

# Simulation of Chemical Reactions on a Quantum Computer

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# **ABSTRACT:** Studying chemical reactions, particularly in the gas phase, relies heavily on computing scattering matrix elements. These elements are essential for characterizing molecular reactions and accurately determining reaction probabilities. However, the intricate nature of quantum interactions poses challenges, necessitating the use of advanced mathematical models and computational approaches to tackle the inherent complexities. In this study, we develop and apply a quantum computing algorithm for the calculation of scattering matrix elements. In our approach, we employ the time-dependent method based on the Møller operator formulation where the S-matrix element between the respective reactant and product channels is determined through the time correlation function of the reactant and product Møller wavepackets. We successfully apply our quantum algorithm to calculate scattering matrix elements for 1D semi-infinite square well potential and on the colinear hydrogen exchange reaction. As we navigate the complexities of quantum interactions, this quantum algorithm is general and emerges as a promising avenue, shedding light on new possibilities for simulating chemical reactions on quantum computers.



I n recent years, there have been significant advancements in the field of quantum information and quantum computing. Both hardware and software have progressed rapidly, leading to the development of algorithms for the current quantum computers. These algorithms show promising results in solving research challenges that are beyond the capabilities of even the most powerful conventional supercomputers.<sup>1,2</sup> Central to the efficacy of such algorithms exist fundamental quantum properties, including superposition, entanglement, coherence, and interference. Recent advancements in quantum hardware have spurred a swift surge in the creation of innovative quantum algorithms.<sup>3-7</sup> The predominant focus of algorithmic development encompasses a diverse array of topics such as spectroscopy,<sup>8–10</sup> electronic structure,<sup>11–15</sup> vibrational structure,<sup>16</sup> quantum many-body problems,<sup>17,18</sup> and open quantum dynamics.<sup>19,20</sup> Notably, the application of these algorithms to address scattering problems has received limited attention thus far. This study aims to bridge this gap by developing a quantum algorithm specifically designed to estimate scattering matrix elements for both elastic and inelastic collision processes.

Quantum scattering calculations play a crucial role in advancing our understanding of fundamental physical and chemical phenomena,<sup>21</sup> making them highly significant across diverse scientific disciplines, including the study of chemical reaction mechanisms in the gaseous phase<sup>22</sup> and atmospheric chemistry.<sup>23–25</sup> These calculations are indispensable for the accurate interpretation of experimental findings in gas-phase interactions, providing intricate insights into bimolecular chemical reactions.<sup>26</sup> Moreover, quantum scattering theory serves as a valuable tool for calculating essential parameters like

cross-section and reaction rate in atomic, and chemical physics, contributing to the study of many scattering processes.<sup>27</sup> The necessity of full-dimensionality in low-energy molecular scattering calculations underscores their pivotal role in comprehensively understanding complex molecular interactions. Additionally, molecular scattering experiments, particularly those conducted under cold<sup>28</sup> and ultracold<sup>29</sup> conditions, yield unparalleled insights into intermolecular interactions. A comprehensive understanding of the quantum dynamics in ultracold environments has the potential to reveal innovative strategies, possibly employing quantum phenomena such as superposition, entanglement, and interference patterns to control reaction outcomes.<sup>30–32</sup>

There are two ways to approach the quantum scattering problem in chemical reactions one can employ either the Time Independent (TI) or the Time Dependent (TD) formalism. Quantitatively accurate simulations of quantum scattering, achieved by directly solving the TI Schrödinger equation through methods like coupled-channel techniques<sup>21,26</sup> or basis set expansion, represents as a computational benchmark. Various techniques in the time-independent formulation have been developed to address this issue, such as the S-matrix version of the Kohn variational principle. This involves applying a variational principle to determine expansion

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coefficients in scattering coordinates, resulting in a more efficient and practical approach for quantum scattering calculations. But in general, the TI approach suffers from the classic "curse of dimensionality" problem meaning the computational scaling scales exponentially as the problem size.

To mitigate this challenge, numerous quantum algorithms have been proposed in the literature for different applications,<sup>33-35</sup> with many relying on the Quantum Phase Estimation (QPE) algorithm. However, as QPE is a faulttolerant algorithm, its implementation is currently unfeasible on utility-scale quantum processors. Consequently, its application is constrained to smaller-scale problem sets. Recently, Xing et al.<sup>36</sup> proposed an innovative solution by employing the S-matrix version of the Kohn variational principle to address the scattering problem. This approach alleviates the intricate task of symmetric matrix inversion through the utilization of the Variational Quantum Linear Solver (VQLS).<sup>37</sup> VQLS employs a parametrized quantum circuit that is easier to implement on the Noisy Intermediate-Scale Quantum (NISQ) devices. Nonetheless, there is a need for further improvement in the scalability of VQLS on Noisy Intermediate-Scale Quantum (NISQ) devices and the trainability of the variational ansatz, especially when addressing larger and more complex problems. In TD formalism of quantum scattering problem, wavepackets are constructed and allowed to evolve using the time-dependent Schrödinger equation. TD methods present the ability to extract information across a range of translational energies in a single computational iteration and exhibit superior scalability compared to their TI counterparts. Furthermore, TD methods offer a more comprehensive understanding of dynamic processes, enabling the investigation of time-evolution phenomena in scattering events. This aspect becomes particularly crucial for reactions involving the formation of new chemical bonds. Despite these potential advantages, as of our current knowledge, there is no existing quantum algorithm based on the TD formalism<sup>38</sup> for the scattering problem.

Here we propose a TD Quantum Algorithm based on the Møller operator formulation of the S-matrix.<sup>39,40</sup> The fundamental technical procedure involves dynamics<sup>41,42</sup> of two wavepackets: one representing an asymptotic reactant localized in a single reactant channel, and the other representing an asymptotic product localized in a single product channel. The selection of specific reactant and product channels dictates the S-matrix elements to be computed. These wavepackets are then advanced toward the interaction region, one forward (reactant) and the other backward (Product) in time. Subsequently, the resulting reactant and product wavepackets are transformed into a common representation, 38,43 and the correlation function  $C_{\gamma_{\prime},\gamma}(t) = \langle \Psi_{-i}^{\gamma'} | \exp\{-iHt\} | \Psi_{+}^{\gamma} \rangle$  is calculated between their subsequent time-dependent evolution. Where,  $|\Psi_{\perp}^{\gamma'}\rangle$  and  $|\Psi_{\perp}^{\gamma}\rangle$ corresponds to the product and reactant Møller states in the  $\gamma'$ and  $\gamma$  channel, and H represents the total Hamiltonian. Calculation of the correlation function is the core computational capability of the proposed quantum algorithm and we employ a modified version of the Hadamard test to estimate the correlation function. Hadamard test is a key Quantum algorithm that is extensively used<sup>15</sup> to estimate the expectation value of operators. The Møller operator formalism is then employed to express S-matrix elements between the chosen reactant and product channels in terms of the Fourier

transform of the correlation function computed. This expression enables the computational effort to be efficiently directed toward computing only the S-matrix elements that are of interest. We discuss the theoretical and computational details in the further sections.

# TIME DEPENDENT FORMULATION OF THE SCATTERING MATRIX

Asymptotic reactant state in the  $\gamma^{th}$  arrangement channel is represented by  $|\Psi_{in}^{\gamma}\rangle$  and the channel Hamiltonian  $H_o^{\gamma}$  governs the asymptotic dynamics of the reactant state wavepacket. Assuming  $H_o^{\gamma}$  is time-independent evolution of the reactant state wavepacket is given by

$$|\Psi_{in}^{\gamma}(x_{\gamma},t)\rangle = \exp\{-iH_{o}^{\gamma}t\}|\Psi_{in}^{\gamma}(x_{\gamma},0)\rangle$$
(1)

In all the derivations we assume atomic units.

The wave function  $|\Psi_{in}^{\gamma}(x_{\gamma}, t)\rangle$  can be represented in the  $|x_{\gamma}\rangle$ =  $|r_{\nu}\rangle|R_{\nu}\rangle$  coordinate representation where  $|r_{\nu}\rangle$  and  $|R_{\nu}\rangle$ represents internal quantum state and relative position of reactants, respectively. Additionally, the center of mass (COM) is stationary in the coordinate representation and the asymptotic Hamiltonian is separable in two parts  $H_o^{\gamma} = H_{rel}^{\gamma} + H_{int}^{\gamma}$ , here  $H_{int}^{\gamma}$  and  $H_{rel}^{\gamma}$  correspond to Hamiltonians which govern the internal dynamics and relative motion, respectively. Eigenfunctions of  $H_{rel}^{\gamma}(|k_{\gamma}\rangle)$  and  $H_{int}^{\gamma}(|\gamma\rangle)$ spans the  $\gamma^{th}$  channel momentum representation. Thus, the  $\gamma^{th}$ channel momentum representation is given by  $|k_{\nu}, \gamma\rangle = |k_{\nu}\rangle|\gamma\rangle$ and the incoming wavepacket is conveniently expressed in the momentum representation. Similarly, an asymptotic product state  $|\Psi_{out}^{\gamma'}\rangle$  belongs to the  $\gamma'$ th channel Hilbert space. In this scenario, the channel label  $\gamma'$  specifies the product arrangement channel along with all the internal quantum numbers of the products. The asymptotic dynamics of the product wavepacket is entirely governed by the  $\gamma'$ th channel Hamiltonian  $H_{\alpha}^{\gamma'}$ . The asymptotic Hilbert space is constructed as the direct sum of all individual channel Hilbert spaces, playing a pivotal role in achieving a complete representation of the scattering operator S.

Near the interaction region, the dynamics of the wavepacket localized in  $\gamma$ th channel is controlled by the complete Hamiltonian  $H = H_o^{\gamma} + V$ , where V denotes the interaction potential. The isometric Møller operator is defined as

$$\Omega_{\pm}^{\gamma} = \lim_{t \to \mp \infty} [\exp\{(iHt)\}\exp\{(-iH_0^{\gamma}t)\}]$$
<sup>(2)</sup>

Møller operator mentioned in eq 2 is fundamentally a composition of time evolution operators, with one corresponding to the asymptotic Hamiltonian of the  $\gamma$ th channel  $H_o^{\gamma}$  and the complete Hamiltonian H. Given an asymptotic state  $|\Psi_{in(out)}^{\gamma}\rangle$  at time t = 0 the impact of applying Møller  $\Omega_{+(-)}^{\gamma}$  involves backward(forward) propagation to time  $t = \tau = -\infty(+\infty)$  under the asymptotic Hamiltonian  $H_o^{\gamma}$  followed by forward (backward) propagation under the full Hamiltonian H from  $t = -\tau(+\tau)$  to t = 0. In the coordinate representation, the asymptotic time limit  $\tau$  is the time required to propagate wave function from the interaction region to the asymptotic region.<sup>44</sup> In brief the impact of Møller operator on  $|k_{\gamma}, \gamma\rangle$  is to create a new set of states  $|k_{\gamma}, \gamma \pm \rangle$ 

$$|\Psi_{\pm}^{\gamma}\rangle = \lim_{t \to \pm \infty} [\exp\{(iHt)\}\exp\{(-iH_{0}^{\gamma}t)\}]|\Psi_{in/out}^{\gamma}\rangle$$
(3)



**Figure 1.** Quantum circuit that calculates the correlation function  $C_{\gamma',\gamma'}(t)$  defined in eq 5. The circuit includes two quantum registers a single qubit ancillary register which is measured and stores information about the correlation function and  $N_q$  qubit quantum register that encodes and manipulates the quantum state.

$$|\Psi_{in(out)}^{\gamma}\rangle = \int_{-\infty}^{+\infty} dk_{\gamma} \eta_{\pm}(k_{\gamma}) |k_{\gamma}, \gamma\rangle$$
(4)

While computing the S matrix elements in the momentum representation it is crucial to note an important property of the basis vectors of the  $\gamma$ th channel. These basis vectors form an eigenbasis for their respective asymptotic Hamiltonians  $H_{\alpha}^{\gamma}$  and the eigenvalues corresponding to  $|k_{\gamma}, \gamma\rangle$  is  $\frac{k_{\gamma}^2}{2} + E_{\gamma}$ . Here  $\frac{k_{\gamma}^2}{2}$ corresponds to the relative kinetic energy and  $E_{\nu}$  relates to the internal energy. One can use the intertwining relation  $\Omega^{\gamma}_{\pm}H^{\gamma}_{o} = H\Omega^{\gamma}_{\pm}$  to show that the  $|k_{\gamma}, \pm \gamma\rangle$  basis set forms an eigen-basis for H with the eigenvalues that corresponds to  $|k_{y}\rangle$  $\gamma$ ).<sup>39</sup> The correlation function between the Møller states is defined in eq 5. One can obtain the correlation function using two different approaches, in the first approach  $|\Psi_{+}^{\gamma}\rangle$  is propagated under the full Hamiltonian H from time t = 0 to  $t = \tau$  and take an inner product of the resulting propagated wavepacket with the product Møller state  $|\Psi^{\gamma}\rangle$ . In an alternative approach the time evolution operator  $(\exp\{-iHt\})$  can be applied symmetrically, first  $\langle \Psi_{\perp}^{\gamma}|$  is propagated from t = 0 to  $t = -\tau$  and then  $|\Psi_{+}^{\gamma}\rangle$  from  $t = -\tau$ to  $t = \tau$ .<sup>40</sup> The scattering matrix elements can be expressed in terms of the Fourier transform of the calculated correlation function (discussed further in the Supporting Information).

$$C_{\gamma',\gamma}(t) = \langle \Psi_{-}^{\gamma} | \exp\{(-iHt)\} | \Psi_{+}^{\gamma} \rangle$$
(5)

#### QUANTUM CIRCUIT IMPLEMENTATION

The quantum algorithm focuses on computing the correlation function  $C_{\gamma',\gamma}$  described in eq 5. While the conventional Hadamard test, can determine the expectation value of an operator U defined as  $\langle \Psi | U | \Psi \rangle$ , it is not capable of calculating the correlation function. The reason behind this limitation is that the correlation function, unlike a straightforward expectation value, involves a computation similar to assessing the overlap ( $\langle \Psi_1 | \Psi_2 \rangle$ ) between two quantum states,  $|\Psi_1 \rangle$  and  $|\Psi_2 \rangle$ . Where  $|\Psi_1\rangle = |\Psi_1'\rangle$  and  $|\Psi_2\rangle = \exp\{(-iHt)\}|\Psi_+'\rangle$ . To calculate the state overlap  $(\langle \Psi_1 | \Psi_2 \rangle)$  a slight modification is required in the conventional Hadamard test. We define operators  $O_{y}(O_{y'})$ such that when we operate them on the vacuum state  $(|000\cdots\rangle)$ they prepare  $|\Psi_1\rangle$  ( $|\Psi_2\rangle$ ) quantum states.

$$O_{y}(t) = e^{-iHt}e^{-iH\tau_{o}}e^{+iH_{o}^{\gamma}\tau_{o}}U_{r}$$
(6)

$$O_{\gamma'} = e^{+iH\tau_o} e^{-iH_o^{\gamma'}\tau_o} U_p \tag{7}$$

In eq 6 operator  $U_r$  corresponds to a state preparation that transforms the initial vacuum state into the asymptotic reactant channel wavepacket  $|\Psi_{in}^{\gamma}\rangle$  similarly  $U_p$  in eq 7 is defined such that  $|\Psi_{out}^{\gamma'}\rangle = U_p|000...\rangle$ . Similar to the Hadamard test here we have two quantum registers Ancillary qubit  $q_a$  that stores the information about the correlation function and qubit  $q_s$  that stores and manipulates the quantum state. We first apply the Hadamard operation on the ancillary qubits (followed by a phase gate  $S^{\dagger}$  if the objective is to calculate Im $(C_{\gamma',\gamma}(t))$ ). Next, we apply two controlled operations which are at this algorithm's core, as shown in Figure 1. In the first controlled operation, we operate the controlled version of the operator  $O_{\gamma}$ eq 6 with ancillary qubit  $q_a$  as a control and the state qubit  $q_s$  as a target with the control state '  $|1\rangle_{q_a}$ '. This means that the operator  $O_{\gamma}$  will operate on the state qubits  $q_a$  only when the quantum state of the ancillary qubit  $q_a$  is  $|1\rangle$ . Similarly we apply another controlled version of the  $O_{\gamma'}$  operator (eq 7) with the ancillary qubit  $q_a$  as control and the control state '  $|0\rangle_q$  '. Finally, we apply the Hadamard operation and measure the ancillary qubit is measured in the  $\sigma_z$  basis.

The wave function is expressed in the momentum representation eq 4 on  $q_s$  and binary encoding<sup>45</sup> is used to map it to the qubit wave function. Please refer to the Supporting Information to get detailed information about the qubit mapping. The wavepacket propagation including the Hamiltonian encoding is done in first quantization by expressing the asymptotic  $H_{\alpha}^{\gamma}$  and total Hamiltonian H in the momentum representation basis and then expressing the Hamiltonian as a linear combination of Pauli strings. The propagators  $\exp\{(\pm iHt)\}$  can be approximated by employing higher order Trotter-Suzuki decompositions.<sup>46</sup> For the secondorder Trotter-Suzuki approximation of the time evolution operator corresponding to the Hamiltonian  $H = \sum_{j=1}^{L} h_j$  the number of gates scales as shown in eq 8. Where, n, L,  $\epsilon$  and  $\Lambda$ corresponds to the number of trotter steps, the number of Pauli terms in the expansion of the Hamiltonian, approximation error and the maximum eigenvalue of the operators. Higher precision requires increasing n and extending simulation time t, resulting in a larger Ngates, thus, this algorithm can be categorized into Fault-Tolerant Quantum Algorithms. Additionally one can use the Qiskit<sup>47</sup> Open Source

(6)

Software Development Kit (SDK) to simulate these quantum circuits (For further details regarding the gate count and quantum simulation, please refer to the Supporting Information).

$$N_{gates} \approx \frac{nL^{5/2}(\Lambda t)^{3/2}}{\sqrt{\epsilon}}$$
 (8)

# APPLICATIONS

A One-dimensional Semi-infinite Well. Evaluating the effectiveness of a new technique often involves applying it to a problem with a well-established analytical solution. In this section, we employ the proposed quantum algorithm to determine the scattering matrix element for a two-nucleon scattering problem. Previous studies<sup>48</sup> have demonstrated that the widely utilized  ${}^{1}S_{0}$  Argonne V18 (AV18) potential<sup>49</sup> which plays a crucial role in describing nucleon–nucleon interactions and is among the most commonly used potentials, can be effectively approximated by a semi-infinite square well with dimensions resembling those of the original potential as shown in Figure 2.

$$V(x) = \begin{cases} 3000 \quad MeV & \text{if } x \le 0.65 fm \\ -100 \quad MeV & \text{if } 0.65 fm < x \le 1.65 fm \\ 0 \quad MeV & \text{if } x > 1.65 fm \end{cases}$$



**Figure 2.** Semi-infinite square well approximation of the  ${}^{1}S_{0}$  potential (Orange Curve). The potential is divided into three different regions, Region I ( $x \le 0.65fm$ ), Region II ( $0.65 < x \le 1.65$ ), and Region III  $x \ge 1.65fm$ .

The functional form of the reactant and product wavepackets at time t = 0 in the coordinate representation is given in eq 9. The reactant/product wavepackets are defined as a Gaussian centered at  $x = x_o$  with the spread of  $\Delta x_o$  and traveling with the momentum of  $k_o$ . The same wave function can be expressed in the momentum representation as shown in eq 10. From Heisenberg's uncertainty principle, it is clear that an increase in the  $\Delta x_o$  spread in the coordinate space results in a decrease in the momentum representation and vice versa.

$$f_{in}(x, t = 0) = \left(\frac{1}{2\pi\Delta x_0^2}\right)^{1/4} \exp\left\{\left[\frac{-(x - x_o)^2}{4\Delta x_o^2} + ik_o(x - x_o)\right]\right\}$$
(9)

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$$\Psi_{in}(k, t = 0) = \left(\frac{2\Delta x_0^2}{\pi}\right)^{1/4} \exp\{\left[-\Delta x_o^2(k - k_o)^2 + ix_o k\right]\}$$
(10)

Parameters are chosen carefully for eq 10 such that the wavepacket should only contain either positive or negative contribution of the momentum else the wavepacket splits up (For more information please refer to the Supporting Information). Figure 3 plots the scaled potential V(x) and



**Figure 3.** Absolute value of the Møller states  $|^{\mp}\Psi_{\pm}^{x}\rangle$  in the position representation eq 9. The potential V(x) is also shown in the solid Azure curve. The potential Absolute values of the wavepacket are scaled by the factor of 0.1 and 15 respectively.

the amplitude of the reactant and product Møller states in the position representation. Figure 3 shows that none of the wave packet is present within the potential, so there is no need to perform the initial propagation of the wave-packets to the asymptotic limit under the channel asymptotic Hamiltonian and subsequent back-propagation under the full channel Hamiltonian (eq 2). Thus, in this specific scenario, these states already correspond to the Møller states as outlined in the eq 3. Figure 4 plots the amplitude of the reactant (Azure) and product(Orange) Møller states in the momentum representation. In the legend ,  $\Psi^k_+$  subscript + (-) corresponds to reactant(product) Møller state and the superscript + (-) corresponds to the sign of contributing k values. The reactant Møller state has contributions from negative values of k and would propagate toward the interaction region and interact with the semi-infinite well.

Referring back to the TD theory of reactive scattering discussed in section we clearly see that there is no internal degree of freedom and we can represent the initial wavepackets eq 10 in the plane wave basis and get the  $\eta_{\pm}(k)$  values and the Hamiltonian matrix (H = T + V) which can be expressed as a linear combination of Pauli matrices. Since we are working with the plane wave basis the Kinetic Energy (KE) *T* matrix will be diagonal and easier to implement. We discretize the *x* and *k* space in 256 grid points since we encode the initial wave



**Figure 4.** Absolute value of the reactant  $| \neg \Psi_{+}^{k} \rangle$ ) and product  $| \neg \Psi_{-}^{k} \rangle$ ) Møller states in the momentum representation eq 10.

function using binary encoding this problem requires 8 qubits  $(\log_2(256))$  to encode the wave function. Since we are already starting from the reactant and product Møller states the operators  $O_{\gamma}(t)$  and  $O_{\gamma'}$  defined in eq 6 and eq 7 reduces down to  $e^{-iHt}U_r$  and  $U_p$  respectively.

The correlation function in this example is defined as  $C_{+k,-k}(t) = \langle +\Psi_-^k | \exp\{-iHt\}|^-\Psi_+^k \rangle$ . In order to calculate the correlation function at time t we need to propagate the reactant Møller state until time t and take the inner product with the product Møller state. Figure 5(a) the peak of the wave packet has progressed toward the interaction region and since the wavepacket is composed of a range of different k values the wavepacket gets broadened (Since, V(x) = 0 in this region). However, no informative data has been gathered at this stage, as the wave packet has not yet entered the interaction region.

The quantum simulation results can be obtained by creating a quantum circuit that only uses the state preparation  $|q_r\rangle$  quantum registers, and initiate the reactant Møller state, then we apply the propagator and implement this quantum circuit using the state vector simulator in Qiskit.

Figure 5(b) shows the scaled absolute value of the reactant propagated wavepacket at  $t = 0.24\tau_v$  The wave packet's higher momentum components have now entered the interaction region, engaging with the barrier. In the course of this interaction, the overall energy within the well area rises, characterized by an exchange of kinetic energy for potential energy. No observable signs of bifurcation are evident. It is evident from Figure 5(c) that at time  $t = 0.56\tau_v$  the wavepacket postcollision begins to exit the interaction region, having acquired information about the potential. Concluding at t = $0.97\tau_{\nu}$  in Figure 5(d) the calculation is essentially complete, with only the lower momentum components yet to exit. The correlation function  $C_{-k,k}(t)$  is plotted in Figure 6 from the figure it is evident that the correlation function was initially zero since the wavepackets were propagating in the opposite directions but once the reactant Møller state gets reflected from the semi-infinite well the correlation function becomes significant and as soon as most of the reflected resultant wavepacket leaves the region around time 1.25  $\tau_v$  the correlation function becomes zero and stays the same.

Figure 7 plots the amplitude of the scattering matrix element. Since the entire waveform should be reflected from the potential barrier we anticipate the scattering amplitude should be equal to one. However, the lower sampling rate fails to align with this expectation due to a suboptimal choice of step size. The lower sampling rate, approximately two samples per femtometer, implies that the square well takes on more of a trapezoidal shape rather than a square one.



**Figure 5.** Scaled absolute value of the Møller states  $|^{\mp}\Psi_{\pm}^{*}\rangle$ ) in the position representation eq 9. The potential V(x) is also shown in the solid Azure curve. Blue curve: product Møller state, Red curve: propagated reactant Møller state at time (a) t = 0.12, (b) t = 0.24, (a) t = 0.56 and (a) t = 0.97. Yellow circles: Quantum simulation of the reactant Møller state propagation.



Figure 6. (a) Real and (b) Imaginary contributions to the correlation function at time *t*. The solid blue curve corresponds to the classical simulation results and the orange discrete points is the result from quantum simulation.



**Figure 7.** Amplitude of the Scattering matrix element  $S_{-k,k}(E)$ . The blue curve corresponds to classical numerical calculation, the dashed orange curve denotes the exact expected analytical result and the red circular markers represent the result from the quantum simulation.

Addressing this limitation, increasing the sampling rate by higher orders of magnitude rectifies the issue, and the anticipated scattering amplitude of one should be achieved. It is essential to note that both solutions reveal a ringing effect at the upper and lower energy limits, which remains consistent regardless of the sampling rate. The occurrence of this ringing phenomenon is attributed to the division by the product of the expansion coefficients  $\eta_{\pm}(k(E))$ , known for their small values in this energy region. In the next example, we include vibrational degrees of freedom and apply the proposed algorithm to calculate scattering matrix elements and reaction probabilities of the colinear hydrogen exchange reaction.

**Colinear Hydrogen Exchange Reaction.** Given its simplistic nature  $H + H_2$  chemical reaction is conventionally recognized as the "Hydrogen atom<sup>50</sup> of chemical reactions" and has held significant importance in theoretical chemistry. In 1929 London, Eyring, and Polanyi demonstrated the existence of a potential energy barrier<sup>51</sup> to the reaction by providing an approximate solution to the electronic Schrödinger equation. Since then the availability of better computational tools along with precise theoretical models fueled the advancement of the field forward which eventually helped to understand different experimental observations.<sup>52</sup>

$$H_a + H_b H_c(\nu) \to H_a H_b(\nu') + H_c \tag{11}$$

In this section, we employ the proposed quantum algorithm to calculate scattering matrix elements of the colinear hydrogen exchange reaction eq 11. The reaction involves in-elastic scattering between the distinguishable hydrogen atoms and a hydrogen molecule. Hydrogen exchange happens during the chemical reaction where one of the hydrogen atoms substitutes another hydrogen atom. Rotationally averaged scattering matrix components are calculated using the time-dependent technique based on the Möller operator formulation of scattering theory (Section). In this chemical process, it proves beneficial to consider three coordinate systems as depicted in Figure 8. The coordinates  $R_1$ ,  $r_1$  ( $R_2$ ,  $r_2$ ) are ideally tailored for



**Figure 8.** Illustration showing linear arrangement of the three distinguishable Hydrogen atoms  $H_a$ ,  $H_b$  abd  $H_c$ . Reactant channel ( $R_1$ ,  $r_1$ ) and product channel ( $R_2$ ,  $r_2$ ) coordinates are along with the bond coordinates (X, Y) are shown. The arrow denotes the direction Hydrogen atom  $H_a$  is traveling.

describing dynamics within the reactant (product) arrangement channel I (II). In channel I the dynamics is solely governed by the asymptotic Hamiltoninan  $H_0^{(1)}$  eq 12 (Which is separable into translation between  $H_a$  and COM of  $H_bH_c$  + Internal vibration in  $H_bH_c$ ). In a similar fashion coordinates labeled  $R_2$  and  $r_2$  in Figure 8 best describes the dynamics in the product channel  $H_aH_b(v') + H_c$  and in the large limit of  $R_2$  the dynamics is explained by asymptotic hamiltoninan  $H_0^{(2)}$  eq 13 (Which is separable into translation between  $H_c$  and COM of  $H_aH_b$  + Internal vibration in  $H_aH_b$ ).

$$H_0^{(1)}(R_1, r_1) = H_{rel}^{(1)}(R_1) + H_{vib}^{(1)}(r_1)$$
(12)

$$H_0^{(2)}(R_2, r_2) = H_{rel}^{(2)}(R_2) + H_{vib}^{(1)}(r_2)$$
(13)

The third coordinate system X and Y as shown in Figure 8 is used to describe Hamiltonian in the interaction region. Being a colinear system the transformation is straightforward is given by the relation eq 14.<sup>53</sup> The dynamics in the interaction region are governed by the kinetically coupled Hamiltonian<sup>54</sup> described in eq 15.  $p_X$  and  $p_Y$  represents momentum in the bond coordinates and V(X, Y) denotes the Liu-Siegbahn-Truhlar-Horowitz (LSTH)<sup>55–57</sup> potential energy surface (PES) as shown in Figure 9.

$$\begin{pmatrix} R_1 - \frac{1}{2}r_1 \\ r_1 \end{pmatrix} = \begin{pmatrix} X \\ Y \end{pmatrix} = \begin{pmatrix} r_2 \\ R_2 - \frac{1}{2}r_2 \end{pmatrix}$$
(14)

$$H = \frac{p_X^2}{m_H} - \frac{p_X p_Y}{m_H} + \frac{p_Y^2}{m_H} + V(X, Y)$$
(15)



**Figure 9.** Illustration showing probability density  $(||\psi_{in}^{1,0}(X, Y)\rangle|^2)$  at time t = 0 of the reactant channel wavepacket described in eq 16. The contour plot of the LSTH PES is also shown.

The reactant wavepacket is created by calculating the direct product between an arbitrary linear combination of onedimensional plane waves characterizing the relative motion of the atom  $H_a$  and the diatom  $H_bH_c(v)$ , and a single vibrational eigenstate, (v) of the diatom  $H_b H_c$ . Similarly, an outgoing channel wavepacket that corresponds to  $H_a H_b(v') + H_c$  is calculated as a direct product between an arbitrary linear combination of one-dimensional plane waves characterizing the relative motion of the atom  $H_c$  and the diatom  $H_aH_b(\nu')$ and a single vibrational eigenstate, (v') of the diatom  $H_aH_b$ . The reaction channel wavepacket  $|\psi_{in}^{1,0}\rangle$  at time t = 0 is created by directly multiplying the translational and vibrational wave functions. In eq 16 N corresponds to the normalization constant, the superscript in  $\psi^{\gamma, \bar{\nu}}$  denotes the channel  $\gamma$  and vibrational quantum number of v, A slice of LSTH- PES taken at a large value of  $R_1$  defines the asymptotic diatomic potential.  $H_{vib}^{1}(r_{1})$  is expressed in the Morse eigenbasis and diagonalized to extract the vibrational wave function  $(|\psi_{vib}^{1,0}(r_1)\rangle)$ . The product channel wavepacket can be defined in a similar fashion (Please refer to the Supporting Information).

$$|\psi_{in}^{1,0}(R_1, r_1)\rangle = N|\psi_{vib}^{1,0}(r_1)\rangle e^{-\Delta k_1^2(R_1 - R_1^0)^2 + ik_1^0(R_1 - R_1^0))}$$
(16)

We calculate S-matrix elements for the two inelastic exchange reactions, where we start with v = 0 in the reactant wavepacket and v' = 0, 1 in the product wavepackets. In this case, 10 qubits are required to represent the quantum state in the algorithm (2 qubits correspond to vibrational encoding and the rest to represent  $2^8 \eta_+(k_{\gamma})$ . The quantum algorithm is executed at each time t and the correlation function is calculated between the reactant  $(|\psi_{\perp}^{\gamma}\rangle)$  and product  $(|\psi_{\perp}^{\gamma'}\rangle)$ Møller states. Figure 10(a) (Figure 10(c)) shows the correlation function for  $H_a + H_b H_c (\nu = 0) \rightarrow H_a H_b (\nu' =$ 0(1) + H<sub>c</sub> case. It is evident that the quantum simulation results go well with the exact classical simulation. The Fourier transform of the calculated correlation function is used to calculate scattering matrix elements. Figure 10(b) and Figure 10(d) plots the transmission coefficient or the reaction probability which is defined as the absolute value square of the corresponding scattering matrix elements  $P_{\nu,\nu}(E) = |S_{+k,-k}^{\nu,\nu}|^2$ . These computations offer an authentic portrayal of the reaction dynamics, capturing all the important aspects of the reaction probabilities. As established in prior research,58 the interplay between direct and resonant components plays a pivotal role in shaping the overall curves depicted in Figure 10(b). The abrupt fluctuations around 0.6 and 1.0 eV arise due to the existence of internal excitation resonances at these energy levels.

# CONCLUSION

In this study, we introduced a quantum algorithm based on the TD Møller to compute scattering matrix elements for both elastic and inelastic scattering processes. To address the requirements for calculating the correlation function, we developed a Modified Hadamard test. The proposed algorithm was successfully applied to two distinct physical problems. Initially, we tackled the 1D semi-infinite well, serving as an approximation for the AV18  ${}^{1}S_{0}$  2-nuclei scattering potential. Subsequently, we extended the application to the colinear Hydrogen exchange reaction. Remarkably, the quantum simulation results demonstrated excellent agreement with classical results in both cases.

Moreover, the algorithm presents two significant sources of errors deserving careful consideration. The first originates from sampling errors associated with the Hadamard test. This error is tied to the estimation of the expected value of the correlation function based on a finite number of sample measurements. Through the application of Chernoff bound,<sup>59</sup> we established that the required number of samples to estimate the expected

value with an absolute error  $\epsilon$  scales as  $O\left(\frac{1}{\epsilon^2}\right)$ .

The other source of error comes from the Trotter-Suzuki approximation of the propagator  $(\exp(-iHt))$ . Accurately assessing Trotter approximation errors is crucial for optimizing Hamiltonian simulations. Efforts<sup>60</sup> have been made to devise a theory that leverages the commutativity of operator summands to yield more tighter error bounds. Despite these endeavors, challenges persist due to the intricacies involved in obtaining analytical expressions for the error bounds and understanding the impact of the approximation on quantum simulation errors. In the future, we would like to extend this formalism from the colinear Hydrogen exchange to include the rotational aspect in



**Figure 10.** (a) Absolute value of the correlation function  $C_{v_p=0,v_p=0}(t)$ , (c) Absolute value of the correlation function  $C_{v_p=1,v_p=0}(t)$ . (b) The probability of the reaction  $P_{v_p=0,v_p=0}$ . (d) The probability of the reaction  $P_{v_p=1,v_p=0}$ . The solid blue curve corresponds to the classical simulation results and the red (black) discrete points is the result from the quantum simulation.

the scattering process. This would open up new avenues to deeply understand molecular processes that exhibit quantum coherent control.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.4c01100.

Detailed expressions for the scattering matrix elements, a thorough look at the quantum algorithm, explanations about Hamiltonian encoding, quantum dynamics parameters, and error analysis (PDF)

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#### Notes

The authors declare no competing financial interest.

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