Statistical product distributions for ultracold reactions in external fields

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Ultracold chemical reactions are often observed and modeled from the loss of reactants, while a thorough understanding of their dynamics is ultimately conditioned by the study of their products. Here, we discuss a rigorous and flexible framework for computing statistical product-state distributions and state-to-state cross sections for ultracold reactions in external fields. We show that fields may have two main effects on statistical reactions, by: (1) modifying the product energy levels thus potentially reshaping the product distributions; and/or (2) changing a reaction’s exothermicity. By discussing these effects and the strength of the formalism to unravel different mechanisms, we argue for statistical predictions as benchmarks for understanding reactivity in the ultracold regime.

Recent advances in producing and trapping species at temperatures below 1 mK have made ultracold chemistry a reality. For the first time, we can explore reactions in the fully quantum regime where resonances, tunneling, quantum degeneracy and other quantum effects may dominate the dynamics. Moreover, controlling all degrees of freedom and scattering conditions becomes possible at such temperatures: reactions can be studied at the state-to-state level, typical and exotic mechanisms scrutinized with unprecedented detail—favored or disfavored at will—and the effects of “tailored” interactions and dimensionality thoroughly probed. Since 2010, pioneering experiments at JILA, Colorado, started addressing many of these issues in reactions involving mixed ultracold samples of K, Rb and KRb [13] by inferring reaction rates through the measurement of reactants losses.

Despite all key findings at JILA, and being commonly acknowledged as one of the most important applications for ultracold species [14], low-temperature chemical reactions are most often considered for their role as obstacles to the stability of quantum gases [15,16]. This seems natural, since the main current experimental focus is on the production of ultracold molecules which reactions obstruct. Nevertheless, the problem of reaction rates and their dependence on external fields have attracted much interest: Quéménéner and Bohn [2,3,10], 11, Idziaszek, Julienne et al. [12,14], and Gao [15,16] developed quantum models to interpret the rate constants measured at JILA, as well as discussed different universality regimes.

Yet, the study of a chemical reaction goes necessarily beyond a description of its rate into that of its products: The question of product-state distributions and state-to-state cross sections is among the biggest experimental and theoretical challenges in the field, with the potential to bring ultracold physics into the realm of chemistry [5]. Product distributions are far more sensitive than reaction rates to finer details of the dynamics, and would provide an integral view and deeper understanding of the underlying physics. In addition, even if neutral products are quite difficult to detect, ionic products may be more easily monitored in experiments on ultracold ion-neutral [17] or Penning-ionization reactions [18], and aid understanding radiative molecular formation, charge transfer and several other mechanisms. The issue seems specially timely for the first product distributions were very recently measured for the closely related process of 3-body recombination in an ultracold atomic gas [19].

A theory that accounts for external fields is essential as these are ubiquitous in ultracold experiments: fields are used for trapping the (ultra)cold species and/or controlling their interactions. In principle, a full description of low-temperature reactions can be derived from the quantum formalism for chemical reactions in electromagnetic fields developed by Tscherbul and Krems [20]. However, such rigorous quantum-mechanical calculations are not currently viable for many cases of experimental interest. This is mainly because—as discussed by Mayle et al. [21,22]—(ultra)cold collisions involving relatively heavy species have associated a huge number of librational states which make full quantum calculations computationally untractable. Moreover, such states produce an enormous number of scattering resonances so that tiny inaccuracies in the interaction potentials may unpredictably modify the calculated cross sections.

Nonetheless, Mayle and coworkers [21,22] have shown that total reaction rates, and answers to a number of important questions regarding the statistics of global properties of such processes, may still be inferred using arguments from Rice-Ramsperger-Kassel-Marcus (RRKM) theory, the random matrix theory of nuclear scattering, and multichannel quantum defect theory (MQDT). The first empirical indication of such statistical behavior was recently reported for ultracold collisions of Er atoms [23].

In this paper, we set up a general and flexible framework for calculating statistical product-state distributions and state-to-state cross sections for ultracold reac-
tions in external fields, by connecting traditional statistical theories [24, 25] and ultracold collision theory [26]. We show that, as in studies of reactions at higher temperatures, product distributions may be used as benchmarks for the founding assumptions of the theory, and provide fundamental tests for the statistical arguments of Mayle et al. [21, 22]. Moreover, they allow to critically evaluate possible departures from statistical behavior, being thus a powerful tool in understanding any kind of reaction.

We consider a reactive collision between two species, $M_\alpha^2$ and $M_\beta^2$, which yields two products, $M_\alpha^1$ and $M_\beta^1$, in the presence of an external field. Here, $\alpha$ and $\beta$ loosely refer to reactants and products; in what follows, $\alpha$ is also used to represent the set of quantum numbers needed to specify the internal states of the reactants, while $\beta$ is its analogous for the products. Product-state distributions are obtained from the reaction cross section $\sigma$, with the probability density associated to a variable $X$, $P(X) = \int \frac{2\pi}{\sigma} dX$ [27]. In general, the only conserved quantity in an external field is the projection $M$ of the total angular momentum, and the total reaction cross section can be obtained by adding all contributions from state-to-state cross sections, $\sigma = \sum_{M_\alpha} \sigma_{\alpha\beta}^M$. The rigorous quantum-mechanical expression for the state-to-state cross section from reactant state $\alpha$ to product state $\beta$, at a given $M$, energy $E$ and field strength $F$ is [20]

$$\sigma_{\alpha\beta}^M(E, F) = \frac{\pi \hbar^2 g_\alpha}{2\mu_\alpha (E - E_\alpha)} \times \sum_{L_\alpha M_{\alpha L_\alpha}} \sum_{L_\beta M_{\beta L_\beta}} \left| S_{\alpha L_\alpha M_{\alpha L_\alpha}; \beta L_\beta M_{\beta L_\beta}}^M (E, F) \right|^2$$

(1)

where $g_\alpha$ is a degeneracy factor that equals 2 if the reactants are indistinguishable and 1 otherwise, $\mu_\alpha$ is the reactants’ reduced mass, $E_\alpha$ ($E_\beta$) is the species energy in state $\alpha$ ($\beta$), and $L_\alpha$ ($L_\beta$) is the space-fixed orbital angular momentum of the reactants (products) with projection $M_{\alpha L_\alpha}$ ($M_{\beta L_\beta}$) on the field axis. The sum over the absolute squares of $S$-matrix elements define the transition probability $P_{\alpha\beta}^M$ from state $\alpha$ to $\beta$. Our model becomes statistical for us assume that reaction always proceeds through complex formation, whose dynamics render the reactant and product channels statistically independent. Following Hauser and Feshbach [21, 24], or Miller [25]

$$P_{\alpha\beta}^M \approx p_{\alpha}^M p_{\beta}^M / \sum_{\gamma} p_{\gamma}^M$$

(2)

where the explicit dependence on $E$ and $F$ has been omitted, as in what follows. The $p^M$ quantities are capture probabilities — i.e., the probability of complex formation, for a given $M$, when the species collide in a specific state. The sum in the denominator runs over all energetically accessible reactant and product channels, hence the ratio $p_{\beta}^M / \sum_{\gamma} p_{\gamma}^M$ is the fraction of collision complexes that dissociate into product state $\beta$. Eq. (2) is statistical for all capture probabilities are considered uncorrelated and is seen to satisfy the principle of detailed balance. In a further approximation, our reasoning may be readily extended to include inelastic processes, thus treating all quenching events statistically — although nonreactive scattering is less likely to involve complex formation.

A distinctive feature of ultracold experiments is the possibility to fully control the reactants’ initial states, thus we fix $\alpha$ in what follows. The statistical state-to-state reaction cross section may be written as

$$\sigma_{\alpha\beta} = \frac{\pi \hbar^2 g_\alpha}{2\mu_\alpha (E - E_\alpha)} \sum_M p_{\alpha}^M p_{\beta}^M / \sum_{\gamma} p_{\gamma}^M$$

(3)

from which the total reaction cross section $\sigma_{\alpha\beta}$ is found by summing over all possible product states $\beta$, and the related total reaction rate $k_{\alpha\beta} = [2(E - E_\alpha)/\mu_\alpha]^{1/2} \sigma_{\alpha\beta}$. Quantities for a specific temperature are obtained by averaging over the corresponding Boltzmann distribution. If reaction occurs, the probability density corresponding to an observable $X$ in the products reads

$$P_{\alpha} (X) = \left( \sum_M p_{\alpha}^M \sum_{\beta} \frac{p_{\beta}^M}{\sum_{\gamma} p_{\gamma}^M} \right)^{-1} \left( \sum_M p_{\alpha}^M \sum_{\beta} \frac{\partial p_{\beta}^M}{\partial X} \sum_{\gamma} p_{\gamma}^M \right)$$

(4)

where the first term in parenthesis acts like a proportionality constant. The form of this distribution is readily visualized by recognizing that the partial derivatives are related to Dirac $\delta$-functions in the form $\delta(X) \sum_{\beta} p_{\beta}^M$, where the sum includes only product states compatible with the value $X$. Contributions from different $M$ values combine with different relative weights that approach the capture probabilities in the entrance channels if many product states are available.

Eqs. (3) and (4) provide detailed statistical predictions for the observables of a chemical reaction in an external field. Kinetic energies in the entrance/elastic (and possibly inelastic) channels are extremely low, hence a quantum-mechanical description is crucial for calculating the corresponding capture probabilities. By comparison, the kinetic energies available to the products are much larger and a simpler (semi)classical description should be appropriate. The issue of capture in the ultracold entrance channels has received much attention in the last few years, mainly to describe the loss rates measured at JILA; various models have been proposed [11–13, 14, 15, 26, 29] that are valid under specific conditions. In addition, we have extended time-independent [30, 31] and time-dependent methods [32], as well as a variety of semiclassical and classical models, to make it possible to evaluate capture probabilities in external fields also for reactions at higher temperatures [33]. The statistical formalism is quite flexible as any specific capture models may be chosen among all of the above, or new models developed, depending on the conditions of the experiment and desired level of sophistication.
To illustrate our formalism, we consider ultracold exothermic reactions involving $^{40}$K, $^{87}$Rb and their diatomic combinations. Reactive collisions between these species are barrierless, with exothermicities ranging from about 10 to 200 cm$^{-1}$, and proceeding through wells up to 8,000 cm$^{-1}$ deep [7, 34]. Such energy differences may lead to statistical behavior. In our calculations, all energy levels ($E_{\alpha}$, $E_{\beta}$) are computed with the Hamiltonian and parameters in Refs. 35, 36. Capture probabilities in the entrance channels are evaluated with a WKB tunneling model for reactions in magnetic fields, and the adiabatic variant of the quantum threshold model (QTM) [10] for those in electric fields. For simplicity, we use a semiclassical model based on phase-space theory (PST) [37–40] to compute capture probabilities from the products, as modified to account for external fields [33]. All dispersion coefficients are taken form ab initio data [41, 42].

We first consider global properties, and remark an important consequence of summing over $\beta$ in Eq. 9 in the common case where there are available many more product than reactant states: $\sum_{\beta} p_{\beta}^{M} / \sum_{\gamma} p_{\gamma}^{M} \to 1$, and global quantities depend exclusively on the capture probabilities for the entrance channels. Such observables thus provide a “one-sided” description of the process and its governing dynamics. Fig. 1 shows experimental and statistical rates for reactions between two ground-state $^{40}$K$^{87}$Rb molecules in magnetic and electric fields. Following our discussion, the statistical predictions are essentially those of the WKB and QTM models [1] [2] [12] chosen to evaluate capture probabilities in the entrance channel(s). The agreement between experimental and statistical predictions is hence a consequence of the known success of these models to account for the quantum effects in reactions of indistinguishable fermions such as $^{40}$K$^{87}$Rb. In these, reaction proceeds via tunneling through dynamical barriers in the entrance channels [1] and may have a strong dependence on $M$ due to long-range anisotropic dipolar interactions induced by external electric fields [2] [10]. Quantitative agreement between theoretical and experimental rates, although a necessary condition, is not conclusive evidence on a reaction’s statistical nature: within capture theory, capture in the entrance channels determine rates in any case with many more product than reactant channels, which is nearly always true in ultracold experiments. In any case, Eq. 4 shows that the key factors that determine product-state distributions are the relative capture probabilities at different $M$.

Given the striking effect of external fields on ultracold reaction rates, it is of great interest to assess what effects can fields have on product-state distributions. Fig. 2 shows statistical translational energy distributions for the products of the ultracold reaction $^{40}$K$^{87}$Rb$_2$ $\to$ $^{40}$K$^{87}$Rb$+$ $^{87}$Rb, at relatively low/high values of an electric field—we focus on the behavior within 30 cm$^{-1}$ of the maximum available energy and neglect nuclear spins.
to keep a manageable number of product states. The smooth curves are obtained by convoluting the calculated distributions (sharp peaks) with an “apparatus” function (i.e., Gaussian convolution), and are included to emphasize their overall behavior. The factors determining the form of field-free statistical distributions have been previously studied 43. In addition, the calculations in Fig. 2 indicate the degree of control over the qualitative form of product distributions that may be attained if fields act directly on the product energy levels. It also highlights the importance of accounting for field effects in the formalism when assessing the statistical nature of a reaction. The fields needed for the strongest effects are high simply because of the small electric dipole of KRb; in principle, it should be possible to tune between the distributions for a rigid rotor and that of pendular states 44 simply by tuning the electric field. Fig. 3 shows statistical translational energy distributions for the prototypical reaction between two ground-state $^{40}$K$^{87}$Rb molecules. In this case, products are nonpolar and the main effect of the field is to reduce the reaction exothermicity 45, while preserving the qualitative form of the distributions. The field effect on the exothermicity is also seen in Fig. 2.

So far, we assumed that interactions in the intermediate complex mix all degrees of freedom (DOFs) considered, leading to a microcanonical distribution of all internal states. There exists, however, the possibility that some DOFs are much less involved and act as “spectators”, being adiabatically conserved during the reaction 46-48. Such behavior would have a distinct signature in product distributions. Our formalism can be readily modified to explore these cases by restricting the sums to product states that fulfill the necessary constraints—also needed to account for the conservation of quantities other than $M$. For instance, Mayle et al. 21 estimated nuclear spin-changing probabilities for typical ultracold reactions and predicted that hyperfine states are very likely to change (be preserved) in processes involving heavier (lighter) species. Fig. 4 shows predicted rotational distributions for the products of the reaction of two ground-state $^{40}$K$^{87}$Rb molecules in an electric field, where the qualitative differences between different schemes is clearly demonstrated. The oscillating pattern predicted when hyperfine DOFs are “active” during the reaction arise because the products are homonuclear $^2S_1$-state molecules and exchange symmetry only allows even/odd values of the total nuclear spin for even/odd rotational states.

In practice, product detection in ultracold collision experiments is particularly challenging. Neutral products do not, in general, remain trapped which makes in-trap measurements impractical. In addition, out-of-trap detection is difficult because the reactions have relatively low yields due to the limited number of reactants, and the complexity of experimental setups makes it troublesome to access the interaction region. On the other hand, ionic products are more easily detected in ion-neutral or Penning-ionization reactions, as these do not suffer from some of these problems.

Nevertheless, a thorough understanding of the physics driving ultracold chemical reactions is ultimately conditioned by the technical advances that make the measurement of product-state distributions possible. For instance, information on the intermediate dynamics in collisions between reactive species (KRb, LiCs, etc.) may be useful in understanding/predicting the dynamics of similar intermediates in inelastic collisions between non-reactive species (RbCs, NaRb, etc.). In addition, experiments may explore reactions in mixed samples of homonuclear dimers such as Rb$_2$+Cs$_2$ → 2RbCs in an attempt to better understand the inverse (non-reactive) processes. All these considerations add to the immediate relevance of alkali-metal dimers that are considered at present as less topical mostly because of their reactivity.
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[1] S. Ospelkaus, K.-K. Ni, D. Wang, M. H. G. de Miranda, B. Neyenhuis, G. Quéméner, P. S. Julienne, J. L. Bohn, D. S. Jin, and J. Ye, Science 327, 853 (2010).

[2] K.-K. Ni, S. Ospelkaus, D. Wang, G. Quéméner, B. Neyenhuis, M. H. G. de Miranda, J. L. Bohn, J. Ye, and D. S. Jin, Nature 464, 1324 (2010).

[3] M. H. G. de Miranda, A. Chotia, B. Neyenhuis, D. Wang, G. Quéméner, S. Ospelkaus, J. L. Bohn, J. Ye, and D. S. Jin, Nat. Phys. 7, 502 (2011).

[4] R. V. Krems, Phys. Chem. Chem. Phys. 10, 4079 (2008).

[5] D. J. Nesbitt, Chem. Rev. 112, 5062 (2012).

[6] P. S. Żuchowski and J. M. Hutson, Phys. Rev. A 81, 060703 (2010).

[7] J. N. Byrd, J. A. Montgomer, and R. Côté, Phys. Rev. A 82, 010502 (2010).

[8] M. Tomza, K. W. Madison, R. Moszynski, and R. V. Krems, Phys. Rev. A 88, 050701 (2013).

[9] B. Zhu, B. Gadway, M. Foss-Feig, J. Schachenmayer, M. L. Wall, K. R. A. Hazzard, B. Yan, S. A. Moses, J. P. Covey, D. S. Jin, et al., Phys. Rev. Lett. 112, 070404 (2014).

[10] G. Quéméner and J. L. Bohn, Phys. Rev. A 81, 022702 (2010).

[11] G. Quéméner and J. L. Bohn, Phys. Rev. A 81, 060701(R) (2010).

[12] Z. Idziaszek and P. S. Julienne, Phys. Rev. Lett. 104, 113202 (2010).

[13] Z. Idziaszek, G. Quéméner, J. L. Bohn, and P. S. Julienne, Phys. Rev. A 82, 020703 (2010).

[14] K. Jachymski, M. Krych, P. S. Julienne, and Z. Idziaszek, Phys. Rev. Lett. 110, 213202 (2013).

[15] B. Gao, Phys. Rev. Lett. 105, 263203 (2010).

[16] B. Gao, Phys. Rev. A 83, 062712 (2011).

[17] P. H. J. Hall, M. Aymar, N. Bouloufa-Maafa, O. Dulieu, and S. Willitsch, Phys. Rev. Lett. 107, 243202 (2011).

[18] J. Jankunas, B. Bertsche, K. Jachymski, M. Hapka, and A. Osterwalder, J. Chem. Phys. 140, 244302 (2014).

[19] A. Härter, A. Krülov, M. Deisz, B. Drews, E. Tiemann, and J. H. Denschlag, Nat. Phys. 9, 512 (2013).

[20] T. V. Tschberbul and R. V. Krems, J. Chem. Phys. 129, 034112 (2008).

[21] M. Mayle, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A 85, 062712 (2012).

[22] M. Mayle, G. Quéméner, B. P. Ruzic, and J. L. Bohn, Phys. Rev. A 87, 012709 (2013).

[23] A. Frisch, M. Mark, K. Aikawa, F. Ferlaino, J. L. Bohn, C. Makrides, A. Petrov, and S. Kotochigova, Nature 507, 475 (2014).

[24] W. Hauser and H. Feshbach, Phys. Rev. 87, 366 (1952).

[25] W. H. Miller, J. Chem. Phys. 52, 543 (1970).

[26] R. V. Krems, B. Friedrich, and W. C. Stwalley, eds., Cold Molecules: Theory, Experiment, Applications (Taylor & Francis, London, 2009), ISBN 978-1-4200-5903-8.

[27] R. D. Levine, Molecular Reaction Dynamics (Cambridge University Press, Cambridge, 2005).

[28] A. A. Buchchenko, Moscow Univ. Chem. Bull. 67, 159 (2012).

[29] A. A. Buchchenko, A. V. Stolyarov, M. M. Szczęśniak, and G. Chalasinski, J. Chem. Phys. 137, 114305 (2012).

[30] E. J. Rackham, F. Huarte-Larranaga, and D. E. Manolopoulos, Chem. Phys. Lett. 343, 356 (2001).

[31] T. González-Lezana, Int. Rev. Phys. Chem. 26, 29 (2007).

[32] H. Guo, Int. Rev. Phys. Chem. 31, 1 (2012).

[33] M. L. González-Martínez, L. Bonnet, and P. Larrégayar (2014), in preparation.

[34] E. R. Meyer and J. L. Bohn, Phys. Rev. A 82, 042707 (2010).

[35] J. Aldegunde, B. A. Rivington, P. S. Żuchowski, and J. M. Hutson, Phys. Rev. A 78, 033434 (2008).

[36] J. Aldegunde and J. M. Hutson, Phys. Rev. A 79, 013401 (2009).

[37] J. C. Light, J. Chem. Phys. 40, 3221 (1964).

[38] P. Pechukas and J. C. Light, J. Chem. Phys. 42, 3281 (1965).

[39] E. E. Nikitin, Teor. Eksp. Khim. Akad. Nauk. Ukr. SSR 1, 135 (1965).

[40] C. Klotz, J. Phys. Chem. 75, 1526 (1971).

[41] P. S. Żuchowski, M. Kosicki, M. Kodrycka, and P. Soldán, Phys. Rev. A 87, 022706 (2013).

[42] M. Kosicki and P. S. Żuchowski (2014), private communication.

[43] L. Bonnet and J.-C. Rayez, Phys. Chem. Chem. Phys. 1, 2383 (1999).

[44] K. Von Meyenn, Z. Physik 231, 154 (1970), in German.

[45] The exothermicity $\Delta E \approx \min (\alpha E_\alpha - \beta E_\beta)$—will in general depend on $F$, which may in principle be used to completely suppress the reaction [34].

[46] M. Quack and J. Troe, Ber. Bunsenges Phys. Chem. 78, 240 (1974).

[47] R. A. Marcus, J. Chem. Phys. 62, 1372 (1975).

[48] G. Worry and R. A. Marcus, J. Chem. Phys. 67, 1636 (1977).