Quantum Molecular Dynamics Calculations on H + H_2 , H_2 + H_2 , H_2 O/Cu(111), and Anthracene with Various Masses

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Abstract: In this work, a theoretical scheme on quantum molecular dynamics in curved Schwarzschild spacetime is developed. To this end, the gravitational field is introduced by revising the kinetics energy operator (KEO) rather than by adding Newtonian gravitational interaction in the potential energy surface (PES) due to the important role of the metric tensor in deriving the KEO. To test the present Schrödinger-type framework, spherically symmetric Schwarzschild spacetime is chosen to explore (1) the H + H₂ reaction dynamics, (2) the H₂ + H₂ scattering dynamics, (3) dynamics of dissociative chemsorption of H₂O on Cu(111), and (4) the spectrum band of anthracene cation. Extensive numerical calculations in curved space predict that reaction or scattering probability and spectrum band decrease abruptly to zero as the gravitational strength increases, indicating the remarkable role of gravitational field in chemical dynamics and naturally leading to effects of gravitational time dilation of the molecular systems. However, it is noteworthy that moderate gravitational field can significantly enhance dynamical resonance in the low-energy region, if such resonance exists in flat space. Finally, based on the present numerical results discussions on the quantum molecular dynamics in curved space are given.

Keywords: Schwarzschild Space; Quantum Molecular Dynamics; Curved Space; kinetics energy operator

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I. INTRODUCTION

As predicted by gravitational time dilation^{1–3}, time passes slower in stronger gravitational field because gravity warps the fabric of spacetime. In this context, an observer closer to a massive object will experience time at a rather slow rate compared to the one further away. In this work, introducing chemistry in curved space we will inspect the effects of gravity for molecular systems in chemical language. On the other hand, our understanding on chemical reaction and molecular properties^{4–11} stems from empirical observations on earth^{12–16} with very weak gravity and low velocit (called classical approximation). However, we inevitably encounter chemical phenomena that demand new explanations when we detect molecules near celestial bodies with enormous mass or navigate in close proximity to them. These scenarios compel us to further develop formalism theory of chemistry in curved space. Main goal of this work is to primitively resolve such problems by developing a theoretical scheme on quantum molecular dynamics in a curved space.

Solving nuclear Schrödinger equation (SE), $i\partial_t \Psi(t) = \hat{H}\Psi(t)$, one can directly explore chemical dynamics^{11,17–20} by either examining the transformation between the eigenstates of reactant and product, known as time-independent quantum scattering, or investigating the time evolution of the wavepacket, known as time-dependent wavepacket propagation. In SE, $\Psi(t)$ represents nuclear wave function and $\hat{H} = \hat{T} + \hat{V}$ nuclear Hamiltonian operator, where \hat{T} and \hat{V} operators are kinetic energy operator (KEO) and potential energy surface (PES), respectively. In above solutions of quantum molecular dynamics, the requirement of a flat spacetime is frequently overlooked and supposed to be always true¹¹. This work, on the other hand, presents a general Schrödinger-type way to unify the theory of chemical reaction and the relativity theory of spacetime to predict quantum molecular dynamics in 4D curved spacetime. To numerically demonstrate such revisions, the H + H₂^{21,22}, H₂ + H₂²², H₂O/Cu(111)²³, and photoelectron (PE) spectrum of anthracene cation²⁴ are employed through the multiconfigurational time-dependent Hartree (MCTDH) product method and its multilayer version (ML-MCTDH)^{14,25–32}.

In addition, by directly adding the Newtonian gravitational potential into the potential term, the Schrödinger-type equation (STE)^{33–36} has drawn increasing attentions to be often employed as the conceptual and technical platforms in understanding the interaction of quantum particle with weak gravity under the classical approximation in flat space. Over the past years, Anastopoulos and Hu^{33,35} explored the structure of STE in relation to the well-tested theories of general relativity and quantum field theory (QFT) which govern the dynamics of classical spacetimes and quantum

matter field. In the STE framework, effects of general relativity are represented by the metric tensor of the spacetime and quantum effects are reproduced by non-relativistic quantum dynamics which is the non-relativistic limit of QFT. Thus, it is easy to slip into believing that STE is a limiting case^{33–36}. However, when the limit of general relativity and non-relativistic limit are taken on face, many theoretical points are ignored. Based on the present theory and calculations, we will discuss on the perspectives of chemical dynamics in curved spacetime beyond the STE framework.

II. THEORY AND CALCULATION

Given in Table I are assumptions of the present work. First, the present thoery requires [3 + 1]decomposition¹⁻³ of the four-dimensional (4D) spacetime which is globally foliated into a oneparameter family of spacelike three-dimensional (3D) slices Σ_t and a time coordinate t leading the Arnowitt-Deser-Misner (ADM) equations 1-3 as equations of motion (EOMs) of the gravitational field. The metric tensors for 4D spacetime and 3D slice are denoted by $g_{\mu\nu}$ and γ_{ij} , respectively. Moreover, the main assumption is that the geometric characteristics of Σ_t remain time-invariant throughout the molecular process. Thus, the temporal coordinate is classical, where the concept of absolute time is accepted, and thus the molecular processes are supposed to be completely decoupled with the evolution of the spacetime. By the above assumptions, incorporating curved spacetime into quantum molecular dynamics in the present work is straightforward through the revised KEO term. Of course, problems start to arise as we go further and include additional effects from relativity. For instance, the inner product between quantum states defined in the case with the existence of absolute time is not Lorentz invariant³⁶. If one wants to describe chemical dynamics in a manner consistent with relativity, a covariant formalism must be adopted to make the EOMs and the inner products Lorentz invariant. The QFT in curved spacetime^{37–39} enables it in the low-energy regime. We will return to this point later.

Turning to chemistry, the conformation of an N-atomic molecule in 3D slice is homeomorphically represented by a single point in a 3N-dimensional smooth manifold, called configuration space, locally homeomorphic to \mathbb{R}^{3N} . Such a homeomorphism mapping between the slice and configuration space exists because they share certainly topological invariants. Like the 3D slice, the geometry of configuration space is characterized by the metric $\tilde{\gamma}^{ij}$ for the Cartesian coordinates. By a set of generalized coordinates q, the KEO has been thoroughly derived through the

polyspherical approach^{40–60} in the form

$$2\hat{T} = -J^{-1}\partial_{\iota}Jg^{\iota\kappa}\partial_{\kappa}, \quad J = \left|\det\left(\frac{\partial x^{(i)}}{\partial q^{(\kappa)}}\right)\right| = \left|\det\left(\partial_{\kappa}x^{(i)}\right)\right|,\tag{1}$$

where the metric $g^{\iota\kappa}$ for \boldsymbol{q} is given by $g^{\iota\kappa} = \tilde{\gamma}^{ij}\partial_i q^{(\iota)}\partial_j q^{(\kappa)}$ and $g_{\iota\kappa} = (g^{\iota\kappa})^{-1}$ leading to J = $(|\det(g^{\iota\kappa})|)^{-1/2}$. Adding the PES, we have got nuclear Hamiltonian operator for subsequent dynamics calculations. By ML-MCTDH, the total time-dependent nuclear wave function is expressed in terms of a tensor in a hierarchical Tucker format, represented by a tree-like structure (called ML-tree). Inserting the multilayer Ansätze into the Dirac-Frenkel variational principle, the ML-MCTDH EOMs for arbitrary layering schemes and for all intermediate quantities have been derived^{29–32}. These coupled non-linear differential equations can be efficiently solved using standard numerical tools^{27,29–31} to obtain time-dependent propagated wavepacket. In computing reaction or scattering probabilities, we analyse the flux of the wave function fraction through the separation surface by adding into the Hamiltonian operator a complex absorbing potential (CAP)^{61,62}, $V_{\text{CAP}} = -\mathrm{i}\eta \cdot (s - s^{(\text{CAP})})^n \cdot \Theta(s - s^{(\text{CAP})}) \cdot \Theta(t - t^{(\text{CAP})})$, where n and η are order and strength of the CAP, while s and $s^{(CAP)}$ represent reaction coordinate and the separation surface, respectively. Here, $\Theta(\cdot)$ is step function and $t^{(CAP)}$ means the time that the CAP appears. By flux analysis through the CAP, we can then compute the probability as function of collision energy E. For the spectrum band of anthracene cation, assuming the Condon approximation, the Fourier transform of autocorrelation function $C(t) = \langle \Psi(0) | \Psi(t) \rangle$ predicts spectrum band²⁴. Here, we also use the so-called t/2-trick for the autocorrelation function, which doubles the length of the autocorrelation function.

For clarity, the Schwarzschild metric is chosen, where the spacetime is around a static and spherically symmetric gravitating source with mass M in vacuum. The event interval in Schwarzschild sapcetime is given by

$$ds^{2} = -\left(1 - \frac{2M}{r}\right)dt^{2} + \left(1 - \frac{2M}{r}\right)^{-1}dr^{2} + r^{2}d\theta^{2} + r^{2}\sin^{2}\theta d\phi^{2}$$
$$= -\left(1 - \varrho\right)dt^{2} + \left(1 - \varrho\right)^{-1}dr^{2} + r^{2}d\theta^{2} + r^{2}\sin^{2}\theta d\phi^{2}, \tag{2}$$

where r_s is the Schwarzschild radius r_s and r the distance between the system and the mass source M. The dimensionless parameter $\varrho = 2M/r = r_s/r$ determines the strength of influence of gravity. According to Equation (1), one can revise the KEOs in flat space obtaining those in Schwarzschild space. To this end, the molecular systems are positioned at a distance r from the origin point and oriented the reaction or scattering coordinate along the radial direction. Moreover, the entire

systems are supposed not to undergo orbital rotation around the spacetime origin. This is possible because we restrict the treatment to the classical regime, where absolute time still exists and thus the molecular velocity must remain relatively low.

III. RESULTS AND DISCUSSIONS

A. Gravitational Time Dilation in Chemistry

Illustrated by Figures 1 and 2 are comparisons of computational results in Schwarzschild sapce with those in flat space for the H + H₂ and H₂ + H₂ systems, respectively. While Figure 3 illustrates similar comparison for the H₂O/Cu(111) system, Figure 4 illustrates the spectrum band of the anthracene cation in the \tilde{B} 2A_u state with various values of ϱ . In these figures, the black lines are computational results in the flat space. The cyan, maroon, light yellow, light green, violet, yellow, green, blue, and red lines represent reactive or scattering probabilities for ϱ values of 0.60, 0.50, 0.40, 0.30, 0.20, 0.10, 0.05, 0.03, and 0.01, respectively. In summary, the present numerical results demonstrate the following two point. First, the gravitational field drastically reduces the reaction probability, scattering probability, spectrum band making these molecular properties approach to zero at ϱ > 0.60. Second, at an appropriate strength, the gravitational field appears to amplify the lowest-energy resonance of the reaction if there exists one. Third, the gravitational field causes the spectrum band to undergo a blueshift.

For the H + H₂ reaction, *i.e.* typical chemical reaction in the gas phase, Figure 1 indicates that in strong gravitational field with $\varrho > 0.10$, all reaction probabilities exhibit a minor peak in the low-energy region around 0.05 eV and a large peak in the high-energy region around 0.4 ~ 0.5 eV. In particular, as ϱ increases from 0.20 to 0.60, the reactive probability at the region of 0.4 ~ 0.5 eV increases and then decreases, reaching its maximum of near unit at approximately $\varrho = 0.30 \sim 0.40$. In this case, the reactive probability drops abruptly to zero once the energy exceeds a certain energy in the range from 0.6 to 1.5 eV, that increases rapidly as ϱ decreases. This is unexpected because the reactive probability tends to approach a non-zero value once the impacting energy exceeds a certain value for typical reactions. Furthermore, this situation changes significantly when ϱ falls below 0.10, and the reaction probability gradually approaches normal when ϱ decreases below 0.05. An interesting phenomenon in the low-energy region of 0.3 ~ 0.6 eV is that the reaction probability initially increases rapidly to nearly 0.95 as ϱ increases from

0.00 to 0.40, then approaches sharply to zero as ϱ continues to increase from 0.40 to 0.60. When ϱ exceeds 0.60, the reaction probability remains almost invariably zero. For typical chemical reaction on the surface, Figure 3 illustrates dissociative chemsorption probabilities of $H_2O \rightarrow H + OH$ on the Cu(111) surface. In flat space, as previously discussed²³ the dissociation probability is approximately equal to zero, when the impacting energy is less than roughly 0.15 eV. At impacting energy of more than 0.15 eV, the dissociation probability increase from 0 to $\sim 10^{-2}$. In curved space, the situation is similar to the results of $H + H_2$, as shown in Figure 1, where the dissociation probabilities of higher-energy region become samller than that in flat space and fast approach to nearly zero when $\varrho > 0.10$. At low-energy region, the situation becomes complex likely caused by numerical calculations.

Having given reaction probabilities of typical reactions in the gas phase and on the surface, now we should turn to examples of molecular properties. For the H₂ + H₂ scattering, as illustrated by Figure 2, the situation is similar to the cases of $H + H_2$ and $H_2O/Cu(111)$, that is the scattering probability depends on the value of ρ . As the impacting energy increases, a larger value of ρ leads to a rapid drop in the scattering probability from unit to nearly zero. Noting that no reaction occurs for the $H_2 + H_2$ scattering process, the scattering probability must be close to unit in the flat space. However, the scattering probabilities with non-zero values of ϱ as shown in Figure 2 imply that the two H₂ molecules form a weak dimer at non-zero impacting energy. This dimer mat be caused by the existence of gravitational field. Furthermore, increasing the value of ρ accelerates the decay rate of the scattering probability. For instance, the scattering probabilities approach to zero at ~ 0.28 , ~ 0.45 , and ~ 1.5 eV for the ϱ values of 0.50, 0.30, and 0.10, respectively. Obviously, this is because of the existence of the curved space. In this context, the enhanced gravity in the curved space may cause two objects to mutually attract and form a dimer. Next, Figure 4 illustrates spectrum bands of the anthracene cation in the \tilde{B}^2A_u state at the cases with various values of ρ . The parameter ρ exerts a dual influence on the spectrum bands. On one hand, the spectral intensity decreases with increasing ρ from zero. When $\rho < 0.10$, the change in spectral intensity remains relatively insignificant. However, it becomes markedly evident once ϱ exceeds 0.10. When ϱ is large enough, the spectral intensity tends to fast approach zero. On the other hand, the band center shifts toward higher energy regions as ϱ increases. When $\varrho < 0.10$, the spectral position shows minimal variation, with the band center shifting slightly toward higher energy regions by approximately 0.01 eV (about 806 cm⁻¹). In contrast, when $\rho > 0.10$, the band shifts rapidly to higher energy regions. For instance, the band positions are 9.21, 9.31, 9.52, and 9.78 eV at the ρ

values of 0.10, 0.30, 0.50, and 0.60, respectively.

B. Discussions

Now, discussions on the present results shown in Section III A must be given. First of all, numerical results predict that the reaction probabilities and spectrum bands in Schwarzschild spacetime clearly depend on the parameter ρ . These results also clearly imply that time flows slower in stronger gravitational fields and faster in weaker ones. This is not surprising because ρ has been introduced in the KEO that plays one of importance roles in quantum dynamics calculations with the other importance component being PES. Essentially, since the Schwarzschild metric (see Equation (2)) characterizes geometry of the curved space, the present KEOs introduce revisions on the masses of the molecular systems. As given by Equation (2), value of ϱ characterizes strength of the gravitational field and thus related with effective mass of the reaction or scattering coordinate (called dynamical coordinate), which is consistent with the fact that curvature of spacetime is associated with the mass. Furthermore, to easily revise the KEO, the molecular systems are set to be positioned at a large enough distance r from the origin of Schwarzschild spacetime and be oriented the dynamical coordinate along its radial direction. The former assumption that r is large enough effectively localizes the entire molecule within an approximately confined region of space, implying that each atom experiences a nearly uniform curvature of the space, that is equivalent to the strength of gravitational field. It allows for a consistent definition of the metric tensor associated with individual atoms. Next, due to the spherical symmetry of Schwarzschild space, the latter assumption implies that the total rotations of the system as well as non-reactive motions remain unaffected by the gravitational field. Therefore, one can ignore the angular elements of the Schwarzschild metric and thus only revise the kinetics energy terms associated with the reaction coordinate. Furthermore, we assume that the entire systems do not undergo orbital rotation around the origin of Schwarzschild space making speed of the entire system remain much smaller than the speed of light, as given in Section II. It allows us to ignore orbital angular-momenta of the entire systems and thus further simplifying the KEOs and subsequent calculations. In addition, it allows us to use the concept of absolute time and to employ revised SE for dynamics calculations.

Second, due to the absolute time, we ignore the time element $-(1 - \varrho)$, like done in Newtonian mechanics, and thus time is just a parameter of dynamics. This is a strong assumption making the spatial and temporal coordinates be treated separately. However, it also implies, as we have

emphasized on various occasions, that time is classical rather than relativistic. Consequently, the resulting Schrödinger-type EOM with only revised KEOs, are not covariant under the Lorentz transformation. Therefore, the present numerical results on quantum dynamics are of qualitative significance only. On the other hand, if the concept of absolute time is still employed, one should note another problem how about the coupling between the system and geometry of the spacetime. This problem might be solved by deriving new EOMs which contain the Schrödinger-type equation and the ADM equations. The former predicts motions of the molecular system, while the latter predicts time-dependent metric tensor and curvature of the slice. Such solution requires covariant characteristic of the EOMs making the question still opens. To overcome this problem, despite the uses of [3 + 1] decomposition and the concept of absolute time, a complete theory should incorporate Lorentz covariant EOMs leading to the chemical dynamics based on QFT. This implies a fundamentally change of the framework of current quantum molecular dynamics in flat Minkowski spacetime where the EOMs are Lorentz covariant. Numerous previously reported attempts¹¹ have demonstrated the feasibility of such change. Then, extension of QFT to curved spacetime should be further made to consider quantum processes in gravitational field^{37–39}. Although it is still not a full theory of quantum gravity, the QFT in curved space is an effective framework^{37–39} for chemistry in curved space.

Finally, since the spherically symmetric Schwarzschild spacetime is neither the sole solution to the ADM equations nor can satisfy general spacetime, let us turn to other kind of curved spacetime. We provide some typical solutions of the ADM equations and their physical insight in the first SI file. As confirmed through experimental observation, the gravitational plane wave represents another distinct type of solution to the ADM equations. The infinitesimal interval in this spacetime with gravitational plane wave which propagates along the *z* axis satisfies

$$ds^{2} = -dt^{2} + dz^{2} + (1 + h_{+}(u))dx^{2} + (1 - h_{+}(u))dy^{2} + 2h_{\times}(u)dxdy,$$
(3)

where u = t - z is retarded time while $h_+(u)$ and $h_\times(u)$ are plus polarization and cross polarization, respectively. For simple, assuming the gravitational plane wave with a single frequency ω , its plus and cross polarizations are given by

$$h_{+}(t-z) = A_{+}\cos\left(\omega(t-z) + \phi_{+}\right), \quad h_{\times}(t-z) = A_{\times}\cos\left(\omega(t-z) + \phi_{\times}\right), \tag{4}$$

where ϕ_+ and ϕ_\times are phases. Equation (4) implies that the gravitational plane wave is a ripple along the z axis in spacetime propagating at the speed of light. The plus and cross polarizations

deform spacetime in quadrupolar patterns. Since the Cartesian coordinates are used to describe the spacetime with gravitational plane wave, it may be influence the PE spectrum band where the vibrational normal modes are linear functions of Cartesian coordinates.

C. Perspectives

Now, we would like to give perspectives on the quantum molecular dynamics in curved space. First of all, as discussed above in Section III B, since the STE framework is not covariant under Lorentz transformation, current goal of the quantum molecular dynamics is to overcome this problem in falt space leading to chemistry of high-speed molecules based on QFT in flat space¹¹. This will be followed by developing EOMs of molecules coupled with the geometry of spacetime based on QFT in curved spacetime making chemistry of molecules with remarkably large velocity possible, such as chemistry on stars S62 and S4714 with \sim 8% the speed of light $^{63-65}$. Now, we must qualitatively examine the relevant scale of QFT in curved spacetime and its matching degree with molecular processes. We would like mention that at this case the molecular system with particles becomes quantum field. The mass and energy of the quantum field must be well below the Planck scale, namely $m_{\rm Planck} \sim 6 \times 10^{18}$ dalton and $E_{\rm Planck} \sim 10^{28}$ eV, ensuring that the back-reaction of the field on the spacetime geometry is small enough. Compton wavelength of the particle in the system must be smaller than the curvature radius making the concept of a localized particle possible. Moreover, spatial scales of the system must be much larger than the Planck length $l_{\rm Planck} \sim 10^{-25}$ Å, while the spacetime changes slowly compared to the characteristic time scale of the quantum field. Rapid changes in geometry can lead to excessive particle creation violating the limitation for chemistry (physically, called semi-classical approximation). Obviously, motions of the molecular system (that is quantum field now) satisfy all of the above restrictions.

Second, it should be noted that the semi-classical approximation, where geometry of the space-time must not change rapidly, effectively ensures the persistence of the one-to-one mapping relationships. This is important in studying chemistry in curved spacetime where no particle creation or annihilation. Furthermore, molecular dynamics based on QFT reformulates the motions of different particles into the dynamics of various types of quantum fields, while the second quantization of these fields conversely allows a return to the description of particle behavior. By the perspectives of field, coupling between matter fields and gravitational field becomes possible implying that one can consider the chemical dynamics beyond the concept of absolute time. Moreover, we

refer to Reference¹¹ for detailed discussions on the applications of QFT to quantum molecular dynamics. Now, we must turn to the separation of electrons and nuclei, which is an important issue in molecular dynamics. The Born-Oppenheimer approximation (BOA) and non-adiabatic methods beyond it are usually adopted to separate chemical dynamics into electronic structure and molecular dynamics, which are connected through the PES term. Similarly, an adiabatic approximation and its non-adiabatic revisions also exist in QFT due to the difference between fast and slow fields. By the adiabatic approximation, a slowly changing field can be treated as a fixed background. The other, fast-reacting quantum fields are then studied as they move and fluctuate within this background. Similar to the Higgs mechanism but unlike the BOA, the field associated with electronic motions is considered as the background (slow field) of the field associated with nuclear motions (fast field). When the adiabatic approximation breaks, the fields become strongly coupled with each other, jumping energy levels, creating new particles, or dumping energy back into the background field.

Finally, as the simplest application of QFT to molecular dynamics, since the effects of nuclear spin are often igonred in considering chemical dynamics, EOM of the quantum field associated with nuclei can be chosen as the generalized Klein-Gordon (KG) equation

$$\left(\Box_g + m^2 + \xi R\right)\phi = V\phi,\tag{5}$$

where *R* is the Ricci scalar curvature, ξ a coupling constant, and ϕ field function for nuclei motions. In Equation (5), \Box_g is the covariant d'Alembertian operator satisfying

$$\Box_g \phi = \frac{1}{\sqrt{-g}} \partial_\mu \Big(\sqrt{-g} g^{\mu\nu} \partial_\nu \phi \Big), \tag{6}$$

where g is the determinant of the metric tensor $g_{\mu\nu}$. Of course, in addition to problematic "negative probability" densities, several theoretical problems arisen from the generalized KG equation need more work to resolve. For instance, introduction of the term of V requires a more general covariant form of Equation (5). To this end, the interaction V should be introduced via minimal coupling by replacing the ordinary derivative with the covariant derivative. In this context, the use of $\partial_{\mu} \rightarrow \nabla_{\mu} = \partial_{\mu} - iA_{\mu}$ makes the interaction become potential field A_{μ} . Moreover, the generalized KG equation as given by Equation (5) is not renormalizable which limits its use to effective theories or external fields.

IV. CONCLUSIONS

The present work proposes a primitive theory on chemical dynamics in curved spacetime to introduce classical gravitational field in chemistry. In particular, the present goal is quantum molecular dynamics in Schwarzschild spacetime which is a spherically symmetric solution to Einstein's equations containing a central black hole at the origin. Within the literature, the Newton-Schrödinger equation provides a framework for describing quantum dynamics in Newtonian gravity assuming a flat spacetime and introducing the gravitational potential as a perturbative term to the PES. This method is unable to study dynamics with slightly stronger gravitational field where the apcetime is curved. In this work, noting the importance role of the metric tensor in deriving the KEO, by revising the KEOs we explore dynamics in curved space for (1) the H + H₂ reaction, (2) the H₂ + H₂ scattering, (3) dissociative chemsorption of H₂O on Cu(111), and (4) the spectrum band of anthracene cation. Extensive numerical MCTDH and ML-MCTDH calculations predict that the curved spacetime makes dynamical properties, such as reaction or scattering probability and spectrum band, decrease abruptly to zero as the gravitational strength increases. These numerical results clearly indicate role of strong gravitational field in molecular properties. This is thus a chemical perspective on so-called gravitational time dilation. Finally, the present theory represents only a preliminary and framework model and thus incorporates several assumptions, which inevitably introduce a considerable degree of approximation. To overcome these limitations, we further propose potential strategies and disucss future plans for addressing these assumptions in subsequent work.

Finally, at the end of this work, we must mention that the present theory on chemistry in curved space differs from the so-called black hole chemistry⁶⁶ completely in substance. Despite its nominal resemblance to the present work, black hole chemistry is an thermodynamic framework for the properties of black holes through the perspectives of chemical-thermodynamic analogies. In black hole chemistry, the cosmological constant is treated as a thermodynamic pressure, leading to a rich phase structure where black holes exhibit behaviors analogous to conventional matter and its thermodynamic properties⁶⁶, such as van der Waals fluids, phase transitions, triple points, and so forth. The mass of the black hole is identified not as internal energy, but as chemical enthalpy, while a newly defined thermodynamic volume allows for the formulation of equations of state and the exploration of mechanical work. It has revealed profound connections between gravity, thermodynamics, and chemistry, opening new ways for understanding quantum gravity and emergent

spacetime. Therefore, black hole chemistry is essentially the physics on black hole with chemical and phase thermodynamics as its tool⁶⁶. Since chemistry is the interplay of matter and a vast subject with many diverse applications, black hole chemistry may prove to be just as multi-faceted.

SUPPLEMENTARY MATERIAL

The Supporting Information documents are available free of charge at https://www.doi.org/XXXX. In the first Supporting Information file, we give details of the present theory and numerical calculations on the benchmarks. In the second Supporting Information file, we give details of the vibrational normal coordinates of anthracene radical cation.

INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

All data have been reported in this work. The data supporting this article have been included as part of the Supplementary Information.

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equation which is further transferred and implemented by the ADM equations while the 4D spacetime is [3 + 1] decomposed. Second, the gravity only provides a geometric background of spacetime. Thus, the lapse function and shift vector are introduced, while the initial data TABLE I: Main assumaptions of the present theory which presents the molecular motions in curved spacetime. The second column gives satisfy Hamiltonian and momentum constraints. Third, the geometric characteristics of the slices Σ_t remain time-invariant throughout the assumptions are actually arisen from three assumptions, as given in the main text. First, the metric tensor is a typical solution of Einstein target of each assumption. The third column describes the assumptions. The rightmost column gives remarks of these assumptions. It should be noted that these assumptions are proposed by assumptions of the quantum field theory in curved space. The present six reaction process. This is arisen from the assumption that curved spacetime only affects the geometry.

No.	Target	Description	Remark
1	metric	classical (non-quantized)	
		Lorentzian metric $g_{\mu\nu}$	It is a typical solution of Einstein equation
2	gravity	not a dynamical field	It provides a geometric background of spacetime
3 a	coordinates transfer	coordinates transfer local Lorentz invariance b	Theories in curved space reduce to
			familiar flat-space theories at each point
4 a	generalization	minimal coupling	Derivatives are replaced with covariant
			derivatives while metric is inserted $^{\rm c}$
5 d	Time	no global time and no unique vacuum ^e	There is no global timelike Killing vector
			and no unique vacuum state
9 t	counteraction	no influence of molecule on the geometry	Semiclassical Einstein equation for the
			back reaction of molecular
			motions is not considered

^a The third and fourth assumptions encode that curved spacetime only affects the geometry but not the molecular motions.

^b Local Lorentz symmetry holds at every point in spacetime.

^c The flat-space equations are generalized to those in curved space by replacing derivatives with covariant derivatives and inserting the metric.

^d This assumption is arisen from the first assumption for metric.

^e This assumption indicates that particle becomes observer-dependent rather than observer-independent as usually expected.

f This assumption is arisen from the second assumption for gravity

FIGURE CAPTIONS

Figure 1: Reaction probability of the H + H₂ system as function of kinetics energy (in eV) of the impacting H atom, together with its dependence on the parameter $\varrho = r_s/r$ defined in the Schwarzschild metric tensor (see Equation (2) for reference). For $\varrho > 0.6$, the computed reaction probabilities are very close to zero and hence ignored here. The cyan, maroon, light yellow, light green, and violet lines represent reactive probabilities for ϱ values of 0.60, 0.50, 0.40, 0.30, and 0.20, respectively. In addition, the yellow, green, blue, and red lines represent those for ϱ of 0.10, 0.05, 0.03, and 0.01, respectively. The black line is the reactive probability in flat space with $\varrho = 0$.

Figure 2: Same as Figure 1, except for the scattering propabilities of the $H_2 + H_2$ system. The maroon, light green, yellow, green, blue, and red lines represent those for ϱ of 0.50, 0.30, 0.10, 0.05, 0.03, and 0.01, respectively, while the black line presents the scattering propability in flat space with $\varrho = 0$. As is well known, the scattering propability in flat space must be equal to unit since no reaction occurs between two H_2 molecules.

Figure 3: Same as Figure 1, except for the dissociative chemsorption propabilities of the H_2O molecule on the Cu(111) surface. The maroon, light green, yellow, green, blue, and red lines represent those for ϱ of 0.50, 0.30, 0.10, 0.05, 0.03, and 0.01, respectively, while the black line presents the propability in flat space with $\varrho = 0$.

Figure 4: Same as Figure 1, except for the spectrum bands of the anthracene cation in the \tilde{B}^2A_u . The maroon, light green, yellow, green, blue, and red lines represent those for ϱ of 0.50, 0.30, 0.10, 0.05, 0.03, and 0.01, respectively, while the black line presents the propability in flat space with $\varrho = 0$.

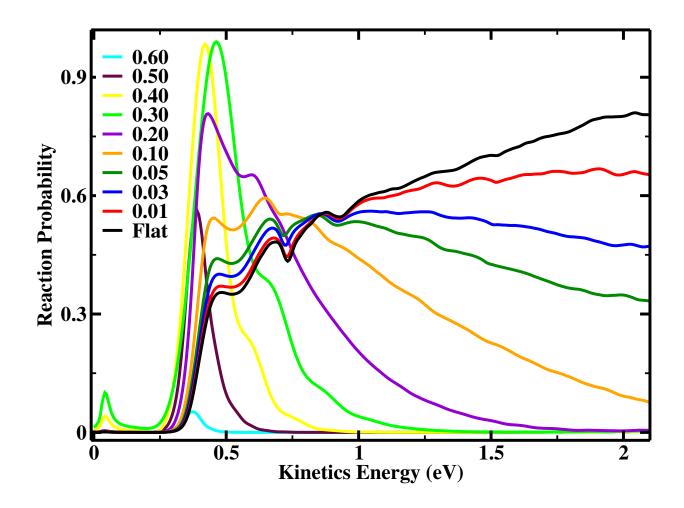


FIG. 1: Chem-Moving-Mol

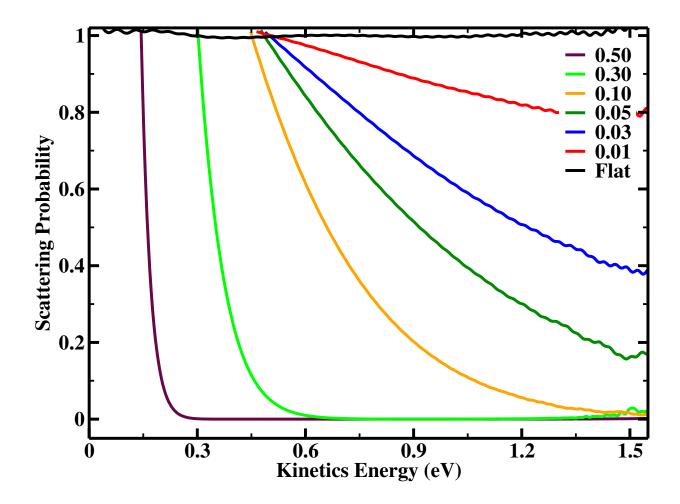


FIG. 2: Chem-Moving-Mol

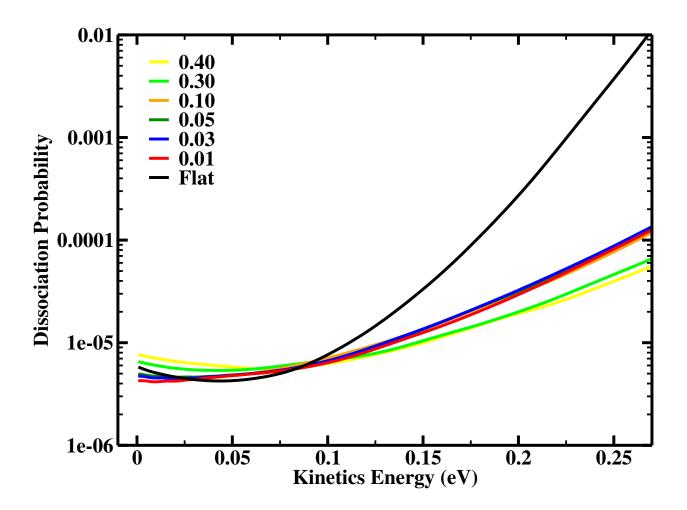


FIG. 3: Chem-Moving-Mol

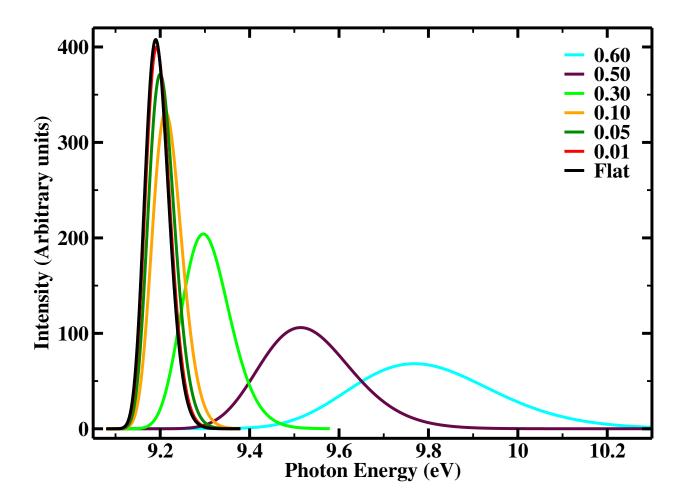


FIG. 4: Chem-Moving-Mol

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