Modeling and simulating formation of neutral hydrogen molecule in Tavis-Cummings-Hubbard model

Miao Hui-hui
Faculty of Computational Mathematics and Cybernetics,
Lomonosov Moscow State University, Vorobyovy Gory, Moscow, Russia

Ozhigov Yuri Igorevich
Faculty of Computational Mathematics and Cybernetics,
Lomonosov Moscow State University, Vorobyovy Gory, Moscow, Russia
K. A. Valiev Institute of physics and technology,
Russian Academy of Sciences, Nakhimovsky Prospekt 32-a, Moscow, Russia

(Dated: September 21, 2022)

A finite-dimensional model of chemistry with two two-level artificial atoms on quantum dots placed in optical cavities, called the association-dissociation model of neutral hydrogen molecule, is described. The initial conditions for formation of the artificial analogue of the neutral hydrogen molecule are discussed. The motion of the nuclei can be represented in quantum form. The association of atoms in the molecule is simulated through a quantum master equation, containing hybridization of atomic orbitals into molecular - depending on the position of the nuclei. Electron spin transitions of electrons and spin-spin interactions between electrons and nuclei are also considered. The influence of temperature variation of photonic modes $\omega^\uparrow$, $\omega^\downarrow$, $\Omega^\uparrow$ and $\Omega^\downarrow$ to unitary evolution and formation of neutral hydrogen molecule is investigated.

Keywords: neutral hydrogen molecule, artificial atom, finite-dimensional quantum electrodynamics, temperature variation.

I. INTRODUCTION

The mathematical modeling of natural phenomena, especially the predictive modeling of chemistry, attracts increasing interest due to the growing capabilities of supercomputers allowing simulation of limited molecular structures in the framework of "quantum chemistry" — stationary states of molecules. This interest has been stimulated in recent years by several theoretical works [1–3]. Compared to classical methods, quantum methods open new perspectives for efficiently simulating known effects and observing fundamentally new phenomena in chemistry even before the building of the full scale quantum computer [2]. One of the main tasks of chemical modeling is the modeling of chemical reactions of hydrogen, especially the formation and decomposition (association and dissociation reactions, respectively) of cation $H_2^+$ and neutral hydrogen molecule $H_2$. Understanding chemical reactions of hydrogen is of undisputed importance if complex molecular structures (especially, biomacromolecule, e.g. protein, deoxyribonucleic acid) are to be constructed. The detailed simulation of association and dissociation of the cation $H_2^+$ is proposed in works [4, 5]. In this paper, we pay more attention to association reaction of neutral hydrogen molecule $H_2$ in Markovian open systems.

In this paper, a seminal contribution is the quantum electrodynamics model (QED), which provides a clear physical picture for exploring interaction between light and matter. This model includes impurity two-level or multi-level systems (usually referred to as atoms) coupled to fields (of cavities). Since the main difficulty represents the description of field, for the "dynamical chemistry" we have to use the models similar to finite dimensional cavity QED models. The ultrastrong-coupling [6–10] (USC) of light and matter (e.g., a cavity mode and a natural or artificial atom, respectively) occurs when their coupling strength $g$ becomes comparable to the atomic ($\omega_a$) or cavity ($\omega_c$) frequencies. More precisely, according to the usual convention, the USC regime occurs when $\eta = \max(\frac{\omega_c}{\omega_a}, \frac{\omega_a}{\omega_c})$ is in the range $[0.1, 1]$. The regime $\eta \geq 1$ is often referred to as deep strong coupling (DSC). The basic model for USC of a single two-level atom in a single-mode cavity is the quantum Rabi model [12] (QRM). Its multi-atom or multi-mode generalizations include the Dicke [14] and Hopfield [15] models. When $\eta < 0.1$, these models for USC can be reduced to the simpler strong coupling (SC) model — the Jaynes-Cummings (JC) model [16]. The JC model describes the dynamics of a two-level atom in an optical cavity, interacting with a single-mode field inside it. Its generalization - the Tavis-Cummings (TC) model [17] describes the dynamics of a group of $N$ two-level atoms in an optical cavity. JC and TC models have been generalized to several cavities coupled by an optical fiber - the Jaynes-Cummings-Hubbard (JCH) and Tavis-Cummings-Hubbard [18] (TCH) models. Since SC is typically easier to realize in experiment than USC and DSC, we reform these SC models to satisfy simulating chemical reaction in this paper. The value of these models and their modifications is also that it allows us to describe a very complex interaction of light and matter...
| Abbreviations/Notations | Descriptions |
|-------------------------|--------------|
| ↑, ↓                    | Spin-up, spin-down |
| \( p \)                | Number of photons (e.g. \( p_1, p_2, p_3, p_4, p_5, p_6 \)) |
| at                     | Atom |
| or                     | Orbital |
| AO, MO                 | Atomic orbital, molecular orbital |
| \( \sigma, \sigma^* \) | Bonding orbital, antibonding orbital |
| \( e \)                | Electron |
| \( s \)                | Spin |
| \( n \)                | Nucleus (e.g. \( n_1, n_2 \)) |
| \( \omega \)           | Cavity frequency |
| \( \omega_n \)         | Transition frequency |
| \( \omega \)           | Transition frequency for electron in molecule (e.g. \( \omega^\uparrow, \omega^\downarrow \)) |
| \( \omega^\uparrow \)  | Transition frequency for electron with \( \uparrow \) in molecule |
| \( \omega^\downarrow \) | Transition frequency for electron with \( \downarrow \) in molecule |
| \( \Omega \) or \( \omega_n \) | Transition frequency for electron in atom (e.g. \( \Omega^\uparrow, \Omega^\downarrow, \Omega^s, \Omega^n \)) |
| \( \Omega^\uparrow \)  | Transition frequency for electron with \( \uparrow \) in atom |
| \( \Omega^\downarrow \) | Transition frequency for electron with \( \downarrow \) in atom |
| \( \Omega^s \)         | Electron spin transition frequency in atom |
| \( \Omega^n \)         | Nuclear spin transition frequency in atom |
| \( a \)                | Photon annihilation operator (e.g. \( a_\omega, a_\Omega \)) and its hermitian conjugate operator — \( a^\dagger \) |
| \( \sigma \)           | Interaction operator of atom with the electromagnetic field of the cavity (e.g. \( \sigma_\omega, \sigma_\Omega, \sigma_{en} \)) and its hermitian conjugate operator — \( \sigma^\dagger \) |
| \( g \) or \( g_n \)   | Coupling strength of photon and the electron (e.g. \( g_\omega, g_n \)) |
| \( \nu_{en} \)         | Slight strength of spin-spin interaction between nucleus and electron |
| \( \zeta \)            | Nucleus tunnelling strength (e.g. \( \zeta_2, \zeta_1, \zeta_0 \)) |
| \( \eta \)             | Maximum ratio of coupling strength to frequency |
| \( C \)                | Space of quantum states for entire system |
| \( A \)                | Subspace of quantum states for associative system (or molecular system) |
| \( D \)                | Subspace of quantum states for dissociative system (or atomic system) |
| \( H \)                | Hamiltonian |
| \( \rho \)             | Density Matrix |
| \( h \)                | Reduced Planck constant or Dirac constant |
| \( A^k \)              | Lindblad or jump operator of system and its hermitian conjugate operator — \( A^k \) |
| \( L^k \)              | Standard dissipation superoperator(e.g. \( \mu_\omega, \mu_\Omega \)) |
| \( L^k \)              | Standard influx superoperator |
| \( \gamma_k \)         | Total spontaneous emission rate for photon |
| \( \gamma_k' \)        | Total spontaneous influx rate for photon |
| \( \mu \)              | Ratio of influx rate to emission rate |
| \( O = H_2, P - H_2 \) | Orthohydrogen, parahydrogen |
| \( I \)                | Nuclear angular momentum quantum number |
| \( M_l \)              | Nuclear magnetic quantum number |
| \( G(T)_{f} \)         | Thermally stationary state |
| \( K \)                | Boltzmann constant |
| \( T \) or \( T_n \)   | Temperature for photonic mode (e.g. \( T_\omega, T_\Omega \)) |
| \( c \)                | Normalization factor |
| \( V \)                | Effective volume of the cavity |
| \( d \)                | Dipole moment of the transition between the ground and the perturbed statesy |
| \( E(x) \)             | Spatial arrangement of the atom in the cavity |
| \( l \)                | Length of the cavity |
| \( \lambda \)          | Photon wavelength |
in the framework of finite-dimensional QED models that allows physical prototypes, among which the most important form is the optical cavity - Fabry-Pérot resonator, and atoms are kepted in it by optical tweezers. In the last time a lot of research has been carried out in the area of modifications of JCH and TCH models: studying phase transitions [19, 20], search for metamaterials [21], studying quantum many-body phenomena [22], evaluating the quality of a quantum gate based on asynchronous atomic excitations [23], etc.

In this paper, we describe modifications of finite-dimensional QED models for interpreting chemical reactions in terms of artificial atoms and molecules on quantum dots placed in optical cavities. Quantum motion of nuclei is permissible between the cavities. Association reaction differ only in the initial states. Chemical processes with two-level atoms are schematically modeled by solving the single quantum master equation (QME) with the Lindblad operators of photon leakage from the cavity to external environment. QME approach has been used to study the dynamics of quantum open system [24], and it is consistent with the laws of quantum thermodynamics [25, 26]. It is only applicable for Markovian approximation.

This paper is organized as follows. After introducing the association-dissociation model of neutral hydrogen molecule in Sec. II describing hybridization and de-hybridization of a couple of two-level artificial atoms, and based on the TCH model [18], we introduce in succession electron spin-flip and spin-spin interaction between electrons and nuclei in Sec. III and in Sec. IV respectively. We also consider influence of temperature variation of external environment. QME approach has been used to study the dynamics of quantum open system [24], and it is consistent with the laws of quantum thermodynamics [25, 26]. It is only applicable for Markovian approximation.

In Sec. VI we introduce a numerical method to achieve reduction of complexity. We do the numerical simulations and get some results in Sec. VII. Some brief comments on our results and extension to future work in Sec. VIII close out the paper.

II. ASSOCIATION-DISSOCIATION MODEL OF NEUTRAL HYDROGEN MOLECULE

In the association-dissociation model, each energy level, both atomic and molecular, is split into two levels with the same energy (approximately the same, with accuracy to stark splitting): spin-up and spin-down, denoted by signs ↑ and ↓ respectively. We will add these signs, designating level of the energy, to separate each level on the spins. Now the levels will be twice as much, and for each level there must be no more than one electron according to Pauli exclusion principle. Photons, that excite the electron, will thus have the same type corresponding to the selected direction of the spin.

In Fig. 1(a) and Fig. 1(b), hybridization of atomic orbitals (AO) and formation of molecular orbitals (MO) are shown, where bonding orbital σ (σ denotes bonding orbital only in pages 3 and 4, denotes interaction operator of atom with the electromagnetic field of the cavity in others) takes the form \( \Phi_\sigma = 1/\sqrt{2}(|0\rangle_1 - |0\rangle_2) \) and antibonding orbital \( \sigma^* \) takes the form \( \Phi_{\sigma^*} = 1/\sqrt{2}(|0\rangle_1 + |0\rangle_2) \). Each nucleus will form a potential well around itself, and the electrons will be bound in these potential wells. The association reaction of \( H_2 \) is shown in Fig. 1(c). Two electrons in the atomic ground orbital \( -1 \) with large distance between nuclei, corresponding to different directions of the spin, absorb respectively photon with mode \( \Omega^\uparrow \) or \( \Omega^\downarrow \), then they rise to atomic excited orbital \( 0 \). When nuclei gather together in one cavity from different cavities through the quantum tunneling effect, the potential barrier between the two potential wells decreases, and since the two electrons are in atomic excited orbitals, the atomic orbitals are hybridized into molecular orbitals, and the electrons are released on the molecular excited orbital \( \Phi_1 \). Then two electrons fleetly release respectively photon with mode \( \omega^\uparrow \) or \( \omega^\downarrow \), and fall to molecular ground orbital \( \Phi_0 \), stable molecule is formed. The dissociation reaction of \( H_2 \) is shown in Fig. 1(d). Two electrons in the molecular ground orbital absorb respectively photon with mode \( \omega^\uparrow \) or \( \omega^\downarrow \), then they rise to molecular excited orbital. When nuclei scatter in different cavities, the potential barrier increases, the molecular orbitals are de-hybridized into atomic orbitals, and the electrons are released on the atomic excited orbital. Finally, two electrons release respectively photon with mode \( \Omega^\uparrow \) or \( \Omega^\downarrow \), and fall to atomic ground orbital, molecule is decomposed. Three-dimensional surface diagrams Fig. 1(e) and Fig. 1(f) can intuitively reveal change of potential wells around nuclei when they are far away or close.

We only consider two electrons with \( \downarrow \) as the initial condition. We assume that the wavelength of all kinds of photons is sufficiently great, so that these photons can interact with electron situated in any cavity. Hamiltonians in this paper are all described based on these conditions as a prerequisite.

The excited states of the electron with the spins for the first nucleus is denoted by \( |0\rangle_1^\uparrow \) and \( |0\rangle_1^\downarrow \) (usually simply written as \( |0\rangle_e \), which can denote any one of \( |0\rangle_1^\uparrow \) and \( |0\rangle_1^\downarrow \)). Then, \( |0\rangle_e \) — ground electron states for the first nucleus. For the second nucleus \( |0\rangle_2 \) and \( |0\rangle_2 \). The ground states are possible only with large distance between nuclei (see Figs. 1(c) and 1(d), where vertical red dashed line means large distance between nuclei).

Hybridization of orbitals — the introduction of molecular states \( \Phi_0 \) and \( \Phi_1 \) corresponding to bonding orbital \( \sigma \) and antibonding orbital \( \sigma^* \) respectively, is possible only for atomic excited states \( |0\rangle_e \). For atomic ground states \( |0\rangle_e \), hybridization is impossible. Hybrid molecular states of the electron energy are denoted by

\[
\Phi_1 = \frac{1}{\sqrt{2}}(|0\rangle_e - |0\rangle_e) \\
\Phi_0 = \frac{1}{\sqrt{2}}(|0\rangle_e + |0\rangle_e)
\]
FIG. 1. (online color) The association-dissociation model of neutral hydrogen molecule. (a) and (b) show the hybridization of orbitals of two hydrogen atoms, and bonding orbital $\sigma$ and antibonding orbital $\sigma^*$. The association of two hydrogen atoms — the formation of $H_2$, is shown in (c). The dissociation of these hydrogen atoms — the decomposition of $H_2$, is shown in (d). (e) describes potential wells of dissociative system when distance between nuclei is large (two nuclei are in different cavities). (f) describes potential wells of associative system when distance between nuclei is small (two nuclei are in the same cavity). Red dots in (b) represent protons. Blue and yellow dots in (c) and (d) represent electrons and photons, respectively.

where $|\Phi_1\rangle_e$ are molecular excited states, $|\Phi_0\rangle_e$ are molecular ground states.

For avoiding complicating problem with antisymmetrization, we introduce second quantization, referred to as occupation number representation [27, 28]. In this approach, the quantum many-body states are represented in the Fock state basis, which are constructed by filling up each single-particle state with a certain number
of identical particles. The second quantization formalism introduces the creation and annihilation operators to construct and handle the Fock states, providing useful tools to the study of the quantum many-body theory.

Thus, the Hilbert space of quantum states of the entire system is \( \mathcal{C} \), having the following form

\[
|\Psi\rangle_\mathcal{C} = |\text{photons}\rangle \otimes |\text{atoms}\rangle \otimes |\text{nuclei}\rangle
\]

where \( p_1, p_2 \) are the numbers of molecular photons with mode \( \omega^\uparrow, \omega^\downarrow \); \( p_3, p_4 \) are the numbers of atomic photons with mode \( \Omega^\uparrow, \Omega^\downarrow \); \( p_5 \) is the number of photons with mode \( \Omega^a \), which can excite the electron spin from \( \downarrow \) to \( \uparrow \) in the atom; \( p_6 \) is the number of photons with mode \( \Omega^c \), which can excite the nuclear spin from \( \downarrow \) to \( \uparrow \) in the atom. \( l_{i, i=1,2} \) describes orbital state (each atom has four orbitals: \( 0^\uparrow, 0^\downarrow, -1^\uparrow \) and \( -1^\downarrow \)); \( l_{i} = 1 \) — the orbital is occupied by one electron, \( l_{i} = 0 \) — the orbital is freed. The states of the nuclei are denoted by \( |k\rangle_n \): \( k = 0 \) — state of nuclei, gathering together in one cavity, \( k = 1 \) — state of nuclei, scattering in different cavities.

The space of quantum states \( \mathcal{C} \) can be absolutely separated to two subspaces \( \mathcal{A} \) and \( \mathcal{D} \), where \( \mathcal{A} \oplus \mathcal{D} = \mathcal{C} \), \( \mathcal{A} \cap \mathcal{D} = \emptyset \). \( \mathcal{A} \) — the subspace for associative system (or molecular system), in which states are corresponding to \( |0\rangle_n \); \( \mathcal{D} \) — the subspace for dissociative system (or atomic system), in which states are corresponding to \( |1\rangle_n \).

In this paper, the association-dissociation model of the neutral hydrogen molecule is a modification of TCH model with multimode electromagnetic field inside optical cavities. The standard TCH model describes the interaction of \( N \) two-level atoms with a single-mode electromagnetic field inside an optical cavity and has been generalized to several cavities coupled by an optical fiber - the standard TCH model. Firstly, the dynamics of system is described by solving the QME for the density matrix with the Lindblad operators of photon leakage from the cavity to external environment. The QME in the Markovian approximation for the density operator \( \rho \) of the system is in following form

\[
\dot{H}\rho = [H, \rho] + iL(\rho)
\]

where \([H, \rho] = H\rho - \rho H\) is the commutator. We have a graph \( K \) of possible allowed photon dissipations between the states. The vertices of \( K \) correspond to the states, the edges correspond to the allowed dissipations. Analogously, \( K' \) is a graph of possible allowed photon influxes. \( L(\rho) \) is in following form

\[
L(\rho) = \sum_{k \in K} L_k(\rho) + \sum_{k' \in K'} L_{k'}(\rho)
\]

where \( L_k(p) \) is the standard dissipation superoperator corresponding to the operator \( A_k \) and taking as an argument on the density matrix \( \rho \)

\[
L_k(\rho) = \gamma_k \left( A_k \rho A_k^\dagger - \frac{1}{2} \{ \rho, A_k A_k^\dagger \} \right)
\]

where \( \{ \rho, A_k A_k^\dagger \} = \rho A_k^\dagger A_k + A_k^\dagger A_k \rho \) is the anticommutator. The total spontaneous emission rate for photon for \( k \in K \) due to photon leakage from the cavity to external environment is denoted \( \gamma_k \). Similarly, \( L_{k'}(\rho) \) is the standard influx superoperator, having the following form

\[
L_{k'}(\rho) = \gamma_{k'} \left( A_k^\dagger \rho A_k - \frac{1}{2} \{ \rho, A_k A_k^\dagger \} \right)
\]

The total spontaneous influx rate for photon for \( k' \in K' \) is denoted by \( \gamma_{k'} \).

The coupled-system Hamiltonian of the association-dissociation model in Eq. (3) is expressed by the total energy operator

\[
H = H_A + H_D + H_{\text{tunnel}}
\]

where \( H_A \) is the associative Hamiltonian corresponding to \( A \), \( H_D \) is the dissipative Hamiltonian corresponding to \( D \), and \( H_{\text{tunnel}} \) describes the quantum tunneling effect between \( H_A \) and \( H_D \).

\[
H_A \text{ has following form}
\]

\[
H_A = \sigma_n^\dagger \sigma_n^\dagger (H_{A,\text{field}} + H_{A,\text{mol}} + H_{A,\text{int}})
\]

where \( \sigma_n^\dagger \sigma_n^\dagger \) verifies that nuclei are close.

Rotating wave approximation (RWA) is considered. In this approximation, terms \( \sigma^\dagger a^\dagger \sigma a \) in a Hamiltonian, which oscillate rapidly, are neglected. This is a valid approximation when the applied electromagnetic radiation is near resonance with an atomic transition, and the intensity is low. Thus,

\[
\frac{g}{\omega_c} \approx \frac{g}{\omega_n} \ll 1
\]

where \( \omega_c \) is cavity frequency, \( \omega_n \) is transition frequency. In general, we assume that \( \omega_c = \omega_n \). Using RWA, we can replace \( \sigma^\dagger a^\dagger (a^\dagger + a) \) with \( \sigma^\dagger a + \sigma a^\dagger \) in Eqs. (10a) and (12c). Thus,

\[
H_{A,\text{field}} = \hbar \omega^\uparrow a^\dagger_{\omega^\uparrow} a_{\omega^\uparrow} + \hbar \omega^\downarrow a^\dagger_{\omega^\downarrow} a_{\omega^\downarrow}
\]

\[
H_{A,\text{mol}} = \sum_{i=1,2} \left( \hbar \omega^\uparrow \sigma^\dagger_{\omega^\uparrow,i} a_{\omega^\uparrow,i} + \hbar \omega^\downarrow \sigma^\dagger_{\omega^\downarrow,i} a_{\omega^\downarrow,i} \right)
\]

\[
H_{A,\text{int}} = \sum_{i=1,2} \left( g_{\omega^\uparrow} \left( \sigma^\dagger_{\omega^\uparrow,i} a_{\omega^\uparrow,i} + \sigma_{\omega^\uparrow,i} a^\dagger_{\omega^\uparrow,i} \right) + g_{\omega^\downarrow} \left( \sigma^\dagger_{\omega^\downarrow,i} a_{\omega^\downarrow,i} + \sigma_{\omega^\downarrow,i} a^\dagger_{\omega^\downarrow,i} \right) \right)
\]

where \( \hbar = h/2\pi \) is the reduced Planck constant or Dirac constant. \( H_{A,\text{field}} \) is the photon energy operator, \( H_{A,\text{mol}} \)
is the molecule energy operator, $H_{A,\text{int}}$ is the molecule-photon interaction operator. $g_\omega$ is the coupling strength between the photon mode $\omega$ (with annihilation and creation operators $a_\omega$ and $a_\omega^\dagger$, respectively) and the electrons in the molecule (with excitation and relaxation operators $\sigma_{\omega,i}^\dagger$ and $\sigma_{\omega,i}$, respectively, where $i$ denotes index of electrons).

Then $H_D$ is described in following form

$$H_D = \sigma_n^\dagger \sigma_n (H_{D,\text{field}} + H_{D,\text{mol}} + H_{D,\text{int}})$$  \hspace{1cm} (11)

where $\sigma_n^\dagger \sigma_n$ verifies that nuclei are far away. Similarly, we introduce RWA,

$$H_{D,\text{field}} = \hbar \Omega^\dagger a_{\Omega}^\dagger a_{\Omega} + \hbar \Omega^\dagger a_{\Omega}^\dagger a_{\Omega}$$  \hspace{1cm} (12a)

$$H_{D,\text{at}} = \sum_{i=1,2} \left( \hbar \Omega^\dagger \sigma_{\Omega,i}^\dagger \sigma_{\Omega,i} + \hbar \Omega^\dagger \sigma_{\Omega,i} \sigma_{\Omega,i}^\dagger \right)$$  \hspace{1cm} (12b)

$$H_{D,\text{int}}^{\text{RW-A}} = \sum_{i=1,2} \left( g_{\Omega,i} \left( \sigma_{\Omega,i}^\dagger a_{\Omega,i}^\dagger + \sigma_{\Omega,i} a_{\Omega,i} \right) + g_{\Omega,i} \left( \sigma_{\Omega,i}^\dagger a_{\Omega,i} + \sigma_{\Omega,i}^\dagger a_{\Omega,i}^\dagger \right) \right)$$  \hspace{1cm} (12c)

where $H_{D,\text{field}}$ is the photon energy operator, $H_{D,\text{at}}$ is the atom energy operator, $H_{D,\text{int}}$ is atom-photon interaction operator. $g_\Omega$ is the coupling strength between the photon mode $\Omega$ (with annihilation and creation operators $a_\Omega$ and $a_\Omega^\dagger$, respectively) and the electrons in the atom (with excitation and relaxation operators $\sigma_{\Omega,i}^\dagger$ and $\sigma_{\Omega,i}$, respectively, here $i$ denotes index of electrons).

Finally, $H_{\text{tun}}$ describe the hybridization and dehybridization, realized by quantum tunneling effect, it takes the form

$$H_{\text{tun}} = \sum_{i_1,i_2=1,2} \left\{ \omega \sigma_{\omega,i_1}^\dagger \sigma_{\omega,i_2} \sigma_{\omega,i_1} \sigma_{\omega,i_2} + \sigma_n^\dagger + \sigma_n \right\}$$

$$+ \zeta_1 \sigma_{\omega,i_1}^\dagger \sigma_{\omega,i_2} \sigma_{\omega,i_1} \sigma_{\omega,i_2} + \sigma_n^\dagger + \sigma_n \right\}$$

$$+ \zeta_2 \sigma_{\omega,i_1}^\dagger \sigma_{\omega,i_2} \sigma_{\omega,i_1} \sigma_{\omega,i_2} + \sigma_n^\dagger + \sigma_n \right\}$$

$$+ \zeta_3 \sigma_{\omega,i_1}^\dagger \sigma_{\omega,i_2} \sigma_{\omega,i_1} \sigma_{\omega,i_2} + \sigma_n^\dagger + \sigma_n \right\}$$

(13)

where $i_1$, $i_2$ denote indices of electrons. $\sigma_{\omega,i}^\dagger$ verifies that two electrons with different spins are at orbital $\Phi_0$ with large tunneling intensity $\zeta_0$, $\sigma_{\omega,i}^\dagger \sigma_{\omega,i}^\dagger$ verifies that electron with $\uparrow$ is at orbital $\Phi_0$ and electron with $\downarrow$ is at orbital $\Phi_1$ with small tunneling intensity $\xi_1$, $\sigma_{\omega,i}^\dagger \sigma_{\omega,i}^\dagger$ verifies that electron with $\uparrow$ is at orbital $\Phi_1$ and electron with $\downarrow$ is at orbital $\Phi_0$ with small tunneling intensity $\xi_1$, $\sigma_{\omega,i}^\dagger \sigma_{\omega,i}^\dagger$ verifies that two electrons with different spins are at orbital $\Phi_0$ with tunneling intensity $\zeta_3$, which equal to 0. In brief, electron falling to molecular ground state, weakens quantum tunneling effect.

The photon annihilation and creation operators on an $p$-photons state, are described as

$$\begin{cases}
  a_\omega |p\rangle_\omega = \sqrt{p} |p-1\rangle_\omega, \\
  a_\omega^\dagger |p\rangle_\omega = \sqrt{p+1} |p+1\rangle_\omega,
\end{cases}$$

if $p > 0$, \hspace{1cm} (14)

$$\begin{cases}
  a_\omega |0\rangle_\omega = |1\rangle_\omega, \\
  a_\omega^\dagger |0\rangle_\omega = |1\rangle_\omega,
\end{cases}$$

if $p = 0$, \hspace{1cm} (15)

The interaction of molecule with the electromagnetic field of the cavity, emitting or absorbing photon with mode $\omega^{\uparrow\downarrow}$, is described as

$$\sigma_{\omega,i} |1\rangle_{\Phi_i} |0\rangle_\phi = |0\rangle_{\Phi_i} |1\rangle_\phi.$$  \hspace{1cm} (16)

In Eqs. (15) and (16) $i$ denotes index of electrons. $\sigma_n, \sigma_n^\dagger$ are tunneling operators of nuclei, having following form

$$\sigma_n |1\rangle_n = |0\rangle_n,$$

$$\sigma_n^\dagger |0\rangle_n = |1\rangle_n.$$  \hspace{1cm} (17)

### III. ELECTRON SPIN TRANSITION

In this section, we introduce spin photons with mode $\Omega^s$ in the association-dissociation model, thus transition between $\uparrow$ and $\downarrow$ is allowed. Electron spins must strictly satisfy the Pauli exclusion principle, which forbids coexistence in same energy level of electrons with same spin.

We stipulate, that electron spin transition is allowed if and only if electrons are in atomic state corresponding to $|1\rangle_n$. Electron spin transition is forbidden when electrons are in molecular state corresponding to $|0\rangle_n$, which covenes Pauli exclusion principle. The stable formation of $H_2$ is only realized through state, where two electrons with differsents spins situated in orbital $\Phi_0$. This situation is just right accord with that the lower the system energy, the more stable. Thus, the formation of $H_2$ are strictly comply with Pauli exclusion principle, principle of minimum energy and Hund’s rules.

Similarly to Eq. (14), the photon annihilation and creation operators on an $p$-photon state with mode $\Omega^s$ are described as

$$\begin{cases}
  a_{\Omega,i} |p\rangle_{\Omega,i} = \sqrt{p} |p-1\rangle_{\Omega,i}, \\
  a_{\Omega,i}^\dagger |p\rangle_{\Omega,i} = \sqrt{p+1} |p+1\rangle_{\Omega,i},
\end{cases}$$

if $p > 0$, \hspace{1cm} (18)

$$\begin{cases}
  a_{\Omega,i}^\dagger |0\rangle_{\Omega,i} = |1\rangle_{\Omega,i},
\end{cases}$$

if $p = 0$, \hspace{1cm} (19)
The situation without consideration of electron spin transition is shown in (a), where formation of neutral hydrogen molecule is impossible when we only put two photons with different modes \( \Omega^\uparrow \) and \( \Omega^\downarrow \) at the start. The situation with consideration of electron spin transition is shown in (b), where formation of neutral hydrogen molecule is possible when we add photon with mode \( \Omega^s \).

Spin-spin interaction between electron and nucleus. (a) shows the spin-spin interaction between electron and nucleus, which only happens when electron falls to atomic ground orbital (electron and nucleus are close). The situation with consideration of spin-spin interaction between nucleus and electron is shown in (b), where formation of neutral hydrogen molecule is possible when we put four photons with different modes \( \Omega^\uparrow \), \( \Omega^\downarrow \), \( \Omega^s \) and \( \Omega^n \) at the start. Red up and down arrows represent nuclear spins \( \uparrow \) and \( \downarrow \), respectively.

And the interaction of atom with the electromagnetic field of the cavity, emitting or absorbing photon with mode \( \Omega^s \) and causing spin-flip, is described as

\[
\begin{align*}
\sigma_{\Omega^s,j}|1\rangle_{\text{or}_{-1}}|0\rangle_{\text{or}_{-1}} &= |0\rangle_{\text{or}_{-1}}|1\rangle_{\text{or}_{-1}}, \\
\sigma_{\Omega^n,j}^\dagger |0\rangle_{\text{or}_{-1}}|1\rangle_{\text{or}_{-1}} &= |1\rangle_{\text{or}_{-1}}|0\rangle_{\text{or}_{-1}},
\end{align*}
\]

where \( i \) denotes index of electrons.

We consider two situations: 1) in Fig. 2(a) we only put two photons with different modes \( \Omega^\uparrow \) and \( \Omega^\downarrow \), and spin photons is provisionally not considered and transition between \( \uparrow \) and \( \downarrow \) is forbidden; 2) in Fig. 2(b) spin photons and corresponding transition is introduced. Thus formation of \( H_2 \) is impossible in Fig. 2(a), and is achieved in Fig. 2(b).
IV. NUCLEAR SPIN AND SPIN-SPIN INTERACTION

Nuclear spin interacts with electrons only when electron fall down to atomic ground state. The interaction is shown in Fig. 3(a). When electron is in atomic ground state and has different spin with nucleus, it can exchange spin with nucleus. This interaction called spin-spin interaction, is denoted $\sigma_{en}$. In Fig. 3(a), with help of this interaction, electron with ↓ absorbs photon with mode $\Omega^s$ and nucleus with ↑ releases photon with mode $\Omega^p$. Conversely, electron with ↑ also can release photon with mode $\Omega^s$ and nucleus with ↓ also can absorb photon with mode $\Omega^p$.

First of all, nuclear state in Eq. (2) is expended as

$$|\text{nuclei}\rangle = |k\rangle_n|k_1\rangle_{n_1}|k_2\rangle_{n_2}$$

(20)

where $k_i$, $i \in \{1, 2\}$ describe spin of the first or second nucleus. $k_i = 1$ — nucleus with ↑, $k_i = 0$ — nucleus with ↓. And spin-spin interaction takes the form

$$\sigma_{en} = \sum_{i,j=1,2} \sigma_{\Omega,i}\sigma_{\Omega,j}^\dagger (\sigma_{\Omega^s,i}\sigma_{\Omega^p,j}^\dagger + \sigma_{\Omega^p,i}\sigma_{\Omega^s,j}^\dagger)$$

(21)

where $i$ denotes index of electrons, $j$ denotes index of nuclei. $\sigma_{\Omega,i}, \sigma_{\Omega,j}^\dagger$ are electron transition operators in atom, described in Eq. (10). $\sigma_{\Omega^s,i}, \sigma_{\Omega^p,i}^\dagger$ means electron fall down to atomic ground state. $\sigma_{\Omega^s,i}, \sigma_{\Omega^p,i}^\dagger$ are electron spin flip operators described in Eq. (12). $\sigma_{\Omega^s,j}, \sigma_{\Omega^p,j}^\dagger$ are spin flip operators for nucleus, which are described as

$$\sigma_{\Omega^s,j}|1\rangle_{n_j} = |0\rangle_{n_j},$$
$$\sigma_{\Omega^p,j}|0\rangle_{n_j} = |1\rangle_{n_j}.$$  

(22)

Similarly to Eq. (14), the photon annihilation and creation operators on an $p$-photon state with mode $\Omega^\mu$ are described as

$$if \ p > 0, \ \left\{ \begin{array}{l} a_{\Omega^\mu}|p\rangle_{\Omega^\mu} = \sqrt{p}|p-1\rangle_{\Omega^\mu}, \\ a_{\Omega^\mu}^\dagger|p\rangle_{\Omega^\mu} = \sqrt{p+1}|p+1\rangle_{\Omega^\mu}. \end{array} \right.$$  

(23)

The initial state $|\Psi'_{\text{initial}}\rangle$ for the association process is shown in Fig. 3(b), where two electron with ↓ are in the same atoms, and two nuclei with ↑ can interact with electrons and exchange spins. We put four photons with different modes $\Omega^1, \Omega^p, \Omega^s$ and $\Omega^p$ at the start. Thus, we have two situations of formation of $H_2$: 1) the first nucleus with ↑ and the second nucleus with ↓, denoted by $|\Psi'_{\text{final}}\rangle$; 2) the first nucleus with ↓ and the second nucleus with ↑, denoted by $|\Psi''_{\text{final}}\rangle$.

Spin-spin interaction between nucleus and electron with slight intensity $u_{en}$ is usually ignored. However experiments indicate that when we introduce spin-spin interaction, molecular hydrogen occurs in two isomeric forms, one with its two proton nuclear spins aligned parallel (orthohydrogen, denoted by $O - H_2$), the other with its two proton spins aligned antiparallel (parahydrogen, denoted by $P - H_2$) [30, 31]. These two forms are often referred to as spin isomers [32] or as nuclear spin isomers [33].

Each hydrogen molecule consists of two hydrogen atoms linked by a covalent bond. Each hydrogen atom consists of one proton and one electron. Each proton has an associated magnetic moment, which is associated with the proton’s spin of $\frac{1}{2}$. In the hydrogen molecule, the spins of the two hydrogen nuclei (protons) couple to form a triplet state known as $O - H_2$, and a singlet state known as $P - H_2$. The triplet state $(O - H_2)$ has nuclear angular momentum quantum number $I = 1$ so that the component along a defined axis can have the three values $M_I = 1, 0, or -1$, where $M_I$ is nuclear magnetic quantum number. The corresponding nuclear spin wavefunctions are $|1\rangle_{n_1}|1\rangle_{n_2}, \frac{1}{\sqrt{2}}(|1\rangle_{n_1}|0\rangle_{n_2} + |0\rangle_{n_1}|1\rangle_{n_2})$ and $|0\rangle_{n_1}|0\rangle_{n_2}$. Each $O - H_2$ energy level then has a (nuclear) spin degeneracy of three, meaning that it corresponds to three states of the same energy (in the absence of a magnetic field) [30]. The singlet state $(P - H_2)$ has $I = 0$ and $M_I = 0$, with wavefunction $\frac{1}{\sqrt{2}}(|0\rangle_{n_1}|1\rangle_{n_2} - |1\rangle_{n_1}|0\rangle_{n_2})$. Since there is only one possibility, each $P - H_2$ level has a spin degeneracy of one and is said to be non-degenerate [30]. $P - H_2$ is in a lower energy state than is $O - H_2$.

Spin-spin interaction is also called hyperfine, which widely exists in the organism.

V. THERMALLY STATIONARY STATE

We define the stationary state of a field with temperature $T$ as a mixed state with a Gibbs distribution of Fock components:

$$\mathcal{G}(T)_f = c \sum_{p=0}^{\infty} \exp(-\frac{\hbar \omega p}{K T})|p\rangle\langle p|,$$  

(24)

where $K$ is the Boltzmann constant, $c$ is the normalization factor, $p$ is the number of photons. We introduce the notation $\gamma_k / \gamma_k = \mu$. The state $\mathcal{G}(T)_f$ will then exist only at $\mu < 1$, because otherwise the temperature will be infinitely large and the state $\mathcal{G}(T)_f$ will be non-normalizable.

The population of the photonic Fock state $|p\rangle$ at temperature $T$ is proportional to $\exp(-\frac{\hbar \omega p}{K T})$. In our model, we assume

$$\mu = \exp(-\frac{\hbar \omega}{K T})$$  

(25)

from where $T = \frac{\hbar \omega}{K \ln(1/\mu)}$.

The following theorem takes place [33]:

The thermally stationary state of atoms and fields at temperature $T$ has the form $\rho_{\text{state}} = \rho_{\text{ph}} \otimes \rho_{\text{at}}$, where $\rho_{\text{ph}}$ is the state of the photon and $\rho_{\text{at}}$ is the state of the atom.
The curves of temperature-dependent function $\mu(T)$ is shown in Fig. 4. When $T = 0$, $\mu = 0$, then $\mu$ rises sharply with the increase of temperature, and reaches plateau when $T$ is large. If $T$ is large enough, $\mu$ will be infinite close to 1.

VI. NUMERICAL METHOD

The solution $\rho(t)$ in Eq. (3) may be approximately found as a sequence of two steps: in the first step we make one step in the solution of the unitary part of Eq. (3)

$$\dot{\rho}(t + dt) = \exp(-\frac{i}{\hbar} H dt) \rho(t) \exp(\frac{i}{\hbar} H dt)$$

and in the second step, make one step in the solution of Eq. (3) with the commutator removed:

$$\rho(t + dt) = \dot{\rho}(t + dt) + \frac{1}{\hbar} L(\dot{\rho}(t + dt)) dt$$

For establishing Hamiltonian in Eq. (26), we have the traditional method called tensor product. We can directly establish Hamiltonian with Eq. (7) through tensor product, however the dimension of Hamiltonian obtained through this method is often very large and there are many excess states, which do not participate in evolution, especially when the degree of freedom of system is large. Besides, we also have to consider antisymmetrization for two-femions system. Here we will introduce another method based on occupation number representation in Eq. (2) and including two steps:

- generate and numbering possible states involved in the unitary evolution according to the initial state and its corresponding possible dissipative states involved in solving QME;
- establish Hamiltonian with these states and possible interactions and dissipations among them.

Now we throw away the excess useless states through this method and obtain anew $\mathcal{C}'$ and $H'$, where $\mathcal{C}' \subset \mathcal{C}$ and $\text{dim}(H') \leq \text{dim}(H)$. Thus, reduction of complexity is achieved. For multi-particle system, with the increase of the degree of freedom, the reduction through this method becomes more effective.

VII. SIMULATIONS AND RESULTS

The coupling strength of photon and the electron in the cavity takes the form:

$$g_n = \sqrt{\hbar \omega_n b/V dE(x)}$$

where $\omega_n$ is transition frequency, $V$ is the effective volume of the cavity, $d$ is the dipole moment of the transition between the ground and the perturbed states and $E(x)$ describes the spatial arrangement of the atom in the cavity, which has the form $E(x) = \sin(\pi x/l)$, here $l$ is the length of the cavity. To ensure the confinement of the photon in the cavity, $l$ has to be chosen such that $l = m\lambda/2$ is a multiple of the photon wavelength $\lambda$. In experiments, $m = 1$ is often chosen to decrease the effective volume of the cavity, which makes it possible to obtain dozens of Rabi oscillations [35]. We assume that $\Omega_{\text{en}} < \Omega^s < \omega^\uparrow = \omega^\downarrow < \Omega^\uparrow = \Omega^\downarrow$, thus $\nu_{\text{en}} < g_{\omega^\downarrow} < g_{\omega^\uparrow} = g_{\Omega^\uparrow} = g_{\Omega^\downarrow}$ according to Eq. (28).

In simulations:

$$\omega^\uparrow = 5 \times 10^9, \Omega^\uparrow = 10^{10}, \Omega^s = 10^9, \Omega^\downarrow = 10^8;$$
$$g_{\omega^\downarrow} = g_{\omega^\uparrow} = 5 \times 10^7, g_{\Omega^\uparrow} = g_{\Omega^\downarrow} = 10^8, g_{\Omega^s} = 10^7, \nu_{\text{en}} = 10^6;$$
The unitary evolution without consideration of electron spin transition. (a) shows the curves of time-dependent probabilities of all possible states involved in the unitary evolution. Probability of state $|\Psi_{\text{initial}}\rangle$ is denoted by cyan solid curve, and probability of state $|\Psi_{\text{final}}\rangle$ is denoted by red solid curve. (b) shows the curves of time-dependent probabilities of subspaces $A$ and $D$. Probability of $A$ is denoted by red solid curve, and probability of $D$ is denoted by blue solid curve.

The unitary evolution with consideration of electron spin transition. In (a), probability of state $|\Psi_{\text{initial}}\rangle$ is denoted by cyan solid curve. Other curves represent as same in Fig. 5. We assume $T_{\omega^\uparrow} = T_{\omega^\downarrow} = 0K$, $T_{\Omega^\uparrow} = T_{\Omega^\downarrow} = 3 \times 10^6 K$, and $\gamma_{\omega^\uparrow} = \gamma_{\omega^\downarrow} = \gamma_{\Omega^\uparrow} = \gamma_{\Omega^\downarrow} = 10^7$.

A. Without consideration of electron spin transition

In this subsection, only a photon with mode $\Omega^\uparrow$ and a photon with mode $\Omega^\downarrow$ are pumped into system at the start, corresponding to the initial state $|\Psi_{\text{initial}}\rangle$, described in Fig. 5 (a), where two electrons with $\downarrow$ are in atomic ground state of different atoms, and photon with mode $\Omega^\uparrow$, which can excite electron from $\downarrow$ to $\uparrow$, is absent. Thus, electron spin transition is forbidden. And only the influx of photons with modes $\omega^\uparrow$ and $\omega^\downarrow$ is considered. The influx of photons with modes $\omega^\uparrow$ and $\omega^\downarrow$ is forbidden. And according to Sec. V, the influx rate is always smaller than the corresponding dissipative rate.

We consider the leakage of all types of photon in Markovian open systems, and its dissipative rate all are equal.

\gamma_{\omega^\uparrow} = \gamma_{\omega^\downarrow} = \gamma_{\Omega^\uparrow} = \gamma_{\Omega^\downarrow} = \gamma_{\Omega^s} = 10^7; \\
\zeta_2 = 10^9, \zeta_1 = 10^7, \zeta_0 = 0.

We assume that $T_{\omega^\uparrow} = T_{\omega^\downarrow} = 0K$, $T_{\Omega^\uparrow} = T_{\Omega^\downarrow} = 3 \times 10^6 K$, thus we get $\mu_{\omega^\uparrow} = \mu_{\omega^\downarrow} = 0$, $\mu_{\Omega^\uparrow} = \mu_{\Omega^\downarrow} \approx 0.485$. Theoretically, $|\Psi_{\text{final}}\rangle$ is impossible to achieved, be-
cause hybridization of atomic orbitals happens only when two electrons both in atomic excited orbitals possess different spins. According to numerical results in Fig. 5(a), we found red solid line representing $|\Psi_{\text{final}}\rangle$ is always equal to 0 during the whole unitary evolution. $|\Psi_{\text{final}}\rangle$ is described in Fig. 2 where two electrons with different spins are fastened in molecular ground orbital. And in Fig. 5(b), red solid line representing $A$, which is the sum of probabilities of all states belonging to dissociative system corresponding to $|0\rangle_n$, is also always equal to 0. And blue solid line representing $D$, which is the sum of probabilities of all states belonging to dissociative system corresponding to $|1\rangle_n$, is always equal to 1. That means entire system of our model keep complete dissociative during the unitary evolution and No energy get into associative system. Thus, we can say that formation of neutral hydrogen molecule is impossible when two electrons are both fastened with same spins, in other words, when electron spin transition is inhibitive.

B. With consideration of electron spin transition

Now we introduce spin-flip photon in the association-dissociation model of neutral hydrogen molecule and electron spin transition is possible. Initial state is $|\Psi_{\text{initial}}\rangle$, described in Fig. 2(b), where photon with mode $\Omega^s$ is added. And we stipulate, that electron spin transition only happens when electron is in atomic state, both excited and ground.

Similarly, for added photon with mode $\Omega^s$, we assume that $T_{\Omega^s} = 3 \times 10^5 K$, thus we get $\mu_{\Omega^s} \approx 0.485$.

According to numerical results in Fig. 3(a), with consideration of electron spin transition, we found red solid line $|\Psi_{\text{final}}\rangle$ rises and reaches 1 at the end. It means that formation of $H_2$ is achieved and free hydrogen atoms are no longer in existence. And in Fig. 5(b), red solid line $A$ also rises and reaches 1, and blue solid line $D$ descends to 0. Thus, we can say that formation of neutral hydrogen molecule is possible when two electrons are with different spins, in other words, when electron spin transition is permissible.

The reason for what is shown in Fig. 6 is that we assume that the dissipative rate of all types of photon are the same, $\mu_{\Omega^\uparrow}$, $\mu_{\Omega^\downarrow}$ and $\mu_{\Omega^*}$ are equal to 0.485, and $\mu_{\omega^\uparrow}$, $\mu_{\omega^\downarrow}$ = 0 (which means that influx rates of photon with mode $\omega^\uparrow$ and $\omega^\downarrow$ are 0). As shown in Fig. 4(d), the decomposition of hydrogen molecules needs to absorb photons with mode $\omega^\uparrow$ and $\omega^\downarrow$ to force electrons to jump from the molecular ground orbital to the excited orbital, but since these photons cannot be replenished, they will gradually leak until they are completely absent in the cavity. Thus the unitary evolution of the system over time eventually leads to the stable formation of neutral hydrogen molecule.

C. Temperature variation

Now we investigate the influence of temperature variation of photonic modes $\omega^\uparrow$, $\omega^\downarrow$ and $\Omega^s$ to the unitary evolution and the formation of neutral hydrogen molecule.

Temperature variation of photonic modes $\omega^\uparrow$ and $\omega^\downarrow$

We assume that $T_{\Omega^\uparrow} = T_{\Omega^\downarrow} = 3 \times 10^6 K$, $T_{\Omega^s} = 3 \times 10^5 K$, thus we get $\mu_{\Omega^\uparrow} = \mu_{\Omega^\downarrow} = \mu_{\Omega^s} \approx 0.485$. And we increase $T_{\omega^\uparrow}(T_{\omega^\downarrow})$ from 0K to $1.5 \times 10^6 K$, and $\mu_{\omega^\uparrow}$( $\mu_{\omega^\downarrow}$) rises from 0 to 0.485.

Now we fix the time $t = 5 \times 10^{-4}$ in Fig. 7 we can intuitively see the tendency of temperature-dependent propabilities of $|\psi_{\text{final}}\rangle$ with the increase of temperature $T_{\omega^\uparrow}(T_{\omega^\downarrow})$. When $T_{\omega^\uparrow}(T_{\omega^\downarrow})$ is close to 0, propability of
$|\psi_{\text{final}}\rangle$ is close to 1. Then when $T_{\omega^i}(T_{\omega^i})$ rises, probability of $|\psi_{\text{final}}\rangle$ descends abruptly. When $T_{\omega^i}(T_{\omega^i})$ is larger enough, probability of $|\psi_{\text{final}}\rangle$ reaches bottom, which is close to 0.

**Temperature variation of photonic modes $\Omega^+$**

We assume that $T_{\omega^1} = T_{\omega^2} = 0 K$, $T_{\Omega^+} = T_{\Omega^-} = 3 \times 10^5 K$, thus we get $\mu_{\omega^1} = \mu_{\omega^2} = 0$, $\mu_{\Omega^+} = \mu_{\Omega^-} \approx 0.485$. And we increase $T_{\Omega^+}$ from $0 K$ to $300000 K$, and $\mu_{\Omega^+}$ rises from 0 to 0.485. We totally investigated 16 situations of temperature of photonic modes $\Omega^+$, which are all written in Tab. II.

In Fig. 8(a), we selected four situations differed in different $T_{\Omega^+}$: $T_{\Omega^1}^1 = 0 K$, $T_{\Omega^2}^2 = 100000 K$, $T_{\Omega^3}^3 = 200000 K$, $T_{\Omega^4}^4 = 300000 K$. Thus we get $\mu_{\Omega^1} = 0$, $\mu_{\Omega^2} = 0.114$, $\mu_{\Omega^3} = 0.337$, $\mu_{\Omega^4} = 0.485$. We found that the higher temperature $T_{\Omega^+}$, the faster formation of neutral hydrogen molecule. When $T_{\Omega^+} = 0 K$, denoted by solid curves, formation is slowest among all situations. When $T_{\Omega^+} = 300000 K$, denoted by dash-dotted curves, formation is fastest among all situations.

Now we fix the time $t = 5 \times 10^{-4}$ in Fig. 8(b), we can intuitively see the tendency of temperature-dependent probabilities of $A$ and $D$ with the increase of temperature $T_{\Omega^+}$. When $T_{\Omega^+}$ is close to 0, probability of $A$ is close to 0 (probability of $D$ is close to 1). Then when $T_{\Omega^+}$ is larger than one threshold (e.g. $T_{\Omega^+} \approx 200000 K$), probability of $A$ rises abruptly (probability of $D$ descends abruptly) as the temperature increases. When $T_{\Omega^+}$ is larger than another threshold (e.g. $T_{\Omega^+} \approx 200000 K$), probability of $A$ reaches plateau, which is close to 1 (probability of $D$ reaches bottom, which is close to 0).

**TABLE II. Temperature-dependent ratio of influx rate to emission rate $\mu$ for photonic modes $\Omega^+$ and $\Omega^-$.

| $T_{\Omega^+}$ ($K$) | $T_{\Omega^-}$ ($K$) | $\mu_{\Omega^+}$ or $\mu_{\Omega^-}$ | $T_{\Omega^+}$ ($K$) | $T_{\Omega^-}$ ($K$) | $\mu_{\Omega^+}$ or $\mu_{\Omega^-}$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0 | 0 | 0.000 | 160000 | 160000 | 0.257 |
| 20000 | 2000 | 1.913e-5 | 180000 | 180000 | 0.299 |
| 40000 | 4000 | 4.373e-3 | 200000 | 200000 | 0.337 |
| 60000 | 6000 | 2.674e-2 | 220000 | 220000 | 0.372 |
| 80000 | 8000 | 6.613e-2 | 240000 | 240000 | 0.404 |
| 100000 | 10000 | 0.114 | 260000 | 260000 | 0.434 |
| 120000 | 12000 | 0.164 | 280000 | 280000 | 0.460 |
| 140000 | 14000 | 0.212 | 300000 | 300000 | 0.485 |

In Sec. VII B we introduced the electron spin transition in model. Now we continue introduce feeble spin-spin interaction between electrons and nuclei and pump a photon with mode $\Omega^n$ into initial system. Initial state is $|\Psi_{\text{initial}}\rangle$, described in Fig. 8(b), where two electrons
FIG. 9. (online color) The unitary evolution with consideration of electron spin transition and spin-spin interaction between electrons and nuclei. In (a), probability of state $|\Psi_{\text{initial}}\rangle$ is denoted by cyan solid curve, and probability of states $|\Psi_{\text{final}}\rangle$ and $|\Psi'_{\text{final}}\rangle$ is denoted by red solid curve. In (b), curves represent as same in Fig. 5(b).

FIG. 10. (online color) Variation of $T_{1,n}$. In (a), time-dependent curves of $A$ and $D$ are corresponding to $T_{1,n}^1$ (solid), $T_{1,n}^2$ (dashed), $T_{1,n}^3$ (dotted) and $T_{1,n}^4$ (dash-dotted), respectively. Here red dotted and dash-dotted for $A$ nearly coincided. Similarly, blue dotted and dash-dotted for $D$ also nearly coincided. In (b), $t = 5 \times 10^{-4}$ is fixed, and gray dots represent $\mu_{\Omega^n}$, red dots represent $A$ and blue dots represent $D$.

with $\downarrow$ are both in atomic ground orbital as above, and besides introduction of spin-flip photon, we also add photon with mode $\Omega^n$. Spin-spin interaction is permissible, and it only happens when electron is in atomic ground orbital, which is close to nucleus. Comparing to electron spin transition strength $g_{33}$, strength of spin-spin interaction between nucleus and electron $\nu_{en}$ is extremely slight. Thus we provisionally neglect spin-flip in ground orbitals in order to study the influence of spin-spin interaction to formation of neutral hydrogen molecule. That is to say, electron spin transition only happens when electron situates in atomic excited orbital.

Similarly, for added photon with mode $\Omega^n$, we assume that $T_{1,n} = 3 \times 10^4 K$, thus we get $\mu_{\Omega^n} \approx 0.485$.

According to numerical results in Fig. 9(a), we found red solid line representing $|\Psi_{\text{final}}\rangle$ and $|\Psi'_{\text{final}}\rangle$ rises and reaches 0.5 at the end (the sum of probabilities of $|\Psi_{\text{final}}\rangle$ and $|\Psi'_{\text{final}}\rangle$ reaches 1). $|\Psi_{\text{final}}\rangle$ and $|\Psi'_{\text{final}}\rangle$ are described in Fig. 3(b), where two electrons with different spins are fastened in molecular ground orbital, corresponding to $|0\rangle_n|1\rangle_{n_1}|0\rangle_{n_2}$ and $|0\rangle_n|0\rangle_{n_1}|1\rangle_{n_2}$, respectively. It also means that formation of $H_2$ is achieved and
free hydrogen atoms are no longer in existence. And in Fig. (b), red solid line A also rises and reaches 1, and blue solid line D descends to 0. The results are similar to those in Fig. (b). Thus, we can say that formation of neutral hydrogen molecule is also possible as above when we introduce spin-spin interaction.

In Fig. (a), two isomers of hydrogen molecule $O - H_2$ and $P - H_2$, described in Sec. [IV] and visualized in Fig. (b), are obtained. They take the forms

$$|O - H_2\rangle = \frac{1}{\sqrt{2}}(|\Psi'_{\text{final}}\rangle + |\Psi''_{\text{final}}\rangle) \quad (29a)$$

$$|P - H_2\rangle = \frac{1}{\sqrt{2}}(|\Psi'_{\text{final}}\rangle - |\Psi''_{\text{final}}\rangle) \quad (29b)$$

And probabilities of these two final states $|\Psi'_{\text{final}}\rangle$ and $|\Psi''_{\text{final}}\rangle$ are equal, thus

$$|O - H_2\rangle : |P - H_2\rangle = \frac{1}{2} : \frac{1}{2} \quad (30)$$

We found that probabilities of these two isomers of hydrogen molecule $O - H_2$ and $P - H_2$ are equal when initial state is $|\Psi''_{\text{initial}}\rangle$.

### Temperature variation of photonic modes $\Omega^n$

Now we investigate the influence of temperature variation of photonic modes $\Omega^n$ to the unitary evolution and the formation of neutral hydrogen molecule.

We assume that $T_{\Omega^1} = T_{\Omega^2} = 0K$, $T_{\Omega^3} = T_{\Omega^4} = 3 \times 10^6 K$, $T_{\Omega^5} = 3 \times 10^5 K$, and $T_{\Omega^6} = 3 \times 10^4 K$, thus we get $\mu_{\Omega^1} = \mu_{\Omega^2} = 0$, $\mu_{\Omega^3} = \mu_{\Omega^4} = \mu_{\Omega^5} = 0.485$. And we increase $T_{\Omega^6}$ from 0K to 30000K, and $\mu_{\Omega^6}$ rises from 0 to 0.485. We totally investigated 16 situations of temperature of photonic modes $\Omega^n$, which also are all written in Tab. [I].

In Fig. (a), we selected four situations differed in $\mu_{\Omega^1}$, $\mu_{\Omega^2}$, $\mu_{\Omega^3}$, $\mu_{\Omega^4}$, $\mu_{\Omega^5}$, and $\mu_{\Omega^6}$. Thus we get $\mu_{\Omega^1} = 0$, $\mu_{\Omega^2} = 0$, $\mu_{\Omega^3} = 0.114$, $\mu_{\Omega^4} = 0.337$, $\mu_{\Omega^5} = 0.485$. We found results as same as above: the higher temperature $T_{\Omega^n}$, the faster formation of neutral hydrogen molecule.

Similarly as above, we fix the time $t = 5 \times 10^{-4}$ in Fig. (b). When $T_{\Omega^n}$ is close to 0, probability of $A$ is close to 0 (probability of $D$ is close to 1). Then when $T_{\Omega^n}$ is larger than one threshold (e.g. $T_{\Omega^n} \approx 2000 K$), probability of $A$ rises abruptly (probability of $D$ descends abruptly) as the temperature increases. When $T_{\Omega^n}$ is larger than another threshold (e.g. $T_{\Omega^n} \approx 2000 K$), probability of $A$ reaches plateau, which is close to 1 (probability of $D$ reaches bottom, which is close to 0).

If we compare Figs. [8] and [10] obtained above, we can see that the temperature of the mode $\Omega^n$ affects the association reaction much more than the temperature of the mode $\Omega^n$.

### VIII. CONCLUDING DISCUSSION AND FUTURE WORK

In this paper, we simulate the association of the neutral hydrogen molecule in the cavity QED model — the TCH model. We have established the association-dissociation model and derived some analytical results of it:

In Secs. VIII A and VIII B we proved hybridization of atomic orbitals and formation of neutral hydrogen molecule only happens when electrons with different spins. Then the influence of variation of $T_{\Omega^1}$, $T_{\Omega^2}$, and $T_{\Omega^3}$ to the unitary evolution and the formation of neutral hydrogen molecule is obtained in Sec. VII C for $T_{\Omega^n}(T_{\Omega^n})$, the higher temperature, the lower probability of formation of neutral hydrogen molecule; for $T_{\Omega^n}$, the higher temperature, the faster process of formation of neutral hydrogen molecule. Finally, we studied spin-spin interaction between electrons and nuclei in Sec. VII D.

In this part, we investigated the formation of two isomers of hydrogen molecule $O - H_2$ and $P - H_2$, and also the influence of variation of $T_{\Omega^n}$ to the unitary evolution and the formation of neutral hydrogen molecule: the higher temperature, the faster process of formation of neutral hydrogen molecule. We have established the adequacy of our model for describing chemical scenarios, taking into account the influence of photons of various modes. In particular, the influence of nuclear spin photons is present, but it is much less than the influence of electron spin photons.

Our model is temporarily rough, but its advantage is in simplicity and scalability. This way it will be more modest. And in future this model can be generalized to many modifications for more complex chemical and biologic models.

### ACKNOWLEDGMENTS

This work was supported by the China Scholarship Council (CSC No.202108090483).

[1] Q. Wang, H.-Y. Liu, Q.-S. Li, Y. Li, Y. Chai, Q. Gong, H. Wang, Y.-C. Wu, Y.-J. Han, G.-C. Guo, and G.-P. Guo, Chemiq: A chemistry simulator for quantum computer (2021).

[2] J. R. McClean, N. C. Rubin, J. Lee, M. P. Harrigan, T. E. O’Brien, R. Babbush, W. J. Huggins, and H.-Y.

Huang, What the foundations of quantum computer science teach us about chemistry, The Journal of Chemical Physics 155, 150901 (2021).

[3] D. Claudino, A. J. McCaskey, and D. I. Lyakh, A backend-agnostic, quantum-classical framework for simulations of chemistry in Japan.
class="monospace"¿++,¿/span¿, ACM Transactions on Quantum Computing 10.1145/3523285 (2022), just Accepted.

[4] J. Zhu, Quantum simulation of dissociative ionization of $h^+ \chi$ in full dimensionality with a time-dependent surface-flux method, Phys. Rev. A 102, 053109 (2020).

[5] A. Vitaliy, K. Zheng, K. Alexei, H. Miao, O. Yuri, L. Wansun, and V. Nadezda, About chemical modifications of finite dimensional qed models, Nonlinear Phenomena in Complex Systems 24, 230 (2021).

[6] S. Haroche, Nobel lecture: Controlling photons in a box and exploring the quantum to classical boundary, Rev. Mod. Phys. 85, 1083 (2013).

[7] X. Gu, A. F. Kockum, A. Miranowicz, Y. xi Liu, and F. Nori, Microwave photonics with superconducting quantum circuits, Physics Reports 718-719, 1 (2017) microwave photonics with superconducting quantum circuits.

[8] A. F. Kockum and F. Nori, Quantum bits with josephson junctions, in Fundamentals and Frontiers of the Josephson Effect, edited by T. Tafuri (Springer International Publishing, Cham, 2019) pp. 703–741.

[9] A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, Nature Reviews Physics 1, 19 (2019).

[10] P. Forn-Díaz, L. Lamata, E. Rico, J. Kono, and E. Solano, Ultrastrong coupling regimes of light–matter interaction, Rev. Mod. Phys. 91, 025005 (2019).

[11] J. Casanova, G. Romero, I. Lizuain, J. J. García-Ripoll, and P. Forn-Díaz, L. Lamata, E. Rico, J. Kono, and E. Solano, Deep strong coupling regime of the jaynes–cummings model, Phys. Rev. Lett. 105, 263603 (2010).

[12] I. L. Rabi, On the process of space quantization, Phys. Rev. 49, 324 (1936).

[13] I. L. Rabi, Space quantization in a gyrating magnetic field, Phys. Rev. 51, 652 (1937).

[14] R. H. Dicke, Coherence in spontaneous radiation processes, Phys. Rev. 93, 99 (1954).

[15] J. J. Hopfield, Theory of the contribution of excitons to the complex dielectric constant of crystals, Phys. Rev. 112, 1555 (1958).

[16] E. Jaynes and F. Cummings, Comparison of quantum and semiclassical radiation theories with application to the beam maser, Proceedings of the IEEE 51, 89 (1963).

[17] M. Tavis and F. W. Cummings, Exact solution for an $n$-molecule—radiation-field hamiltonian, Phys. Rev. 170, 379 (1968).

[18] D. G. Angelakis, M. F. Santos, and S. Bose, Photon-blockade-induced mott transitions and $xy$ spin models in coupled cavity arrays, Phys. Rev. A 76, 031805 (2007).

[19] H. Wei, J. Zhang, S. Greschner, T. C. Scott, and W. Zhang, Quantum monte carlo study of superradiant supersons in the extended jaynes-cummings-hubbard model, Phys. Rev. B 103, 184501 (2021).

[20] S. Prasad and A. Martin, Effective three-body interac-

[21] tions in jaynes-cummings-hubbard systems, Sci Rep 8, 16253 (2018).

[22] L. Guo, S. Greschner, S. Zhu, and W. Zhang, Supersolid and pair correlations of the extended jaynes-cummings-hubbard model on triangular lattices, Phys. Rev. A 100, 033614 (2019).

[23] R. Düll, A. Kulagin, W. Lee, Y. Ozhigov, H. Miao, and K. Zheng, Quality of control in the tavis–cummings–hubbard model, Computational Mathematics and Modeling 32, 75 (2021).

[24] H.-P. Breuer, F. Petruccione, et al., The theory of open quantum systems (Oxford University Press, 2002).

[25] R. Alicki, The quantum open system as a model of the heat engine, Journal of Physics A: Mathematical and General 12, L103 (1979).

[26] R. Kosloff, Quantum thermodynamics: A dynamical viewpoint, Entropy 15, 2100 (2013).

[27] P. A. M. Dirac, The quantum theory of the emission and absorption of radiation, Proc. R. Soc. A, 243 (1927).

[28] V. Fock, Konfigurationsraum und zweite quantelung, Zeitschrift für Physik 75, 622 (1932).

[29] Y. Wu and X. Yang, Strong-coupling theory of periodically driven two-level systems, Phys. Rev. Lett. 98, 013601 (2007).

[30] A. P., P. J., and K. J., Atkins’ Physical Chemistry (Oxford University Press, 2017).

[31] M. J. Nye, Michael Polanyi and His Generation: Origins of the Social Construction of Science (University of Chicago Press, 2011).

[32] M. J. Matthews, G. Petitpas, and S. M. Aceves, A study of spin isomer conversion kinetics in supercritical fluid hydrogen for cryogenic fuel storage technologies, Applied Physics Letters 99, 081906 (2011).

[33] J. Y.-C. Chen, Y. Li, M. Frunzli, X. Lei, Y. Murata, R. G. Lawler, and N. J. Turro, Nuclear spin isomers of guest molecules in $h_{2}/sub@c/sub@60/sub@h$ and other endo-fullerenes, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 371, 20110628 (2013).

[34] A. Kulagin, V. Ladunov, Y. Ozhigov, N. Skovoroda, and N. Victorova, Homogeneous atomic ensembles and single-mode field: review of simulation results, in International Conference on Micro-and Nano-Electronics 2018 Vol. 11022 (SPIE, 2019) pp. 600–611.

[35] G. Rempe, H. Walther, and N. Klein, Observation of quantum collapse and revival in a one-atom maser, Phys. Rev. Lett. 58, 353 (1987).