Symmetry and the Geometric Phase in Ultracold Hydrogen-Exchange Reactions

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Quantum reactive scattering calculations are reported for the ultracold hydrogen-exchange reaction and its non-reactive atom-exchange isotopic counterparts, proceeding from excited rotational states. It is shown that while the geometric phase (GP) does not necessarily control the reaction to all final states one can always find final states where it does. For the isotopic counterpart reactions these states can be used to make a measurement of the GP effect by separately measuring the even and odd symmetry contributions, which experimentally requires nuclear-spin final-state resolution. This follows from symmetry considerations that make the even and odd identical-particle exchange symmetry wavefunctions which include the GP locally equivalent to the opposite symmetry wavefunctions which do not. This equivalence reflects the important role discrete symmetries play in ultracold chemistry generally and highlights the key role ultracold reactions can play in understanding fundamental aspects of chemical reactivity.

The hydrogen exchange reaction is referred to as “the simplest reaction”. Consisting of only 3 protons and 3 electrons the forces on the nuclei can be accurately calculated from first-principles quantum mechanics. Consequently this reaction has been extensively studied which has led to many advances in our understanding of chemical reactions 1–3.

In the ultracold regime chemical reactions can be studied at the single quantum state level 4–9. Reactions proceed through a single partial wave and quantum mechanical effects are magnified. The essence of all chemical reactions is quantum mechanical, as such the ultracold regime is a window on reactions at their most fundamental level. A perfect illustration of this is the ultracold reaction between two fermionic KRb molecules, Ospelkaus et al. showed that the requirement that the total wavefunction be anti-symmetric with respect to exchange of identical fermions suppresses the reaction between two KRb molecules in the same internal state 3. Taking advantage of this they were able to turn the reaction on and off by changing the internal state of one of the molecules.

Studying the ultracold hydrogen exchange reaction therefore offers the perfect testbed to study fundamental aspects of chemical reactivity, such as symmetry effects, isotopic substitution and the GP effect. The GP effect is purely quantum mechanical in origin, relating to the phase of the wavefunction encircling a conical intersection (CI) 10–14. Being quantum mechanical in origin the GP does not readily manifest itself at higher collision energies where high quantum numbers lead to classical behaviour 15. However in the ultracold regime it has been shown that the GP controls the O + OH → H + O2 reaction 16, just as the identical particle symmetry does in the KRb reaction.

In quantum mechanics two wavefunctions can interfere either constructively or destructively, depending on their relative sign (or phase). A change of sign for either one of the wavefunctions will change destructive interference to constructive interference or vice versa. Often such a change of sign is a consequence of symmetry considerations. This is the case for the hydrogen exchange reaction where the inclusion of the GP introduces a change of relative sign between the dominant reaction pathways 17.

In the ultracold regime phases are quantized, leading to maximally constructive or destructive interference between reaction pathways. Furthermore, when two reaction pathways are of similar magnitude they will either cancel each other out or double up: the reaction can only be on or off. This is exactly the case for the ultracold hydrogen exchange reaction proceeding from \( v = 4 \ j = 0 \), where the sign change associated with the GP turns the reaction on and off 18, 19. This is what is meant by the GP controlling ultracold reactions 16.

In each of these ultracold reactions the on/off character is due to a discrete symmetry. Discrete symmetries are of fundamental importance in quantum mechanics, but have no corresponding classical physical meaning. In this work we examine the ultracold hydrogen exchange reaction, and its non-reactive atom-exchange isotopic counterparts, proceeding from excited rotational states. In doing so we will highlight the important role discrete symmetries play in ultracold chemistry and under what conditions we should expect them to control ultracold chemical reactions in general.

I. METHODS

We use the atom-diatom scattering formalism as developed by Pack and Parker 20, 21. In the short range we use adiabatically-adjusting-principle-axis hyperspherical coordinates, an approach which ensures that all arrangements are treated fully equivalently, while in the long range we use Delves hyperspherical coordinates for each arrangement channel. Calculations were performed on the BKMP2 potential energy surface 22 and the vector potential approach of Mead and Truhler was used to include the GP effect 12. The coupled equations were propagated using the log-derivative method of Johnson 23. Results are well converged in the ultracold regime with total angular momentum up to and including 4 used in all calculations. This approach has been
FIG. 1. Reaction rate coefficients for the $\text{H} + \text{H}_2(j = 1, 2) \rightarrow \text{H} + \text{H}_2(v',j')$ reaction at 1 $\mu$K. Results include all values of total angular momentum ($J$) up to and including 4. The upper and lower panels show reactions proceeding from $j = 1$ and 2 respectively. The GP and NGP labels denote rates which do and do not include the GP effect respectively.

used extensively in recent years to study the role of the GP in the ultracold hydrogen exchange reaction and its isotopic counterparts [18, 19, 24, 25].

II. RESULTS

A. $\text{H} + \text{H}_2 \rightarrow \text{H} + \text{H}_2$

Ultracold reactions proceeding from $v = 4 \ j = 0$ have been shown to be controlled by the GP [18, 19]. The excited vibrational state is needed to overcome the reaction barrier while remaining in the ultracold regime. As such all reactions in this paper proceed from $v = 4$ and the $v$ is omitted from state-to-state labels for clarity. As discussed in the introduction the GP controls these reaction due to a number of factors: the quantization of phase shifts in the ultracold; the sign change due to the GP; and the similar magnitude of the two dominant reaction pathways. In this work we will use the term “controlled by the GP” to mean state resolved rates which change by over an order of magnitude when the GP is included. Such state-to-state rates offer an excellent way to directly measure the GP effect in chemical reactions.

We begin by studying the ultracold hydrogen exchange reaction proceeding from excited rotational states. Figure II shows $j$-resolved reaction rate coefficients for $\text{H} + \text{H}_2(j = 1, 2) \rightarrow \text{H} + \text{H}_2(v',j')$ calculated at 1 $\mu$K, in the Wigner threshold regime. These rates include contributions from both the exchange and non-exchange pathways [17]. It is seen that for reactions proceeding from $j = 1$ the reaction is, just as for $j = 0$, either on or off. The GP and NGP (no geometric phase) rates differ by about an order of magnitude, with the NGP reaction
FIG. 2. Reaction rate coefficients for the \( D + HD(\nu' = 1, 2) \rightarrow D + HD(\nu', j') \) reaction at 1 \( \mu \text{K} \). Results include all values of total angular momentum \( (J) \) up to and including 4. The upper and lower panels show reactions proceeding from \( j = 1 \) and 2 respectively.

being on and the GP turning the reaction off. A couple of final states buck this trend, notably \( \nu' = 0 \), \( j' = 15 \) where this is reversed. However these correspond to final states with rates orders of magnitude smaller than for the dominant final states. As such the vibrational resolved rates also show this on/off character. Reactions proceeding from \( j = 2 \) however show weaker influence of the GP. Here we find that while many channels do not exhibit a strong GP effect many do, such as \( \nu' = 2 \), \( j' = 10 \).

\( \text{H}_2 \) exists in either para or ortho form, for \( j = 1 \) there is no pure rotational quenching whereas for \( j = 2 \) there is pure rotational quenching to \( j = 0 \). We find that the rate for pure rotational quenching is around 2 orders of magnitude larger than the rates to inelastic channels and does not exhibit a strong GP effect. This is because when there is pure rotational quenching the non-exchange pathway dominates the reaction and the sign change along the exchange pathway due to the GP has a small effect.

B. \( D + HD \rightarrow D + HD \) & \( H + HD \rightarrow H + HD \)

We now move on to examine the non-reactive atom-exchange isotopic counterparts. These reactions proceeding from \( j = 0 \) have been studied in the ultracold regime and shown to exhibit large GP effects in the state-to-state rates \([24, 25]\). Figure 2 shows \( j \)-resolved reaction rate coefficients for \( D + HD(\nu' = 1, 2) \rightarrow D + HD(\nu', j') \) at \( 1 \mu \text{K} \). Just as for \( \text{H}_2 \) these rates include contributions from both the exchange and non-exchange pathways. Here we see that for \( j = 1 \) the GP still controls the reaction, for even symmetry it turns the reaction on while for odd symmetry it turns the reaction off. For
FIG. 3. Reaction rate coefficients for the $H + HD(j = 1, 2) \rightarrow H + HD(v', j')$ reaction at $1 \mu K$. Results include all values of total angular momentum ($J$) up to and including 4. The upper and lower panels show reactions proceeding from $j = 1$ and $2$ respectively.

reactions proceeding from $j = 2$ the trend is mostly reversed and weaker, however there are many final states where the GP changes the rate by over an order of magnitude.

Figure 4 shows the same data as figure 2 but for the $H + HD(j = 1, 2) \rightarrow H + HD(v', j')$ reaction. In this case there is not a consistent trend across all final states. However there are regions where the GP controls the reaction, most clearly for $v' = 0$ $j' \lesssim 5$ where for $j = 1$ (2) the GP turns on (off) the even symmetry case and turns off (on) the odd symmetry case. Just as in the $H_2$ case we find that pure rotational quenching dominates the rate to inelastic channels and does not exhibit a strong GP effect for either of the non-reactive atom-exchange isotopic counterparts (here $j = 1 \rightarrow 0$ and $j = 2 \rightarrow 0 \& 1$ are allowed).

It is clear from figures 2 and 4 that the GP and exchange symmetry play complementary roles in the non-reactive atom-exchange isotopic counterparts to the hydrogen exchange reaction. The GP rates for each symmetry are well approximated by the NGP rate of the opposite symmetry, this is most clear when the GP controls the reaction but it is also true generally. This complementarity follows from the symmetry of the wavefunction when the GP is included. The characteristic of the GP is that the wavefunction around the CI is double valued and exhibits even symmetry on one-side and odd symmetry on the other side. The double-valued GP wavefunction can therefore be accurately represented by a NGP wavefunction (of either even or odd symmetry) but only locally (i.e. only on one side of the CI or the other but not both simultaneously). A NGP wavefunction of suitable symmetry therefore accurately approximates the double-valued GP wavefunction in $H_3$ type systems as only one
The total state resolved rates are computed by adding the rates for even and odd exchange symmetry multiplied by the appropriate nuclear spin statistical factor. This summation reduces the overall GP effect in the total rates since the rate is on for one of the symmetries and off for the other. For the D + HD case since D is a spin 1 boson the even and odd factors are 2/3 and 1/3 respectively. For the H + HD case since H is a spin 1/2 fermion the even and odd factors are 2/3 and 1/3 respectively. The difference between the GP and NGP total rates is thus primarily due to the nuclear spin weighting factor.

On the other hand with nuclear-spin final-state resolution the even and odd symmetry GP rates can be measured directly. The rates shown in figures 3 and 5 are then obtained by multiplying by the appropriate nuclear spin weighting factors. For example the total experimental rate for D + HD is $k_{\text{tot}}^{\exp} = \frac{2}{3}k_{\text{evn}}^{\exp} + \frac{1}{3}k_{\text{odd}}^{\exp}$.

For the non-reactive atom-exchange isotopic counter-
parts to the hydrogen exchange reaction, just as in the H$_3$ case, we find that there are always final states which exhibit a strong GP effect. Due to symmetry, for these reactions, state-to-state rates including the GP are well approximated by NGP rates of the opposite identical-particle exchange symmetry. This symmetry effect can be used to make a measurement of the GP effect. Experimentally this amounts to finding a final state with a large difference between even and odd symmetry, which requires nuclear-spin final-state resolution.

The importance of the GP and identical-particle symmetry shown here reflects the importance of discrete symmetries in ultracold chemical reactions generally, where their effect is magnified. Discrete symmetries have been shown to play a key role in a diverse range of ultracold reactions: KRb + KRb $\rightarrow$ K$_2$ + Rb$_2$ [4], O + OH $\rightarrow$ O$_2$ + H [16], and the hydrogen exchange reaction [18]. Discrete symmetries are present in all quantum systems exhibiting reflection symmetry and this on/off character is expected to be ubiquitous across ultracold chemistry. This highlights the important role ultracold reactions can play in understanding fundamental chemical processes more generally.

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