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Entanglement and Energy for Vibrationally Localized States in Molecule CS₂

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The dynamics of quantum entanglement described by the von Neumann entropy is studied for the localized states of Fermi-resonance coupling vibrations in molecule CS₂, where the interacting energy between the stretching and the bending modes is considered to establish a connection between entanglement and energy. It is shown that entanglement reveals dominant anti-correlation with the interacting energy for the stretch-localized state, while that exhibits dominantly positive correlation for the bend-localized state. The entanglement and the energy for the dislocalized states are discussed as well. Those are useful for molecular quantum computing and quantum information in high dimensional states.

Key words: Entanglement, Quantum entropy, Vibrational analysis

I. INTRODUCTION

In recent years, a lot of interest has been generated in characterizing quantum entanglement in various systems [1–5]. In particular, the dynamics of entanglement for vibrational states in small molecules is well quantified in terms of several indicators such as the von Neumann entropy [6], the linear entropy [7], concurrence [8], and so forth. For example, the concurrence of the pendular qubit states can be equivalently measured by the frequency shift in two linear dipoles in the weak coupling realm [3]. The entanglement of vibrational states with local-mode character is more regular than that of states with normal-mode character [4, 5]. Those investigations [3–5] are of importance for molecular quantum computing since the interplay of the anharmonicity and the interacting between different vibrational modes play a primary role in such computing based on vibrational qubits [9]. However, those studies are restricted to two stretching vibrations in molecules [4, 5].

In the present work, we study the dynamics of entanglement for the bending and the stretching vibrations based on a spectroscopic Hamiltonian of molecule CS₂ [10], where the bend and the stretch are coupled with 2:1 Fermi resonance. Fermi resonance has become an important interaction in the analysis of complex experimental spectra in polyatomic molecules [11, 12]. Moreover, we consider the dynamics of the interacting energy so as to explore the relationship between quantum entanglement and intramolecular energy. That is further motivated by a recent work [5], the dynamics between

entanglement and coherence in two stretching modes displays a similar oscillation under suitable conditions [5]. It is thus of importance to investigate the dynamical correlation between entanglement and energy in another spectroscopic model. In order to examine such dynamics, we choose the stretching and the bending vibrationally localized states as initial states in a representative molecule, CS₂. The dynamics of entanglement and energy for a typically dislocalized state is calculated for comparison.

II. SPECTROSCOPIC HAMILTONIAN

We are interested in molecule CS₂ since its stretching and bending vibrational spectra up to 12000 cm⁻¹ have been measured with high resolution [10]. Moreover, a spectroscopic Hamiltonian has been introduced for the understanding of the major bands in the overtone region with a good insight into the nature of the vibrations.

The Hamiltonian is given by [10]

$$H = H_0(v_1, v_2) + K_{122}(a_1^\dagger a_2 a_2 + a_1 a_2^\dagger a_2^\dagger) \quad (1)$$
$$H_0(v_1, v_2) = \omega_1 \left(v_1 + \frac{1}{2} \right) + \omega_2 (v_2 + 1) + X_{11} \left(v_1 + \frac{1}{2} \right)^2 + X_{22} (v_2 + 1)^2 + X_{12} \left(v_1 + \frac{1}{2} \right) (v_2 + 1) + Y_{222} (v_2 + 1)^3 \quad (2)$$

where v_i is quantum number on the stretch (bend), indexes 1 and 2 stand for the degree of freedom on the stretching and the bending modes, respectively, a_i and a_i^\dagger ($i=1,2$) are the annihilation and

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creation operators on mode i , ω_1 , ω_2 , X_{11} , X_{22} , X_{12} , Y_{22} , and K_{122} have their usual spectroscopic meaning with K_{122} being the Fermi coupling between the stretch and the bend. Pique and coworkers have optimized those parameters [10], which are reproduced: $\omega_1=661.83\text{ cm}^{-1}$, $\omega_2=396.79\text{ cm}^{-1}$, $X_{11}=-0.181\text{ cm}^{-1}$, $X_{22}=0.719\text{ cm}^{-1}$, $X_{12}=-1.206\text{ cm}^{-1}$, $Y_{22}=-0.0112\text{ cm}^{-1}$, and $K_{122}=41.114\text{ cm}^{-1}$ for reference. Using those parameters, Pique and coworkers have made Fourier transform and phase space analysis [10]. Additionally, the dynamics of fidelity and mutual entropy has been discussed for vibrational states in this molecule [13]. Details for spectroscopic Hamiltonian are referred to Refs.[14, 15]. We use those parameters for molecule CS_2 to explore the dynamics of entanglement and energy.

III. DYNAMICS OF ENTANGLEMENT AND ENERGY

We are concerned with entanglement and energy due to their central role in the theory of quantum information. Two kinds of initial states, the stretching and the bending vibrationally localized states, are used to study the time-evolution of entanglement and energy. The importance of studying both quantities in different initial states is twofold. It may be viewed as a key to the understanding of some of the striking difference between the quantum and classical description of the world. Previous investigations [4, 5, 16] were mostly focused on quantum dynamics of the stretching vibrational localized states in small molecules. In particular, the problem of entanglement and energy transfer was discussed for an integrable model [5, 17]. The energy transfer by 1:2 and 1:1 resonance in two anharmonic oscillators was investigated in classical mechanics and quantum mechanics [18], where the conditions of complete energy exchange are given for an initial pure state. However, little is known about entanglement dynamics for the bending vibrationally localized states in a molecule. Therefore, it is interesting and necessary to investigate dynamics of entanglement and energy for both kinds of states.

The stretching and the bending vibrationally localized states are respectively given by $|v_1, 0\rangle$ and $|0, v_2\rangle$, where $|v_1, v_2\rangle=|v_1\rangle\otimes|v_2\rangle$ with v_i being the excited quantum number on vibrational mode i in molecule CS_2 . Of particular interest is a typical dislocalized state, which can be given by $|v_1, v_2\rangle$ with nonzero v_1 and v_2 . Since those states are pure states, we are able to use the von Neumann entropy of subsystems as a measure of entanglement. The entropy of vibrational mode 1(2) is given by the von Neumann entropy [6]

$$S_{1(2)} = -\text{Tr}[\rho_{1(2)}\ln\rho_{1(2)}] \quad (3)$$

where $\rho_{1(2)}=\text{Tr}_{2(1)}\rho_{12}$ is the reduced-density matrix. The purity of mode 1(2) is given by $\text{Tr}[\rho_{1(2)}]^2$. Thus, the increase in the von Neumann entropy is parallel to the

decrease in purity. For a pure state we have $S_1=S_2\equiv S$ and use a single S to describe the entanglement entropy. The density matrix ρ_{12} of full system evolves in time with the Liouville equation,

$$\dot{\rho}_{12}(t) = -i[H, \rho_{12}(t)] \quad (4)$$

Once the entropy of a subsystem is defined, it is natural to consider a basic well-known quantity, the energy of each vibrational mode. For the energy of individual vibrational mode we calculate the mean value of the relevant restriction of the free Hamiltonian:

$$E_{1(2)} = \text{Tr}[\rho_{12}H_{1(2)}] \quad (5)$$

$$H_1 = \omega_1 \left(v_1 + \frac{1}{2} \right) + X_{11} \left(v_1 + \frac{1}{2} \right)^2 \quad (6)$$

$$H_2 = \omega_2(v_2 + 1) + X_{22}(v_2 + 1)^2 + Y_{222}(v_2 + 1)^3 \quad (7)$$

As a result, it is easy to simulate the interacting energy between two modes,

$$E = \text{Tr}[\rho_{12}(H - H_1 - H_2)] \quad (8)$$

Thereby it is possible to compare the interaction energy with the entanglement entropy given by Eq.(3).

Figure 1 shows the time-evolution of the von Neumann entropy $S(t)$ and the interacting energy $E(t)$ for three initial states, the stretching vibrationally localized state $|6, 0\rangle$, the bending vibrationally localized state $|0, 12\rangle$, and the typically dislocalized state $|3, 6\rangle$ in molecule CS_2 , where the energy is scaled by 200 cm^{-1} so that it is dimensionless and comparable with the entropy. It is seen that the increasing rate of the entanglement entropy at the early-time evolution of state $|3, 6\rangle$ is the largest while that of state $|6, 0\rangle$ is the smallest. Moreover, the oscillation of the entropy in state $|3, 6\rangle$ is the fastest with smaller oscillatory amplitude. Those coming from that state $|3, 6\rangle$ are interacted with more states via Fermi resonances. However, the increasing rate of the interacting energy in the early-time evolution is negative for initial state $|6, 0\rangle$, while that is positive for state $|0, 12\rangle$. That implies that the initially excited energy in one mode is transferred into another mode without initial excitation. Although the dynamics of entropy and energy is irregular, one can observe two different kinds of correlation between entropy and energy in Fig.1. The first kind of correlation is a case in which both quantities rise and lower together, and another kind is a case where they are anti-correlated, that is, one quantity increases with the increase of time while another decreases or vice versa. It is noted that entropy and energy display dominant anti-correlation for the stretching vibrationally localized state $|6, 0\rangle$, whereas they are dominantly positive correlated for the bending vibrationally localized state $|0, 12\rangle$. For the typically dislocalized state $|3, 6\rangle$ the positive- or anti-correlation between both quantities occurs in irregular

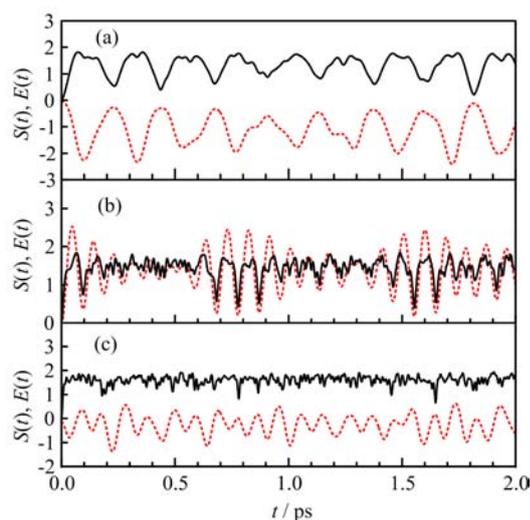


FIG. 1 von Neumann entropy $S(t)$ (solid line) and interacting energy $E(t)$ (dotted line) for three initial states, (a) stretch-localized state $|6,0\rangle$, (b) bend-localized state $|0,12\rangle$, and (c) typically dislocalized state $|3,6\rangle$ in molecule CS₂, where the energy is divided by 200 cm^{-1} .

manner. However, the oscillation of the entropy is much faster than that of energy for those states.

Figure 2 shows another example for the dynamics of entropy and energy, with different initial states, $|10,0\rangle$, $|0,20\rangle$, and $|5,15\rangle$, and the energy is divided by 300 cm^{-1} . The above argument for Fig.1 can be applied to Fig.2. We would like to stress the difference in the entropy between Fig.1 and Fig.2. For those stretching and bending vibrationally localized states, the maximal value and the increasing rate of entropy at the early-time evolution increase as the quantum number increases, where the entropic oscillation becomes faster. Moreover, for the same excitation in both kinds of initial states, the increasing rate of entropy at the early-time evolution for the bend-localized state is larger than that for the stretch-localized state. However, the maximal value of latter state is larger. That indicates that the maximal entanglement can be available for this molecule prepared in the stretch-localized state.

Finally, it should be remarked that we have made more calculations for other initial states. In particular, if the initial state is taken to be $|1,0\rangle$ and $|0,2\rangle$, the entropies for both states are equal, analytically given by

$$S = -\lambda \ln \lambda - (1 - \lambda) \ln(1 - \lambda) \quad (9)$$

$$\lambda = \frac{2K_{122}^2}{\Omega^2} [1 - \cos(\Omega t)] \quad (10)$$

$$\Omega = \sqrt{[H_0(1,0) - H_0(0,2)]^2 + 4K_{122}^2} \quad (11)$$

which clearly states that the dynamical entanglement between two vibrational modes becomes significant if

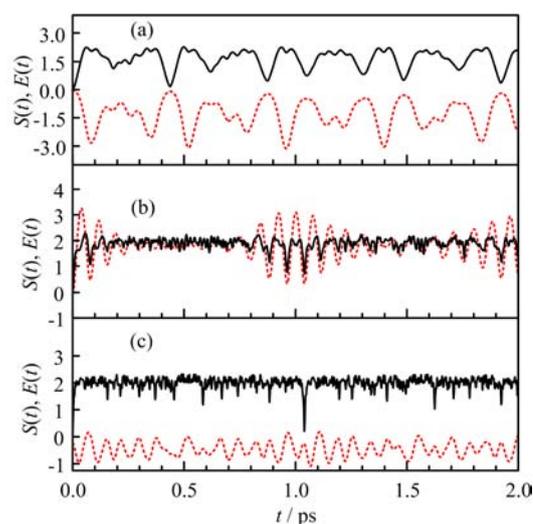


FIG. 2 von Neumann entropy $S(t)$ (solid line) and interacting energy $E(t)$ (dotted line) for initial states, (a) $|10,0\rangle$, (b) $|0,20\rangle$, and (c) $|5,15\rangle$, with the energy scaled by 300 cm^{-1} .

and only if Fermi coupling (K_{122}) is nonzero. In this case the interacting energy respectively reads

$$E = \mp \frac{1}{2} \left\{ [H_0(0,2) - H_0(1,0)] \left(1 - 4 \frac{K_{122}^2}{\Omega^2} \right) + \frac{3}{8} X_{12} \left(60 - \frac{7\Omega^2}{K_{122}^2} \right) \right\} [1 - \cos(\Omega t)] \quad (12)$$

indicating that the entropy is completely anti-(positive-) correlated with the interacting energy for the stretch- (bend-) localized state. More simulations demonstrate that the above conclusions can be applied under suitable conditions, that is, for the localized state with initial excitations on the stretching or the bending mode, the dynamics of entropy and energy can reveal dominant positive- or anti-correlation. Moreover, for the localized state with high excitations in one vibrational mode and lower or no excitations in another mode, such property remains. We believe the studied dynamics is useful in the understanding of the complicated entanglement in high dimensional states from intramolecular energy.

IV. CONCLUSION

We have studied the dynamics of entanglement and energy for different initial states in the stretching and bending vibrations of molecule CS₂. It is shown that the maximal entanglement can be obtained for the stretching vibrationally localized state. Moreover, we consider the relation between the entanglement and the interacting energy between the stretching and the bending modes. It is demonstrated that the entanglement measured by the von Neumann entropy is the most distinct

in dominant anti-correlation with the interacting energy for the stretch-localized state, while that is dominantly positive correlation for the bend-localized state. That implies that the interacting energy can provide some information of quantum entanglement. However, for the dislocalized states, the positive- or anti-correlation between the entanglement entropy and the interacting energy happens in an irregular way. Those can be utilized in quantum computation [9] based on vibrational states in high dimensions.

It is possible to explore the entanglement quantified by other measures [1, 2] so as to establish a link among entanglement and other well-known quantities for mixed states, and results will be discussed elsewhere.

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