Universal Model for Exoergic Bimolecular Reactions and Inelastic Processes

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From a rigorous multichannel quantum-defect formulation of bimolecular processes, we derive a fully quantal and analytic model for the total rate of exoergic bimolecular reactions or inelastic processes that is applicable over a wide range of temperatures including the ultracold regime. The theory establishes a connection between the ultracold chemistry and the regular chemistry by showing that the same theory that gives the quantum threshold behavior agrees with the classical Gorin model at higher temperatures. In between, it predicts that the rates for identical bosonic molecules and distinguishable molecules would first decrease with temperature outside of the Wigner threshold region, before rising after a minimum is reached.

The recent experiment by the JILA group [1] represents a milestone in studies of chemical reactions. For the first time, reactions are studied in a temperature regime where the quantum nature of the relative motion of the reactants becomes unequivocally important, as reflected in the quantum threshold behavior and in the importance of quantum statistics. More importantly, the experiment strongly suggests that bimolecular reactions in the ultracold regime follow universal behaviors determined by the long-range interaction, as spelled out in more detail in related theoretical works by Julienne and Idziaszek [2,3] and by Quéméner and Bohn [4].

The significance of such experiments goes beyond exploring chemical reactions in a new temperature regime with many unique characteristics, such as controllability via moderate external fields [4–6]. By forcing a new perspective on the quantum theory of reactions, as demanded by their interpretation, they have the potential to improve our understanding of reactions and inelastic processes at all temperatures. This Letter is an illustration of such an outcome. From a rigorous multichannel quantum-defect formulation of bimolecular processes, we derive here a fully quantal model for the total rate of exoergic bimolecular reactions or inelastic processes that is applicable over a wide range of temperatures. The theory establishes a connection between the ultracold chemistry and the regular chemistry by showing that the same theory that gives the quantum threshold behavior [1–3] agrees with the classical Gorin model [7,8] at higher temperatures. In between, it shows that the rates for identical bosonic molecules and distinguishable molecules would first decrease with temperature outside of the Wigner threshold region, before rising after a minimum is reached. The theory further illustrates explicitly how the quantum effects, including effects of quantum statistics, gradually diminish at higher temperatures, and establishes the van der Waals temperature scale as the one that separates the quantum and the semiclassical behaviors of reactions. The same formalism

is applicable to ion-molecule reactions where our quantum model, with details to be presented in a separated publication, would approach the classical Langevin model [8,9] at high temperatures.

Consider the collision of two distinguishable molecules A and B in the absence of any external fields. The cross section for a transition from an entrance channel i to an exit channel f can be written in terms of the S matrix as [10]

$$\sigma_{fi}(\epsilon) = \frac{\pi}{(2F_{Ai} + 1)(2F_{Bi} + 1)k_i^2} \times \sum_{F_t, F_i, l_i, \{q_f\}} (2F_t + 1)|S_{fi}^{(F_t)} - \delta_{fi}|^2. \quad (1)$$

Here $\epsilon \equiv E - E_i = \hbar^2 k_i^2/2\mu$ is the energy relative to the entrance channel i, with μ being the reduced mass. F_A and F_B are the total (internal) angular momenta of molecules A and B, respectively. $\mathbf{F} = \mathbf{F}_A + \mathbf{F}_B$ is the total angular momentum excluding l, which is the relative angular momentum between A and B. F_t is the total angular momentum of the system, which is conserved in the absence of external fields. $\{q_f\}$ represents the quantum numbers, excluding F_t, that are required to characterize an exit channel f.

The exit channels can be classified into elastic channels, labeled by $\{e\}$, inelastic channels, labeled by $\{u\}$, and reactive channels, labels by $\{r\}$. From the unitarity of the S matrix [10], the total cross section, $\sigma_{ur} \equiv \sum_{f\in\{u,r\}}\sigma_{fi}$, for the combination of all inelastic and reactive processes, can be written as

$$\sigma_{ur}(\epsilon) = \frac{\pi}{(2F_{Ai} + 1)(2F_{Bi} + 1)k_i^2} \sum_{F_t, F_i, l_i} (2F_t + 1) \times \left[1 - \sum_{F_e, l_e}|S_{ei}^{(F_t)}|^2\right]. \quad (2)$$

The implication is that such a total cross section is completely determined by the S matrix elements for elastic

channels only. The corresponding rate constant at temperature T is given in terms of σ_{ur} by

$$K(T) = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\frac{1}{(k_BT)^2}\int_0^\infty \epsilon\sigma_{ur}(\epsilon)\exp(-\epsilon/k_BT)d\epsilon, \quad (3)$$

where k_B is the Boltzmann constant.

Considerably further understanding of bimolecular processes can be achieved through a multichannel quantum-defect theory (MQDT) (see Ref. [11] and references therein), especially through an S matrix formulation in terms of quantum reflection and transmission amplitudes associated with the long-range potential [12]. The theory, which is a multichannel generalization of the S matrix formulation of Ref. [12], gives

$$S^{(F_t)} = -(-1)^l\{r_{oo}^{(oi)} + t_{oo}^{(io)}S_{\text{eff}}^c[I - r_{oo}^{(io)}S_{\text{eff}}^c]^{-1}t_{oo}^{(oi)}\}, \quad (4)$$

$$= -(-1)^l\left\{r_{oo}^{(oi)} + t_{oo}^{(io)}S_{\text{eff}}^c\left[\sum_{m=0}^\infty(r_{oo}^{\{io\}}S_{\text{eff}}^c)^m\right]t_{oo}^{(oi)}\right\}. \quad (5)$$

Here $(-1)^l$ is a diagonal matrix with elements $(-1)^{l_j}$ for channel j. The $r_{oo}^{(oi)}$ and $t_{oo}^{(oi)}$ are diagonal matrices for the open channels with elements $r_{l_j}^{(oi)}(\epsilon_{sj})$ and $t_{l_j}^{(oi)}(\epsilon_{sj})$ representing the (complex) quantum reflection and the quantum transmission amplitudes, respectively, for molecules going outside-in (approaching each other) [12]. They are universal functions of scaled energies, $\epsilon_{sj} \equiv (E - E_j)/s_{Ej}$, that are uniquely determined by the exponent, α_j, of the long-range interaction, $-C_{\alpha j}/R_j^{\alpha_j}$, in channel j, and the l_j. Such long-range interactions have length scales $\beta_{\alpha j} = (2\mu_j C_{\alpha j}/\hbar^2)^{1/(\alpha_j-2)}$ and corresponding energy scales $s_{Ej} = (\hbar^2/2\mu_j)(1/\beta_{\alpha j}^2)$, associated with them. The $r_{oo}^{(io)}$ and $t_{oo}^{(io)}$ are similar, except that their elements are amplitudes for molecules going inside-out (moving away from each other) [12]. The S_{eff}^c is an effective short-range S matrix [12], after the elimination of the closed channels [11]. It has the physical meaning of being an effective reflection amplitudes by the inner potential. We note that all quantities are defined in standard Jacobi coordinates, which implies that in cases of reactions, μ_j, the reduced mass in channel j, and R_j, the separation between the fragments in channel j, are different for different arrangements of atoms.

Equation (4) for the S matrix has a clear physical interpretation as discussed in Ref. [12]. In particular, the mth term in its expansion, Eq. (5), corresponds to the contribution from a path in which the fragments are reflected $m + 1$ times by the inner potential. Further simplification can be achieved by recognizing that $r_{l_j}^{(io)}(\epsilon_{sj}) \approx 0$ for $\epsilon_{sj} \gg s_{Ej}$ [12]. Dividing all open channels into elastic and near-degenerate channels with $\epsilon_{sj} < {\sim}s_{Ej}$, and other channels with $\epsilon_{sj} \gg s_{Ej}$, we have

$$S_{ei}^{(F_t)} \approx -(-1)^{l_e}\{r_{l_i}^{(oi)}\delta_{ei} + t_{l_e}^{(io)}[\tilde{S}_{\text{eff}}^c(1 - r^{\{io\}}\tilde{S}_{\text{eff}}^c)^{-1}]_{ei}t_{l_i}^{(oi)}\}, \quad (6)$$

where $\tilde{S}_{\text{eff}}^c$ is a submatrix of the effective short-range S_{eff}^c that includes only the elastic and other near-degenerate channels for which the quantum reflection amplitude $r_l^{(io)}$ differs substantially from zero.

A number of different theories and models, both exact and approximate, can be derived from Eq. (2), and either Eq. (4) or (6). The universal model to be presented here, which we call the quantum Langevin (QL) model, results from the assumption of no reflection by the inner potential, namely,

$$\tilde{S}_{\text{eff}}^c \approx 0. \quad (7)$$

It is a rigorous mathematical representation of the Langevin assumption [8,9] in a quantum theory. In plain language, it assumes that whenever two molecules come sufficiently close to each other, so many "bad" things can happen that they can never get out of it in their initial configurations. It can be expected to be a good approximation whenever there are a large number of open exit channels that are strongly coupled to the entrance channel in the inner region. For it to be satisfied in the limit of zero energy, the reactions and inelastic processes under consideration have to be at least exoergic.

Under the Langevin assumption, Eq. (6) gives

$$S_{ei}^{(F_t)} \approx -(-1)^{l_i}r_{l_i}^{(oi)}\delta_{ei}. \quad (8)$$

It implies that the elastic S matrix elements in the QL model, and therefore the total cross section and the corresponding total rate for inelastic and reactive processes, are all described by universal functions that are uniquely determined by the long-range interaction in the entrance channel. Substituting Eq. (8) into Eq. (2) and subsequently into Eq. (3), the total rate of inelastic and reactive processes in the QL model can be written as

$$K(T) = s_K\mathcal{K}^{(\alpha)}(T_s). \quad (9)$$

Here s_K is the rate scale corresponding to the long-range, $-C_\alpha/R^\alpha$, interaction in the entrance channel.

$$s_K = (\hbar/\mu\beta_\alpha)\pi\beta_\alpha^2 = \pi\hbar\beta_\alpha/\mu, \quad (10)$$

in which $\hbar/\mu\beta_\alpha$ is the velocity scale corresponding to the length scale β_α. $\mathcal{K}^{(\alpha)}(T_s)$ is a universal function of the scaled temperature, $T_s = T/(s_E/k_B)$, that is uniquely determined by the exponent α. Specifically,

$$\mathcal{K}^{(\alpha)}(T_s) = \frac{2}{\sqrt{\pi}}\int_0^\infty dx\, x^{1/2}e^{-x}\mathcal{W}^{(\alpha)}(T_s x), \quad (11)$$

where $\mathcal{W}^{(\alpha)}(\epsilon_s)$ is a scaled total rate before thermal averaging. It depends on energy only through the scaled energy $\epsilon_s = \epsilon/s_E$, and has contributions from all partial waves

$$\mathcal{W}^{(\alpha)}(\epsilon_s) = \sum_l \mathcal{W}_l^{(\alpha)}(\epsilon_s). \qquad (12)$$

Here $\mathcal{W}_l^{(\alpha)}$ is a scaled partial rate given by

$$\mathcal{W}_l^{(\alpha)}(\epsilon_s) = (2l+1)\mathcal{T}_l^{c(\alpha)}(\epsilon_s)/\epsilon_s^{1/2}, \qquad (13)$$

in which $\mathcal{T}_l^{c(\alpha)}(\epsilon_s) = |t_l^{(oi)}(\epsilon_s)|^2$ is the quantum transmission probability through the long-range potential at the scaled energy ϵ_s and for partial wave l [12].

This QL model for reactions and inelastic processes is applicable to both neutral-neutral systems, for which $\alpha = 6$ corresponding to the van der Waals potential, and charge-neutral systems, for which $\alpha = 4$ corresponding to the polarization potential. We focus here on the neutral-neutral case to make a connection with existing theories and experiments [1–4]. The results for charge-neutral systems will be presented elsewhere.

For $\alpha = 6$, the quantum transmission probability through the long-range potential, $\mathcal{T}_l^{c(\alpha)}(\epsilon_s)$, which is the only quantity required to determine the universal rate functions in the QL model, can be found analytically by substituting Eqs. (A1)–(A4) of Ref. [12] into the Eq. (52) of the same reference. The result is

$$\mathcal{T}_l^{c(6)}(\epsilon_s) = \frac{2M_{\epsilon_s l}[\cos(\pi\nu) - \cos(3\pi\nu)]}{1 - 2M_{\epsilon_s l}\cos(3\pi\nu) + M_{\epsilon_s l}^2}, \qquad (14)$$

where ν is the characteristic exponent and $M_{\epsilon_s l}$ is one of the universal QDT functions for $-1/R^6$ potential [13]. The resulting universal rate function, $\mathcal{K}^{(\alpha)}(T_s)$, applicable to neutral-neutral distinguishable molecules, is illustrated in Fig. 1. Similar results can be obtained for neutral-neutral interactions of identical molecules, following considerations similar to those of Ref. [14]. They are given generally by a combination of two universal rate functions defined by
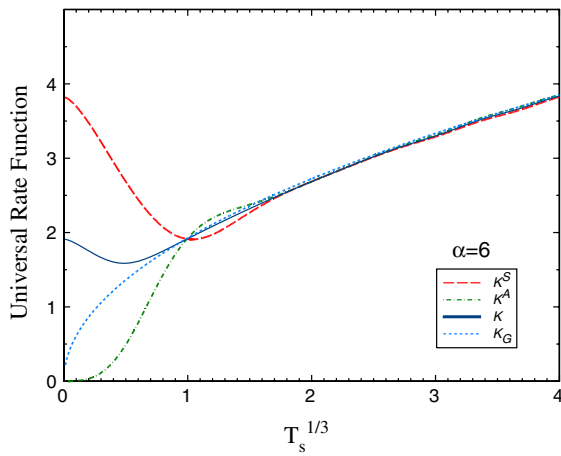

FIG. 1 (color online). The universal rate functions $\mathcal{K}^{S(\alpha)}(T_s)$, $\mathcal{K}^{A(\alpha)}(T_s)$, and $\mathcal{K}^{(\alpha)}(T_s)$ for $\alpha = 6$, corresponding to $-1/R^6$ type of interaction in the entrance channel. Here $\mathcal{K}_G$ refers to the prediction of the classical Gorin model, as given by Eq. (22). All results include summations over all relevant partial waves.

$$\mathcal{K}^{S(\alpha)}(T_s) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx\, x^{1/2} e^{-x} \mathcal{W}^{S(\alpha)}(T_s x), \qquad (15)$$

where

$$\mathcal{W}^{S(\alpha)}(\epsilon_s) = 2\sum_{l=\text{even}} \mathcal{W}_l^{(\alpha)}(\epsilon_s), \qquad (16)$$

and

$$\mathcal{K}^{A(\alpha)}(T_s) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx\, x^{1/2} e^{-x} \mathcal{W}^{A(\alpha)}(T_s x), \qquad (17)$$

where

$$\mathcal{W}^{A(\alpha)}(\epsilon_s) = 2\sum_{l=\text{odd}} \mathcal{W}_l^{(\alpha)}(\epsilon_s). \qquad (18)$$

For example, in terms of $\mathcal{K}^{S(\alpha)}$ and $\mathcal{K}^{A(\alpha)}$, $K^S(T) = s_K \mathcal{K}^{S(\alpha)}$ gives the rate for identical bosonic molecules in the same internal (M) state, and $K^A(T) = s_K \mathcal{K}^{A(\alpha)}$ gives the rate for identical fermionic molecules in the same internal state. The three rate functions are related by $\mathcal{K}^{(\alpha)} = [\mathcal{K}^{S(\alpha)} + \mathcal{K}^{A(\alpha)}]/2$, and are all illustrated in Fig. 1 for $\alpha = 6$.

At ultracold temperatures such that $T_s \ll 1$, a QDT expansion [15] of $\mathcal{T}_l^{c(6)}(\epsilon_s)$ gives

$$\mathcal{K}^{S(6)}(T_s) = 8\bar{a}_{sl=0}\Big[1 - \frac{4\bar{a}_{sl=0}}{\sqrt{\pi}} T_s^{1/2} + 3\bar{a}_{sl=0}^2 T_s + O(T_s^{3/2}) \Big], \qquad (19)$$

where $\bar{a}_{sl=0} = 2\pi/[\Gamma(1/4)]^2 \approx 0.4779888$ is the scaled mean scattering length for $l = 0$ [15],

$$\mathcal{K}^{A(6)}(T_s) = 36\bar{a}_{sl=1}T_s\Big[1 - \frac{16\bar{a}_{sl=1}}{\sqrt{\pi}} T_s^{3/2} + O(T_s^2) \Big], \qquad (20)$$

where $\bar{a}_{sl=1} = [\Gamma(1/4)]^2/36\pi \approx 0.1162277$ is the scaled mean scattering length for $l = 1$ [15], and

$$\mathcal{K}^{(6)}(T_s) = 4\bar{a}_{sl=0} - \frac{(4\bar{a}_{sl=0})^2}{\sqrt{\pi}} T_s^{1/2} + (12\bar{a}_{sl=0}^3 + 18\bar{a}_{sl=1})T_s + O(T_s^{3/2}). \qquad (21)$$

At high temperatures as characterized by $T_s \gg 1$, it is straightforward to show, from the semiclassical limit of the transmission probabilities [12], that

$$\mathcal{K}^{S(6)}(T_s) \approx \mathcal{K}^{A(6)}(T_s) \approx \mathcal{K}^{(6)}(T_s) \sim \frac{2^{4/3}\Gamma(2/3)}{\sqrt{\pi}} T_s^{1/6}, \qquad (22)$$

in agreement with the classical Gorin model [7,8]. All scaled results can be put on absolute scales using a single parameter, the C_6 coefficient for the entrance channel, from which both the temperature scale s_E/k_B and the rate scale s_K can be determined [16].

In the Wigner threshold region, in which the rates are accurately characterized by the first terms of Eqs. (19)–(21), our results are consistent with those of Julienne and Idziaszek [2,3]. Outside of this region, both $\mathcal{K}^{(6)}$ and $\mathcal{K}^{S(6)}$ are predicted to first decrease with temperature, a behavior that deviates strongly from the prediction of the classical Gorin model. Specifically, $\mathcal{K}^{(6)}$ is predicted to reach a minimum value of $\mathcal{K}^{(6)}_{\min} \approx 1.587$ at $T^{(6)}_{s\min} \approx 0.1154$, for a drop of about 17% from its value at zero temperature. The $\mathcal{K}^{S(6)}$ is predicted to reach a minimum value of $\mathcal{K}^{S(6)}_{\min} \approx 1.908$ at $T^{S(6)}_{s\min} \approx 1.114$, for a drop of about 50% from its value at zero temperature. For the JILA experiment [1], $T^{(6)}_{s\min}$ translates, using the C_6 coefficients of Kotochigova [16,17], to $T^{(6)}_{\min} \approx 2.58\ \mu K$ for $^{40}K^{87}Rb + {}^{40}K^{87}Rb$ in different internal states, and to $T^{(6)}_{\min} \approx 11.9\ \mu K$ for $^{40}K + {}^{40}K^{87}Rb$. It is worth noting that an experimental measurement of either $T^{(6)}_{\min}$ or $T^{S(6)}_{\min}$ would constitute a measurement of the C_6 coefficient, a fact that can be valuable especially for more complex molecules for which theoretical calculations of C_6 [17,18] become increasingly difficult and unreliable. At higher temperatures, our results show how the quantum effects, including that of quantum statistics, gradually diminish, and all rates approach that of the classical Gorin model [7,8]. As illustrated in Fig. 1, such a transition from quantum to semiclassical behavior occurs over a range of the van der Waals temperature scale s_E/k_B.

The QL model gives the total rate that includes both reactive and inelastic processes. For experiments with only reactive channels open [1], it give the total rate of reactions. For experiments with no open reactive channels, it gives the total rate of inelastic processes. In all cases, the requirement for its validity is that there are many open channels that are strongly coupled to the entrance channel by the short-range interactions, a condition that is expected to be well satisfied by most barrierless (in the inner region) reactions. Of interest in the context of cold-atom physics, the QL model serves to unify theories of ultracold chemistry [2–4,17] with theories for atom-atom [19], atom-molecule [20], and molecule-molecule inelastic processes. For example, for a vibrational highly excited molecule, except Feshbach molecules with very small binding energies [21], the theory predicts that its collisional lifetime is approximately independent of its initial state, and that the rates for atom-molecule and molecule-molecule inelastic processes are related. More specifically, for Cs_2 in a highly excited rovibrational state [22], it predicts that the $Cs_2 - Cs_2$ inelastic rate should have a minimum around $6.31\ \mu K$ (assuming that they are prepared in the same state), and $Cs_2 - Cs$ inelastic rate has a minimum around

$1.70\ \mu K$. More detailed discussion of such applications will be presented elsewhere.

In conclusion, we have presented a universal model of exoergic bimolecular reactions or inelastic processes that is applicable over a wide range of temperatures, illustrating the evolution from quantum behavior to semiclassical behavior. It is an important baseline model in which rates for different systems differ from each other only in scaling, and has an intriguing and useful property of being more accurate for more complex systems. Simple analytic formulas, to higher orders than those of Julienne and Idziaszek [2,3], and applicable over a substantially wider range of temperatures, are also presented. Equally important, we believe, is that the underlying MQDT formulation, such as Eq. (6), lays a solid foundation for new types of theories of reactions and inelastic processes, either rigorous or approximate, that goes further beyond the QL model.

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