

Semiclassical spin exchange via temperature-dependent transition states

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Spin-exchange collisions have been widely studied in recent years, and various quantum-mechanical scattering approaches have been developed to calculate the rates. However, these methods based on global knowledge of wave functions can be computationally demanding, are limited to small systems, and do not offer a mechanistic interpretation. Here, we present a semiclassical transition-state theory (SCTST) derived from first principles to describe the nonadiabatic transition between two states that differ only in their spins, where classical TST and Landau-Zener theory fail. We apply our theory to describe the spin-exchange collision between the nuclear spin of ^3He and the electronic spin of ^{23}Na . SCTST reveals that the reaction proceeds via temperature-dependent transition states, determined by an intricate compromise between minimizing the activation energy and maximizing the hyperfine coupling. It further demonstrates the importance of quantum delocalization effects prevalent in spin exchange even when tunneling is suppressed and successfully explains the observed weak temperature dependence of the rate. Finally, we showcase the power of SCTST by making predictions for the $^3\text{He} + \text{CH}_3$ spin-exchange collision in full dimensionality, where we find that the internal degrees of freedom induce symmetry-broken transition states.

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I. INTRODUCTION

Utilizing the spin degree of freedom for information storage and fabrication of quantum materials has been one of the key goals in the field of spintronics [1]. The bottleneck for this process is the generation and control of the spin while preserving the charge of the system [2]. The nuclear spins of odd isotopes of noble gases have a nonzero quantum number and a long coherence time [3], as they are well shielded by the electron cloud from external agents. However, these nuclear spins can be coherently controlled by coupling them with the electronic spins of alkali metals via spin-exchange processes [4,5], making them important candidates for constructing quantum materials [6]. Other forms of spin exchange are prevalent in atom-photon collisions [7] and have recently been shown to cause energy transfer between atomic hyperfine and molecular rotational states [8]. Thus, it is crucial to understand the mechanism of the spin-exchange process in order to aid the rational design of quantum materials.

Various quantum scattering methods have been proposed over the years to calculate the rate constants for spin-exchange processes [9–14]. For instance, the exchange between the nuclear spin of ^3He and the electronic spin of the valence electron of ^{23}Na is known to be mediated by short-range hyperfine couplings [15], of which the isotropic Fermi contact interaction plays the dominant role [9]. After removing the center-of-mass motion, the Hamiltonian for the spin-exchange

process in the absence of a magnetic field is [16]

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hat{L}^2}{2mr^2} + V(r) + A(r)\hat{I} \cdot \hat{S}, \quad (1)$$

where m is the reduced mass, r is the internuclear distance, $\hat{L}$ is the spatial angular-momentum operator, and $V(r)$ is the potential energy. The final term couples the nuclear and electronic spin angular-momentum operators, $\hat{I}$ and $\hat{S}$, via the Fermi contact interaction,

$$A(r) = \frac{16\pi}{3} \frac{\mu_0 \mu_{\text{He}}}{I} \rho_{\text{He}}(r). \quad (2)$$

Here, μ_0 and μ_{He} are the Bohr magneton and nuclear magnetic moment of ^3He , $I = \frac{1}{2}$ is the nuclear spin quantum number, and $\rho_{\text{He}}(r)$ is the electron spin density at the nucleus of He. We neglect the long-range anisotropic spin-dipolar part of the hyperfine coupling, which only becomes important at very low temperatures [14]. Additionally, since we are describing spin exchange and not spin relaxation, the spin-rotation term, which couples the electronic spin with the spatial angular momentum (and is proportional to Na's weak spin-orbit coupling [16]), has been omitted in the expression.

Although quantum scattering methods can in principle solve this problem numerically exactly, they involve tedious calculations of the partial waves and do not provide an intuitive understanding of the spin-exchange mechanism. Moreover, these scattering methods are limited to a few degrees of freedom and even with modern computation power it is impossible to tackle collisions with polyatomic molecules. Furthermore, they require global knowledge of the system and calculating the potential as well as the hyperfine coupling between the collision partners at large distances can be difficult because of the effects of various long-range interactions.

On the other hand, classical methods such as Marcus theory [17] and nonadiabatic transition-state theory (TST)

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[18,19] utilize Landau-Zener transmission coefficients [20,21] based on information at the minimum-energy crossing point (MECP) of the reactant and product potential energy surface (PES) and have been used to calculate spin-flip rates (also known as intersystem crossing) in molecules in an elegant manner [22]. However, in the case of spin-exchange collisions, the reactant and product PESs are identical and thus “cross” at every point, which causes the classical rates to diverge. Moreover, due to the absence of a unique transition state, the mechanism is unclear. Hence, it is necessary to devise a more powerful type of transition-state theory that can describe the spin-exchange process.

In this article, we describe a semiclassical transition-state theory (SCTST) that stems from instanton theory [23–25] and its generalization to nonadiabatic reactions [26,27]. It uses path integrals rather than wave functions and thus offers a different way of looking at the phenomenon. The resulting method requires only local knowledge of the system at a single geometry, called the “hopping point,” which is defined as the minimum of the *temperature-dependent effective potential*, thus significantly reducing the computational cost. Nonetheless, it is able to predict the spin-exchange rates with good accuracy, which confirms that the hopping point is the key to understanding the mechanism and can thus be thought of as the *transition state* for this process.

II. DERIVATION OF THE SCTST RATE

We take the initial (reactant) state of the system to be $|R\rangle = |\uparrow\downarrow\rangle$ and the final (product) state to be $|P\rangle = |\downarrow\uparrow\rangle$, where the two arrows represent the nuclear and electronic spins. The Hamiltonians for each state are thus $\hat{H}_n = \langle n|\hat{H}|n\rangle$ for $n \in \{R, P\}$, which have kinetic energy identical to the first two terms of Eq. (1) and potential energy $V_n(r) = V(r) + A(r)/4 \approx V(r)$. The two states are coupled by

$$\Delta(r) = \langle \uparrow\downarrow | A(r) \hat{f} \cdot \hat{S} | \downarrow\uparrow \rangle = \frac{A(r)}{2}. \quad (3)$$

The thermal rate is given by

$$k Z_R = \frac{1}{2\pi\hbar} \int_0^\infty N(E) e^{-\beta E} dE, \quad (4)$$

where the cumulative reaction probability (assuming the coupling to be weak) is defined using Fermi’s golden rule [28]

$$N(E_R) = (2\pi)^2 \sum_\ell (2\ell + 1) \int |\Delta^\ell(E_R, E_P)|^2 \times \delta(E_R - E_P) dE_P. \quad (5)$$

Here, the scattering states (with angular-momentum quantum number ℓ and collision energy E_n) obey $\hat{H}_n \psi_n^\ell(E_n) = E_n \psi_n^\ell(E_n)$ and are coupled by $\Delta^\ell(E_R, E_P) = \langle \psi_R^\ell(E_R) | \Delta | \psi_P^\ell(E_P) \rangle$. Finally, $Z_R = (m/2\pi\beta\hbar^2)^{3/2}$ is the reactant partition function per unit volume.

As we wish to avoid computing scattering wave functions, we now present an alternative formula in a basis-independent representation obtained using the Fourier transform of the delta function [27,29]:

$$k Z_R = \frac{1}{\hbar^2} \int_{-\infty}^\infty \text{Tr} \left[\hat{\Delta} e^{-(\beta\hbar - \tau - i\tau)\hat{H}_R/\hbar} \hat{\Delta} e^{-(\tau + i\tau)\hat{H}_P/\hbar} \right] dt, \quad (6)$$

where we have introduced an arbitrary component of imaginary time, τ .

The most direct way to obtain a classical rate equation is by evaluating the trace as a phase-space integral [30],

$$k_{cl} Z_R = \frac{1}{\hbar^2} \frac{1}{(2\pi\hbar)^3} \iiint_{-\infty}^\infty \Delta^2(\mathbf{x}) e^{-\beta\|\mathbf{p}\|^2/2m} \times e^{-\beta V_R - (V_P - V_R)(\tau + i\tau)/\hbar} dt d\mathbf{p} d\mathbf{x}, \quad (7)$$

with $\mathbf{x}$ being the internuclear vector and $\mathbf{p}$ its conjugate momentum. In the general case, the integral over time results in a factor of $\delta[V_R(\mathbf{x}) - V_P(\mathbf{x})]$ and thus forces the hop to occur at a crossing point, as in Marcus theory. However, it becomes immediately evident that for completely overlapping potentials where $V_R(\mathbf{x}) = V_P(\mathbf{x})$ for all $\mathbf{x}$, which is the case for spin-exchange collisions, the time integral becomes undefined and the classical approach completely breaks down.

To solve this problem, we return to quantum mechanics and express the trace in the path-integral formalism. First, we consider a general case where V_R and V_P are different functions before studying the implications of setting them to be identical. Writing Eq. (4) in terms of the quantum-mechanical propagators $K_n(\mathbf{x}', \mathbf{x}'', \tau_n) = \langle \mathbf{x}' | e^{-\tau_n \hat{H}_n/\hbar} | \mathbf{x}'' \rangle$, the rate expression becomes [29,31]

$$k Z_R = \frac{1}{\hbar^2} \iiint \Delta(\mathbf{x}') K_R(\mathbf{x}', \mathbf{x}'', \beta\hbar - \tau - i\tau) \times \Delta(\mathbf{x}'') K_P(\mathbf{x}'', \mathbf{x}', \tau + i\tau) d\mathbf{x}' d\mathbf{x}'' dt. \quad (8)$$

To obtain a high-temperature limit for the rate, we approximate the propagators in the semiclassical short-time limit [31–33], as discussed further in the Supplemental Material [34]: $K_n(\mathbf{x}', \mathbf{x}'', \tau_n) \simeq (m/2\pi\hbar\tau_n)^{3/2} e^{-S_n/\hbar}$, with the classical limit of the action [35–37]:

$$S_n(\boldsymbol{\xi}, \mathbf{x}, \tau_n) \simeq \frac{m}{2\tau_n} \|\boldsymbol{\xi}\|^2 + \tau_n V_n(\mathbf{x}). \quad (9)$$

For simplicity, we have transformed the variables to $\mathbf{x} = \frac{1}{2}(\mathbf{x}' + \mathbf{x}'')$ and $\boldsymbol{\xi} = (\mathbf{x}' - \mathbf{x}'')$. The rate constant now becomes

$$k Z_R \simeq \frac{1}{\hbar^2} \iiint \left(\frac{m}{2\pi\hbar\tau_R} \right)^{3/2} \left(\frac{m}{2\pi\hbar\tau_P} \right)^{3/2} \times \Delta(\mathbf{x})^2 e^{-(S_R + S_P)/\hbar} d\boldsymbol{\xi} d\mathbf{x} dt, \quad (10)$$

where we have approximated $\Delta(\mathbf{x} \pm \frac{1}{2}\boldsymbol{\xi}) \simeq \Delta(\mathbf{x})$, which is valid in the high-temperature limit. The resulting Gaussian integral over $\boldsymbol{\xi}$ is trivially performed.

In many golden-rule processes [27], one can treat $\Delta(\mathbf{x})$ as slowly varying; however, this so-called Condon approximation is no longer valid here as it leads to divergent rates. To extend the theory for a coupling that strongly depends on the internuclear position, we move the $\Delta(\mathbf{x})$ terms to the exponential [38] by introducing the effective action $S_{\text{eff}} = S_R(\mathbf{0}, \mathbf{x}, \tau_R) + S_P(\mathbf{0}, \mathbf{x}, \tau_P) - 2\hbar \ln \frac{\Delta(\mathbf{x})}{\Delta_0}$, where Δ_0 is an arbitrary constant required to take care of the units. Finally, we convert $\mathbf{x}$ to polar coordinates:

$$k Z_R \simeq \frac{\Delta_0^2}{\hbar^2} \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \iint 4\pi r^2 e^{-S_{\text{eff}}/\hbar} dr dt. \quad (11)$$

We then perform a steepest-descent integration in r and t around the stationary point of the effective action:

$$k_{\text{cl}} Z_{\text{R}} = \sqrt{2\pi\hbar} \frac{\Delta_0^2}{\hbar^2} Z_{\text{rot}} \sqrt{\frac{m}{\beta\hbar}} \sqrt{\frac{1}{-\Sigma_{\text{eff}}}} e^{-S_{\text{eff}}/\hbar}, \quad (12)$$

where $Z_{\text{rot}} = 2mr^2/\beta\hbar^2$ is the rotational partition function measured at the hopping point. Additionally, $\tau_{\text{R}} = \beta\hbar - \tau$ and $\tau_{\text{P}} = \tau$ correspond to the imaginary time spent on the reactant and product states (which is determined by the stationary-action condition). The negative sign before Σ_{eff} comes from the Cauchy-Riemann relations that allow us to evaluate the derivatives in imaginary time:

$$\Sigma_{\text{eff}} = \begin{vmatrix} \frac{\partial^2 S_{\text{eff}}}{\partial r^2} & \frac{\partial^2 S_{\text{eff}}}{\partial r \partial \tau} \\ \frac{\partial^2 S_{\text{eff}}}{\partial \tau \partial r} & \frac{\partial^2 S_{\text{eff}}}{\partial \tau^2} \end{vmatrix}. \quad (13)$$

Performing the derivatives using Eq. (9) in the short-time limit gives the determinant

$$\Sigma_{\text{eff}}^{\text{cl}} = \begin{vmatrix} \beta\hbar\bar{\Omega} - 2\Xi & \kappa_{\text{R}} - \kappa_{\text{P}} \\ \kappa_{\text{R}} - \kappa_{\text{P}} & 0 \end{vmatrix}, \quad (14)$$

with $\bar{\Omega} = (\tau_{\text{R}}\Omega_{\text{R}} + \tau_{\text{P}}\Omega_{\text{P}})/\beta\hbar$ and $\Xi = \hbar \frac{\partial^2 \ln \Delta}{\partial r^2}$, where κ_n and Ω_n are the first and second derivatives of the potential $V_n(r)$ at the hopping point $r^\ddagger$. These expressions are similar to the ones derived in previous works [37,39] except for the introduction of the effective action. In fact, in the high-temperature limit, we recover a form identical to that of nonadiabatic TST,

$$k_{\text{cl}} = \sqrt{\frac{2\pi m}{\beta\hbar^2}} \frac{\Delta(r^\ddagger)^2}{\hbar|\kappa_{\text{R}} - \kappa_{\text{P}}|} \frac{Z_{\text{rot}}}{Z_{\text{R}}} e^{-\beta V^\ddagger(\beta)}. \quad (15)$$

This formula is related to Marcus theory, which is recovered from the additional assumption of harmonic potentials. One recognizes that the prefactor is proportional to the Landau-Zener factor in the weak-coupling limit. The key difference is that the hopping point is determined by the optimization of an effective potential, $V_{\text{eff}}(r; \beta) = V_{\text{R}}(r) - \frac{2}{\beta} \ln \frac{\Delta(r)}{\Delta_0}$ on the crossing seam $V_{\text{R}}(r) = V_{\text{P}}(r)$, which leads to the concept of a temperature-dependent MECP with $V^\ddagger(\beta) = V_{\text{R}}(r^\ddagger)$.

An interesting phenomenon arises when we attempt to apply this classical theory to spin-exchange collision. In this case, the reactant and product surfaces are identical everywhere, such that the gradients $\kappa_{\text{R}} = \kappa_{\text{P}}$ are equal, which causes the Landau-Zener factor and hence the classical rate Eq. (15) to diverge. However, in contrast to the phase-space approach of Eq. (7), it is now clear how the issue can be fixed.

The problem stems from the fact that the determinant $\Sigma_{\text{eff}}^{\text{cl}}$ is zero when $\kappa_{\text{R}} = \kappa_{\text{P}}$. Thus, instead of truncating the action at the lowest order, we are forced to include some quantum-mechanical effects [34],

$$S_n(\xi, \mathbf{x}, \tau_n) \simeq \frac{m}{2\tau_n} \|\xi\|^2 + \tau_n V_n(\mathbf{x}) - \frac{\kappa_n^2 \tau_n^3}{24m}, \quad (16)$$

where the final term is recognized from the action of a linear potential [35,39] and accounts for quantum-mechanical delocalization. In this way, SCTST goes beyond classical rate theories by including certain quantum effects, which, as we now show, are crucial to describe the spin-exchange process.

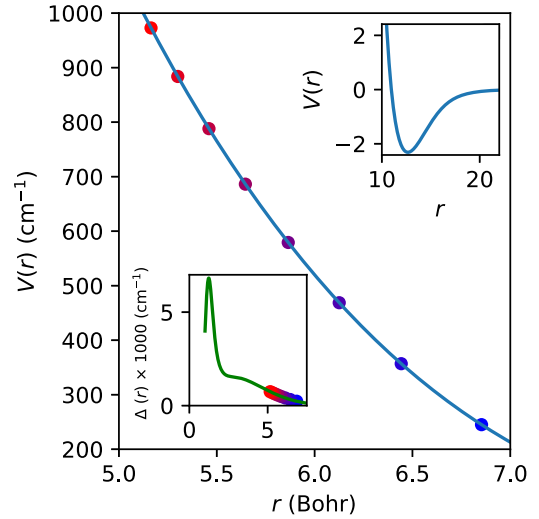


FIG. 1. Hopping points, $r^\ddagger$, for spin-exchange collisions between ^3He and ^{23}Na from 200 to 900 K in steps of 100 K. With increasing temperature, the hopping point (also known as the transition state) climbs to higher energies to access larger coupling. The insets show the potential energy curve and the coupling along a wider range of internuclear distances. The shallow minimum in the potential plays no role in the semiclassical theory.

The semiclassical determinant now becomes

$$\Sigma_{\text{eff}}^{\text{sc}} \simeq \begin{vmatrix} \beta\hbar\bar{\Omega} - 2\Xi & 0 \\ 0 & -\frac{\beta\hbar\kappa^2}{4m} \end{vmatrix}, \quad (17)$$

where because of the symmetry of the problem, $\kappa = \kappa_{\text{R}} = \kappa_{\text{P}}$, $\bar{\Omega} = \Omega_{\text{R}} = \Omega_{\text{P}}$, and $\tau_{\text{R}} = \tau_{\text{P}} = \beta\hbar/2$. Note that the final term in Eq. (16) is clearly subdominant in the high-temperature limit. However, it is nonetheless essential to describe the quantum fluctuations correctly to obtain a nonzero determinant and hence a well-defined rate.

The semiclassical rate constant is therefore defined by combining Eqs. (12) and (17) as

$$k_{\text{SCTST}} = \sqrt{\frac{2\pi m}{\beta\hbar^2}} \frac{\Delta^2(r^\ddagger)}{\hbar|\kappa/2|} \frac{Z_{\text{rot}}}{Z_{\text{R}}} \frac{1}{\beta\hbar\omega} e^{-\beta V^\ddagger(\beta)}, \quad (18)$$

where $m\omega^2 = \Omega - 2\Xi/\beta\hbar$. This rate expression for SCTST appears strikingly similar to Eq. (15). However, it is marked by certain important differences, in particular, that the prefactor differs from the Landau-Zener form and thus avoids the problem of divergence.

In this way, SCTST provides an intuitive picture of the whole spin-exchange mechanism where the most probable approach distance is described by the hopping point, $r^\ddagger$, also known as the transition state. As shown in Fig. 1, there is a competition between the activation energy required to reach this point and the gain in increasing the coupling. For this reason, the spin-exchange process does not follow the usual Arrhenius law, as increasing the temperature raises the activation energy in such a way that the rate constant only changes slightly. This is in agreement with experiments [40,41], where no significant temperature dependence of the spin-exchange rate was observed over the measured small temperature range.

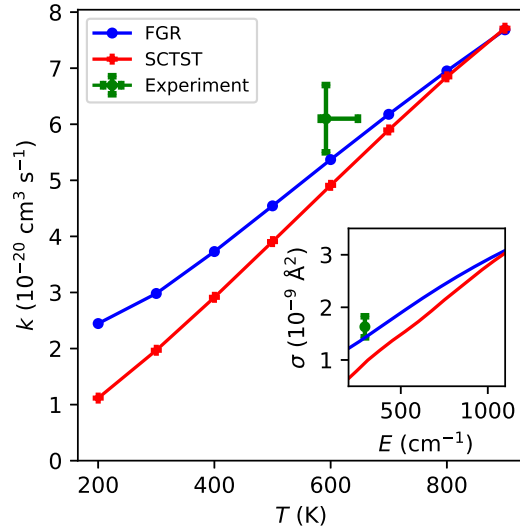


FIG. 2. Rate constants for the spin-exchange between ^3He and ^{23}Na compared with the experimental measurement of Ref. [40]. The semiclassical rates converge to the quantum-mechanical rate (FGR) at high temperatures. The inset shows the reaction cross sections, $\sigma(E)$, compared with experimental measurements of Ref. [42]. Experiments suggest that the rate is roughly constant (within error bars) over the small temperature range measured (as indicated), which is in line with our calculations in which the rate constant only has a mild temperature dependence, rather than the usual exponential Arrhenius behavior.

III. RESULTS

SCTST was used to calculate the spin-exchange rates for the $^3\text{He}+\text{Na}$ reaction. Figure 2 shows that the SCTST rates are in good agreement with the quantum rates calculated via Fermi's golden rule with scattering wave functions. In particular, SCTST captures the qualitative trend of the rates decreasing roughly linearly with temperature [34] as suggested previously by Walter *et al.* [13], who had proposed an empirical temperature scaling relation for the rate constant. However, this apparent linear dependence of the rate constant on temperature is fortuitous and we see a deviation from linearity when the Fermi contact interaction is replaced by a simpler exponential function (not shown).

Note that the strong deviation from the usual exponential Arrhenius form is a consequence of the *temperature-dependent transition states* and not an indication of tunneling effects. In fact, the close agreement between our SCTST rate (which neglects tunneling) and quantum results confirms that tunneling is not important in this case. In particular, including the higher-order term from Eq. (16) into the exponent has a very minor effect on the result.

Our first-principles study also agrees with previous works [11,12], where an atomic model was used to approximate the Fermi contact with an empirical enhancement factor obtained by comparing theoretical calculations of the frequency-shift enhancement factor with experiment. The experimental rate constant reported by Borel *et al.* [40] is $(6.1 \pm 0.6) \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ at 319 °C, which is very close to our quantum rate of $5.3 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ and our SCTST rate of $4.8 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$. This highlights that the error made by

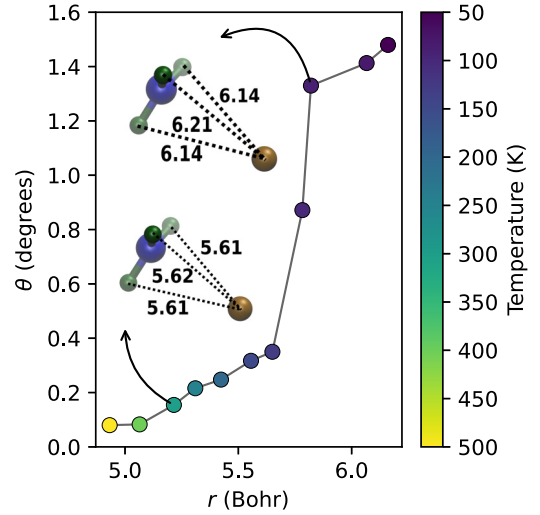


FIG. 3. Temperature-dependent transition states for spin-exchange between ^3He and CH_3 at different temperatures. r is defined as the He-C distance. θ is defined as the angle between the normal of the plane of H atoms and the He-C vector. With increasing temperature, the intermolecular distance decreases so that Δ increases [34]. We also notice a sudden change in the angle at which the He approaches the methyl radical, leading to symmetry breaking at low temperatures. The insets show the structure of the transition states at 300 and 90 K, with the H-He distances labeled.

SCTST with respect to the quantum-mechanical rate is less than the uncertainty of the experimental result.

In addition to calculating thermal rates, we can also predict reaction cross sections using SCTST. Formally, the cumulative reaction probabilities are related to the thermal rate by an inverse Laplace transform of Eq. (4),

$$N(E) = \frac{\hbar}{i} \int_{\beta_{\text{sp}} - i\infty}^{\beta_{\text{sp}} + i\infty} e^{\beta E + \ln \Phi(\beta)} d\beta, \quad (19)$$

where $\Phi(\beta) = k(\beta) Z_R(\beta)$. The stationary point β_{sp} satisfies $E = -(\frac{d \ln \Phi(\beta)}{d\beta})_{\beta=\beta_{\text{sp}}}$, which is assumed to be larger than the real part of all the singularities of $\Phi(\beta)$. Making the stationary-phase approximation [43,44] for a given energy, we obtain the cumulative reaction probability

$$N(E) \simeq \left(\frac{1}{2\pi} \frac{d^2 \ln \Phi(\beta)}{d\beta^2} \right)^{-1/2}_{\beta=\beta_{\text{sp}}} e^{\beta_{\text{sp}} E + \ln \Phi(\beta_{\text{sp}})}. \quad (20)$$

Finally, the spin-exchange cross section can be obtained as $\sigma(E) = \pi \hbar^2 N(E) / 2mE$ [45].

The results in the inset of Fig. 2 show that at higher energies the semiclassical approximation approaches the quantum result and shows only a minor error at lower energies. Our calculations are also in good agreement with the spin-exchange cross section measured by Soboll [42].

Another advantage of SCTST is that it is trivially generalized to multidimensional systems [34], allowing the description of polyatomic molecules with internal degrees of freedom. We demonstrate this by studying the spin-exchange mechanism for $^3\text{He} + \text{CH}_3$ in full dimensionality using on-the-fly electronic-structure theory [34,46]. Figure 3 shows a significant change in the structure of the transition states

with temperature. The spin density of the methyl radical is primarily distributed perpendicular to the plane of the hydrogen atoms since the lone electron is in a p orbital; consequently, the He nucleus tends to approach along this direction to access more coupling. For this reason, in the high-temperature limit, the transition state has a C_{3v} symmetry with He at the center of methyl. However, at low temperatures, we notice symmetry breaking in the transition state as the He atom moves away from the center. The resulting decrease in coupling is compensated by a reduction of the intermolecular repulsion. Furthermore, we also notice changes in the umbrella mode of the methyl [34], where at high temperatures it assumes a less planar structure due to steric effects from the He atom.

IV. CONCLUSION

In conclusion, we have developed a semiclassical transition-state theory for nonadiabatic transitions between two identical PESs and used it to explain the mechanism of the spin-exchange phenomenon in a simple way. This clarifies the role of quantum effects in the process—although there is negligible tunneling, it is necessary to include quantum delocalization even at high temperatures in order to avoid divergences. The results are in good agreement with experiment and could in principle be systematically improved by increasing the accuracy of the electronic-structure calculations as well as by perturbatively incorporating extra effects such as anharmonicity and higher-order contributions beyond

Fermi's golden rule [47–49]. SCTST can be extended further to include anisotropic, spin-rotation and spin-orbit couplings [14,16,50] along with the effects of electric and magnetic fields [51–53] either perturbatively or by incorporating them explicitly in the electronic-structure calculations. Some of these interactions can split the surfaces such that they do not cross anywhere. Once again, standard classical approaches fail. However, SCTST can be generalized to these systems, as the existence of a transition state on the effective potential is well defined even in the absence of a crossing point [34]. Moreover, as shown, the method is not limited to atom-atom scattering but can also be used to study spin-exchange collisions with polyatomic molecules or even nanoclusters and the surfaces of bulk materials. In this way, the SCTST approach opens up possibilities for a better understanding of the spin-exchange process to aid the rational design of quantum technologies by controlling the spin-polarization timescales.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

- [1] I. Žutić, J. Fabian, and S. Das Sarma, Spintronics: Fundamentals and applications, *Rev. Mod. Phys.* **76**, 323 (2004).
- [2] W. Han, Y. Otani, and S. Maekawa, Quantum materials for spin and charge conversion, *npj Quantum Mater.* **3**, 27 (2018).
- [3] T. R. Gentile, P. J. Nacher, B. Saam, and T. G. Walker, Optically polarized ^3He , *Rev. Mod. Phys.* **89**, 045004 (2017).
- [4] R. Shaham, O. Katz, and O. Firstenberg, Strong coupling of alkali-metal spins to noble-gas spins with an hour-long coherence time, *Nat. Phys.* **18**, 506 (2022).
- [5] O. Katz, O. Peleg, and O. Firstenberg, Coherent coupling of alkali atoms by random collisions, *Phys. Rev. Lett.* **115**, 113003 (2015).
- [6] O. Katz, R. Shaham, and O. Firstenberg, Quantum interface for noble-gas spins based on spin-exchange collisions, *PRX Quantum* **3**, 010305 (2022).
- [7] F. Yang, Y.-C. Liu, and L. You, Atom-photon spin-exchange collisions mediated by Rydberg dressing, *Phys. Rev. Lett.* **125**, 143601 (2020).
- [8] Y.-X. Liu, L. Zhu, J. Luke, M. C. Babin, M. Gronowski, H. Ladjimi, M. Tomza, J. L. Bohn, T. V. Tscherbul, and K.-K. Ni, Hyperfine-to-rotational energy transfer in ultracold atom-molecule collisions of Rb and KRb, *Nat. Chem.* **17**, 688 (2025).
- [9] B. Chann, E. Babcock, L. W. Anderson, and T. G. Walker, Measurements of ^3He spin-exchange rates, *Phys. Rev. A* **66**, 032703 (2002).
- [10] S. Appelt, A. B.-A. Baranga, C. J. Erickson, M. V. Romalis, A. R. Young, and W. Happer, Theory of spin-exchange optical pumping of ^3He and ^{129}Xe , *Phys. Rev. A* **58**, 1412 (1998).
- [11] T. V. Tscherbul, P. Zhang, H. R. Sadeghpour, and A. Dalgarno, Collision-induced spin exchange of alkali-metal atoms with ^3He : An *ab initio* study, *Phys. Rev. A* **79**, 062707 (2009).
- [12] T. G. Walker, Estimates of spin-exchange parameters for alkali-metal–noble-gas pairs, *Phys. Rev. A* **40**, 4959 (1989).
- [13] D. K. Walter, W. Happer, and T. G. Walker, Estimates of the relative magnitudes of the isotropic and anisotropic magnetic-dipole hyperfine interactions in alkali-metal–noble-gas systems, *Phys. Rev. A* **58**, 3642 (1998).
- [14] T. Tscherbul, P. Zhang, H. R. Sadeghpour, and A. Dalgarno, Anisotropic hyperfine interactions limit the efficiency of spin-exchange optical pumping of ^3He nuclei, *Phys. Rev. Lett.* **107**, 023204 (2011).
- [15] N. F. Ramsey, Electron coupled interactions between nuclear spins in molecules, *Phys. Rev.* **91**, 303 (1953).
- [16] T. G. Walker and W. Happer, Spin-exchange optical pumping of noble-gas nuclei, *Rev. Mod. Phys.* **69**, 629 (1997).
- [17] R. A. Marcus, Electron transfer reactions in chemistry. Theory and experiment, *Rev. Mod. Phys.* **65**, 599 (1993).
- [18] J. C. Lorquet and B. Leyh-Nihant, Nonadiabatic unimolecular reactions. 1. A statistical formulation for the rate constants, *J. Phys. Chem.* **92**, 4778 (1988).
- [19] A. O. Lykhin, D. S. Kaliakin, G. E. dePolo, A. A. Kuzubov, and S. A. Varganov, Nonadiabatic transition state theory: Application to intersystem crossings in the active sites of metal-sulfur proteins, *Int. J. Quantum Chem.* **116**, 750 (2016).
- [20] L. D. Landau, Zur Theorie der Energieübertragung. II, *Phys. Z. Sowjetunion* **2**, 46 (1932).

- [21] C. Zener, Non-adiabatic crossing of energy levels, *Proc. R. Soc. London A* **137**, 696 (1932).
- [22] J. N. Harvey, Spin-forbidden reactions: Computational insight into mechanisms and kinetics, *WIREs Comput. Mol. Sci.* **4**, 1 (2014).
- [23] W. H. Miller, Semiclassical limit of quantum mechanical transition state theory for nonseparable systems, *J. Chem. Phys.* **62**, 1899 (1975).
- [24] W. H. Miller, R. Hernandez, N. C. Handy, D. Jayatilaka, and A. Willetts, *Ab initio* calculation of anharmonic constants for a transition state, with application to semiclassical transition state tunneling probabilities, *Chem. Phys. Lett.* **172**, 62 (1990).
- [25] S. Coleman, Fate of the false vacuum: Semiclassical theory, *Phys. Rev. D* **15**, 2929 (1977).
- [26] E. R. Heller and J. O. Richardson, Instanton formulation of Fermi's golden rule in the Marcus inverted regime, *J. Chem. Phys.* **152**, 034106 (2020).
- [27] J. O. Richardson, Nonadiabatic tunneling in chemical reactions, *J. Phys. Chem. Lett.* **15**, 7387 (2024).
- [28] P. A. M. Dirac, The quantum theory of the emission and absorption of radiation, *Proc. R. Soc. London A* **114**, 243 (1927).
- [29] P. G. Wolynes, Imaginary time path integral Monte Carlo route to rate coefficients for nonadiabatic barrier crossing, *J. Chem. Phys.* **87**, 6559 (1987).
- [30] D. Chandler, Electron transfer in water and other polar environments, how it happens, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne, G. Cicciotti, and D. F. Coker (World Scientific, Singapore, 1998), Chap. 2, pp. 25–49.
- [31] J. O. Richardson, Ring-polymer instanton theory, *Int. Rev. Phys. Chem.* **37**, 171 (2018).
- [32] M. C. Gutzwiller, *Chaos in Classical and Quantum Mechanics* (Springer, New York, 1990).
- [33] W. H. Miller, Classical path approximation for the Boltzmann density matrix, *J. Chem. Phys.* **55**, 3146 (1971).
- [34] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/glys-ydzp> for computational details, further details on the derivations as well as additional results for the $^3\text{He} + \text{CH}_3$ reaction.
- [35] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
- [36] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics and Financial Markets*, 5th ed. (World Scientific, Singapore, 2009).
- [37] J. O. Richardson, R. Bauer, and M. Thoss, Semiclassical Green's functions and an instanton formulation of electron-transfer rates in the nonadiabatic limit, *J. Chem. Phys.* **143**, 134115 (2015).
- [38] W. Fang, E. R. Heller, and J. O. Richardson, Competing quantum effects in heavy-atom tunnelling through conical intersections, *Chem. Sci.* **14**, 10777 (2023).
- [39] I. M. Ansari, E. R. Heller, G. Trenins, and J. O. Richardson, Instanton theory for Fermi's golden rule and beyond, *Philos. Trans. R. Soc. A* **380**, 20200378 (2022).
- [40] P. I. Borel, L. V. Sogaard, W. E. Svendsen, and N. Andersen, Spin-exchange and spin-destruction rates for the ^3He –Na system, *Phys. Rev. A* **67**, 062705 (2003).
- [41] A. Ben-Amar Baranga, S. Appelt, M. V. Romalis, C. J. Erickson, A. R. Young, G. D. Cates, and W. Happer, Polarization of ^3He by spin exchange with optically pumped Rb and K vapors, *Phys. Rev. Lett.* **80**, 2801 (1998).
- [42] H. Soboll, Spin exchange between optically oriented sodium and foreign gas nuclei, *Phys. Lett. A* **41**, 373 (1972).
- [43] W. Fang, P. Winter, and J. O. Richardson, Microcanonical tunneling rates from density-of-states instanton theory, *J. Chem. Theory Comput.* **17**, 40 (2021).
- [44] J. E. Lawrence and J. O. Richardson, Improved microcanonical instanton theory, *Faraday Discuss.* **238**, 204 (2022).
- [45] R. D. Levine, *Molecular Reaction Dynamics* (Cambridge University Press, Cambridge, 2005).
- [46] F. Neese, The ORCA program system, *WIREs Comput. Mol. Sci.* **2**, 73 (2012).
- [47] J. E. Lawrence, J. Dušek, and J. O. Richardson, Perturbatively corrected ring-polymer instanton theory for accurate tunneling splittings, *J. Chem. Phys.* **159**, 014111 (2023).
- [48] J. Dušek, J. E. Lawrence, and J. O. Richardson, Perturbatively corrected ring-polymer instanton rate theory rigorously captures anharmonicity and deep tunneling, *J. Chem. Phys.* **164**, 024104 (2026).
- [49] G. Trenins and J. O. Richardson, Nonadiabatic instanton rate theory beyond the golden-rule limit, *J. Chem. Phys.* **156**, 174115 (2022).
- [50] T. V. Tscherbul, P. Brumer, and A. A. Buchachenko, Spin-orbit interactions and quantum spin dynamics in cold ion-atom collisions, *Phys. Rev. Lett.* **117**, 143201 (2016).
- [51] T. V. Tscherbul and R. V. Krems, Controlling electronic spin relaxation of cold molecules with electric fields, *Phys. Rev. Lett.* **97**, 083201 (2006).
- [52] R. Krems and A. Dalgarno, Quantum-mechanical theory of atom-molecule and molecular collisions in a magnetic field: Spin depolarization, *J. Chem. Phys.* **120**, 2296 (2004).
- [53] M. Dikopoltsev, A. Berrebi, U. Levy, and O. Katz, Suppressing the decoherence of alkali-metal spins at low magnetic fields, *Phys. Rev. Lett.* **134**, 143201 (2025).