Quantum Langevin model for exoergic ion-molecule reactions and inelastic processes

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We presents a fully quantal version of the Langevin model for the total rate of exoergic ion-molecule reactions or inelastic processes. The model, which is derived from a rigorous multichannel quantum-defect formulation of bimolecular processes, agrees with the classical Langevin model at sufficiently high temperatures. It also gives the first analytic description of ion-molecule reactions and inelastic processes in the ultracold regime where the quantum nature of the relative motion between the reactants becomes important.

The classical Langevin model for exoergic ion-molecule reactions [1, 2] is one of the most fundamental and powerful results in the theory of reactions. It has been shown to be applicable to a variety of systems and over a wide range of temperatures [2, 3]. As a model based on the long-range interaction, it can be expected to be more accurate the lower the temperature [4], until one reaches a regime where quantum effects, more specifically the quantum effects associated with the relative motion of the reactants, become important.

An experimental study of reactions in this temperature regime, often referred as the ultracold regime, has recently been realized for neutral-neutral reactions in a landmark experiment by the JILA group [5]. While it is not yet realized for charge-neutral systems, the growing ability of making cold molecular samples [6] and manipulating cold ions [7], implies that it may soon become a reality. A sample process, likely among the first investigated, would include the type

$$A^+ + B_2 \rightarrow AB + B^+ \; , \qquad (1a)$$
$$\rightarrow A + B_2^+ \; , \qquad (1b)$$
$$\rightarrow (AB)^+ + B \; , \qquad (1c)$$
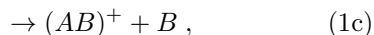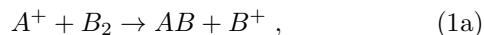
where all reactions can be expected to be exoergic if the ionization potential of atom A is considerably greater than that of atom B. They can proceed with substantial rates even in the limit of zero temperature as ion-molecule interactions are generally expected to be barrierless at the short range [8].

The theory presented here, to be called the quantum Langevin (QL) model for the total rate of exoergic ion-molecule reactions or inelastic processes, gives the first theoretical prediction on where and how the quantum effects come into play and how the resulting behavior deviates from the classical Langevin model. It is another application of a new quantum framework for reactions [9] that differs considerably from existing formulations [10], and is used here to further illustrate the concepts behind the theory.

In a conventional quantum theory of reactions [10], little can be known about a reaction without a detailed

knowledge of the potential energy surface (PES), the accuracy of which is often insufficient for quantitative predications, especially at low temperatures. This has been true even for ultracold atom-atom and ion-atom interactions, where, to the best of our knowledge, no *ab initio* PES for alkali metal systems has ever been sufficiently accurate to predict the scattering length. All potentials had to be modified by incorporating a substantial amount of spectroscopic data (see, e.g., Ref. [11]). The same issue becomes *much* more severe for multidimensional PES in reactions, and will remain so for many years to come. This difficulty, coupled with the exponential growth of the Hilbert space beyond two-body [12], has limited the conventional approach to a few simple systems such as $D+H_2$, with little hope for more complex systems.

The multichannel quantum-defect theory for reactions (MQDTR), as outline in Ref. [9], with important motivations and ingredients that come before it [5, 13–16], offers a different perspective on reactions and inelastic processes. It comes from a much wider assertion that much can be known about a quantum system, specifically its behavior around a fragmentation threshold, simply from the *types* of long-range interactions among its constituents. Whatever not yet known can be characterized by a few energy-insensitive parameters, which can be further determined from a few experimental measurements without any knowledge of the short-range interaction, or even the strength of the long-range interaction. This physical picture, which goes back to the original quantum-defect theory for the Coulomb interaction [17], has been well established in recent years for atom-atom [18, 19] and ion-atom interactions [20], and to a lesser degree for few-atom [21] and many-atom systems [22]. Its realization for reactions [9], as is further illustrated in this work, frees the theory from being held hostage by the details of PES, while ready to take advantage of them when they are available. It also resolves a conceptual disparity in existing theories of reactions. While many classical models [2, 4] are based on the recognition of the importance of the long-range interaction, the same physical concept gets lost in the conventional quantum formulations [10]. It is primarily due to this omission that they have missed the universality and the simplicity in reactions that have been uncovered in the landmark

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JILA experiment [5].

The QL model for ion-molecule reactions or inelastic processes, to be presented here, is a special case of a more general QL model [9] that is formally applicable to bimolecular processes with arbitrary $-C_n/R^n$ ($n > 2$) type of long-range interaction in the entrance channel. Other than the exponent n, the most important characteristic of such a potential is its length scale $\beta_n = (2\mu C_n/\hbar^2)^{1/(n-2)}$, where μ is the reduced mass in the entrance channel. It determines the scale parameters for other relevant physical observables, such as the energy, with a scale of $s_E = (\hbar^2/2\mu)(1/\beta_n)^2$, the temperature, with a scale of s_E/k_B, and the rate of reactions, with a scale of $s_K = \pi\hbar\beta_n/\mu$ [9]. For ion-molecule interactions, $n = 4$ and $C_4 = \alpha q^2/2$, corresponding to the polarization potential, with α being the average polarizability of the molecule and q the charge of the ion. The realization of the QL model for this class of systems is made possible by a recent reformulation of the quantum-defect theory (QDT) for $-1/R^4$ potential [20], which gives, in particular, analytic results for the quantum transmission probability to be used in this work.

In Ref. [9], we have shown that under the Langevin assumption, corresponding to the assumption of no reflection by the inner potential, the total rate of reactions and inelastic processes follows a universal behavior uniquely determined by the exponent n characterizing the type of long-range interaction in the entrance channel. Different systems with the same type of potentials differ from each other only in scaling. Specifically, the rate constant for the total rate of reactions and inelastic processes can be written as

$$K(T) = s_K \mathcal{K}^{(n)}(T_s) , \qquad (2)$$

where s_K is the rate scale defined earlier, and $\mathcal{K}^{(n)}(T_s)$ is a universal function of the scaled temperature, $T_s = T/(s_E/k_B)$, given by

$$\mathcal{K}^{(n)}(T_s) = \frac{2}{\sqrt{\pi}} \int_0^\infty dx \, x^{1/2} e^{-x} \mathcal{W}^{(n)}(T_s x) . \qquad (3)$$

Here $\mathcal{W}^{(n)}(\epsilon_s)$ 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

$$\mathcal{W}^{(n)}(\epsilon_s) = \sum_{l=0}^\infty \mathcal{W}_l^{(n)}(\epsilon_s) , \qquad (4)$$

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

$$\mathcal{W}_l^{(n)}(\epsilon_s) = (2l+1)\mathcal{T}_l^{c(n)}(\epsilon_s)/\epsilon_s^{1/2} , \qquad (5)$$

in which $\mathcal{T}_l^{c(n)}(\epsilon_s) = |t_l^{(oi)}(\epsilon_s)|^2$ is the quantum transmission probability through the long-range potential at the scaled energy ϵ_s and for partial wave l [19].

For $n = 4$, corresponding to the ion-molecule interaction, the quantum transmission probability, $\mathcal{T}_l^{c(4)}(\epsilon_s)$,
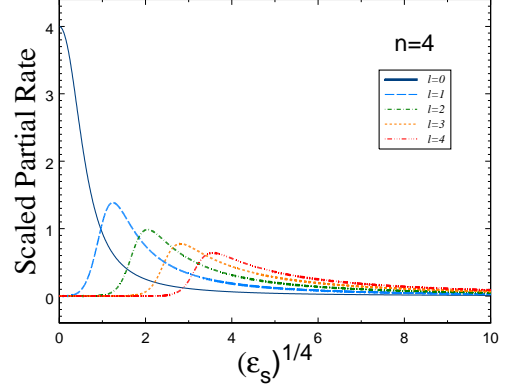

FIG. 1. (color online) The scaled partial rates $\mathcal{W}_l^{(n)}(\epsilon_s)$ for $n = 4$, corresponding to $-1/R^4$ type of interaction in the entrance channel.
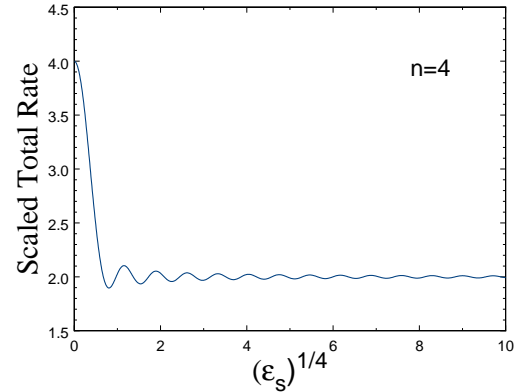

FIG. 2. (color online) The scaled total rate $\mathcal{W}^{(n)}(\epsilon_s)$ for $n = 4$, corresponding to $-1/R^4$ type of interaction in the entrance channel.

which is the only quantity required to determine the universal rate function in the QL model, can be found analytically as a part of the QDT for $-1/R^4$ potential [19, 20]. The result is

$$\mathcal{T}_l^{c(4)}(\epsilon_s) = \frac{2M_{\epsilon_s l}^2[1 - \cos(2\pi\nu)]}{1 - 2M_{\epsilon_s l}^2 \cos(2\pi\nu) + M_{\epsilon_s l}^4} , \qquad (6)$$

where ν is the characteristic exponent and $M_{\epsilon_s l}$ is one of the universal QDT functions for the $-1/R^4$ potential, both of which are as given in Ref. [20].

Figure 1 illustrates the resulting scaled partial rates $\mathcal{W}_l^{(n)}$ for $n = 4$. Figure 2 shows the corresponding total rate $\mathcal{W}^{(n)}$. We note that the oscillatory structure in the total rate is neither a resonance nor an interference phenomenon. It is instead a result of the quantization of angular momentum, with contributions from a discrete set of partial waves peaking at different energies, as illus-
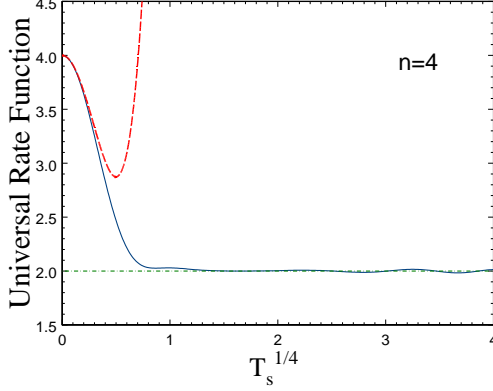
FIG. 3. (color online) The universal rate function $\mathcal{K}^{(n)}(T_s)$ for $-1/R^4$ type of interaction in the entrance channel (solid line). The dash-dot line represents the prediction of the classical Langevin model, as given by Eq. (12). The dashed line represents the QDT expansion as given by Eq. (11).

trated in Fig. 1. The $\mathcal{W}^{(n)}$ is related to the total reactive and inelastic cross section, σ_{ur}, by $\sigma_{\mathrm{ur}} = (\pi\beta_n^2)\Sigma_{\mathrm{ur}}^{(n)}(\epsilon_s)$, in which $\Sigma_{\mathrm{ur}}^{(n)}(\epsilon_s) = \mathcal{W}^{(n)}/\epsilon_s^{1/2}$ is the scaled total inelastic and reactive cross section. We note that the oscillatory structure in $\mathcal{W}^{(n)}$ is much less visible in the cross section, making it difficult to detect experimentally.

Figure 3 illustrates the universal rate function $\mathcal{K}^{(n)}(T_s)$ for $n = 4$, which is the thermal average of the total rate shown in Fig. 2. In the ultracold regime of $T_s \ll 1$, simpler analytic formulas for rates and cross sections can be derived using the QDT expansion [23] of the transmission probability. For small scaled energies ϵ_s, it can be shown from the QDT for $n = 4$ [20] that

$$\mathcal{T}_{l=0}^{c(4)} = \frac{4\bar{a}_{sl=0}^{(4)}\epsilon_s^{1/2}}{(1 + \bar{a}_{sl=0}^{(4)}\epsilon_s^{1/2})^2} + O(\epsilon_s^{5/2}) , \qquad (7)$$

$$\mathcal{T}_{l=1}^{c(4)} = \frac{4\bar{a}_{sl=1}^{(4)}\epsilon_s^{3/2}}{(1 + \bar{a}_{sl=1}^{(4)}\epsilon_s^{3/2})^2} + O(\epsilon_s^{7/2}) , \qquad (8)$$

and

$$\mathcal{T}_{l\geq 2}^{c(4)} = 4\bar{a}_{sl}^{(4)}\epsilon_s^{l+1/2} + O(\epsilon_s^{l+5/2}) , \qquad (9)$$

where

$$\bar{a}_{sl}^{(4)} = \frac{(2l+1)^2}{[(2l+1)!!]^4} , \qquad (10)$$

is called the scaled mean scattering lengths for a $-1/R^4$ potential, after similar quantities for $-1/R^6$ potential [23]. We note that such analytic expansions could not have been derived from either the WKB theory [24], or the top-of-barrier analysis [25], as to be discussed in more details elsewhere [26]. Substituting Eqs. (7)-(9) into

TABLE I. Sample scale parameters for ion-molecule reactions and inelastic processes. The $\beta_4 = (2\mu C_4/\hbar^2)^{1/2}$ is the length scale associated with the polarization potential $-C_4/R^4$, where $C_4 = \alpha q^2/2$ with α being the average polarizability of the molecule. $s_E/k_B = (\hbar^2/2\mu)(1/\beta_4)^2/k_B$ is the corresponding temperature scale. $s_K = \pi\hbar\beta_4/\mu$ is the rate scale corresponding to β_4. It is given here in units of 10^{-9} cm^{3}s^{-1}.

System	α (a.u.)	β_4 (a.u.)	s_E/k_B (K)	s_K
D$^+$-^{1}H$_2$	5.41[a]	99.7	8.65×10^{-3}	1.05
^{1}H$^+$-^{7}Li$_2$	216[b]	608	2.49×10^{-4}	6.83
^{7}Li$^+$-^{87}Rb$_2$	553[b]	2610	1.90×10^{-6}	4.08
^{138}Ba$^+$-^{87}Rb$_2$	553[b]	8800	1.45×10^{-8}	1.21
^{40}Ca$^+$-^{133}Cs$_2$	675[b]	6540	5.83×10^{-8}	1.99
^{40}Ca$^+$-^{40}K^{87}Rb	526[b]	5400	9.78×10^{-8}	1.88

[a] From Ref. [27].
[b] From Ref. [28].

Eqs. (3)-(5) gives the expansion of $\mathcal{K}^{(4)}(T_s)$ in the ultracold regime of $T_s \ll 1$,

$$\mathcal{K}^{(4)}(T_s) = 4\bar{a}_{sl=0}^{(4)} - \frac{16(\bar{a}_{sl=0}^{(4)})^2}{\sqrt{\pi}}T_s^{1/2}$$
$$+ 18\left[(\bar{a}_{sl=0}^{(4)})^3 + \bar{a}_{sl=1}^{(4)}\right]T_s + O(T_s^2) . \quad (11)$$

Here $\bar{a}_{sl=0}^{(4)} = 1$ and $\bar{a}_{sl=1}^{(4)} = 1/225$ are the scaled mean scattering lengths for $l = 0$ and $l = 1$, respectively. A comparison of this QDT expansion with the exact result is shown in Fig. 3.

At high temperatures as characterized by $T_s \gg 1$, it is straightforward to show, from the semiclassical limit of the transmission probabilities [19], that

$$\mathcal{K}^{(4)}(T_s) \sim 2 , \qquad (12)$$

in agreement with the classical Langevin model [1, 2]. Figure 3 shows that the transition from quantum to semiclassical behavior occurs over a temperature range of s_E/k_B, which we generally refers as the van der Waals temperature scale. The rate goes from $4s_K$ at the threshold to approximately the Langevin rate of $2s_K$ beyond s_E/k_B. Figure 3 also shows that the oscillatory structure present in $\mathcal{W}^{(n)}$ has mostly been washed out by thermal averaging.

All scaled results can be put on absolute scales using a single parameter, the average polarizability of the molecule α. It determines both the rate scale s_K and the temperature scale s_E/k_B. Sample scale parameters are given in Table I. They are chosen to illustrate that the meaning of the ultracold regime, if defined as the range of temperatures over which the quantum effects are important, is very different for different systems. It covers a much broader temperature range for lighter systems than for heavier ones. They are also chosen to imply that we expect the QL model to be applicable not only to nonpolar molecules, but also to small polar molecules such

as KRb [5], with the main difference being that its upper range of applicability will be more limited. It is interesting to note from the table that despite wide variations of temperature scales for different systems, the rate scales are of the same order of magnitude, $\sim 10^{-9}$ cm^{3}s^{-1}, which is roughly 100 times greater than those for neutral-neutral reactions [9].

In conclusion, we have presented a fully quantal version of the Langevin model for exoergic charge-neutral reactions and inelastic processes. It is a universal model in which different systems differ only in scaling, further illustrating the concept that even in a purely quantum theory, there are important aspects of reactions that can be understood without detailed knowledge of the PES at the short range. Such aspects include not only the total rate of reactions and inelastic processes, presented here, but also the elastic cross section and the total cross section, to be presented elsewhere. For a state-to-state partial cross section, it can be shown from the underlying MQDTR [9] that while its absolute value requires the short-range PES, its energy dependence can still be parametrized using the same universal transmission probabilities $\mathcal{T}_l^{c(n)}(\epsilon_s)$. We point out that the QL model is applicable not only to molecules in the ground or low-lying states, but also to molecules in vibrationally highly excited states and to atoms in selective Rydberg states (ones with significant quantum defect). In such applications, the theory connects with quantum few-body physics [29], and provides a description of their behavior outside of the so-called universal regime, a region that has been difficult to treat using other methods because of the large number of open channels. In a mathematical abstraction with even broader implications, the QL models presented here and earlier in Ref. [9] represents one type of universal behaviors that can emerge whenever the number of open channels in a set of coupled channel (or close-coupling) equations becomes large. It is our belief that uncovering and taking advantage of such universal behaviors will be the key to a more systemic understanding of quantum systems beyond two-body.

At higher temperatures where the molecules start to explore interactions of shorter range, the universal behavior as represented by the QL model will be broken, and be replaced by more system-specific behaviors that will distinguish, e.g., between a polar and a nonpolar molecule. Extracting universal behaviors at such shorter length scales will require explicit treatment of anisotropic interactions, such as charge-dipole for a polar molecule, within the MQDTR framework, and will be the next challenge for the theory.

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