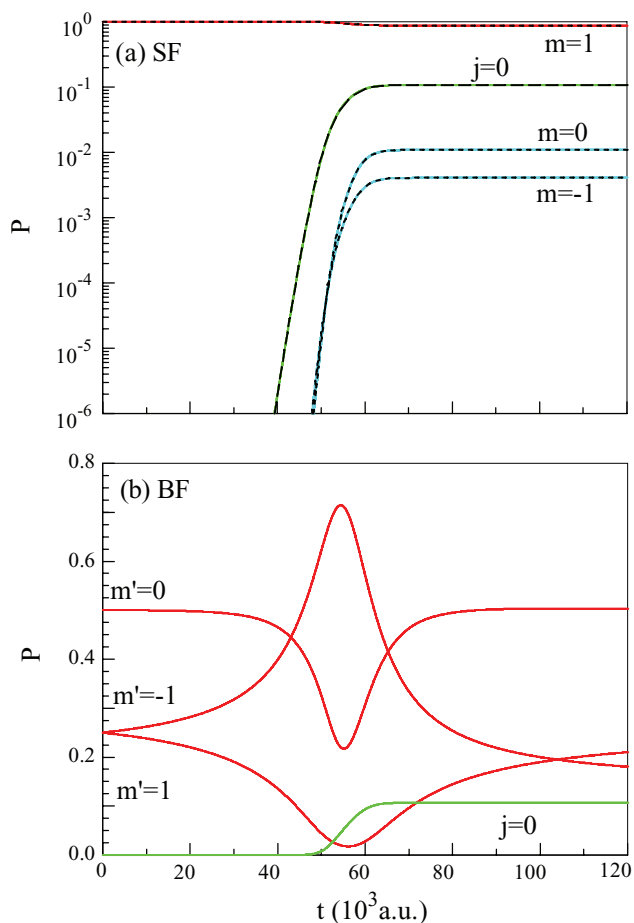

FIG. 4. Time evolution of rotational state populations in SF reference frame (a) and BF reference frame (b) for a typical trajectory. The initial quantum state was $j = 1$, $m = 1$ in the SF reference frame. Red curve in (a) corresponds to this state. Green curve in (a) and (b) corresponds to the ground state $j = 0$ and describes quenching. Blue curves in (a) correspond to the inter-multiplet transitions. Red curves in (b) correspond to different states of $j = 1$ level in the BF, all populated (arbitrarily) at the initial moment of time. Black dashed lines in (a) are obtained by projection of the BF results (b) onto SF basis functions. They entirely coincide with SF results.

identical to those of the previous example. Results are plotted in Fig. 5. As expected, transition to $j = 0$ is suppressed, but transitions between m'-states are still there. The peaks in Fig. 5 correspond to the distance of closest approach, not to the maximum of any interaction (the interaction is zero in this test). Overall, time evolution is very similar to what we saw in the previous test, Fig. 4(b). This is because the scattering angle of the trajectory in the previous test was relatively small, less than 13°. Without interaction the trajectory is a straight line, of course.

E. Testing impact parameter

In this test (SF only) we scanned the impact parameter along z-axis for the initial state $m = 0$ and separately for the initial state $(m^+ - m^-)/\sqrt{2}$ of $j = 1$. These two initial states correspond to mainly perpendicular and mainly parallel relative orientation of the molecular axis and the collision velocity vector, respectively. While such calculations are restricted, they scan pretty well the range of possible transition
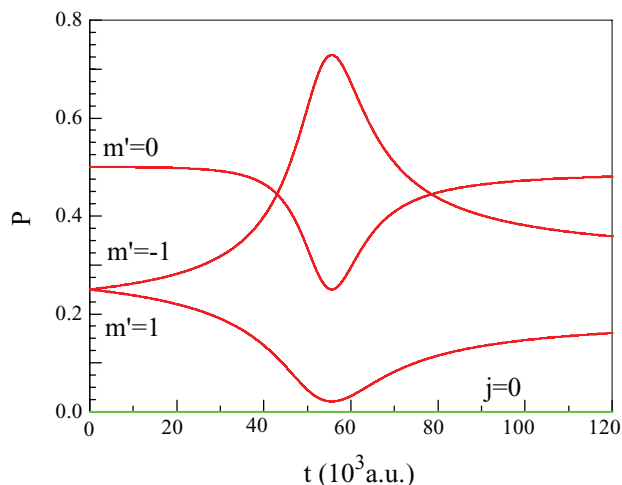
FIG. 5. Same as in Fig. 4(b), but with interaction potential "switched-off." No quenching to $j = 0$ occur, but population of different multiplet states within $j = 1$ level evolves continuously in the BF reference frame, and very similar to that in Fig. 4(b).

probabilities. Results are presented in Fig. 6. We see that transition probability is higher for perpendicular arrangement. This property carries rather clear classical meaning. However, the transition probability oscillates (as a function of impact parameter), which reflects quantum properties of these calculations.

F. Testing microscopic reversibility

Here we carried out calculations of excitation probability (SF only), in order to compare with probability of quenching and assess how well the principle of microscopic reversibility is satisfied (or how badly it is violated). It is known that the principle of microscopic reversibility is not immediately built into the MQCT,[34] but expected that it is approximately satisfied when the value of internal energy quantum is small, compared to scattering energy. Thus, we performed calculations with different scattering energies. Results are presented
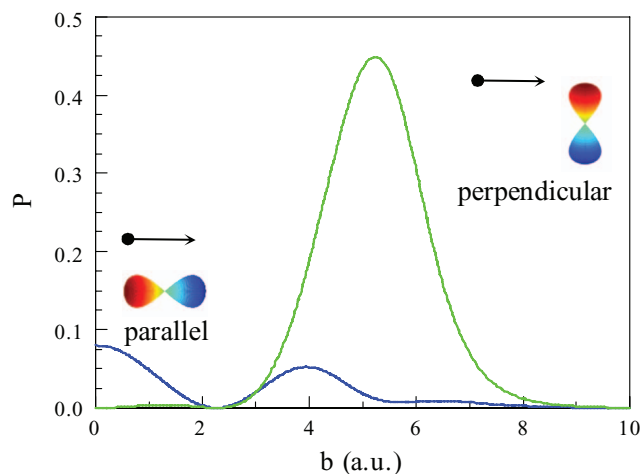

FIG. 6. Probability of $j = 1$ quenching as a function of impact parameter for perpendicular (green) and parallel (blue) initial orientations of the wave function of AB with respect to the velocity vector of M.
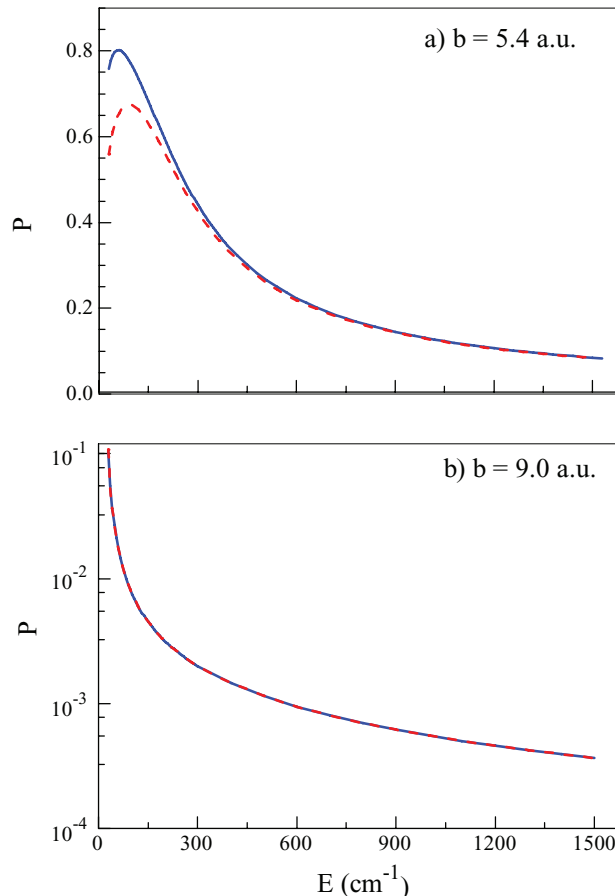

FIG. 7. Probabilities of quenching (solid blue line) and excitation (dashed red line) as functions of collision energy for two typical trajectories with small (a) and large (b) values of impact parameter.

in Figs. 7(a) and 7(b) that correspond two different trajectories, one with intermediate impact parameter $b = 5.4a_0$, and one with larger impact parameter $b = 9a_0$. As expected, the microscopic reversibility is violated at low collision energies. Here the value of rotational quantum is 1.6 cm^{-1}. In Fig. 7(a) the difference between excitation and quenching probabilities changes smoothly and reaches $\sim$35% when the collision energy is reduced to 25 cm^{-1}. In Fig. 7(b) the difference between excitation and quenching remains small even at 25 cm^{-1}. Conclusion is that the microscopic reversibility is not automatically satisfied at low collision energies, particularly when the transition probability is large. In order to build it into the MQCT one has to use the idea of collision energy symmetrization.[31,33]

IV. CONCLUSIONS

We formulated the mixed quantum/classical theory, MQCT, for rotationally (and vibrationally) inelastic scattering process in the diatomic molecule + atom system. Two versions of theory are presented: first in the SF and second in the BF reference frames. The SF version is easy to derive and the resultant equations of motion are transparent, but the state-to-state transition matrix is complex-valued and dense (many non-zero elements). Such calculations may be computationally demanding for heavier molecules and/or higher

temperatures, when the number of accessible channels becomes large. In contrast, the BF version of theory requires some tedious derivations and the final equations of motion are rather complicated (not particularly intuitive). However, the state-to-state transitions are driven by real-valued near-diagonal matrixes of smaller size. Thus, the BF formulation is the method of choice from the computational point of view, while the SF formulation can serve as a test of the BF equations of motion, and the code. Rigorous numerical tests were carried out for a model system to ensure that all equations, matrixes and computer codes in both SF and BF reference frames are correct. These tests also helped to better understand differences and similarities of two physically equivalent but mathematically different formulations.

We want to emphasize again that MQCT is not thought to replace the full-quantum calculations. At low temperatures and/or light collision partners the full-quantum calculations are indispensable (accurate and affordable). It is at higher temperatures and for heavier molecules/quenchers we expect that MQCT can successfully complement the existing methods. In its current form this theory can be applied to a number of important diatomic molecule + atom inelastic scattering processes, such as SO + He,[44] NH + He,[45] and CO + Ar.[46] Our recent MQCT calculations of rotational state-to-state transition cross sections for N_2 + Na system show excellent agreement with full quantum results for both excitation and quenching processes in a broad range of collision energies.[39] Another ongoing project is to develop MQCT further, for treatment of general asymmetric top rotor molecules (bent triatomics and small polyatomic molecules) in order to treat the quenching of H_2O and SOMs. Some (very) preliminary data for H_2O + He scattering are also encouraging.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATIVE OF WIGNER ROTATION FUNCTION

Transformation of the basis set of rotational eigenstates is

$$Y_{jm'}(\gamma, \varphi') = \sum_{m=-j}^{j} D^j_{mm'}(\Phi, \Theta, 0) Y_{jm}(\theta, \varphi). \quad (A1)$$

In general:

$$D^j_{mm'}(\Phi, \Theta, \Lambda) = \exp(-im\Phi) d^j_{mm'}(\Theta) \exp(-im'\Lambda), \quad (A2)$$

where $d^j_{mm'}(\Theta)$ are small Wigner d-functions, or explicitly:

$$d^j_{mm'}(\Theta) = \left[(j+m')!(j-m')!(j+m)!(j-m)!\right]^{1/2}$$
$$\times \sum_s \frac{(-1)^{m-m'+s}}{(j+m'-s)!s!(m-m'+s)!(j-m-s)!}$$
$$\times \left(\cos\left(\frac{\Theta}{2}\right)\right)^{2j+m'-2s-m} \left(\sin\left(\frac{\Theta}{2}\right)\right)^{m+2s-m'}.$$
$$(A3)$$

The index s takes only such values that the factorials are non-negative. The d-matrix elements defined here are real and correspond to the $z - y - z$ convention.[41, 42]

For an atomic quencher the last rotation (by angle Λ around the mole-quencher axis) is meaningless. So, one can set $\Lambda = 0$ without loss of generality. The purpose of this appendix is to derive expressions for $\partial D^j_{mm'}(\Phi, \Theta, \Lambda)/\partial\Phi$ and $\partial D^j_{mm'}(\Phi, \Theta, \Lambda)/\partial\Theta$. It is quite clear that

$$\partial D^j_{mm'}(\Phi, \Theta, \Lambda)/\partial\Lambda = -im' D^j_{mm'}(\Phi, \Theta, \Lambda). \quad (A4)$$

One could also write immediately $\partial D^j_{mm'}(\Phi, \Theta, \Lambda)/\partial\Phi = -im D^j_{mm'}(\Phi, \Theta, \Lambda)$ but this expression is useless because it contains m, while the sum in Eq. (28) is also over m. In order to obtain a useful expression for $\partial/\partial\Phi$, and derive the expression for $\partial/\partial\Theta$ without differentiating Eq. (A3) for d-function directly, we will use the raising and lowering operators as explained below.

There is a deep connection between Wigner d-functions and a quantum rotation of the symmetric top. D-function is an eigenfunction of the symmetric top Hamiltonian. In terms of Schrodinger equation: $\Im^2 D^j_{mm'} = j(j+1) D^j_{mm'}$, where the kinetic energy operator is

$$\Im^2 = -\frac{1}{\sin\Theta}\frac{\partial}{\partial\Theta}\sin\Theta\frac{\partial}{\partial\Theta}$$
$$-\frac{1}{\sin^2\Theta}\left(\frac{\partial^2}{\partial^2\Lambda} + \frac{\partial^2}{\partial^2\Phi} + 2\cos\Theta\frac{\partial^2}{\partial\Lambda\partial\Phi}\right).$$

Reference 40 emphasizes that Wigner functions have the same properties as spherical harmonics. We know that for spherical harmonics there are raising and lowering operators, e.g.,

$$(\hat{j}_x \pm i\,\hat{j}_y) Y_{jm} = \hat{j}_\pm Y_{jm} = \sqrt{j(j+1) - m(m\pm 1)} Y_{jm\pm 1}.$$

Similar operators exist for Wigner functions. They are called the *space fixed angular momentum operators of rigid rotor*:

$$\Im_x = i\left(\cos\Lambda\cot\Theta\frac{\partial}{\partial\Lambda} + \sin\Lambda\frac{\partial}{\partial\Theta} - \frac{\cos\Lambda}{\sin\Theta}\frac{\partial}{\partial\Phi}\right), \quad (A5)$$

$$\Im_y = i\left(\sin\Lambda\cot\Theta\frac{\partial}{\partial\Lambda} - \cos\Lambda\frac{\partial}{\partial\Theta} - \frac{\sin\Lambda}{\sin\Theta}\frac{\partial}{\partial\Phi}\right), \quad (A6)$$

$$\Im_z = -i\frac{\partial}{\partial\Lambda}. \quad (A7)$$

Then, the raising and lowering operators $\Im_+ = \Im_x - i\Im_y$ and $\Im_- = \Im_x + i\Im_y$ (note: minus sign in raising and plus sign in lowering) result in

$$\Im_\pm D^j_{mm'} = \overline{j(j+1) - m'(m'\pm 1)} D^j_{mm'\pm 1}. \quad (A8)$$

The kinetic energy operator can be expressed as $\Im^2 = \Im_+\Im_- + \Im_-\Im_+ + \Im_z^2$. Raising and lowering operators allow expressing the partial derivatives of D-function through other D-functions. In other words, action of a derivative operator is a mapping of one quantum state (the rotational state of symmetric top) onto other states.

In the $\Lambda = 0$ case relevant to the diatomic molecule Eqs. (A5)–(A7) simplify to

$$\tilde{\Im}_x = i\left(\cot\Theta\frac{\partial}{\partial\Lambda} - \frac{1}{\sin\Theta}\frac{\partial}{\partial\Phi}\right), \tag{A9}$$

$$\tilde{\Im}_y = -i\frac{\partial}{\partial\Theta}, \tag{A10}$$

$$\tilde{\Im}_z = -i\frac{\partial}{\partial\Lambda}. \tag{A11}$$

Derivative over Θ is obtained from the second of these equations, which gives $\partial/\partial\Theta = i\tilde{\Im}_y$.

Using $\tilde{\Im}_y = (\tilde{\Im}_- - \tilde{\Im}_+)/2i$ one arrives to

$$\frac{\partial}{\partial\Theta} = \frac{(\tilde{\Im}_- - \tilde{\Im}_+)}{2}. \tag{A12}$$

One can also restrict consideration to $\Phi = 0$ and $\Lambda = 0$ using the following relation:

$$\frac{\partial D^j_{mm'}(\Phi,\Theta,\Lambda)}{\partial\Theta} = \exp(-i\Phi m - im'\Lambda)\frac{\partial D^j_{mm'}(0,\Theta,0)}{\partial\Theta}. \tag{A13}$$

This is so because only $d^j_{mm'}(\Theta)$ depend on Θ. So

$$\frac{\partial D^j_{mm'}(0,\Theta,0)}{\partial\Theta}$$
$$= \left(\frac{\tilde{\Im}_- - \tilde{\Im}_+}{2}\right)D^j_{mm'}(0,\Theta,0)$$
$$= \frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}D^j_{mm'-1}(0,\Theta,0)$$
$$-\sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(0,\Theta,0)]. \tag{A14}$$

Finally, for derivative over Θ we obtain

$$\frac{\partial D^j_{mm'}(\Phi,\Theta,0)}{\partial\Theta}$$
$$= \exp(-im\Phi)\frac{\partial D^j_{mm'}(0,\Theta,0)}{\partial\Theta}$$
$$= \exp(-im\Phi)\frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}D^j_{mm'-1}(0,\Theta,0)$$
$$-\sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(0,\Theta,0)]$$
$$= \frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}\exp(-im\Phi)D^j_{mm'-1}(0,\Theta,0)$$
$$-\sqrt{j(j+1)-m'(m'+1)}\exp(-im\Phi)D^j_{mm'+1}(0,\Theta,0)]$$
$$= \frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}D^j_{mm'-1}(\Phi,\Theta,0)$$
$$-\sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(\Phi,\Theta,0)]. \tag{A15}$$

This is the final expression for $\partial/\partial\Theta$.

Now focus on derivative over Φ. Combining Eq. (A8) with $\Im_+ = \Im_x - i\Im_y$ and using Eqs. (A9) and (A10), one obtains:

$$\Im_+ D^j_{mm'}(\Phi,\Theta,0)$$
$$= \sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(\Phi,\Theta,0)$$
$$= \left\{i\left(\cot\Theta\frac{\partial}{\partial\Lambda} - \frac{1}{\sin\Theta}\frac{\partial}{\partial\Phi}\right) - \frac{\partial}{\partial\Theta}\right\}D^j_{mm'}(\Phi,\Theta,0). \tag{A16}$$

Using Eq. (A15) for derivative over Θ and Eq. (A4) for derivative over Λ one obtains

$$\frac{\partial D^j_{mm'}(\Phi,\Theta,0)}{\partial\Phi}$$
$$= i\frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}D^j_{mm'-1}(\Phi,\Theta,0)$$
$$+ \sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(\Phi,\Theta,0)]\sin\Theta$$
$$- im'D^j_{mm}(\Phi,\Theta,0)\cos\Theta. \tag{A17}$$

This is the final expression for $\partial/\partial\Phi$. Note that this expression depends on m' (not on m) so that summation in Eq. (19) can be carried out analytically as follows:

$$\sum_m \frac{\partial}{\partial\Phi}D^j_{mm'}(\Phi,\Theta,0)Y_{jm}(\theta,\varphi)$$
$$= \sum_m \left(i\frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}D^j_{mm'-1}(\Phi,\Theta,0)\right.$$
$$+ \sqrt{j(j+1)-m'(m'+1)}D^j_{mm'+1}(\Phi,\Theta,0)]\sin\Theta$$
$$\left. - im'D^j_{mm'}(\Phi,\Theta,0)\cos\Theta\right)Y_{jm}(\theta,\varphi)$$
$$= i\frac{1}{2}[\sqrt{j(j+1)-m'(m'-1)}Y_{jm'-1}(\gamma,\varphi')$$
$$+ \sqrt{j(j+1)-m'(m'+1)}Y_{jm'+1}(\gamma,\varphi')]\sin\Theta$$
$$- im'Y_{jm'}(\gamma,\varphi')\cos\Theta. \tag{A18}$$

Expressions (A15) and (A17) can be found in the handbook,[43] where they are given without any prove.

APPENDIX B: MATRIX ELEMENTS IN THE BF

Using the expansions of Eqs. (17) and (18) and the expression (A15) for partial derivative over Θ

we can write:

$$
\frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} = \sum_{n'j'm'} a_{n'j'm'} \phi_{n'j'}(r) \frac{\partial Y_{j'm'}(\gamma, \varphi')}{\partial \Theta} \exp\left\{-\frac{i E_{n'j'} t}{\hbar}\right\}
$$

$$
= \sum_{n'j'm'} a_{n'j'm'} \phi_{n'j'}(r) \sum_m \frac{\partial D^{j'}_{mm'}(\Phi, \Theta, 0)}{\partial \Theta} Y_{j'm}(\theta, \varphi) \exp\left\{-\frac{i E_{n'j'} t}{\hbar}\right\}
$$

$$
= \sum_{n'j'm'} a_{n'j'm'} \phi_{n'j'}(r) \frac{1}{2} [\sqrt{j'(j'+1) - m'(m'-1)} Y_{j'm'-1}(\gamma, \varphi') - \sqrt{j'(j'+1) - m'(m'+1)} Y_{j'm'+1}(\gamma, \varphi')] \exp\left\{-\frac{i E_{n'j'} t}{\hbar}\right\}.
$$

(B1)

Now we need to substitute (B1) into the first of term of Eq. (27a), which for convenience can be split onto two terms as follows:

$$
-2\mathrm{Re}\langle \psi(r, \gamma, \varphi') | V(R, r, \gamma) | \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} \rangle
$$

$$
= -\langle \psi(r, \gamma, \varphi') | V(R, r, \gamma) | \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} \rangle - \langle \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} | V(R, r, \gamma) | \psi(r, \gamma, \varphi') \rangle.
$$

(B2)

The substitution gives

$$
\langle \psi(r, \gamma, \varphi') | V(R, r, \gamma) | \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} \rangle
$$

$$
= \sum_{n''j''m''} \sum_{n'j'm'} a^*_{n''j''m''} a_{n'j'm'} \exp\left(i \frac{E_{n''j''} - E_{n'j'}}{\hbar} t\right) \langle \phi_{n''j''}(r) Y_{j''m''}(\gamma, \varphi') | V(R, r, \gamma) |
$$

$$
\times \phi_{n'j'}(r) \frac{1}{2} [\sqrt{j'(j'+1) - m'(m'-1)} Y_{j'm'-1}(\gamma, \varphi') - \sqrt{j'(j'+1) - m'(m'+1)} Y_{j'm'+1}(\gamma, \varphi')] \rangle
$$

$$
= \sum_{n''j''m''} \sum_{n'j'm'} a^*_{n''j''m''} a_{n'j'm'} \exp\left(i \frac{E_{n''j''} - E_{n'j'}}{\hbar} t\right)
$$

$$
\times \frac{1}{2} [\sqrt{j'(j'+1) - m'(m'-1)} \langle \phi_{n''j''}(r) Y_{j''m''}(\gamma, \varphi') | V(R, r, \gamma) | \phi_{n'j'}(r) Y_{j'm'-1}(\gamma, \varphi') \rangle
$$

$$
- \sqrt{j'(j'+1) - m'(m'+1)} \langle \phi_{n''j''}(r) Y_{j''m''}(\gamma, \varphi') | V(R, r, \gamma) | \phi_{n'j'}(r) Y_{j'm'+1}(\gamma, \varphi') \rangle]
$$

$$
= \sum_{n''j''m''} \sum_{n'j'm'} a^*_{n''j''m''} a_{n'j'm'} \exp\left(i \frac{E_{n''j''} - E_{n'j'}}{\hbar} t\right)
$$

$$
\times \frac{1}{2} [\sqrt{j'(j'+1) - m'(m'+1)} M^{n''j''m''}_{n'j'm'+1}(R) - \sqrt{j'(j'-1) - m'(m'-1)} M^{n''j''m''}_{n'j'm'-1}(R)],
$$

(B3)

and similarly

$$
\langle \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} | V(R, r, \gamma) | \psi(r, \gamma, \varphi') \rangle = \sum_{n''j''m''} \sum_{n'j'm'} a^*_{n''j''m''} a_{n'j'm'} \exp\left(i \frac{E_{n''j''} - E_{n'j'}}{\hbar} t\right)
$$

$$
\times \frac{1}{2} [\sqrt{j''(j''+1) - m''(m''+1)} M^{n''j''m''+1}_{n'j'm'}(R) - \sqrt{j''(j''-1) - m''(m''-1)} M^{n''j''m''-1}_{n'j'm'}(R)].
$$

(B4)

Combining these two expressions we finally obtain

$$
-2\mathrm{Re}\langle \psi(r, \gamma, \varphi') | V(R, r, \gamma) | \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} \rangle = -\langle \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} | V(R, r, \gamma) | \psi(r, \gamma, \varphi') \rangle - \langle \psi(r, \gamma, \varphi') | V(R, r, \gamma) | \frac{\partial \psi(r, \gamma, \varphi')}{\partial \Theta} \rangle
$$

$$
= \sum_{n''j''m''} \sum_{n'j'm'} a^*_{n''j''m''} a_{n'j'm'} \exp\left(i \frac{E_{n''j''} - E_{n'j'}}{\hbar} t\right) \frac{1}{2} \big[M^{n''j''m''-1}_{n'j'm'} \sqrt{j''(j''+1) - m''(m''-1)}
$$

$$
- M^{n''j''m''+1}_{n'j'm'} \sqrt{j''(j''+1) - m''(m''+1)} + \sqrt{j'(j'+1) - m'(m'-1)} M^{n'j'm'-1}_{n''j''m''} - \sqrt{j'(j'+1) - m'(m'+1)} M^{n'j'm'+1}_{n''j''m''} \big].
$$

(B5)

It is shown in Appendix C that this expression can be conveniently re-written through the commutator of matrixes **M** and **U**:

$$-2\mathrm{Re}\langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial \psi(r,\gamma,\varphi')}{\partial \Theta}\rangle$$

$$= \sum_{n''j''m''}\sum_{n'j'm'} a^*_{n''j''m''}a_{n'j'm'}$$

$$\times \exp\left(i\frac{E_{n''j''}-E_{n'j'}}{\hbar}t\right)[\mathbf{M},\mathbf{U}]^{n''j''m''}_{n'j'm'}. \qquad (B6)$$

which leads to Eq. (28a). Furthermore, we can split the sum in Eq. (B6) onto a pair of terms:

$$a^*_{n''j''m''}a_{n'j'm'}\exp\left(i\frac{E_{n''j''}-E_{n'j'}}{\hbar}t\right)[\mathbf{M},\mathbf{U}]^{n''j''m''}_{n'j'm'}$$

and

$$a_{n''j''m''}a^*_{n'j'm'}\exp\left(i\frac{E_{n'j'}-E_{n''j''}}{\hbar}t\right)[\mathbf{M},\mathbf{U}]^{n'j'm'}_{n''j''m''}.$$

Because [**M**, **U**] is symmetric and real (according to Eq. (C17)) we have the sum of these two numbers is a real number. If $n'j'm' = n''j''m''$ the diagonal term (which does not have a pair) is real by itself: $|a_{n'j'm'}|^2[\mathbf{M},\mathbf{U}]^{n'j'm'}_{n'j'm'}$. Thus, the expression of Eq. (B6) always gives real numbers. Its physical meaning corresponds to the torque.

Now consider $\partial \psi/\partial \Phi$ in Eq. (27b):

$$\frac{\partial \psi(r,\gamma,\varphi')}{\partial \Phi} = \sum_{n'j'm'} a_{n'j'm'}\phi_{n'j'}(r)\frac{\partial Y_{j'm'}(\gamma,\varphi')}{\partial \Phi}\exp\left\{-\frac{iE_{n'j'}t}{\hbar}\right\} = i\sum_{n'j'm'} a_{n'j'm'}\phi_{n'j'}(r)\exp\left\{-\frac{iE_{n'j'}t}{\hbar}\right\}$$

$$\times \left(\sin\Theta\frac{1}{2}[\sqrt{j'(j'+1)-m'(m'-1)}Y_{j'm'-1}(\gamma,\varphi') + \sqrt{j'(j'+1)-m'(m'+1)}Y_{j'm'+1}(\gamma,\varphi')] - m'\cos\Theta Y_{j'm'}(\gamma,\varphi')\right). \qquad (B7)$$

Then, for the matrix element in Eq. (27b) we can write:

$$\langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial \psi(r,\gamma,\varphi')}{\partial \Phi}\rangle = i\sum_{n''j''m''}\sum_{n'j'm'} a^*_{n''j''m''}a_{n'j'm'}\exp\left(i\frac{E_{n''j''}-E_{n'j'}}{\hbar}t\right)$$

$$\times \left(\sin\Theta\frac{1}{2}[\sqrt{j'(j'+1)-m'(m'-1)}M^{n'j'm'-1}_{n''j''m''} + \sqrt{j'(j'+1)-m'(m'+1)}M^{j'm'+1}_{n''j''m''}] - m'\cos\Theta M^{n''j''m''}_{n'j'm'}\right), \qquad (B8)$$

and similarly

$$\langle \frac{\partial \psi(r,\gamma,\varphi')}{\partial \Phi}|V(R,r,\gamma)|\psi(r,\gamma,\varphi')\rangle = -i\sum_{n''j''m''}\sum_{n'j'm'} a^*_{n''j''m''}a_{n'j'm'}\exp\left(i\frac{E_{n''j''}-E_{n'j'}}{\hbar}t\right)$$

$$\times \left(\frac{1}{2}\sin\Theta[\sqrt{j''(j''+1)-m''(m''-1)}M^{n''j''m''-1}_{n'j'm'} + \sqrt{j''(j''+1)-m''(m''+1)}M^{n''j''m''+1}_{n'j'm'}] - m''\cos\Theta M^{n''j''m''}_{n'j'm'}\right). \qquad (B9)$$

Combining these two expressions:

$$2\mathrm{Re}\langle \psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial \psi(r,\gamma,\varphi')}{\partial \Phi}\rangle = i\sum_{n''j''m''}\sum_{n'j'm'} a^*_{n''j''m''}a_{n'j'm'}\exp\left(i\frac{E_{n''j''}-E_{n'j'}}{\hbar}t\right)$$

$$\times \left(\sin\Theta\frac{1}{2}[\sqrt{j''(j''+1)-m''(m''-1)}M^{n''j''m''-1}_{n'j'm'} + \sqrt{j''(j''+1)-m''(m''+1)}M^{n''j''m''+1}_{n'j'm'}] - m''\cos\Theta M^{n''j''m''}_{n'j'm'}\right.$$

$$\left.- \sin\Theta\frac{1}{2}[\sqrt{j'(j'+1)-m'(m'-1)}M^{n'j'm'-1}_{n''j''m''} + \sqrt{j'(j'+1)-m'(m'+1)}M^{n'j'm'+1}_{n''j''m''}] + m'\cos\Theta M^{n'j'm'}_{n''j''m''}\right). \qquad (B10)$$

According to (C1) $m' M_{n''j''m''}^{n'j'm'} = m'' M_{n'j'm'}^{n''j''m''}$ and Appendix C shows that this expression can be conveniently rewritten through the commutator of matrixes **M** and **V**:

$$-2\text{Re}\langle\psi(r,\gamma,\varphi')|V(R,r,\gamma)|\frac{\partial\psi(r,\gamma,\varphi')}{\partial\Phi}\rangle$$

$$= -i\sum_{n''j''m''}\sum_{n'j'm'} a_{n''j''m''}^* a_{n'j'm'}$$

$$\times \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right)[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''} . \quad (B11)$$

This leads to Eq. (28b). Furthermore, we can split the sum in Eq. (B11) onto a pair of terms:

$$-ia_{n''j''m''}^* a_{n'j'm'} \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right)[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}$$

and

$$-ia_{n'j'm'}^* a_{n''j''m''} \exp\left(i\frac{E_{n'j'} - E_{n''j''}}{\hbar}t\right)[\mathbf{M},\mathbf{V}]_{n''j''m''}^{n'j'm'} .$$

Due to Eq. (C8) we have

$$-ia_{n''j''m''}^* a_{n'j'm'} \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right)[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}$$

$$-ia_{n'j'm'}^* a_{n''j''m''} \exp\left(i\frac{E_{n'j'} - E_{n''j''}}{\hbar}t\right)[\mathbf{M},\mathbf{V}]_{n''j''m''}^{n'j'm'}$$

$$= -i\left\{a_{n''j''m''}^* a_{n'j'm'} \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right)\right.$$

$$\left. - a_{n'j'm'}^* a_{n''j''m''} \exp\left(i\frac{E_{n'j'} - E_{n''j''}}{\hbar}t\right)\right\}[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''} .$$

$$(B12)$$

Because

$$a_{n''j''m''}^* a_{n'j'm'} \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right) - a_{n'j'm'}^* a_{n''j''m''}$$

$$\times \exp\left(i\frac{E_{n'j'} - E_{n''j''}}{\hbar}t\right) = 2i\,\text{Im}\,a_{n''j''m''}^* a_{n'j'm'}$$

$$\times \exp\left(i\frac{E_{n''j''} - E_{n'j'}}{\hbar}t\right)$$

is an imaginary number, the value of (B12) is always real and $[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}$ is real too. Note that the diagonal term in this matrix is null: $[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n'j'm'} = 0$, i.e., also real. This demonstrates that the torque (B11) in the classical equation of motion (28) is always a real number.

APPENDIX C: PROPERTIES OF M, U, V, AND THEIR COMMUTATORS

The expanded matrix **M** (labeled by three indexes) is obtained by combining the smaller matrixes (labelled by two indexes) for different values of m' given by Eq. (31) in the following way:

$$M_{n'j'm'}^{n''j''m''}(R) = \delta_{m'm''} M_{n'j'}^{n''j''}(R). \quad (C1)$$

By this construction, and according to the definition of Eq. (22), the entire matrix **M** is symmetric, $M_{n'j'm'}^{n''j''m''} = M_{n''j''m''}^{n'j'm'}$, and is diagonal in m': $M_{n'j'm'}^{n''j''m''} = 0$ if $m'' \neq m'$.

Similarly, the expanded matrixes **U** and **V** (labeled by three indexes) are obtained by combining the smaller matrixes (labelled by one index) for different values of (nj) given by Eqs. (24a) and (24b). Namely:

$$U_{n'j'm'}^{n''j''m''} = \delta_{n'j',n''j''} U_{m'}^{m''} \quad \text{and} \quad V_{n'j'm'}^{n''j''m''} = \delta_{n'j',n''j''} V_{m'}^{m''}.$$

$$(C2)$$

So, the matrixes **U** and **V** are diagonal in (nj). Their elements are zero if $n'' \neq n'$ or $j'' \neq j'$. Consider $m'' = m' + 1$. In this case, due to the first term in Eq. (24a), we obtain

$$U_{n'j'm'}^{n''j''m'+1} = \delta_{n'j',n''j''}\frac{1}{2}\sqrt{j'(j'+1) - m'(m'+1)}. \quad (C3)$$

Here we replaced m'' by $m' + 1$, including the expression,

$$\sqrt{j'(j'+1) - m''(m''-1)} = \sqrt{j'(j'+1) - (m'+1)m'}.$$

$$(C4)$$

Now consider $m'' = m' - 1$. In this case, due to the second term in Eq. (24a), we obtain

$$U_{n'j'm'+1}^{n''j''m'} = -\delta_{n'j',n''j''}\frac{1}{2}\sqrt{j'(j'+1) - m'(m'+1)}. \quad (C5)$$

Here we deliberately used $m' + 1$ and m' as lower and upper indexes, respectively. Comparing Eqs. (C3) and (C5) we conclude that:

$$U_{n'j'm'+1}^{n''j''m'} = -U_{n'j'm'}^{n''j''m'+1} = U_{n''j''m'}^{n'j'm'+1}. \quad (C6)$$

Since $U_{n'j'm'}^{n''j''m''} = 0$ if $m'' \neq m' \pm 1$ (according to the definition of Eq. (24a) and by construction) we also obtain from Eq. (C6) that

$$U_{n'j'm'}^{n''j''m''} = -U_{n''j''m''}^{n'j'm'}. \quad (C7)$$

Thus, matrix **U** is anti-symmetric.

Similar considerations apply to the matrix **V**, but it appears to be symmetric:

$$V_{n'j'm'}^{n''j''m''} = V_{n''j''m''}^{n'j'm'}. \quad (C8)$$

The commutator of **M** and **U** is by definition:

$$[\mathbf{M},\mathbf{U}]_{n'j'm'}^{n''j''m''}$$

$$= \sum_{n'''j'''m'''} M_{n'j'm'}^{n'''j'''m'''} U_{n'''j'''m'''}^{n''j''m''} - U_{n'j'm'}^{n'''j'''m'''} M_{n'''j'''m'''}^{n''j''m''}. \quad (C9)$$

Consider the first term in this expression. Using Eq. (24a) we obtain

$$\sum_{n'''j'''m'''} M_{n'j'm'}^{n'''j'''m'''} U_{n'''j'''m'''}^{n''j''m''}$$

$$= \sum_{m'''}\frac{1}{2} M_{n'j'm'}^{n''j''m'''} [\delta_{m''',m''-1}\sqrt{j''(j''+1) - m''(m''-1)}$$

$$-\delta_{m''',m''+1}\sqrt{j''(j''+1) - m''(m''+1)}]$$

$$= \frac{1}{2}\left[M_{n'j'm'}^{n''j''m''-1}\sqrt{j''(j''+1) - m''(m''-1)}\right.$$

$$\left. - M_{n'j'm'}^{n''j''m''+1}\sqrt{j''(j''+1) - m''(m''+1)}\right]. \quad (C10)$$

And similar expression for the second term in Eq. (C9):

$$\sum_{n'''j'''m'''} U_{n'j'm'}^{n'''j'''m'''} M_{n''j''m''}^{n'''j'''m'''}$$

$$= \sum_{m'''} U_{n'j'm'}^{n'j'm'''} M_{n''j''m''}^{n'j'm'''}$$

$$= \sum_{m'''} \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'''}\delta_{m',m'''-1}\sqrt{j'(j'+1)-m'''(m'''-1)} \right.$$

$$\left. - M_{n''j''m''}^{n'j'm'''}\delta_{m',m'''+1}\sqrt{j'(j'+1)-m'''(m'''+1)} \right]$$

$$= \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'+1}\sqrt{j'(j'+1)-m'(m'+1)} \right.$$

$$\left. - M_{n''j''m''}^{n'j'm'-1}\sqrt{j'(j'+1)-m'(m'-1)} \right] \quad (C11)$$

or

$$-\sum_{n'''j'''m'''} U_{n'''j'''m'''}^{n'j'm'} M_{n''j''m''}^{n'''j'''m'''}$$

$$= \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'-1}\sqrt{j'(j'+1)-m'(m'-1)} \right.$$

$$\left. - M_{n''j''m''}^{n'j'm'+1}\sqrt{j'(j'+1)-m'(m'+1)} \right]. \quad (C12)$$

Finally, substitution of expressions (C10) and (C12) into (C8) gives

$$[\mathbf{M},\mathbf{U}]_{n'j'm'}^{n''j''m''}$$

$$= \frac{1}{2}\left[M_{n''j''m''+1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''+1)} \right.$$

$$\left. - M_{n''j''m''-1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''-1)} \right]$$

$$+ \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'+1}\sqrt{j'(j'+1)-m'(m'+1)} \right.$$

$$\left. - M_{n''j''m''}^{n'j'm'-1}\sqrt{j'(j'+1)-m'(m'-1)} \right]. \quad (C13)$$

All similar considerations apply to the commutator of **M** and **V**:

$$\sum_{n'''j'''m'''} M_{n'j'm'}^{n'''j'''m'''} V_{n'''j'''m'''}^{n''j''m''}$$

$$= \frac{1}{2}\left[M_{n''j''m''+1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''+1)} \right.$$

$$\left. + M_{n''j''m''-1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''-1)} \right] \quad (C14)$$

and

$$\sum_{n'''j'''m'''} V_{n'''j'''m'''}^{n'j'm'} M_{n''j''m''}^{n'''j'''m'''}$$

$$= \sum_{m'''} V_{n'j'm'''}^{n'j'm'} M_{n''j''m''}^{n'j'm'''}$$

$$= \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'+1}\sqrt{j'(j'+1)-m'(m'+1)} \right.$$

$$\left. + M_{n''j''m''}^{n'j'm'-1}\sqrt{j'(j'+1)-m'(m'-1)} \right], \quad (C15)$$

and finally

$$[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}$$

$$= \frac{1}{2}\left[M_{n''j''m''+1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''+1)} \right.$$

$$\left. + M_{n''j''m''-1}^{n'j'm'}\sqrt{j''(j''+1)-m''(m''-1)} \right]$$

$$- \frac{1}{2}\left[M_{n''j''m''}^{n'j'm'+1}\sqrt{j'(j'+1)-m'(m'+1)} \right.$$

$$\left. + M_{n''j''m''}^{n'j'm'-1}\sqrt{j'(j'+1)-m'(m'-1)} \right]. \quad (C16)$$

Several properties of the commutator matrixes are worth noting. Namely,

$$[\mathbf{M},\mathbf{U}]_{n'j'm'}^{n''j''m''} = [\mathbf{M},\mathbf{U}]_{n''j''m''}^{n'j'm'}, \quad (C17)$$

which means that this matrix is symmetric. This is easy to prove using the properties (C1) and (C7) as follows:

$$[\mathbf{M},\mathbf{U}]_{n'j'm'}^{n''j''m''}$$

$$= \sum_{n'''j'''m'''} M_{n'j'm'}^{n'''j'''m'''} U_{n'''j'''m'''}^{n''j''m''} - U_{n'j'm'}^{n'''j'''m'''} M_{n'''j'''m'''}^{n''j''m''}$$

$$= \sum_{n'''j'''m'''} U_{n'''j'''m'''}^{n'j'm'} M_{n''j''m''}^{n'''j'''m'''} - M_{n'''j'''m'''}^{n'j'm'} U_{n''j''m''}^{n'''j'''m'''}$$

$$= \sum_{n'''j'''m'''} M_{n''j''m''}^{n'''j'''m'''} U_{n'''j'''m'''}^{n'j'm'} - U_{n''j''m''}^{n'''j'''m'''} M_{n'''j'''m'''}^{n'j'm'}$$

$$= [\mathbf{M},\mathbf{U}]_{n''j''m''}^{n'j'm'}.$$

In contrast, the commutator

$$[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''} = -[\mathbf{M},\mathbf{V}]_{n''j''m''}^{n'j'm'} \quad (C18)$$

is an anti-symmetric matrix. This is shown using Eq. (C8) as follows:

$$[\mathbf{M},\mathbf{V}]_{n'j'm'}^{n''j''m''}$$

$$= \sum_{n'''j'''m'''} M_{n'j'm'}^{n'''j'''m'''} V_{n'''j'''m'''}^{n''j''m''} - V_{n'j'm'}^{n'''j'''m'''} M_{n'''j'''m'''}^{n''j''m''}$$

$$= \sum_{n'''j'''m'''} M_{n''j''m''}^{n'''j'''m'''} V_{n'''j'''m'''}^{n'j'm'} - V_{n''j''m''}^{n'''j'''m'''} M_{n'''j'''m'''}^{n'j'm'}$$

$$= -\left(\sum_{n'''j'''m'''} M_{n''j''m''}^{n'''j'''m'''} V_{n'''j'''m'''}^{n'j'm'} - V_{n''j''m''}^{n'''j'''m'''} M_{n'''j'''m'''}^{n'j'm'} \right)$$

$$= -[\mathbf{M},\mathbf{V}]_{n''j''m''}^{n'j'm'}.$$

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