

Model for nuclear spin product-state distributions of ultracold chemical reactions in magnetic fieldsGoulven Quémener *Université Paris-Saclay, CNRS, Laboratoire Aimé Cotton, 91405, Orsay, France*Ming-Guang Hu , Yu Liu, Matthew A. Nichols , Lingbang Zhu, and Kang-Kuen Ni*Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA;**Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA;**and Harvard-MIT Center for Ultracold Atoms, Cambridge, Massachusetts 02138, USA*

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Based on a theoretical model where the nuclear spins remain unchanged during a collision, we provide an analytical and general expression for the nuclear spin state-to-state distribution of an ultracold diatom-diatom chemical reaction in a magnetic field, for given rotational transitions of the molecules. It simply requires knowledge of the field-dependent eigenfunctions of the molecular reactants and products of the chemical reaction. The final state-to-state distribution drastically changes with the magnetic field. When the distribution is summed over all the final products, a simplified expression is found where only the knowledge of the eigenfunctions of the molecular reactants is required. The present theoretical formalism has been successfully used to explain the magnetic field behavior of the product-state distribution in chemical reactions of ultracold KRb molecules [Hu *et al.*, *Nat. Chem.* **13**, 435 (2021)].

DOI: [10.1103/PhysRevA.104.052817](https://doi.org/10.1103/PhysRevA.104.052817)**I. INTRODUCTION**

The fate of a chemical reaction is a fascinating subject [1–5]. It is governed by a potential energy surface and it tells about the influence of the numerous and complicated many-body electronic interactions when the atoms of the molecules are close to each other, in the region where chemistry prevails. Ultracold molecules can be used to probe such chemical reactions with an unprecedented control at the quantum level [6–10]. All the fragments of an ultracold chemical reaction can now be observed by ionization spectroscopy and velocity-map imaging [11–14], from reactants to products, including intermediate complexes. Molecules possess electronic, vibrational, rotational, and spin degrees of freedom and the way they end up in a chemical reaction via the rearrangement of the atoms is complicated. Full-dimensional potential energy surfaces of heavy tetra-atomic systems have recently started to become available [15–17]. While the dynamics of triatomic systems such as ultracold atom-diatom reactions is numerically tractable using time-independent formalisms either for heavy systems [18–23] and for light systems [24] or using time-dependent formalisms for light systems [25], tetra-atomic systems are more challenging. Time-dependent collisional codes based on Jacobi coordinates are now performant enough to reach the ultracold collision energy regime for light diatom-diatom systems [26] but are not yet capable of describing heavy systems. Similarly, time-independent collisional codes for the dynamics of heavy alkali-metal diatom-diatom reactions based on hyperspherical coordinates are still lacking. Therefore, a full quantum treatment of all degrees of freedom for these heavy alkali-metal systems is for the moment impractical. However, a much simpler statistical

model [27,28] can shed light on the rotational state-to-state distribution of the products. This has been observed in a recent experiment [29] where the overall agreement indicates the global statistical nature of the chemical reaction when the released final kinetic energies of the products are higher than the ultralow initial kinetic energy.

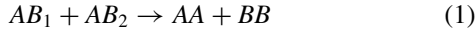
Besides the rotational structure, other important points to investigate are the role of the hyperfine structure in ultracold collisions [30–33] and to what extent the nuclear spin degrees of freedom are linked to the remaining ones in a chemical reaction [34]. This is the scope of the present paper. Despite being generally weak compared to the other type of interactions that occur in a chemical reaction, interactions involving the nuclear spins are important in ortho-para conversion of molecules [34–37]. A recent experimental study showed that they mainly act as spectators in chemical reactions of ultracold bi-alkali-metal molecules in magnetic fields [38], leading to selected values of the rotation parities of the molecular products. In that study, the theoretical model used to explain the experimental data focused on the specific type of molecule employed in the experiment and on the specific initial quantum state that was prepared. Here we provide a complete analytic generalization of the theoretical model. The model is mainly based on the knowledge of the eigenfunctions of the reactants and the products dressed by the magnetic field.

This paper is organized as follows. In Sec. II we present the full theory of our model where we define the bare and dressed states of both reactants and products, as well as the unsymmetrized and symmetrized states, and provide an expression to compute the nuclear spin state-to-state probability distribution in a magnetic field. In Sec. III we apply our

formalism to ${}^6\text{Li} {}^{40}\text{K} + {}^6\text{Li} {}^{40}\text{K}$ and ${}^{41}\text{K} {}^{87}\text{Rb} + {}^{41}\text{K} {}^{87}\text{Rb}$ ultracold reactions. We present the nuclear spin distribution from a given initial quantum state of the reactants to the possible final nuclear spin states of the products as a function of an applied magnetic field, for rotational transitions where all molecules are in their ground rotational state. We summarize in Sec. IV.

II. THEORY

We are interested in the general chemical reaction



in a magnetic field. Here AB_1 and AB_2 are the two reactants and AA and BB are the products. In the following, the subscripts 1 and 2 denote the first and second entities, whether it is an atom or a molecule: A_1 and A_2 will denote the first and second A atoms, B_1 and B_2 the first and second B atoms, and AB_1 and AB_2 the first and second reactant molecules. For the sake of simplicity, we will consider diatomic molecules with no electronic orbital and spin momentum involved (namely, ${}^1\Sigma$ molecules), so $\Lambda_1 = \Lambda_2 = 0$ and $S_1 = S_2 = 0$. Similarly, we do not include the vibrational quantum numbers v_1 and v_2 in the formalism. The rotational quantum numbers of reactant AB_1 (AB_2) are denoted by n_1 and m_{n_1} (n_2 and m_{n_2}), while for AA (BB) they are denoted by n_A and m_{n_A} (n_B and m_{n_B}). Finally, the nuclear spins of the atoms A_1 , B_1 , A_2 , and B_2 are denoted by i_{A_1} , i_{B_1} , i_{A_2} , and i_{B_2} , respectively. The numbers m_{A_1} , m_{B_1} , m_{A_2} , and m_{B_2} are abbreviations for the nuclear spin projection quantum numbers m_i of each individual nuclear spins onto the magnetic field axis, taken as the quantization axis. As we consider here identical reactants, we have $i_{A_1} = i_{A_2} = i_A$ and $i_{B_1} = i_{B_2} = i_B$. The nuclear spin projection quantum numbers of molecules AB_1 , AB_2 , AA , and BB are defined, respectively, by $m_1 = m_{A_1} + m_{B_1}$, $m_2 = m_{A_2} + m_{B_2}$, $m_A = m_{A_1} + m_{A_2}$, and $m_B = m_{B_1} + m_{B_2}$. The total projection quantum number of the first (second) reactant molecule AB_1 (AB_2) is denoted by M_1 (M_2), with $M_1 = m_{n_1} + m_{A_1} + m_{B_1}$ ($M_2 = m_{n_2} + m_{A_2} + m_{B_2}$). Similarly, the total projection quantum number of the products AA (BB) is denoted by M_A (M_B), with $M_A = m_{n_A} + m_{A_1} + m_{A_2}$ ($M_B = m_{n_B} + m_{B_1} + m_{B_2}$). Here M_1 , M_2 , M_A , and M_B are good quantum numbers in a magnetic field. Depending on the state preparation of the reactants, the molecules can have the same values $M_1 = M_2$ or different ones $M_1 \neq M_2$. If they are prepared in the same internal state, they are often called indistinguishable (and necessarily $M_1 = M_2$). If not, they are prepared in different internal states and they are called distinguishable ($M_1 = M_2$ or $M_1 \neq M_2$ are both possible). In this study, we are interested in finding the state-to-state probabilities of the products of the chemical reaction (1). For that, we propose a model based on three assumptions.

First assumption. Before the collision takes place, the two reactant molecules are quite far apart. The magnetic field is then strong enough to polarize them as the molecules feel the field via the Zeeman interaction. As they approach each other and start to collide, the molecules will feel the magnetic field less and less while they will feel the presence of the other molecule more and more. In the short-range region of the tetra-atomic complex where the four atoms are close to each other, the nuclear spins are prone to other interactions with

the other (nuclear and electronic) spins or with the overall rotation. These interactions can compete with the Zeeman interaction. Therefore, the nuclear spins do not remain necessarily polarized throughout the entire reaction and could spin flip in the short-range region. However, including all those spin interactions in the short-range region is difficult and complicated due to the few-body tetra-atomic aspect of the process. To circumvent that, we assume that the nuclear spins remain spectators and unchanged during the time they spend in the tetramer complex [34]. Then they do not participate in the dynamics at short range, as confirmed by a recent experiment [38] and as can also be seen in studies of ultracold atom-diatom collisions and reactions [30,33]. The atoms of the molecular products then simply inherit the nuclear spin projection quantum numbers of the atoms that are included in the linear combination of the wave function of the reactants in a magnetic field. This is as if the nuclear spins were spectators in the short-range region and then the process is only driven by the physics at long range, typically the interaction of the reactants and products with the magnetic field. This is what we adopt in the present theoretical model. The final state-to-state distribution is then mainly governed by permutation symmetry considerations for the two identical reactants, permutation symmetry considerations for the two identical atoms of the products, and the interaction of the molecules with the magnetic field at long range. If we consider now two molecules AB_1 and AB_2 with an orbital angular momentum between the reactants denoted by l_r , m_{l_r} , the total projection quantum number of the colliding system is $M = M_1 + M_2 + m_{l_r}$ and it is a conserved quantity. Then for the products we have $M_A + M_B + m_{l_p} = M$, where the orbital angular momentum of the products is denoted by l_p , m_{l_p} . From the above assumption of the model that the nuclear spins do not change, this implies that $m_{n_1} + m_{n_2} + m_{l_r} = m_{n_A} + m_{n_B} + m_{l_p}$. As it will be done in Sec. III, simplifications can arise if we consider reactants in the ground rotational state $n_1 = n_2 = 0$ so that $m_{n_1} = m_{n_2} = 0$.

Second assumption. We will consider molecular systems in which the couplings between different rotational quantum numbers do not significantly affect the nuclear spin structure. For example, this is the case for bi-alkali-metal molecules where the hyperfine couplings involving rotation, namely, the rotation–nuclear spin interaction, the rotation–magnetic field interaction, and the nuclei electric quadrupole moment gradient of field interaction are weak compared to the rotational constant B_{rot} of the corresponding molecule [39–41]. Due to these weak couplings, we do not consider couplings between different rotational quantum numbers of the molecules, that is, between different values of n_1 , n_2 , n_A , or n_B . However, within a given rotational manifold n_1 , n_2 , n_A , or n_B , these hyperfine terms give rise to couplings between different values of m_{n_1} , m_{n_2} , m_{n_A} , or m_{n_B} . In the following, it will be implicit that we focus on a given state-to-state transition of Eq. (1), from initial quantum numbers n_1 , m_{n_1} , n_2 , m_{n_2} , l_r , and m_{l_r} to final ones n_A , m_{n_A} , n_B , m_{n_B} , l_p , and m_{l_p} .

Third assumption. We finally consider that we can separate the final state-to-state probabilities into two independent parts, a rotational one and a nuclear spin one, and that the rotational part depends on n_1 , n_2 , n_A , and n_B but not on m_{n_1} , m_{n_2} , m_{n_A} , and m_{n_B} . This assumption is somewhat confirmed by a recent

experiment [29] which observed that the rotational state-to-state distribution of the reaction is globally statistical in nature [27,28], when the products have a release of the final kinetic energy larger than the initial one, and that the probabilities are the same for any m_{n_1} , m_{n_2} , m_{n_A} , and m_{n_B} quantum numbers.

A. Bare and dressed states of the reactants and the products:

Unsymmetrized states

We note the unsymmetrized bare state (b for bare) of the reactants AB_1 and AB_2 ,

$$\begin{aligned} |b_{AB_1}\rangle &= |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle, \\ |b_{AB_2}\rangle &= |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle, \end{aligned} \quad (2)$$

and the unsymmetrized bare state of the products AA and BB ,

$$\begin{aligned} |b_{AA}\rangle &= |n_A m_{n_A} m_{A_1} m_{A_2}\rangle, \\ |b_{BB}\rangle &= |n_B m_{n_B} m_{B_1} m_{B_2}\rangle. \end{aligned} \quad (3)$$

In a magnetic field, the unsymmetrized bare states become unsymmetrized dressed states (d for dressed), written for reactant AB_1 as

$$\begin{aligned} |d_{AB_1}\rangle &= \sum_{b_{AB_1}} |b_{AB_1}\rangle \langle b_{AB_1} | d_{AB_1} \rangle \\ &= \sum_{m_{n_1}} \sum_{m_{A_1}, m_{B_1}} |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle \langle n_1 m_{n_1} m_{A_1} m_{B_1} | d_{AB_1} \rangle \end{aligned} \quad (4)$$

and for AB_2 as

$$\begin{aligned} |d_{AB_2}\rangle &= \sum_{b_{AB_2}} |b_{AB_2}\rangle \langle b_{AB_2} | d_{AB_2} \rangle \\ &= \sum_{m_{n_2}} \sum_{m_{A_2}, m_{B_2}} |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle \langle n_2 m_{n_2} m_{A_2} m_{B_2} | d_{AB_2} \rangle. \end{aligned} \quad (5)$$

Similarly for the products, the unsymmetrized dressed states for AA are given by

$$\begin{aligned} |d_{AA}\rangle &= \sum_{b_{AA}} |b_{AA}\rangle \langle b_{AA} | d_{AA} \rangle \\ &= \sum_{m_{n_A}} \sum_{m_{A_1}, m_{A_2}} |n_A m_{n_A} m_{A_1} m_{A_2}\rangle \langle n_A m_{n_A} m_{A_1} m_{A_2} | d_{AA} \rangle \end{aligned} \quad (6)$$

and for BB by

$$\begin{aligned} |d_{BB}\rangle &= \sum_{b_{BB}} |b_{BB}\rangle \langle b_{BB} | d_{BB} \rangle \\ &= \sum_{m_{n_B}} \sum_{m_{B_1}, m_{B_2}} |n_B m_{n_B} m_{B_1} m_{B_2}\rangle \langle n_B m_{n_B} m_{B_1} m_{B_2} | d_{BB} \rangle. \end{aligned} \quad (7)$$

In all cases, we keep explicitly the rotational quantum numbers in the notation of the kets, which are fixed once for a given rotational state-to-state transition.

B. Symmetrized states

1. For the reactants

As the two AB molecules are identical, symmetrized states of the combined reactants $AB_1 + AB_2$ have to be built. The

bare symmetrized states are

$$\begin{aligned} |b_{AB_1}, b_{AB_2}; \eta\rangle &= \frac{1}{\sqrt{\Delta_b}} \{ |b_{AB_1}\rangle \otimes |b_{AB_2}\rangle + \eta |b_{AB_2}\rangle \otimes |b_{AB_1}\rangle \} \\ &= \frac{1}{\sqrt{\Delta_b}} \{ |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle \otimes |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle \\ &\quad + \eta |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle \otimes |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle \}, \end{aligned} \quad (8)$$

where $\Delta_b = 2(1 + \delta_{b_{AB_1}, b_{AB_2}})$, with $\eta = +1$ for symmetric states and $\eta = -1$ for antisymmetric states. The counting of these states has to be well ordered [42]. Here $b_{AB_1} = 1, 2, \dots, (2i_A + 1) \times (2i_B + 1) \times (2n_1 + 1)$ and $b_{AB_2} = 1, 2, \dots, (2i_A + 1) \times (2i_B + 1) \times (2n_2 + 1)$ are indices to count the states, for given numbers n_1 and n_2 in the rotational basis. To avoid double counting the symmetrized states of the reactants, the condition $b_{AB_2} \geq b_{AB_1}$ or $b_{AB_2} \leq b_{AB_1}$ has to be made. Here we choose arbitrarily $b_{AB_2} \geq b_{AB_1}$. Note that when the symmetrized antisymmetric states ($\eta = -1$) are considered, b_{AB_2} cannot be equal to b_{AB_1} , which implies $b_{AB_2} > b_{AB_1}$. These general arguments hold whenever the well-ordered states are mentioned hereafter.

In the presence of a magnetic field, the symmetrized bare states transform into the symmetrized dressed states

$$\begin{aligned} |d_{AB_1}, d_{AB_2}; \eta\rangle &= \frac{1}{\sqrt{\Delta_d}} \{ |d_{AB_1}\rangle \otimes |d_{AB_2}\rangle + \eta |d_{AB_2}\rangle \otimes |d_{AB_1}\rangle \} \\ &= \frac{1}{\sqrt{\Delta_d}} \sum_{b_{AB_1}} \sum_{b_{AB_2}} \langle b_{AB_1} | d_{AB_1} \rangle \langle b_{AB_2} | d_{AB_2} \rangle \\ &\quad \{ |b_{AB_1}\rangle \otimes |b_{AB_2}\rangle + \eta |b_{AB_2}\rangle \otimes |b_{AB_1}\rangle \} \\ &= \sum_{m_{n_1}} \sum_{m_{n_2}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{A_2} = -i_A}^{+i_A} \sum_{m_{B_2} = -i_B}^{+i_B} \\ &\quad \langle n_1 m_{n_1} m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_2} | d_{AB_2} \rangle \\ &\quad \times \delta_{m_{n_1} + m_{A_1} + m_{B_1}, M_1} \delta_{m_{n_2} + m_{A_2} + m_{B_2}, M_2} \\ &\quad \times \frac{1}{\sqrt{\Delta_d}} \{ |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle \otimes |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle \\ &\quad + \eta |n_2 m_{n_2} m_{A_2} m_{B_2}\rangle \otimes |n_1 m_{n_1} m_{A_1} m_{B_1}\rangle \}, \end{aligned} \quad (9)$$

where now $\Delta_d = 2(1 + \delta_{d_{AB_1}, d_{AB_2}})$ and the well ordering of the states is chosen to be $d_{AB_2} \geq d_{AB_1}$. It is important to note that here there is no well ordering of the b_{AB_1} and b_{AB_2} states, as they span all values that come from the dressing of the bare states (4) and (5). The Kronecker δ terms ensure the conservation of the total projection quantum number of each molecule AB_1 and AB_2 , as is the case in a magnetic field.

2. For the products

In contrast with the two identical reactants AB , the products AA and BB are different molecules. Therefore, there is no symmetrization of the wave function of the combined products that is required. However, as the A atoms (B atoms) are

identical, we have to symmetrize the wave function of the individual molecule AA (BB). The bare symmetrized states are

$$|b_{AA}, b_{BB}; \eta_A, \eta_B\rangle = |b_{AA}; \eta_A\rangle \otimes |b_{BB}; \eta_B\rangle, \quad (10)$$

with

$$\begin{aligned} |b_{AA}; \eta_A\rangle &= |n_A m_{n_A}\rangle \times \frac{1}{\sqrt{\Delta_A}} \{ |m_{A_1} m_{A_2}\rangle + \eta_A |m_{A_2} m_{A_1}\rangle \} \\ &= \frac{1}{\sqrt{\Delta_A}} \{ |n_A m_{n_A} m_{A_1} m_{A_2}\rangle + \eta_A |n_A m_{n_A} m_{A_2} m_{A_1}\rangle \} \\ &\equiv |n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A\rangle, \\ |b_{BB}; \eta_B\rangle &= |n_B m_{n_B}\rangle \times \frac{1}{\sqrt{\Delta_B}} \{ |m_{B_1} m_{B_2}\rangle + \eta_B |m_{B_2} m_{B_1}\rangle \} \\ &= \frac{1}{\sqrt{\Delta_B}} \{ |n_B m_{n_B} m_{B_1} m_{B_2}\rangle + \eta_B |n_B m_{n_B} m_{B_2} m_{B_1}\rangle \} \\ &\equiv |n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B\rangle. \end{aligned} \quad (11)$$

Here $\Delta_A = 2(1 + \delta_{m_{A_1}, m_{A_2}})$, $\Delta_B = 2(1 + \delta_{m_{B_1}, m_{B_2}})$, and $\eta_A = \pm 1$ and $\eta_B = \pm 1$ for symmetric or antisymmetric states of AA and BB . Again, these states have to be well ordered. The nuclear spin indices span $m_{A_{1,2}} = -i_A, +i_A$ and $m_{B_{1,2}} = -i_B, +i_B$. We choose $m_{A_2} \geq m_{A_1}$ as well as $m_{B_2} \leq m_{B_1}$. This is arbitrary but convenient for the case when the molecules have $m_1 = m_2$. In such a case, the conservation of $m_{A_1} + m_{B_1} = m_{A_2} + m_{B_2}$ implies that if $m_{A_2} \geq m_{A_1}$, then $m_{B_2} \leq m_{B_1}$.

In the presence of a magnetic field, the symmetrized bare states transform into the symmetrized dressed states for each individual molecule

$$\begin{aligned} |d_{AA}; \eta_A\rangle &= \sum_{b_{AA}} |b_{AA}; \eta_A\rangle \langle b_{AA}; \eta_A | d_{AA}; \eta_A\rangle \\ &= \sum_{m_{n_A}} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} |n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A\rangle \\ &\quad \times \langle n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A | d_{AA}; \eta_A\rangle, \\ |d_{BB}; \eta_B\rangle &= \sum_{b_{BB}} |b_{BB}; \eta_B\rangle \langle b_{BB}; \eta_B | d_{BB}; \eta_B\rangle \\ &= \sum_{m_{n_B}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} |n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B\rangle \\ &\quad \times \langle n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B | d_{BB}; \eta_B\rangle. \end{aligned} \quad (12)$$

Then we get the following symmetrized dressed state for the products:

$$\begin{aligned} |d_{AA}, d_{BB}; \eta_A, \eta_B\rangle &= |d_{AA}; \eta_A\rangle \otimes |d_{BB}; \eta_B\rangle \\ &= \sum_{b_{AA}} \sum_{b_{BB}} |b_{AA}, b_{BB}; \eta_A, \eta_B\rangle \\ &\quad \langle b_{AA}; \eta_A | d_{AA}; \eta_A\rangle \langle b_{BB}; \eta_B | d_{BB}; \eta_B\rangle \\ &= \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \\ &\quad \langle n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A | d_{AA}; \eta_A\rangle \\ &\quad \times \langle n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B | d_{BB}; \eta_B\rangle \\ &\quad \times \delta_{m_A + m_B, m_1 + m_2} \end{aligned}$$

$$\begin{aligned} &\times \delta_{m_{n_A} + m_{A_1} + m_{A_2} + m_{n_B} + m_{B_1} + m_{B_2} + m_{l_r}, M} \\ &\times \frac{1}{\sqrt{\Delta_A}} \{ |n_A m_{n_A} m_{A_1} m_{A_2}\rangle + \eta_A |n_A m_{n_A} m_{A_2} m_{A_1}\rangle \} \\ &\otimes \frac{1}{\sqrt{\Delta_B}} \{ |n_B m_{n_B} m_{B_1} m_{B_2}\rangle + \eta_B |n_B m_{n_B} m_{B_2} m_{B_1}\rangle \}. \end{aligned} \quad (13)$$

Among the multiple possible combined nuclear spin states of the molecular products AA and BB , only those which satisfy the conservation of $m_A + m_B = m_{A_1} + m_{A_2} + m_{B_1} + m_{B_2} = m_1 + m_2$ are retained, as imposed by the first Kronecker δ term. This is a consequence of the first assumption. Also, only those which satisfy the conservation of the total M are retained, as imposed by the second Kronecker δ term. Note that because $M = m_{n_A} + m_{A_1} + m_{B_1} + m_{n_2} + m_{A_2} + m_{B_2} + m_{l_r}$, the second Kronecker symbol can be recast as $\delta_{m_{n_A} + m_{n_B}, m_{n_1} + m_{n_2} + m_{l_r} - m_{l_p}}$, and this is what we will employ in the following.

C. State-to-state probabilities

Our model will consider that the state-to-state probability $P_{i \rightarrow j}$, from the combined dressed state of the indistinguishable reactants $|d_{AB_1}, d_{AB_2}; \eta\rangle$ denoted by $|i\rangle$ to the combined dressed state of the products $|d_{AA}, d_{BB}; \eta_A, \eta_B\rangle$ denoted by $|j\rangle$, is simply the modulus square of the probability amplitude, the overlap between those two states

$$P_{i \rightarrow j} = |\langle j | i \rangle|^2 = |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle|^2. \quad (14)$$

It reflects the amount of the molecular product wave function obtained from the molecular reactant wave function, both dressed by the magnetic field, taking into account the appropriate permutation symmetry considerations characterized by η_A , η_B , and η . This probability is for a transition from initial quantum numbers $n_1, m_{n_1}, n_2, m_{n_2}, l_r$, and m_{l_r} to final ones $n_A, m_{n_A}, n_B, m_{n_B}, l_p$, and m_{l_p} . The conservation of the total angular momentum M , as mentioned above, is implicit here and leads to the selection rule $m_{n_1} + m_{n_2} + m_{l_r} = m_{n_A} + m_{n_B} + m_{l_p}$. From the assumptions made in the model and as shown in Appendix A, the probability amplitude related to Eq. (14) can be recast into the product of two parts, namely, $\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}}$ for the nuclear spin degree of freedom and $\langle n_A n_B | n_1 n_2 \rangle$ for the rotational degree of freedom (or all the other degrees of freedom but the nuclear spin if we consider, for example, vibration). This implies that Eq. (14) becomes a product of two probabilities

$$P_{i \rightarrow j} = P^{\text{rot}} \times P_{i \rightarrow j}^{\text{ns}}, \quad (15)$$

with a global one related to a given rotational transition $P^{\text{rot}} = |\langle n_A n_B | n_1 n_2 \rangle|^2$ and a state-to-state specific one related to a nuclear spin transition (of a given rotational transition) $P_{i \rightarrow j}^{\text{ns}} = |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}}|^2$. The probability P^{rot} highly depends on the complicated short-range dynamics of the tetramer complex and the different angular momenta couplings. It is not treated in our study as mentioned above but can be represented by the statistical expressions developed

in Refs. [27–29]. The probability $P_{i \rightarrow j}^{\text{ns}}$ (and the amplitude) is treated in our study and depending on the initial preparation

of the reactants, different simplifications occur as derived in Appendixes A and B. This is what we focus on now.

1. General case of reactants in nonzero rotational states

For the general case where the reactants are in a nonzero rotational state, the probability amplitude for the nuclear spin is given by the general expression

$$\begin{aligned}
 & \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} \\
 &= \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1}=-i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}=-i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 & \times \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \sum_{m_{n_1}} \sum_{m_{n_2}} \delta_{m_{n_A}+m_{n_B}, m_{n_1}+m_{n_2}+m_{l_r}-m_{l_p}} \\
 & \times \{ \langle n_1 m_{n_1} m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_2} | d_{AB_2} \rangle [1 + \eta_A \eta_B \eta] \delta_{m_{n_1}+m_{A_1}+m_{B_1}, M_1} \delta_{m_{n_2}+m_{A_2}+m_{B_2}, M_2} \\
 & \times \langle n_1 m_{n_1} m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A \eta_B + \eta] \delta_{m_{n_1}+m_{A_2}+m_{B_2}, M_1} \delta_{m_{n_2}+m_{A_1}+m_{B_1}, M_2} \\
 & \times \langle n_1 m_{n_1} m_{A_1} m_{B_2} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_1} | d_{AB_2} \rangle [\eta_B + \eta_A \eta] \delta_{m_{n_1}+m_{A_1}+m_{B_2}, M_1} \delta_{m_{n_2}+m_{A_2}+m_{B_1}, M_2} \\
 & \times \langle n_1 m_{n_1} m_{A_2} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_1} m_{B_2} | d_{AB_2} \rangle [\eta_A + \eta_B \eta] \delta_{m_{n_1}+m_{A_2}+m_{B_1}, M_1} \delta_{m_{n_2}+m_{A_1}+m_{B_2}, M_2} \}. \tag{16}
 \end{aligned}$$

Important to note is the fact that the Kronecker δ term $\delta_{\eta_A \eta_B, \eta}$ imposes a selection rule for the symmetry of the AA and BB molecular products. If $\eta = +1$, only the cases $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$ are allowed. If $\eta = -1$, only the cases $\eta_A = +1$ and $\eta_B = -1$ or $\eta_A = -1$ and $\eta_B = +1$ are allowed.

2. Specific case of reactants in zero rotational states

Now if the reactants are in a zero rotational state, we have $n_1 = n_2 = 0$ and $m_{n_1} = m_{n_2} = 0$, which implies $M_1 \equiv m_1$ and $M_2 \equiv m_2$. Equation (16) simplifies to

$$\begin{aligned}
 & \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} = \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A}+m_{n_B}, m_{l_r}-m_{l_p}} \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \\
 & \times \sum_{m_{A_1}=-i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}=-i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle [1 + \eta_A \eta_B \eta] \delta_{m_{A_1}+m_{B_1}, m_1} \delta_{m_{A_2}+m_{B_2}, m_2} \\
 & + \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A \eta_B + \eta] \delta_{m_{A_2}+m_{B_2}, m_1} \delta_{m_{A_1}+m_{B_1}, m_2} \\
 & + \langle m_{A_1} m_{B_2} | d_{AB_1} \rangle \langle m_{A_2} m_{B_1} | d_{AB_2} \rangle [\eta_B + \eta_A \eta] \delta_{m_{A_1}+m_{B_2}, m_1} \delta_{m_{A_2}+m_{B_1}, m_2} \\
 & + \langle m_{A_2} m_{B_1} | d_{AB_1} \rangle \langle m_{A_1} m_{B_2} | d_{AB_2} \rangle [\eta_A + \eta_B \eta] \delta_{m_{A_2}+m_{B_1}, m_1} \delta_{m_{A_1}+m_{B_2}, m_2} \}. \tag{17}
 \end{aligned}$$

3. Specific case of reactants in zero rotational states with $m_1 = m_2$

When the molecules (indistinguishable or not) have the same values $m_1 = m_2$, Eq. (17) simplifies to

$$\begin{aligned}
 & \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} = \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A}+m_{n_B}, m_{l_r}-m_{l_p}} \\
 & \times \frac{1}{\sqrt{\Delta_d}} \sum_{m_{A_1}=-i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}=-i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle + \eta \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \} \delta_{m_{A_1}+m_{B_1}, m_1} \delta_{m_{A_2}+m_{B_2}, m_1}. \tag{18}
 \end{aligned}$$

The Kronecker δ terms $\delta_{m_{A_1}+m_{B_1}, m_1}$ and $\delta_{m_{A_2}+m_{B_2}, m_1}$ impose some restrictions for the quadruple sum of the nuclear spins. If $m_{A_2} = m_{A_1}$, this implies automatically $m_{B_2} = m_{B_1}$. There is no case with $m_{A_2} = m_{A_1}$ and $m_{B_2} \neq m_{B_1}$ or the reverse, $m_{B_2} = m_{B_1}$ and

$m_{A_2} \neq m_{A_1}$, for the same reasons. Therefore, only the cases $m_{A_2} = m_{A_1}$ and $m_{B_2} = m_{B_1}$ and the cases $m_{A_2} > m_{A_1}$ and $m_{B_2} < m_{B_1}$ have to be considered for $\eta = +1$ and only $m_{A_2} > m_{A_1}$ and $m_{B_2} < m_{B_1}$ for $\eta = -1$ (see Appendix B).

a. Indistinguishable case. In addition, if the reactants are indistinguishable $d_{AB_2} \equiv d_{AB_1} \equiv d_{AB}$ and only the component $\eta = +1$ has to be computed. The selection rule necessarily implies $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$. Equation (18) further simplifies to

$$\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB}, d_{AB}; +1 \rangle^{\text{ns}} = \delta_{\eta_A \eta_B, +1} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \quad (19)$$

This is the case treated in Sec. III. In that section we will also define a symmetric state probability

$$P_{i \rightarrow j}^{\text{S ns}} = |\langle d_{AA}, d_{BB}; +1, +1 | d_{AB}, d_{AB}; +1 \rangle^{\text{ns}}|^2, \quad (20)$$

the probability that corresponds to the case of a nuclear spin symmetric wave function of the *AA* and *BB* products $\eta_A = \eta_B = +1$, and an antisymmetric state probability

$$P_{i \rightarrow j}^{\text{A ns}} = |\langle d_{AA}, d_{BB}; -1, -1 | d_{AB}, d_{AB}; +1 \rangle^{\text{ns}}|^2, \quad (21)$$

the one that corresponds to the case of a nuclear spin antisymmetric wave function of the *AA* and *BB* products $\eta_A = \eta_B = -1$. As it will be discussed in Sec. III, the symmetric or antisymmetric state probabilities imply a specific parity of the rotational quantum numbers of the molecular products, depending on the bosonic or fermionic character of the involved atoms.

b. Distinguishable case. If the reactants are distinguishable, both components $\eta = \pm 1$ have to be computed and Eq. (18) becomes

$$\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} = \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \frac{1}{\sqrt{2}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle + \eta \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \} \times \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \quad (22)$$

D. Sum of the state-to-state probabilities over the final states of the products

For a given rotational transition, the probability summed over all the final states of the products $|j\rangle$ simplifies due to appropriate closure relations as derived in Appendix C and is given by

$$\sum_j P_{i \rightarrow j} = P^{\text{rot}} \times \sum_j P_{i \rightarrow j}^{\text{ns}}. \quad (23)$$

We quote only the expression for the indistinguishable case here:

$$\sum_j P_{i \rightarrow j}^{\text{ns}} = \delta_{\eta_A \eta_B, +1} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle^2 \times \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \quad (24)$$

This is the generalized form of the expression used in Ref. [38] to compare with experimental data. Similar to Eqs. (20) and (21), two types of sums can be computed, $\sum_j P_{i \rightarrow j}^{\text{S ns}}$ and $\sum_j P_{i \rightarrow j}^{\text{A ns}}$. From the conservation of the total probability, the sum of them has to be unity: $\sum_j P_{i \rightarrow j}^{\text{S ns}} + \sum_j P_{i \rightarrow j}^{\text{A ns}} = 1$. We show here that this summed probability only requires the

eigenfunctions of the dressed reactants in the magnetic field, not the ones of the dressed products. Similar simplifications are found for the other cases, as discussed in Appendix C.

III. APPLICATION TO STATE-TO-STATE CHEMICAL REACTIONS

To illustrate our model, we present results of nuclear spin state-to-state distributions in a magnetic field B for reactants in the ground rotational states $n_1 = n_2 = 0$ starting with bi-alkali-metal molecules in indistinguishable states (so that $m_{n_1} = m_{n_2} = 0$, $\eta = +1$, and $m_1 = m_2$). We assume the molecules being prepared in their electronic $X^1\Sigma^+$ and vibrational $v = 0$ ground state. To simplify the calculation of the interaction of the molecules with the magnetic field, we also consider products in the ground rotational states $n_A = 0$ and $n_B = 0$ [so that $m_{n_A} = m_{n_B} = 0$, $(\eta_A, \eta_B) = (+1, +1)$ or $(\eta_A, \eta_B) = (-1, -1)$, and $m_1 = m_2$]. Due to symmetry reasons, having both type of products in the zero rotational state implies necessarily both molecular products with all the atoms involved of either bosonic character or fermionic character. When the atoms are all fermionic, the only possible reaction with bi-alkali-metal molecules is ${}^6\text{Li} {}^{40}\text{K} + {}^6\text{Li} {}^{40}\text{K} \rightarrow {}^6\text{Li}_2 + {}^{40}\text{K}_2$ and the nuclear spin state distribution is symmetric $(\eta_A, \eta_B) = (+1, +1)$. When the atoms are all bosonic,

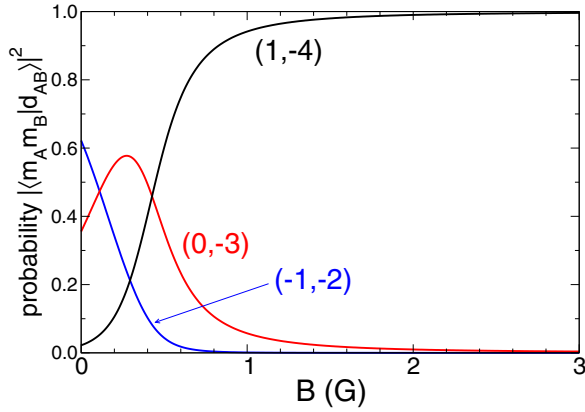


FIG. 1. The quantity $|\langle m_A m_B | d_{AB} \rangle|^2$ gives the probability of a component of the wave function of a ${}^6\text{Li}{}^{40}\text{K}$ molecule in the zero rotational state as a function of the magnetic field B , for its first dressed state $|d_{AB}\rangle = 1$ of the $m_1 = m_2 = -3$ manifold. The components of the wave function are denoted by (m_A, m_B) . The black, red, and blue curves correspond to the components $(1, -4)$, $(0, -3)$, and $(-1, -2)$, respectively.

for example, in the reaction ${}^{41}\text{K}{}^{87}\text{Rb} + {}^{41}\text{K}{}^{87}\text{Rb} \rightarrow {}^{41}\text{K}_2 + {}^{87}\text{Rb}_2$, the nuclear spin state distribution is antisymmetric $(\eta_A, \eta_B) = (-1, -1)$. We discuss these two types of distribution in the following, applying the present model to these two systems taken as examples.

A. The ${}^6\text{Li}{}^{40}\text{K} + {}^6\text{Li}{}^{40}\text{K} \rightarrow {}^6\text{Li}_2 + {}^{40}\text{K}_2$ chemical reaction

Among the list of the ten bi-alkali-metal possible as reactants, only the bosonic ${}^6\text{Li}{}^{40}\text{K}$ molecule can illustrate the example of a distribution with symmetric nuclear spin states with both products in the ground rotational state. For symmetry reasons, this is indeed the only heteronuclear bi-alkali-metal molecule that can be made with two different fermionic atoms. We consider that they are all prepared in the lowest state of the $m_1 = m_2 = -3$ manifold. At large magnetic fields, the Zeeman interaction starts to dominate over the other hyperfine interactions ($B > 1$ G for this system) and the nuclear spin projections become good quantum numbers. Therefore, the dressed states correspond to a nearly pure character of m_{Li} and m_{K} , the quantum numbers associated with projections of the nuclear spins of the corresponding isotopes $i_{\text{Li}} = 1$ and $i_{\text{K}} = 4$ onto the magnetic field axis. This can be seen in Fig. 1 as a black line, where the probability of a component of the wave function of a ${}^6\text{Li}{}^{40}\text{K}$ molecule is plotted as a function of the magnetic field B in its first dressed state $|d_{AB}\rangle = 1$ for $m_1 = m_2 = -3$. At lower magnetic fields, $|d_{AB}\rangle = 1$ can gain other characters, as other components of the LiK wave function, plotted as the red and blue lines, are also present due to the fact that other hyperfine interactions cannot be neglected. As the formalism assumes that the nuclear spins are spectators during the chemical reaction, we expect that the chemical reaction favors at large magnetic fields a simple rearrangement of the original nuclear spins of the initial reactants $(1, -4) + (1, -4)$ into the products, namely, $(1, 1) + (-4, -4)$ by simply swapping them. In the following, the abbreviation $(m_{A_1}, m_{B_1}) + (m_{A_2}, m_{B_2})$ will

sometimes be used to express the main characters of the reactants and $(m_{A_1}, m_{A_2}) + (m_{B_1}, m_{B_2})$ of the products.

To obtain the eigenfunctions and eigenenergies of the LiK, Li_2 , and K_2 molecules in a magnetic field, we diagonalize the corresponding molecular Hamiltonians using the basis sets of the nuclear spin states (2) and (3). In the following we will take $A = {}^6\text{Li}$ and $B = {}^{40}\text{K}$. It is then obvious that the denotations AA and BB used for the theoretical developments in the previous section stand for the molecules Li_2 and K_2 in the following. As we consider only molecules in zero rotational states (see the discussion about the second assumption), the form of the molecular Hamiltonian simplifies and reduces to [39–41]

$$H = H_{hf} + H_Z, \quad (25)$$

with the hyperfine and Zeeman Hamiltonians for the AB molecule given, respectively, by

$$\begin{aligned} H_{hf} &= c_{AB} \vec{i}_A \cdot \vec{i}_B, \\ H_Z &= -g_A \mu_N \vec{i}_A \cdot \vec{B} (1 - \sigma_{A \text{ of } AB}) \\ &\quad - g_B \mu_N \vec{i}_B \cdot \vec{B} (1 - \sigma_{B \text{ of } AB}), \end{aligned} \quad (26)$$

for the AA molecule given by

$$\begin{aligned} H_{hf} &= c_{AA} \vec{i}_{A_1} \cdot \vec{i}_{A_2}, \\ H_Z &= -g_A \mu_N \vec{i}_{A_1} \cdot \vec{B} (1 - \sigma_{A \text{ of } AA}) \\ &\quad - g_A \mu_N \vec{i}_{A_2} \cdot \vec{B} (1 - \sigma_{A \text{ of } AA}), \end{aligned} \quad (27)$$

and for the BB molecule by

$$\begin{aligned} H_{hf} &= c_{BB} \vec{i}_{B_1} \cdot \vec{i}_{B_2}, \\ H_Z &= -g_B \mu_N \vec{i}_{B_1} \cdot \vec{B} (1 - \sigma_{B \text{ of } BB}) \\ &\quad - g_B \mu_N \vec{i}_{B_2} \cdot \vec{B} (1 - \sigma_{B \text{ of } BB}). \end{aligned} \quad (28)$$

We took $c_{AB} = 48.2$ Hz, $g_A = 0.822$, $g_B = -0.324$, $\sigma_{A \text{ of } AB} = 104.1$ ppm, and $\sigma_{B \text{ of } AB} = 1296.8$ ppm from Ref. [41]. We took $c_{AA} = 161$ Hz, $c_{BB} = -42$ Hz, $\sigma_{A \text{ of } AA} = 102$ ppm, and $\sigma_{B \text{ of } BB} = 1313$ ppm from Ref. [40]. For two molecules, we have $m_1 + m_2 = -6$, which is conserved during the collision. The products of the chemical reaction ${}^6\text{Li}_2$ and ${}^{40}\text{K}_2$ are formed in their ground electronic state $X^1\Sigma_g^+$, ground vibrational state $v = 0$, and ground rotational state $n_A = n_B = 0$.

Figure 2 presents the energies of the combined dressed states of the reactants $AB + AB = {}^6\text{Li}{}^{40}\text{K} + {}^6\text{Li}{}^{40}\text{K}$ in the zero rotational states as a function of the magnetic field, for $m_1 + m_2 = -6$ and $\eta = +1$ for the case of indistinguishable states. There are six dressed states denoted by $|i\rangle = 1, \dots, 6$, which correspond to different combinations of the individual dressed states $|d_{AB}\rangle$ in the $m_1 + m_2 = -6$ manifold. Table I provides the nomenclature for these states. We take $|i\rangle = 1$ as an example of initial state that could be prepared in experiments, presented as a red bold line in the figure. The $|i\rangle = 1$ state corresponds to two molecules in the first dressed state $|d_{AB}\rangle = 1$. At large magnetic fields, the initial state $|i\rangle = 1$ has a main character of $m_{A_1} = 1$, $m_{B_1} = -4$, $m_{A_2} = 1$, and $m_{B_2} = -4$ and at lower fields it can gain other characters, as discussed above for the individual reactants.

Similarly, Fig. 3 presents the energies of the combined dressed states of the products $AA + BB = {}^6\text{Li}_2 + {}^{40}\text{K}_2$ in the

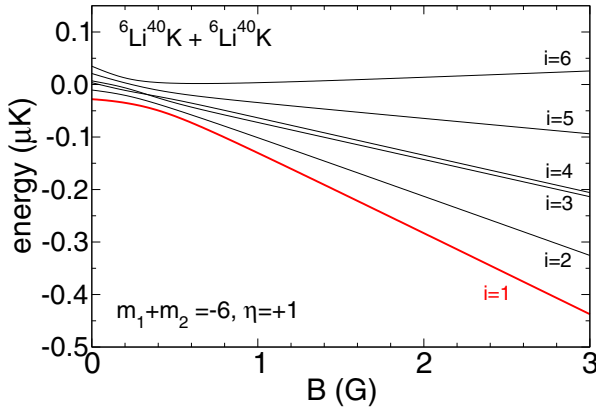


FIG. 2. Energies of the combined dressed states of the reactants ${}^6\text{Li}^{40}\text{K} + {}^6\text{Li}^{40}\text{K}$ in the zero rotational states as a function of the magnetic field B , for $m_1 + m_2 = -6$ and $\eta = +1$. There are six possible $|i\rangle$ states as labeled in the figure. The $|i\rangle = 1$ state corresponds to two molecules in the state $|d_{AB_1}\rangle = |d_{AB_2}\rangle = 1$.

zero rotational states as a function of the magnetic field, for $m_A + m_B = m_1 + m_2 = -6$, and $\eta_A = +1$ and $\eta_B = +1$ (nuclear spin symmetric states). The ${}^6\text{Li}$ and ${}^{40}\text{K}$ nuclei are composite bosons. The permutation of two identical bosonic nuclei in the ${}^6\text{Li}_2$ molecule and in the ${}^{40}\text{K}_2$ molecule should obey the symmetrization principle and lead to an overall symmetric wave function for each molecule. As the rotational wave functions of the ${}^6\text{Li}_2$ and ${}^{40}\text{K}_2$ molecules in the zero rotational state are symmetric under the interchange of the nuclei, their nuclear spin wave functions have to be symmetric as well and hence described by values of $\eta_A = +1$ and $\eta_B = +1$. There are 11 dressed states denoted by $|j\rangle = 1, \dots, 11$, which correspond to different combinations of the individual dressed states $|d_{AA}; +1\rangle$ and $|d_{BB}; +1\rangle$. Table II provides the nomenclature for the states. These are all the possible final product states of the chemical reaction, for the nuclear spin symmetric states of the molecules.

From the eigenvectors of the combined dressed states expressed in the nuclear spin state basis set, namely,

TABLE I. Nomenclature for the combined dressed states of the reactants $AB + AB = {}^6\text{Li}^{40}\text{K} + {}^6\text{Li}^{40}\text{K}$ in the zero rotational states for $\eta = +1$ and $m_1 + m_2 = -6$, with $A = {}^6\text{Li}$ and $B = {}^{40}\text{K}$. The combined dressed states are denoted by $|i\rangle$, corresponding to the combination of the dressed states $|d_{AB_1}\rangle$ and $|d_{AB_2}\rangle$. In this study, the initial state will be $|i\rangle = 1$, corresponding to the case where $|d_{AB_2}\rangle \equiv |d_{AB_1}\rangle$. The second and third columns display the main character of $|d_{AB_1}\rangle$ and $|d_{AB_2}\rangle$. This is given at a large magnetic field, typically $B > 1$ G for this system, as the dressed states tend to be nearly pure bare states.

$ i\rangle$	$ d_{AB_1}\rangle$	$ d_{AB_2}\rangle$	m_{A_1}	m_{B_1}	m_{A_2}	m_{B_2}
1	1	1	1	-4	1	-4
2	1	2	1	-4	0	-3
3	1	3	1	-4	-1	-2
4	2	2	0	-3	0	-3
5	2	3	0	-3	-1	-2
6	3	3	-1	-2	-1	-2

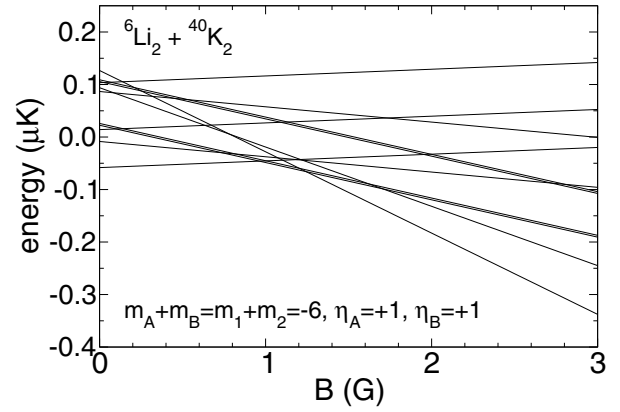


FIG. 3. Energies of the combined dressed states of the products ${}^6\text{Li}_2 + {}^{40}\text{K}_2$ in the zero rotational states for $m_A + m_B = m_1 + m_2 = -6$, and $\eta_A = +1$ and $\eta_B = +1$ (nuclear spin symmetric states).

$\langle m_{A_1} m_{B_1} | d_{AB} \rangle$ and $\langle m_{A_2} m_{B_2} | d_{AB} \rangle$ for the reactants and $\langle m_{A_1} m_{A_2}; \eta_A | d_{AA}; \eta_A \rangle$ and $\langle m_{B_1} m_{B_2}; \eta_B | d_{BB}; \eta_B \rangle$ for the products (we omit the numbers n_A , m_{n_A} , n_B , and m_{n_B}), one can plot the nuclear spin state-to-state probability $P_{i \rightarrow j}^{S_{ns}}$ expressed by Eqs. (20) and (19) from the initial state $|i\rangle = 1$ to all final states $|j\rangle$. This is presented in Figs. 4(a) and 4(b) as a function of the magnetic field. The behavior of the probabilities as functions of B really depends on the many admixtures of the bare states for the dressed states of the two reactants and the two products. The probabilities $P_{i \rightarrow j}^{S_{ns}}$ are also plotted as functions of the final states $|j\rangle$ for different magnetic fields in Figs. 4(c)–4(f). It can be seen that the state-to-state distribution drastically changes with B populating different final states. For $P_{i \rightarrow j}^{S_{ns}}$, the $|j\rangle = 11$ final state (green curve) is favored at high field, while at low field it vanishes and other values of $|j\rangle$ are now more probable. From Table II, the $|j\rangle = 11$ state corresponds to a main character of $(1, 1) + (-4, -4)$, entailing ${}^6\text{Li}_2$ and ${}^{40}\text{K}_2$ molecules with the same components of their atomic nuclear spins. This state corresponds exactly to the original one $(1, -4) + (1, -4)$ of the reactants in the $|i\rangle = 1$ state, but with just a swap. For lower magnetic fields [see Fig. 4(b)], the chemical reaction ends up dominantly in other final product states $|j\rangle = 10$ (orange curve), $|j\rangle = 9$ (gray curve), $|j\rangle = 5$ (brown curve), and $|j\rangle = 2$ (red curve) for decreasing B , with a main character in $(0, 1) + (-3, -4)$, $(0, 0) + (-3, -3)$, $(-1, 0) + (-2, -3)$, and $(-1, -1) + (0, -4)$, respectively. Then, depending on the magnetic field that is applied, different types of states of the molecular products can be predominantly composed. Those with different nuclear spins, for example, $(0, 1) + (-3, -4)$ for $|j\rangle = 10$ in the range $B = [0.35 - 0.4]$ G, take the form of an entangled state, namely, $\{|0, 1\rangle + |1, 0\rangle\}/\sqrt{2}$ for the ${}^6\text{Li}$ nuclei and $\{|-3, -4\rangle + |-4, -3\rangle\}/\sqrt{2}$ for the ${}^{40}\text{K}$ nuclei. Those with the same nuclear spins, for example, $(1, 1) + (-4, -4)$ for $|j\rangle = 11$ at $B > 0.5$ G, take the form of a separable state, namely, $|1\rangle|1\rangle$ for the ${}^6\text{Li}$ nuclei and $|-4\rangle|-4\rangle$ for the ${}^{40}\text{K}$ nuclei.

The total probability $\sum_j P_{i \rightarrow j}^{S_{ns}}$, summed over all the final combined dressed states of the products $|j\rangle$, is shown as a thick black line in Fig. 4 and consists of the sum of all individual curves given by Eq. (20). The thick black line is compared

TABLE II. Nomenclature for the combined dressed states of the products $AA + BB = {}^6\text{Li}_2 + {}^{40}\text{K}_2$ for $\eta_A = +1$ and $\eta_B = +1$ (nuclear spin symmetric states), with $A = {}^6\text{Li}$ and $B = {}^{40}\text{K}$. The combined dressed states are denoted by $|j\rangle$, corresponding to the combination of the dressed states $|d_{AA}; \eta_A\rangle$ and $|d_{BB}; \eta_B\rangle$. Columns 4,5,6,7 display the main character of $|d_{AA}; \eta_A\rangle$ and $|d_{BB}; \eta_B\rangle$, while columns 8,9,10,11 display the second main character, if any. This is given for large magnetic fields, typically $B > 1$ G for this system.

$ j\rangle$	$ d_{AA}; +1\rangle$	$ d_{BB}; +1\rangle$	m_{A_1}	m_{A_2}	m_{B_1}	m_{B_2}	m_{A_1}	m_{A_2}	m_{B_1}	m_{B_2}
1	1	7	-1	-1	-1	-3			0	-4
2	1	8	-1	-1	0	-4			-2	-2
3	1	9	-1	-1	-1	-3			-2	-2
4	2	5	-1	0	-1	-4			-2	-3
5	2	6	-1	0	-2	-3			-1	-4
6	3	3	-1	1	-2	-4	0	0	-3	-3
7	3	4	-1	1	-3	-3	0	0	-2	-4
8	4	3	0	0	-2	-4	-1	1	-3	-3
9	4	4	0	0	-3	-3	-1	1	-2	-4
10	5	2	0	1	-3	-4				
11	6	1	1	1	-4	-4				

with the simplified expression given by Eq. (24), presented as open circles for each figure. We can see that the curve and the circle data are identical, so this confirms that one can use the simplified formula (24) directly, which requires only the knowledge of the eigenfunctions of the dressed states of the reactants. There is no need to compute the dressed states of the products in a magnetic field as far as the total probability summed over all $|j\rangle$ is concerned. This is what was done in [38] for fermionic ${}^{40}\text{K}$ ${}^{87}\text{Rb}$ molecules, as the experimental data involved a measurement of the total probability, summed over all possible nuclear spin states of the products. Equation (24) was used to fit the y axis of the experimental data, which

consisted of counting the product molecules (more precisely, counting the ionized form of the product molecules). Very good agreement was found in the trend of the data with the magnetic field, confirming that the nuclear spin structure in the magnetic field is treated correctly and that the assumption of conserved nuclear spins is sufficient. An overall fitting parameter was used to account for the overall magnitude of the counting for each observed rotational state of the products, which is a characteristic of the intrinsic complicated effect of the rotational structure of the molecules in the chemical reaction at short range, something that is not taken into account in the present model. As the long-range physics where

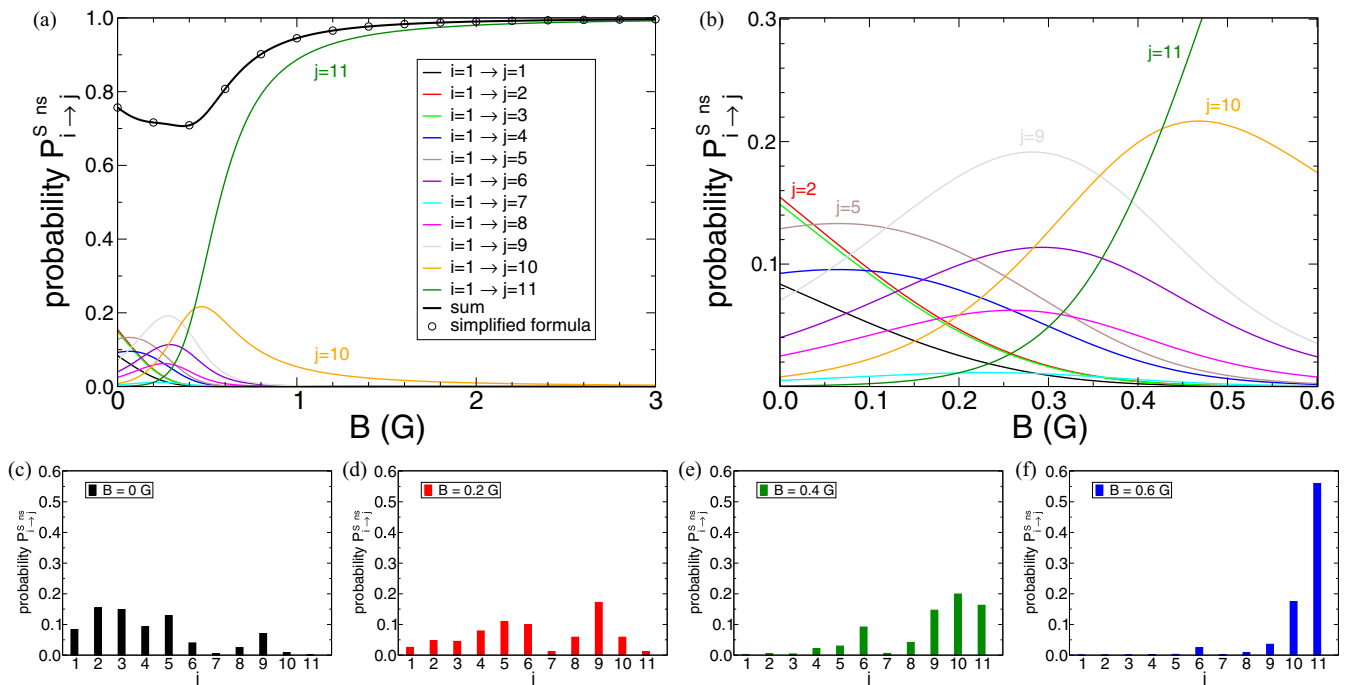


FIG. 4. (a) Probability $P_{i=1 \rightarrow j}^{S ns}$ for ${}^6\text{Li}_2 + {}^{40}\text{K}_2$ in zero rotational states as a function of the magnetic field B . The total sum is displayed as a thick black line. The simplified formula (open circles) corresponds to Eq. (24). (b) Close-up of (a). (c)–(f) Probability $P_{i=1 \rightarrow j}^{S ns}$ as a function of the final states $|j\rangle = 1, \dots, 11$ with $|i\rangle = 1$, for different magnetic fields: (c) $B = 0$ G, (d) $B = 0.2$ G, (e) $B = 0.4$ G, and (f) $B = 0.6$ G.

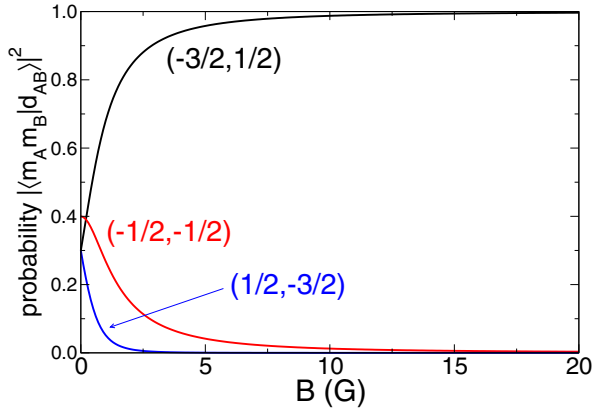


FIG. 5. Same as Fig. 1 but for the $^{41}\text{K}^{87}\text{Rb}$ molecule in the $m_1 = -1$ manifold. The black, red, and blue curves correspond to the components $(-3/2, 1/2)$, $(-1/2, -1/2)$, and $(1/2, -3/2)$, respectively.

interactions between the magnetic field and nuclear spins occur is fully taken into account in our model, this overall fitting parameter depends only on the short-range physics. A recent experiment [29] suggested that this fitting parameter can be simply obtained by a state-counting model based on a statistical theory argument [27,28], when the products have a release of final kinetic energy larger than the initial one.

B. The $^{41}\text{K}^{87}\text{Rb} + ^{41}\text{K}^{87}\text{Rb} \rightarrow ^{41}\text{K}_2 + ^{87}\text{Rb}_2$ chemical reaction

The previous system is the only one involving a state-to-state distribution of nuclear spin symmetric states $(\eta_A, \eta_B) = (+1, +1)$ if both products are in their ground rotational states. To illustrate now a state-to-state distribution of nuclear spin antisymmetric states $(\eta_A, \eta_B) = (-1, -1)$, we take the example of bosonic $^{41}\text{K}^{87}\text{Rb}$ molecules. We consider that they are all prepared in the lowest state of the $m_1 = m_2 = -1$ manifold.

Figure 5 shows the probability of a component of the wave function of a $^{41}\text{K}^{87}\text{Rb}$ molecule plotted as a function of the magnetic field B in its first dressed state $|d_{AB}\rangle = 1$ for $m_1 = m_2 = -1$. As can be seen with the black line, the dressed state at large magnetic field ($B > 5$ G for this system) corresponds to a nearly pure character with $m_K = -3/2$ and $m_{\text{Rb}} = 1/2$, the nuclear spins of the corresponding isotopes being $i_K = 3/2$ and $i_{\text{Rb}} = 3/2$. In the following we will take $A = ^{41}\text{K}$ and $B = ^{87}\text{Rb}$. The products of the chemical reaction $^{41}\text{K}_2$ and $^{87}\text{Rb}_2$ are formed in their ground electronic state $X^1\Sigma_g^+$, ground vibrational state $v = 0$, and ground rotational state $n_A = n_B = 0$. To obtain the eigenfunctions and eigenenergies of the KRb, K_2 , and Rb_2 molecules in a magnetic field, we diagonalize the corresponding molecular Hamiltonians in Eq. (25). As hyperfine parameters, we took $c_{AB} = 896.2$ Hz, $g_A = 0.143$, $g_B = 1.834$, $\sigma_{A \text{ of } AB} = 1321$ ppm, and $\sigma_{B \text{ of } AB} = 3469$ ppm from Ref. [39]. We took $c_{AA} = 32$ Hz, $c_{BB} = 25021$ Hz, $\sigma_{A \text{ of } AA} = 1313$ ppm, and $\sigma_{B \text{ of } BB} = 3489$ ppm from Ref. [40].

Figure 6 presents the energies of the combined dressed states of the reactants $AB + AB = ^{41}\text{K}^{87}\text{Rb} + ^{41}\text{K}^{87}\text{Rb}$ in the zero rotational states as a function of the magnetic field, for

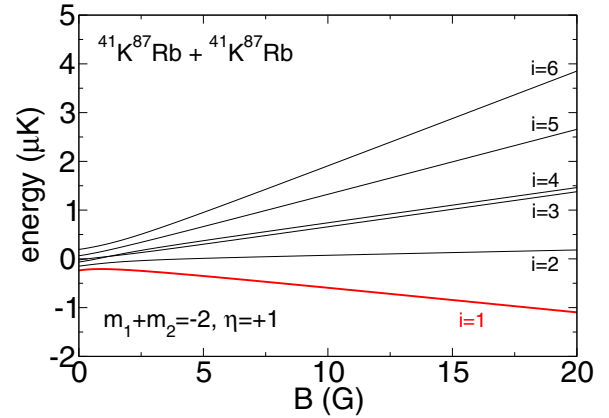


FIG. 6. Same as Fig. 2 but for $^{41}\text{K}^{87}\text{Rb} + ^{41}\text{K}^{87}\text{Rb}$ with $m_1 + m_2 = -2$.

$m_1 + m_2 = -2$ and $\eta = +1$ for the case of indistinguishable states. There are six dressed states denoted by $|i\rangle = 1, \dots, 6$. Table III provides the nomenclature for these states. We take $|i\rangle = 1$ as an example of the initial state (red bold line in the figure). At large magnetic fields, the initial state $|i\rangle = 1$ has a main character of $m_{A_1} = -3/2$, $m_{B_1} = 1/2$, $m_{A_2} = -3/2$, and $m_{B_2} = 1/2$, as can be seen with the black line in Fig. 5 for the individual reactants, but at lower fields $|i\rangle = 1$ gains other characters (red and blue lines in Fig. 1).

Figure 7 presents the energies of the combined dressed states of the products $AA + BB = ^{41}\text{K}_2 + ^{87}\text{Rb}_2$ in the zero rotational states as a function of the magnetic field, for $m_A + m_B = m_1 + m_2 = -2$, and $\eta_A = -1$ and $\eta_B = -1$ (nuclear spin antisymmetric states). The ^{41}K and ^{87}Rb nuclei are composite fermions. The permutation of two identical fermionic nuclei in the $^{41}\text{K}_2$ molecule and in the $^{87}\text{Rb}_2$ molecule should lead to an overall antisymmetric wave function for each molecules. As the rotational wave functions of the $^{41}\text{K}_2$ and $^{87}\text{Rb}_2$ molecules in the zero rotational state are symmetric under the interchange of the nuclei, their nuclear spin wave functions have to be antisymmetric and hence described by values of $\eta_A = -1$ and $\eta_B = -1$. There are now five dressed states denoted by $|j\rangle = 1, \dots, 5$, which correspond to different combinations of the individual dressed states $|d_{AA}; -1\rangle$ and $|d_{BB}; -1\rangle$. Table IV provides the nomenclature for the states. These are all the possible final product states of the chemical reaction, for the nuclear spin antisymmetric states of the molecules.

TABLE III. Same as Table I but for $AB + AB = ^{41}\text{K}^{87}\text{Rb} + ^{41}\text{K}^{87}\text{Rb}$ with $m_1 + m_2 = -1$, and $A = ^{41}\text{K}$ and $B = ^{87}\text{Rb}$.

$ i\rangle$	$ d_{AB_1}\rangle$	$ d_{AB_2}\rangle$	m_{A_1}	m_{B_1}	m_{A_2}	m_{B_2}
1	1	1	-3/2	1/2	-3/2	1/2
2	1	2	-3/2	1/2	-1/2	-1/2
3	1	3	-3/2	1/2	1/2	-3/2
4	2	2	-1/2	-1/2	-1/2	-1/2
5	2	3	-1/2	-1/2	1/2	-3/2
6	3	3	1/2	-3/2	1/2	-3/2

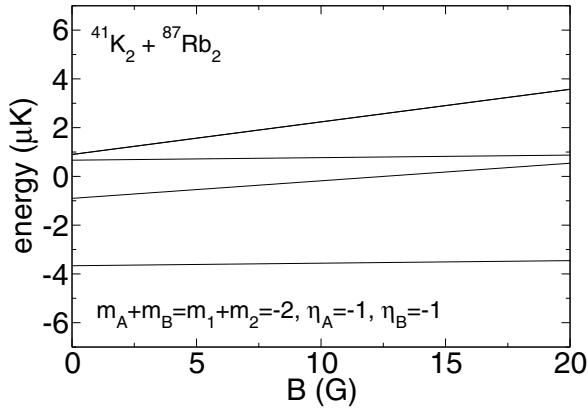


FIG. 7. Same as Fig. 3 but for $^{41}\text{K}_2 + ^{87}\text{Rb}_2$ for $m_A + m_B = m_1 + m_2 = -2$, and $\eta_A = -1$ and $\eta_B = -1$ (nuclear spin antisymmetric states).

Finally, the probability $P_{i \rightarrow j}^{A_{ns}}$ expressed by Eq. (21) for the nuclear spin antisymmetric states is presented in Fig. 8 as a function of the magnetic field [Figs. 8(a) and 8(b)] and as a function of the final states $|j\rangle$ for different magnetic fields [Figs. 8(c)–8(f)]. We find a conclusion similar to that for the case of the nuclear spin symmetric states, that the behavior of the probabilities depends on the magnetic field and on the admixtures of the bare states for the dressed states of the reactants and products. For all values of B , the $|j\rangle = 2$ (red curve) dominates. From Table IV, this state corresponds to a main character of $(-3/2, -1/2) + (1/2, -1/2)$. Around $B \sim 0$ G, the $|j\rangle = 5$ (brown curve) with a main character of $(-1/2, 1/2) + (-1/2, -3/2)$ and the $|j\rangle = 3$ (green curve) with a main character of $(-3/2, 1/2) + (1/2, -3/2)$ become as important as $|j\rangle = 2$. All of these states take the form of an entangled state for the nuclei. For example, for $|j\rangle = 2$ the wave function is $\{| -3/2, -1/2\rangle - | -1/2, -3/2\rangle\}/\sqrt{2}$ for the ^{41}K nuclei and $\{| 1/2, -1/2\rangle - | -1/2, 1/2\rangle\}/\sqrt{2}$ for the ^{87}Rb nuclei. These entangled states carry now a minus sign in contrast with the entangled states of the products discussed above for the case of nuclear spin symmetric states. Therefore, symmetry considerations also impose the type of entangled state (plus or minus). At large magnetic fields, because both molecular states are antisymmetric, there cannot be a character in the symmetric states $(-3/2, -3/2) + (1/2, 1/2)$, the character coming from the swap of the original nuclear spins in the reactants, for the present example. The probabilities

from the reactant state $|i\rangle = 1$ to all these antisymmetric states must then vanish. Therefore, identical reactants in indistinguishable states at large magnetic fields will always populate nuclear spin symmetric states of the molecular products, for the assumptions considered in our study. In the present case, this will correspond to populating the first excited rotational state $n_A = n_B = 1$ of the products, not the ground rotational states. The same arguments explain the selected values of the rotation parities of the molecular products observed in [38].

IV. CONCLUSION

We have presented in this study a theoretical model to compute nuclear spin state-to-state distributions of ultracold chemical reactions, from reactants to products. This distribution can be modified by an applied magnetic field. The formalism is based on the fact that atomic nuclear spins of the products of a chemical reaction inherit the ones of the reactants in the magnetic field. The mechanism is then driven by long-range physics only and not by short-range interactions when the atoms are close together. A simple atomic rearrangement in the chemical reaction and symmetry considerations of identical particles are used to explain the symmetric or antisymmetric character of the nuclear spin wave functions, hence the even or odd parity of the rotational wave function of the molecular products. Depending on the magnetic field that is applied, among the symmetric nuclear spin wave functions, the molecular products can end up in the form of a separable state or of an entangled state of the atomic nuclear spins. Again depending on the magnetic field, for antisymmetric states, the molecular products can end up only in the form of an entangled state. Otherwise the probability tends to zero, which is responsible for the selected values of the rotational parities that have been observed in a recent experiment [38]. The state-to-state probabilities can be computed as functions of the magnetic field. It requires the knowledge of the eigenfunctions of the molecular reactants and products in the magnetic field. We showed that the final state-to-state distribution drastically changes with the magnetic field. When the probability is summed over all the final product states, we showed that, after an analytic development, the probability requires only the knowledge of the eigenfunctions of the reactants. This expression of the summed probabilities was used to explain and understand the magnetic field dependence for the product distribution of a recent experiment [38], validating the assumption that nuclear spins remain unchanged during an ultracold chemical reaction of bi-alkali-metal molecules.

TABLE IV. Same as Table II but for $AA + BB = ^{41}\text{K}_2 + ^{87}\text{Rb}_2$, and $\eta_A = -1$ and $\eta_B = -1$ (nuclear spin antisymmetric states), with $A = ^{41}\text{K}$ and $B = ^{87}\text{Rb}$. The main and second main characters are given for large magnetic fields, typically $B > 5$ G.

$ j\rangle$	$ d_{AA}; -1\rangle$	$ d_{BB}; -1\rangle$	m_{A_1}	m_{A_2}	m_{B_1}	m_{B_2}	m_{A_1}	m_{A_2}	m_{B_1}	m_{B_2}
1	1	3	$-3/2$	$-1/2$	$3/2$	$-3/2$			$1/2$	$-1/2$
2	1	4	$-3/2$	$-1/2$	$1/2$	$-1/2$			$3/2$	$-3/2$
3	2	2	$-3/2$	$1/2$	$1/2$	$-3/2$				
4	3	1	$-3/2$	$3/2$	$-1/2$	$-3/2$	$-1/2$	$1/2$		
5	4	1	$-1/2$	$1/2$	$-1/2$	$-3/2$	$-3/2$	$3/2$		

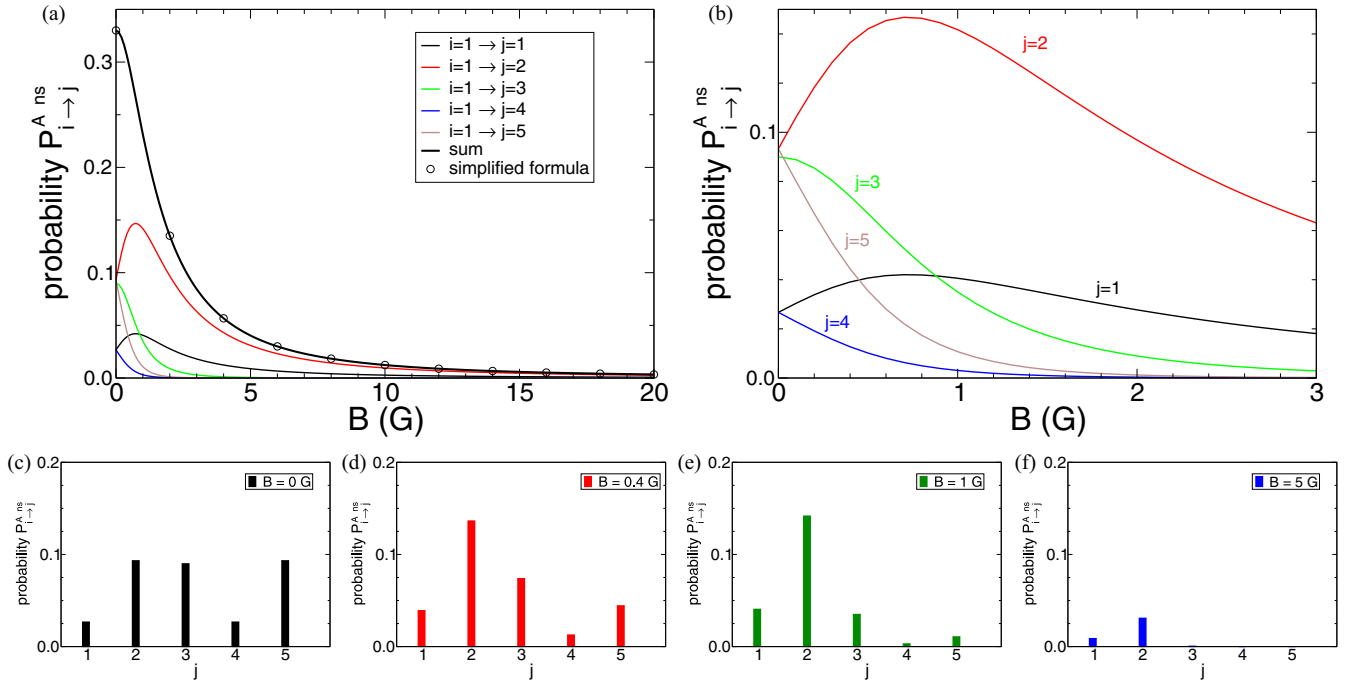


FIG. 8. Same as Fig. 4 but for $P_{i \rightarrow j}^{A ns}$ for $^{41}\text{K}_2 + ^{87}\text{Rb}_2$ and (c) $B = 0$ G, (d) $B = 0.4$ G, (e) $B = 1$ G, and (f) $B = 5$ G.

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APPENDIX A: STATE-TO-STATE PROBABILITIES AND AMPLITUDES

We want to evaluate the probability amplitude $\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle$ in Eq. (14), using Eqs. (9) and (13). We have

$$\begin{aligned}
 & \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle \\
 &= \sum_{m'_{n_A}} \sum_{m'_{n_B}} \sum_{m'_{A_1} = -i_A}^{+i_A} \sum_{m'_{A_2} \geq m'_{A_1}} \sum_{m'_{B_1} = -i_B}^{+i_B} \sum_{m'_{B_2} \leq m'_{B_1}} \langle d_{AA}; \eta_A | n'_A m'_{n_A} m'_{A_1} m'_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n'_B m'_{n_B} m'_{B_1} m'_{B_2}; \eta_B \rangle \\
 & \times \sum_{m_{n_1}} \sum_{m_{n_2}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{A_2} = -i_A}^{+i_A} \sum_{m_{B_2} = -i_B}^{+i_B} \langle n_1 m_{n_1} m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_2} | d_{AB_2} \rangle \\
 & \times \delta_{m'_{n_A} + m'_{n_B}, m_{n_1} + m_{n_2} + m_r - m_p} \delta_{m_{n_1} + m_{A_1} + m_{B_1}, M_1} \delta_{m_{n_2} + m_{A_2} + m_{B_2}, M_2} \\
 & \times \left(\frac{1}{\sqrt{\Delta_A}} \{ |n'_A m'_{n_A} m'_{A_1} m'_{A_2}| + \eta_A \langle n'_A m'_{n_A} m'_{A_2} m'_{A_1} | \} \otimes \frac{1}{\sqrt{\Delta_B}} \{ |n'_B m'_{n_B} m'_{B_1} m'_{B_2}| + \eta_B \langle n'_B m'_{n_B} m'_{B_2} m'_{B_1} | \} \right) \\
 & \times \left(\frac{1}{\sqrt{\Delta_d}} \{ |n_1 m_{n_1} m_{A_1} m_{B_1} \rangle \otimes |n_2 m_{n_2} m_{A_2} m_{B_2} \rangle + \eta |n_2 m_{n_2} m_{A_2} m_{B_2} \rangle \otimes |n_1 m_{n_1} m_{A_1} m_{B_1} \rangle \right). \tag{A1}
 \end{aligned}$$

We rewrite the last line of Eq. (A1) using the first assumption of the model that the nuclear spins remain spectators in the region of the tetra-atomic complex, so that after the reaction they remain the same in the basis of the bare states. Then we can replace the kets $|n_1 m_{n_1} m_{A_1} m_{B_1} \rangle \otimes |n_2 m_{n_2} m_{A_2} m_{B_2} \rangle$ and $|n_2 m_{n_2} m_{A_2} m_{B_2} \rangle \otimes |n_1 m_{n_1} m_{A_1} m_{B_1} \rangle$ by $|n_1 m_{n_1} m_{A_1} m_{A_2} \rangle \otimes |n_2 m_{n_2} m_{B_1} m_{B_2} \rangle$ and $|n_2 m_{n_2} m_{A_2} m_{A_1} \rangle \otimes |n_1 m_{n_1} m_{B_2} m_{B_1} \rangle$, regardless of the order of the nuclear spins in the kets. Note that the two atoms A and B are swapped at the same time, as the total wave function is invariant under the permutation of the molecules as a whole. One cannot

therefore have a swap of atoms A without a swap of atoms B . We now develop the last two lines of Eq. (A1):

$$\begin{aligned}
& \left(\frac{1}{\sqrt{\Delta_A}} \{ \langle n_A' m_{n_A}' m_{A_1}' m_{A_2}' | + \eta_A \langle n_A' m_{n_A}' m_{A_2}' m_{A_1}' | \} \otimes \frac{1}{\sqrt{\Delta_B}} \{ \langle n_B' m_{n_B}' m_{B_1}' m_{B_2}' | + \eta_B \langle n_B' m_{n_B}' m_{B_2}' m_{B_1}' | \} \right) \\
& \quad \times \left(\frac{1}{\sqrt{\Delta_d}} \{ |n_1 m_{n_1} m_{A_1} m_{A_2}\rangle \otimes |n_2 m_{n_2} m_{B_1} m_{B_2}\rangle + \eta |n_2 m_{n_2} m_{A_2} m_{A_1}\rangle \otimes |n_1 m_{n_1} m_{B_2} m_{B_1}\rangle \right) \\
& = \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \left(\langle n_A' m_{n_A}' m_{A_1}' m_{A_2}' | \otimes \langle n_B' m_{n_B}' m_{B_1}' m_{B_2}' | + \eta_A \langle n_A' m_{n_A}' m_{A_2}' m_{A_1}' | \otimes \langle n_B' m_{n_B}' m_{B_1}' m_{B_2}' | \right. \\
& \quad \left. + \eta_B \langle n_A' m_{n_A}' m_{A_1}' m_{A_2}' | \otimes \langle n_B' m_{n_B}' m_{B_2}' m_{B_1}' | + \eta_A \eta_B \langle n_A' m_{n_A}' m_{A_2}' m_{A_1}' | \otimes \langle n_B' m_{n_B}' m_{B_2}' m_{B_1}' | \right) \\
& \quad \times \left(|n_1 m_{n_1} m_{A_1} m_{A_2}\rangle \otimes |n_2 m_{n_2} m_{B_1} m_{B_2}\rangle + \eta |n_2 m_{n_2} m_{A_2} m_{A_1}\rangle \otimes |n_1 m_{n_1} m_{B_2} m_{B_1}\rangle \right) \\
& = \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \left\{ \delta_{m_{A_1}, m_{A_1}'} \delta_{m_{A_2}, m_{A_2}'} \delta_{m_{B_1}, m_{B_1}'} \delta_{m_{B_2}, m_{B_2}'} \left[\langle n_A' m_{n_A}' n_B' m_{n_B}' | n_1 m_{n_1} n_2 m_{n_2} \rangle + \eta_A \eta_B \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_2 m_{n_2} n_1 m_{n_1} \rangle \right] \right. \\
& \quad \left. + \delta_{m_{A_1}, m_{A_2}'} \delta_{m_{A_2}, m_{A_1}'} \delta_{m_{B_1}, m_{B_2}'} \delta_{m_{B_2}, m_{B_1}'} \left[\eta_A \eta_B \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_1 m_{n_1} n_2 m_{n_2} \rangle + \eta \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_2 m_{n_2} n_1 m_{n_1} \rangle \right] \right. \\
& \quad \left. + \delta_{m_{A_1}, m_{A_1}'} \delta_{m_{A_2}, m_{A_2}'} \delta_{m_{B_1}, m_{B_2}'} \delta_{m_{B_2}, m_{B_1}'} \left[\eta_B \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_1 m_{n_1} n_2 m_{n_2} \rangle + \eta_A \eta \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_2 m_{n_2} n_1 m_{n_1} \rangle \right] \right. \\
& \quad \left. + \delta_{m_{A_1}, m_{A_2}'} \delta_{m_{A_2}, m_{A_1}'} \delta_{m_{B_1}, m_{B_2}'} \delta_{m_{B_2}, m_{B_1}'} \left[\eta_A \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_1 m_{n_1} n_2 m_{n_2} \rangle + \eta_B \eta \langle n_A' m_{n_A}' n_B' m_{n_B}' | n_2 m_{n_2} n_1 m_{n_1} \rangle \right] \right\}. \tag{A2}
\end{aligned}$$

From the third assumption, we assume that the terms $\langle n_A' m_{n_A}' n_B' m_{n_B}' | n_1 m_{n_1} n_2 m_{n_2} \rangle$ and $\langle n_A' m_{n_A}' n_B' m_{n_B}' | n_2 m_{n_2} n_1 m_{n_1} \rangle$ are independent of the projection quantum numbers and are equal regardless of the order of the rotational quantum numbers. We then rewrite these terms as $\langle n_A' n_B' | n_1 n_2 \rangle$. If we get rid of the dummy prime variables, we get the general expression

$$\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle = \langle n_A n_B | n_1 n_2 \rangle \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}}, \tag{A3}$$

with

$$\begin{aligned}
& \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} \\
& = \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
& \quad \times \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \sum_{m_{n_1}} \sum_{m_{n_2}} \delta_{m_{n_A} + m_{n_B}, m_{n_1} + m_{n_2} + m_{i_r} - m_{i_p}} \\
& \quad \times \{ \langle n_1 m_{n_1} m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_2} | d_{AB_2} \rangle [1 + \eta_A \eta_B \eta] \delta_{m_{n_1} + m_{A_1} + m_{B_1}, M_1} \delta_{m_{n_2} + m_{A_2} + m_{B_2}, M_2} \\
& \quad \times \langle n_1 m_{n_1} m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A \eta_B + \eta] \delta_{m_{n_1} + m_{A_2} + m_{B_2}, M_1} \delta_{m_{n_2} + m_{A_1} + m_{B_1}, M_2} \\
& \quad \times \langle n_1 m_{n_1} m_{A_1} m_{B_2} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_2} m_{B_1} | d_{AB_2} \rangle [\eta_B + \eta_A \eta] \delta_{m_{n_1} + m_{A_1} + m_{B_2}, M_1} \delta_{m_{n_2} + m_{A_2} + m_{B_1}, M_2} \\
& \quad \times \langle n_1 m_{n_1} m_{A_2} m_{B_1} | d_{AB_1} \rangle \langle n_2 m_{n_2} m_{A_1} m_{B_2} | d_{AB_2} \rangle [\eta_A + \eta_B \eta] \delta_{m_{n_1} + m_{A_2} + m_{B_1}, M_1} \delta_{m_{n_2} + m_{A_1} + m_{B_2}, M_2} \}. \tag{A4}
\end{aligned}$$

The Kronecker symbol $\delta_{\eta_A \eta_B, \eta}$ has been added explicitly from the related selection rules in the square brackets. The expression has been separated into two parts with a part related to the rotational degree of freedom $\langle n_A n_B | n_1 n_2 \rangle$ and for a given transition from initial rotational quantum numbers n_1 and n_2 to final ones n_A and n_B , a part related to the nuclear spin degree of freedom $\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}}$. The corresponding probability is the modulus square of the amplitude

$$P_{i \rightarrow j} = |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle|^2 = P^{\text{rot}} \times P_{i \rightarrow j}^{\text{ns}}, \tag{A5}$$

with

$$P^{\text{rot}} = |\langle n_A n_B | n_1 n_2 \rangle|^2, \quad P_{i \rightarrow j}^{\text{ns}} = |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}}|^2. \tag{A6}$$

APPENDIX B: SIMPLIFICATIONS FOR REACTANTS IN ZERO ROTATIONAL STATES

If we consider reactants in $n_1 = n_2 = 0$, then $m_{n_1} = m_{n_2} = 0$, and $M_1 \equiv m_1$ and $M_2 \equiv m_2$.

1. Distinguishable case with $m_1 \neq m_2$

We consider first reactants with $m_1 \neq m_2$. Equation (A4) can be simplified to

$$\begin{aligned}
 \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} &= \delta_{\eta_A \eta_B, \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \\
 &\times \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\times \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \frac{1}{\sqrt{\Delta_d}} \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle [1 + \eta_A \eta_B \eta] \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_2} \\
 &+ \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A \eta_B + \eta] \delta_{m_{A_2} + m_{B_2}, m_1} \delta_{m_{A_1} + m_{B_1}, m_2} \\
 &+ \langle m_{A_1} m_{B_2} | d_{AB_1} \rangle \langle m_{A_2} m_{B_1} | d_{AB_2} \rangle [\eta_B + \eta_A \eta] \delta_{m_{A_1} + m_{B_2}, m_1} \delta_{m_{A_2} + m_{B_1}, m_2} \\
 &+ \langle m_{A_2} m_{B_1} | d_{AB_1} \rangle \langle m_{A_1} m_{B_2} | d_{AB_2} \rangle [\eta_A + \eta_B \eta] \delta_{m_{A_2} + m_{B_1}, m_1} \delta_{m_{A_1} + m_{B_2}, m_2} \}. \tag{B1}
 \end{aligned}$$

2. Indistinguishable case with $m_1 = m_2$

We further develop the expression (B1) when, in addition, the reactants are indistinguishable. In this case $d_{AB_1} = d_{AB_2} = d_{AB}$, $\eta = +1$, and $\Delta_d = 4$. From the first Kronecker δ term, this implies necessarily $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$. Also, molecules have necessarily the same values of projection so that $m_1 = m_2$. Equation (B1) simplifies to

$$\begin{aligned}
 \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB}, d_{AB}; +1 \rangle^{\text{ns}} &= \delta_{\eta_A \eta_B, +1} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \\
 &\times \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\times \frac{1}{\sqrt{\Delta_A}} \frac{1}{\sqrt{\Delta_B}} \{ \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle [1 + \eta_A \eta_B] \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1} \\
 &+ \langle m_{A_1} m_{B_2} | d_{AB} \rangle \langle m_{A_2} m_{B_1} | d_{AB} \rangle [\eta_A + \eta_B] \delta_{m_{A_1} + m_{B_2}, m_1} \delta_{m_{A_2} + m_{B_1}, m_1} \}. \tag{B2}
 \end{aligned}$$

Let us consider the case of $m_{A_2} = m_{A_1}$ and $m_{B_2} = m_{B_1}$ in the quadruple sum of nuclear spins, with necessarily $\eta_A = +1$, $\eta_B = +1$, and $\Delta_A = \Delta_B = 4$. After simplifications, this gives the term

$$\langle d_{AA}; +1 | n_A m_{n_A} m_{A_1} m_{A_1}; +1 \rangle \langle d_{BB}; +1 | n_B m_{n_B} m_{B_1} m_{B_1}; +1 \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle. \tag{B3}$$

The case of $m_{A_2} > m_{A_1}$ and $m_{B_2} < m_{B_1}$ in the quadruple sum, with $\Delta_A = \Delta_B = 2$ and $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$, gives

$$\langle d_{AA}; \pm 1 | n_A m_{n_A} m_{A_1} m_{A_1}; \pm 1 \rangle \langle d_{BB}; \pm 1 | n_B m_{n_B} m_{B_1} m_{B_1}; \pm 1 \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle. \tag{B4}$$

We used the fact that the coefficients $\langle m_{A_1} m_{B_2} | d_{AB} \rangle$ and $\langle m_{A_2} m_{B_1} | d_{AB} \rangle$ in Eq. (B2) both necessarily vanish when the A or B atoms are swapped, because when $m_{A_2} > m_{A_1}$ ($m_{B_2} < m_{B_1}$), $m_{A_2} + m_{B_1} > m_{A_1} + m_{B_2}$ ($m_{A_1} + m_{B_2} < m_{A_2} + m_{B_1}$), so that $m_{A_2} + m_{B_1} > m_1$ ($m_{A_1} + m_{B_2} < m_1$). For the same reasons, we cannot have a case $m_{A_2} = m_{A_1}$ and $m_{B_2} < m_{B_1}$, or $m_{A_2} > m_{A_1}$ and $m_{B_2} = m_{B_1}$. Therefore, one can write Eq. (B2) in a compact form

$$\begin{aligned}
 \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB}, d_{AB}; +1 \rangle^{\text{ns}} &= \delta_{\eta_A \eta_B, +1} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \\
 &\times \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\times \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \tag{B5}
 \end{aligned}$$

3. Distinguishable case with $m_1 = m_2$

We further develop Eq. (A4) when the reactants are distinguishable. In this case $d_{AB_1} \neq d_{AB_2}$, $\Delta_d = 2$, and both $\eta = \pm 1$ components have to be computed. From the first Kronecker δ term, this implies necessarily $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$ when $\eta = +1$, and $\eta_A = +1$ and $\eta_B = -1$ or $\eta_A = -1$ and $\eta_B = +1$ when $\eta = -1$. We focus on the case where molecules have the same values of projection so that $m_1 = m_2$. Let us start with the component $\eta = +1$. The case of $m_{A_2} = m_{A_1}$ and $m_{B_2} = m_{B_1}$

in the quadruple sum of nuclear spins, with necessarily $\eta_A = +1$, $\eta_B = +1$, $\Delta_A = \Delta_B = 4$, and $\eta = +1$, gives the term

$$\sqrt{2} \langle d_{AA}; +1 | n_A m_{n_A} m_{A_1} m_{A_1}; +1 \rangle \langle d_{BB}; +1 | n_B m_{n_B} m_{B_1} m_{B_1}; +1 \rangle \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle. \quad (\text{B6})$$

We prefer the following form for later general notation convenience:

$$\begin{aligned} & \frac{1}{\sqrt{2}} \langle d_{AA}; +1 | n_A m_{n_A} m_{A_1} m_{A_1}; +1 \rangle \langle d_{BB}; +1 | n_B m_{n_B} m_{B_1} m_{B_1}; +1 \rangle \\ & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle + \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \}. \end{aligned} \quad (\text{B7})$$

The case of $m_{A_2} > m_{A_1}$ and $m_{B_2} < m_{B_1}$ in the quadruple sum, with $\Delta_A = \Delta_B = 2$ and $\eta_A = \eta_B = +1$ or $\eta_A = \eta_B = -1$, gives

$$\begin{aligned} & \frac{1}{\sqrt{2}} \langle d_{AA}; \pm 1 | n_A m_{n_A} m_{A_1} m_{A_1}; \pm 1 \rangle \langle d_{BB}; \pm 1 | n_B m_{n_B} m_{B_1} m_{B_1}; \pm 1 \rangle \\ & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle + \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \}. \end{aligned} \quad (\text{B8})$$

For the same reasons as above, the coefficients $\langle m_{A_1} m_{B_2} | d_{AB_1} \rangle$, $\langle m_{A_2} m_{B_1} | d_{AB_1} \rangle$, $\langle m_{A_1} m_{B_2} | d_{AB_2} \rangle$, and $\langle m_{A_2} m_{B_1} | d_{AB_2} \rangle$ all vanish. Similarly, we cannot have a case $m_{A_2} = m_{A_1}$ and $m_{B_2} < m_{B_1}$, or $m_{A_2} > m_{A_1}$ and $m_{B_2} = m_{B_1}$. For $\eta = -1$, similar arguments hold, in addition to the fact that the case of $m_{A_2} = m_{A_1}$ and $m_{B_2} = m_{B_1}$ cannot exist. The case of $m_{A_2} > m_{A_1}$ and $m_{B_2} < m_{B_1}$ in the quadruple sum, with $\Delta_A = \Delta_B = 2$, $\eta_A = +1$, and $\eta_B = -1$, or $\eta_A = -1$ and $\eta_B = +1$, gives

$$\begin{aligned} & \frac{1}{\sqrt{2}} \langle d_{AA}; \pm 1 | n_A m_{n_A} m_{A_1} m_{A_2}; \pm 1 \rangle \langle d_{BB}; \mp 1 | n_B m_{n_B} m_{B_1} m_{B_2}; \mp 1 \rangle \\ & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle - \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \} \end{aligned} \quad (\text{B9})$$

with now a destructive term inside the curly brackets. Gathering these expressions all together, Eq. (A4) can then be written in a compact form

$$\begin{aligned} \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} &= \delta_{\eta_A \eta_B \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \\ & \times \frac{1}{\sqrt{2}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\ & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle + \eta \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \} \\ & \times \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \end{aligned} \quad (\text{B10})$$

4. Compact form for molecules with the same projection quantum numbers $m_1 = m_2$

Both Eqs. (B5) and (B10) can be written in an even more compact form, whether the molecules, with same projection quantum numbers $m_1 = m_2$, are indistinguishable or not:

$$\begin{aligned} \langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB_1}, d_{AB_2}; \eta \rangle^{\text{ns}} &= \delta_{\eta_A \eta_B \eta} \sum_{m_{n_A}} \sum_{m_{n_B}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \\ & \times \frac{1}{\sqrt{\Delta d}} \sum_{m_{A_1} = -i_A}^{+i_A} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1} = -i_B}^{+i_B} \sum_{m_{B_2} \leq m_{B_1}} \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\ & \times \{ \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle + \eta \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle \} \\ & \times \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \end{aligned} \quad (\text{B11})$$

APPENDIX C: SUM OF THE STATE-TO-STATE PROBABILITIES OVER THE FINAL STATES OF THE PRODUCTS

We consider here the case of reactants in $n_1 = n_2 = m_{n_1} = m_{n_2} = 0$ but we explicitly include the quantum numbers. We consider first Eq. (B5) for the case of indistinguishable molecules as the expression is easier to work for the derivation, but we use the intermediate form in Eq. (A2), explicitly including the term $\langle n_A m_{n_A} n_B m_{n_B} | n_1 m_{n_1} n_2 m_{n_2} \rangle$ inside the sum. We use the fact that it is the same regardless of the order of the rotational quantum numbers, but we do not necessarily use the fact that it is independent of the projection quantum numbers. Therefore, we keep explicit the projection quantum numbers for the purpose of the derivation. Recall that we have $d_{AB_1} = d_{AB_2} = d_{AB}$ and $m_1 = m_2$. The total probability summed over all the final states of the

products is given by

$$\begin{aligned}
 \sum_j P_{i \rightarrow j} &= \sum_{|d_{AA}, d_{BB}; \eta_A, \eta_B\rangle} |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB}, d_{AB}; +1 \rangle|^2 \\
 &= \sum_{|d_{AA}; \eta_A\rangle} \sum_{|d_{BB}; \eta_B\rangle} |\langle d_{AA}, d_{BB}; \eta_A, \eta_B | d_{AB}, d_{AB}; +1 \rangle|^2 \\
 &= \delta_{\eta_A \eta_B, +1} \sum_{|d_{AA}; \eta_A\rangle} \sum_{|d_{BB}; \eta_B\rangle} \left| \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \right. \\
 &\quad \times \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\quad \times \langle n_A m_{n_A} n_B m_{n_B} | n_1 m_{n_1} n_2 m_{n_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \\
 &\quad \times \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1} \left. \right|^2 \\
 &= \delta_{\eta_A \eta_B, +1} \times \sum_{|d_{AA}; \eta_A\rangle} \sum_{|d_{BB}; \eta_B\rangle} \sum_{m'_{n_A}} \sum_{m'_{n_B}} \sum_{m'_{A_1}} \sum_{m'_{A_2} \geq m'_{A_1}} \sum_{m'_{B_1}} \sum_{m'_{B_2} \leq m'_{B_1}} \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \\
 &\quad \times \langle n_A m'_{n_A} m'_{A_1} m'_{A_2}; \eta_A | d_{AA}; \eta_A \rangle \langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \\
 &\quad \times \langle n_B m'_{n_B} m'_{B_1} m'_{B_2}; \eta_B | d_{BB}; \eta_B \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\quad \times \langle n_1 m_{n_1} n_2 m_{n_2} | n_A m'_{n_A} n_B m'_{n_B} \rangle \langle n_A m_{n_A} n_B m_{n_B} | n_1 m_{n_1} n_2 m_{n_2} \rangle \\
 &\quad \times \langle d_{AB} | m'_{A_1} m'_{B_1} \rangle \langle d_{AB} | m'_{A_2} m'_{B_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \\
 &\quad \times \delta_{m'_{n_A} + m'_{n_B}, m_{i_r} - m_{i_p}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \delta_{m'_{A_1} + m'_{B_1}, m_1} \delta_{m'_{A_2} + m'_{B_2}, m_1} \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1} \\
 &= \delta_{\eta_A \eta_B, +1} \times \sum_{m'_{n_A}} \sum_{m'_{n_B}} \sum_{m'_{A_1}} \sum_{m'_{A_2} \geq m'_{A_1}} \sum_{m'_{B_1}} \sum_{m'_{B_2} \leq m'_{B_1}} \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \\
 &\quad \times \langle n_A m'_{n_A} m'_{A_1} m'_{A_2}; \eta_A | \left(\sum_{|d_{AA}; \eta_A\rangle} |d_{AA}; \eta_A\rangle \langle d_{AA}; \eta_A| \right) | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \\
 &\quad \times \langle n_B m'_{n_B} m'_{B_1} m'_{B_2}; \eta_B | \left(\sum_{|d_{BB}; \eta_B\rangle} |d_{BB}; \eta_B\rangle \langle d_{BB}; \eta_B| \right) | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\quad \times \langle n_1 m_{n_1} n_2 m_{n_2} | n_A m'_{n_A} n_B m'_{n_B} \rangle \langle n_A m_{n_A} n_B m_{n_B} | n_1 m_{n_1} n_2 m_{n_2} \rangle \\
 &\quad \times \langle d_{AB} | m'_{A_1} m'_{B_1} \rangle \langle d_{AB} | m'_{A_2} m'_{B_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \\
 &\quad \times \delta_{m'_{n_A} + m'_{n_B}, m_{i_r} - m_{i_p}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \delta_{m'_{A_1} + m'_{B_1}, m_1} \delta_{m'_{A_2} + m'_{B_2}, m_1} \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}.
 \end{aligned}$$

We can use the closure relations $\sum_{|d_{AA}; \eta_A\rangle} |d_{AA}; \eta_A\rangle \langle d_{AA}; \eta_A| = 1$ and $\sum_{|d_{BB}; \eta_B\rangle} |d_{BB}; \eta_B\rangle \langle d_{BB}; \eta_B| = 1$. We get

$$\begin{aligned}
 \sum_j P_{i \rightarrow j} &= \delta_{\eta_A \eta_B, +1} \sum_{m'_{n_A}} \sum_{m'_{n_B}} \sum_{m'_{A_1}} \sum_{m'_{A_2} \geq m'_{A_1}} \sum_{m'_{B_1}} \sum_{m'_{B_2} \leq m'_{B_1}} \sum_{m_{n_A}} \sum_{m_{n_B}} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \\
 &\quad \times \langle n_A m'_{n_A} m'_{A_1} m'_{A_2}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle n_B m'_{n_B} m'_{B_1} m'_{B_2}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle \\
 &\quad \times \langle n_1 m_{n_1} n_2 m_{n_2} | n_A m'_{n_A} n_B m'_{n_B} \rangle \langle n_A m_{n_A} n_B m_{n_B} | n_1 m_{n_1} n_2 m_{n_2} \rangle \langle d_{AB} | m'_{A_1} m'_{B_1} \rangle \langle d_{AB} | m'_{A_2} m'_{B_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \\
 &\quad \times \delta_{m'_{n_A} + m'_{n_B}, m_{i_r} - m_{i_p}} \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \delta_{m'_{A_1} + m'_{B_1}, m_1} \delta_{m'_{A_2} + m'_{B_2}, m_1} \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}.
 \end{aligned}$$

We now use the fact that $\langle n_A m'_{n_A} m'_{A_1} m'_{A_2}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle = \delta_{m_{n_A}, m'_{n_A}} \delta_{m_{A_1}, m'_{A_1}} \delta_{m_{A_2}, m'_{A_2}}$ and $\langle n_B m'_{n_B} m'_{B_1} m'_{B_2}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle = \delta_{m_{n_B}, m'_{n_B}} \delta_{m_{B_1}, m'_{B_1}} \delta_{m_{B_2}, m'_{B_2}}$. Then

$$\begin{aligned}
 \sum_j P_{i \rightarrow j} &= \delta_{\eta_A \eta_B, +1} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \langle n_1 m_{n_1} n_2 m_{n_2} | \left(\sum_{m_{n_A}} \sum_{m_{n_B}} |n_A m_{n_A} n_B m_{n_B}\rangle \langle n_A m_{n_A} n_B m_{n_B}| \right) | n_1 m_{n_1} n_2 m_{n_2} \rangle \\
 &\quad \times \langle d_{AB} | m'_{A_1} m'_{B_1} \rangle \langle d_{AB} | m'_{A_2} m'_{B_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \delta_{m_{n_A} + m_{n_B}, m_{i_r} - m_{i_p}} \delta_{m_{A_1} + m_{B_1}, m_1} \delta_{m_{A_2} + m_{B_2}, m_1}. \tag{C1}
 \end{aligned}$$

We use the closure relation $\sum_{m_{n_A}} \sum_{m_{n_B}} |m_{n_A} m_{n_B}\rangle \langle m_{n_A} m_{n_B}| = 1$ (the term $\delta_{m_{n_A}+m_{n_B}, m_r-m_l}$ disappears), so that

$$\sum_j P_{i \rightarrow j} = \delta_{\eta_A \eta_B, +1} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \langle n_1 m_{n_1} n_2 m_{n_2} | n_A n_B \rangle \langle n_A n_B | n_1 m_{n_1} n_2 m_{n_2} \rangle \\ \times \langle d_{AB} | m'_{A_1} m'_{B_1} \rangle \langle d_{AB} | m'_{A_2} m'_{B_2} \rangle \langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle \delta_{m_{n_A}+m_{n_B}, m_r-m_l} \delta_{m_{A_1}+m_{B_1}, m_l} \delta_{m_{A_2}+m_{B_2}, m_1}. \quad (\text{C2})$$

Using the fact that $\langle n_1 m_{n_1} n_2 m_{n_2} | n_A n_B \rangle \langle n_A n_B | n_1 m_{n_1} n_2 m_{n_2} \rangle \equiv |\langle n_A n_B | n_1 n_2 \rangle|^2 = P^{\text{rot}}$ (see arguments in Appendix A), we get at the end

$$\sum_j P_{i \rightarrow j} = P^{\text{rot}} \times \sum_j P_{i \rightarrow j}^{\text{ns}}, \quad (\text{C3})$$

with

$$\sum_j P_{i \rightarrow j}^{\text{ns}} = \delta_{\eta_A \eta_B, +1} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} |\langle m_{A_1} m_{B_1} | d_{AB} \rangle \langle m_{A_2} m_{B_2} | d_{AB} \rangle|^2 \delta_{m_{A_1}+m_{B_1}, m_l} \delta_{m_{A_2}+m_{B_2}, m_1}. \quad (\text{C4})$$

The previous derivation remains similar for the other cases, as the element $\langle d_{AA}; \eta_A | n_A m_{n_A} m_{A_1} m_{A_2}; \eta_A \rangle \langle d_{BB}; \eta_B | n_B m_{n_B} m_{B_1} m_{B_2}; \eta_B \rangle$ factorizes as well in front of the full expression. The same overall procedure is used and this element disappears due to the closure relations. The case $m_1 \neq m_2$ in Eq. (B1) would give

$$\sum_j P_{i \rightarrow j}^{\text{ns}} = \delta_{\eta_A \eta_B, \eta} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \frac{1}{\Delta_A} \frac{1}{\Delta_B} \frac{1}{\Delta_d} |\langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle| [1 + \eta_A \eta_B \eta] \delta_{m_{A_1}+m_{B_1}, m_l} \delta_{m_{A_2}+m_{B_2}, m_2} \\ + \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A \eta_B + \eta] \delta_{m_{A_2}+m_{B_2}, m_1} \delta_{m_{A_1}+m_{B_1}, m_2} + \langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle [\eta_B + \eta_A \eta] \\ \times \delta_{m_{A_1}+m_{B_1}, m_1} \delta_{m_{A_2}+m_{B_2}, m_2} + \langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle [\eta_A + \eta_B \eta] \delta_{m_{A_2}+m_{B_2}, m_1} \delta_{m_{A_1}+m_{B_1}, m_2}^2 \quad (\text{C5})$$

and the case of molecules with same values $m_1 = m_2$, indistinguishable or not, in Eq. (B11) would give

$$\sum_j P_{i \rightarrow j}^{\text{ns}} = \delta_{\eta_A \eta_B, \eta} \sum_{m_{A_1}} \sum_{m_{A_2} \geq m_{A_1}} \sum_{m_{B_1}} \sum_{m_{B_2} \leq m_{B_1}} \frac{1}{\Delta_d} |\langle m_{A_1} m_{B_1} | d_{AB_1} \rangle \langle m_{A_2} m_{B_2} | d_{AB_2} \rangle| \\ + \eta |\langle m_{A_2} m_{B_2} | d_{AB_1} \rangle \langle m_{A_1} m_{B_1} | d_{AB_2} \rangle|^2 \delta_{m_{A_1}+m_{B_1}, m_l} \delta_{m_{A_2}+m_{B_2}, m_1}. \quad (\text{C6})$$

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