Lie Algebraic Approach to Dynamical Entanglement of Vibrations in Triatomic Molecules

Hairan Feng,1,∗ Peng Li,1 Yujun Zheng2 and Shiliang Ding2

1 Department of Physics and Information Engineering, Jining University, Jining 273155, China
2 School of Physics, Shandong University, Jinan 250100, China

(Received November 10, 2009)

The relation between dynamics of quantum entanglement and dynamics of molecular vibrations is explored by the Lie-algebraic approach. The analytical expression of reduced-density matrices is obtained by using the algebraic model. The linear entropy, von Neumann entropy and the Lyapunov function are employed to measure the quantum entanglement for various initial states, respectively. The mean values of entropy and the Lyapunov function are also discussed.

Subject Index: 061

§1. Introduction

Quantum entanglement has many applications in the emerging technologies of quantum computation, quantum teleportation and quantum cryptography.1)–5) Among the best known applications of entanglement are superdense coding6), 7) and quantum state teleportation.8), 9) In brief, entanglement has been a resource of great utility in quantum computation and quantum information. The creation and transformation of entanglement are dynamical processes of interest in quantum information theory. Many studies are devoted to explore the dynamical properties of entanglement.10), 11) Recently much attention has been given to the theoretical studies of entanglement dynamics in ideal molecular systems12)–15) and using molecular vibrational states for quantum computing.16), 17) In this work we explore the entanglement dynamics of realistic molecular anharmonic stretching vibrations in triatomic molecules by the Lie-algebraic approach. Entropy provides one tool which can be used to quantify entanglement. It measures how much uncertainty there is in the state of a physical system. Here we choose the linear entropy and von Neumann entropy as measures of quantum entanglement. Both of them are decided by the density operator or density matrix of quantum systems. The density operator can be applied to described individual subsystems of a composite quantum system.1) Such a description is provided by the reduced density operator, so it is so useful as to be virtually indispensable in the analysis of composite quantum systems. In this research, we give analytical expression of reduced-density matrices by using the algebraic Hamiltonian which is presented by the quadratic anharmonic oscillators model.18), 20), 21) We have successfully studied the infrared multiphoton resonant transition and selective vibrational excitation for small molecules23), 24) by using the

∗) Corresponding author. E-mail: hairanfeng@mail.sdu.edu.cn
Here we employ the Hamiltonian to study the entanglement dynamics of molecular vibrations for various initial states. The linear triatomic molecules HCN and DCN are taken as examples. It is shown that the entanglement of vibrations displays quite different behaviors for different initial states. The properties of dynamical entanglement also depend on the vibrational transitions in molecules.

The paper proceeds as follows. In §2, the analytical expression of reduced-density matrices is derived by the Lie algebraic method. Then the linear entropy, von Neumann entropy and the Lyapunov function can be analytically obtained. The mean values of entropy and the Lyapunov function are also calculated. In §3, the time evolution of the entropy and the Lyapunov function for various initial states in molecules HCN and DCN are investigated. The different dynamical properties of entanglement of vibrations in HCN and DCN are discussed. The paper ends with conclusions and some discussions in §4.

§2. Theory

2.1. The general theoretical framework

For a quantum system with time-independent Hamiltonian, the time-dependent wave function can be obtained by

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle = e^{-it\hat{H}}|\psi(0)\rangle,$$

where $|\psi(0)\rangle$ is the initial state of the quantum system. Here $\hbar = 1$ as we choose atomic units.

Then the total density operator and the reduced density matrices can be described as

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)|,$$

$$\rho_1(t) = \text{Tr}_2\rho(t) = \text{Tr}_2|\psi(t)\rangle\langle\psi(t)|.$$

where Tr$_2$ denotes the partial trace over the second subsystem.

The linear entropy $S_l(t)$ and von Neumann entropy $S_n(t)$ are defined by, respectively,$^{25,26}$

$$S_l(t) = 1 - \text{Tr}_1\rho_1(t)^2,$$

$$S_n(t) = -\text{Tr}_1[\rho_1(t)\ln\rho_1(t)].$$

The stability of the quantum control system can be described by the Lyapunov function$^{27,28}$

$$L_y(t) = 1 - |\langle\psi(0)|\psi(t)\rangle|^2.$$

Here the Lyapunov function is used to investigate the “distance” between the state $|\psi(t)\rangle$ and the initial state $|\psi(0)\rangle$. 

Downloaded from https://academic.oup.com/ptp/article-abstract/123/2/215/1895586 by guest on 07 March 2019
The mean values of the linear entropy, von Neumann entropy and the Lyapunov function over long time $T$ are defined by

$$\bar{S}_l = \frac{1}{T} \int_0^T S_l(t) dt,$$

$$\bar{S}_n = \frac{1}{T} \int_0^T S_n(t) dt,$$

$$\bar{L}_y = \frac{1}{T} \int_0^T L_y(t) dt.$$  \hfill (2.6)

2.2. Dynamical Lie algebraic model

We consider the one-dimensional vibrational motion of a diatomic molecule firstly. For completeness, we briefly review the well-known results for the $U(2)$ dynamical symmetry of diatomic molecules. The $U(2)$ algebra is successfully applied to describe vibrations, and $U(2)$ possesses two dynamical symmetry chains: \hfill (2.7)

$$U(2) \supset U(1),$$

$$U(2) \supset O(2).$$

The Hamiltonian of a non-rotating Morse oscillator could be written as

$$\hat{H}_{mol} = \hbar \omega_0 \left( \frac{\hat{P}^2}{2} + \frac{\hat{Q}^2}{2} \right),$$  \hfill (2.8)

where $\omega_0$ is the frequency of the anharmonic oscillator, and $\hat{P}$ and $\hat{Q}$ are the bilinear products constructed by the generators of $U(2)$ algebra. \hfill (2.10)

An equivalent quadratic expression of Morse oscillator Hamiltonian (2.8) is

$$\hat{H}_{mol} = \hbar \omega_0 \left( \hat{A}^\dagger \hat{A} + \frac{\hat{I}_0}{2} \right),$$  \hfill (2.9)

where the creation ($\hat{A}^\dagger$) and annihilation ($\hat{A}$) operators are defined as

$$\hat{A}^\dagger = \frac{1}{\sqrt{2}} (\hat{Q} - i \hat{P}),$$

$$\hat{A} = \frac{1}{\sqrt{2}} (\hat{Q} + i \hat{P}),$$  \hfill (2.10)

which obey the commutation relations

$$[\hat{A}, \hat{A}^\dagger] = \hat{I}_0, \quad [\hat{I}_0, \hat{A}] = -2x_0 \hat{A}, \quad [\hat{I}_0, \hat{A}^\dagger] = 2x_0 \hat{A}^\dagger.$$  \hfill (2.11)

It should be noted that $\hat{I}_0$ tends to the identity operator in the harmonic limits, and $x_0 \to 0$ in these limits. The anharmonic correction is given in order of $x_0 = 1/N$. \hfill (2.12)

The triatomic molecule could be thought as the two coupled Morse oscillators, i.e., the dynamical symmetry group of a triatomic molecule is

$$U_1(2) \otimes U_2(2).$$  \hfill (2.12)
Then for stretching vibrations in a triatomic molecule, the algebraic Hamiltonian reads
\[ \hat{H}_{\text{tri}} = \hbar \omega_0 \left( \frac{\hat{P}_1^2}{2} + \frac{Q_1^2}{2} \right) + \hbar \omega_2 \left( \frac{\hat{P}_2^2}{2} + \frac{Q_2^2}{2} \right) - \lambda (\hat{Q}_1 \hat{Q}_2 + \hat{P}_1 \hat{P}_2), \] (2.13)
where the ‘1’ and ‘2’ subscripts denote one of the two bonds of the molecule, respectively, \( \lambda \) is the coupling coefficient, and we here include the kinetic and potential linear couple terms.

The Hamiltonian (2.13) could be rewritten, by using Eq. (2.10), as
\[ \hat{H} = \hbar \omega_0 \left( \hat{A}_1^{\dagger} \hat{A}_1 + \frac{\hat{I}_{01}}{2} \right) + \hbar \omega_2 \left( \hat{A}_2^{\dagger} \hat{A}_2 + \frac{\hat{I}_{02}}{2} \right) - \lambda \left( \hat{A}_1^{\dagger} \hat{A}_2 + \hat{A}_2^{\dagger} \hat{A}_1 \right), \] (2.14)
where \( \omega_0 \) and \( \omega_2 \) are the angular frequencies of the triatomic molecule corresponding to the bond 1 and bond 2. \( \lambda \) is the coupling coefficient which can be determined by the experimental values. This Hamiltonian can reproduce the real situations of vibrations in the linear triatomic molecules.\(^{23,24}\)

The initial states are taken to be
\[ |\psi(0)\rangle = |N_1, v_1\rangle \otimes |N_2, v_2\rangle \equiv |v_0, v_n - v_0\rangle, \] (2.15)
where \( v_0 = v_1 \) can be arbitrary value between 0 and \( v_n (= v_1 + v_2) \).

The quadratic operators \( \hat{A}_i^{\dagger}, \hat{A}_i, \hat{I}_{0i} \) in the Hamiltonian (2.14) act on the state \( |N_i, v_i\rangle \).\(^{18}\)

\[ \hat{A}_i^{\dagger} |N_i, v_i\rangle = \sqrt{1 - x_{0i} v_i} |v_i + 1\rangle |N_i, v_i + 1\rangle, \]
\[ \hat{A}_i |N_i, v_i\rangle = \sqrt{1 - x_{0i} v_i} |v_i - 1\rangle |N_i, v_i - 1\rangle, \]
\[ \hat{I}_{0i} |N_i, v_i\rangle = (1 - 2x_{0i} v_i) |N_i, v_i\rangle. \] (2.16)

According to Eqs. (2.1), (2.14) and (2.16), the time-dependent wave function can be written as
\[ |\psi(t)\rangle = e^{-it\hat{H}} |\psi(0)\rangle \]
\[ = e^{-it\hat{H}} |v_0, v_n - v_0\rangle \]
\[ = \sum_{k=0}^{\infty} \frac{(-it)^k}{k!} \hat{H}^k |v_0, v_n - v_0\rangle \]
\[ = \sum_{k=0}^{\infty} \sum_{\min\{k, v_n-v_0\}}^{\infty} \Gamma_k^m(t) |v_0 + m, v_n - v_0 - m\rangle \]
\[ = \sum_{m=-v_0}^{v_n-v_0} P^m(t) |v_0 + m, v_n - v_0 - m\rangle, \] (2.17)
where \( P^m(t) = \sum_{k=0}^{\infty} \Gamma_k^m(t) \). When \( k = 0 \), \( \Gamma_0^m(t) = \delta_{0,m} \), and when \( k = 1, 2, 3, ..., \infty \), the recursive expression \( \Gamma_k^m(t) \) is
\[ \Gamma_k^m(t) = -\frac{i}{k} \cdot \{ \gamma_0(v_0 + m, v_n - v_0 - m) \Gamma_{k-1}^m(t) \} \]
\[ + \gamma_+(v_0 + m, v_n - v_0 - m)I_{k-1}^{m+1}(t) \\
+ \gamma_-(v_0 + m, v_n - v_0 - m)I_{k-1}^{m-1}(t) \} \]

(2.18)

in which the function \( \gamma_0, \gamma_+, \gamma_- \) can be obtained using algebraic operations

\[
\begin{align*}
\gamma_0(v_1, v_2) &= \hbar \omega_0 (v_1^2 - x_0 v_1^2) + \hbar \omega_2 (v_2^2 - x_0 v_2^2), \\
\gamma_+(v_1, v_2) &= -\lambda \sqrt{(1 - x_0 v_1)(v_1 + 1) \cdot \sqrt{1 - x_0 v_2(v_2 - 1)v_2}}, \\
\gamma_-(v_1, v_2) &= -\lambda \sqrt{(1 - x_0 v_1(v_1 - 1))v_1 \cdot \sqrt{1 - x_0 v_2(v_2 + 1)}},
\end{align*}
\]

(2.19)

where \( v_1 = v_0 + m, v_2 = v_n - v_0 - m \).

The analytical expression of reduced-density matrices can be given by using Eqs. (2.3) and (2.17),

\[
\rho_1(t) = \text{Tr}_2 \rho(t) \\
= \text{Tr}_2 \{ |\psi(t)\rangle \langle \psi(t)| \} \\
= \sum_{m=-v_0}^{v_n-v_0} \sum_{m'=-v_0}^{v_n-n_0} P^m(t)P^{m'}(t)^* |v_0 + m\rangle \langle v_0 + m'| \delta_{m,m'} \\
= \sum_{m=-v_0}^{v_n-v_0} |P^m(t)|^2 |v_0 + m\rangle \langle v_0 + m|. 
\]

(2.20)

Putting Eq. (2.20) into Eq. (2.4), the linear entropy and von Neumann entropy can be written as, respectively,

\[
S_l(t) = 1 - \text{Tr}_1 \rho_1(t)^2 = 1 - \sum_{m=-v_0}^{v_n-v_0} |P^m(t)|^4, 
\]

(2.21)

\[
S_n(t) = -\text{Tr}_1 [\rho_1(t) \ln \rho_1(t)] = \sum_{m=-v_0}^{v_n-v_0} |P^m(t)|^2 \ln |P^m(t)|^2. 
\]

(2.22)

The Lyapunov function can be obtained by using Eqs. (2.5) and (2.17),

\[
L_\psi(t) = 1 - |\langle \psi(0) | \psi(t) \rangle|^2 = 1 - |P^0(t)|^2. 
\]

(2.23)

Then the mean values of entropy and Lyapunov function can be directly calculated by putting Eqs. (2.21), (2.22) and (2.23) into Eq. (2.6).

**§3. Dynamical entanglement of vibrations**

In this section we study the dynamics of entanglement of vibrations in molecules HCN and DCN. The Hamiltonian (see Eq. (2.14)) has been used to calculate the stretching vibrational energies of HCN and DCN molecules successfully\textsuperscript{23} and got a good agreement with the experimental values. See the parameters of HCN and DCN molecules in the reference.\textsuperscript{23} We choose three kinds of initial states \( |0, v_n\rangle \),
Fig. 1. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n-v_0\rangle$ in HCN with $v_0 = 0$ and $v_n = 3, 6, 9, 12, 15$.

Fig. 2. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n-v_0\rangle$ in DCN with $v_0 = 0$ and $v_n = 3, 6, 9, 12, 15$.

$|\frac{v_n}{2}, \frac{v_n}{2}\rangle$ (or $|\frac{(v_n-1)}{2}, \frac{(v_n+1)}{2}\rangle$) and $|v_n, 0\rangle$. The first and third kinds of initial states are of local-mode character and the second kind of initial states are of normal-mode character. We calculate the linear entropy and von Neumann entropy with those various initial states, the results are given in Figs. 1–8. From these figures, we can see the linear entropy and von Neumann entropy have the similar behaviors for the same quantum system which is consistent with other research.29,30

Figures 1 and 2 show the entanglement dynamics of vibrations in HCN and DCN for initial states $|0, v_n\rangle$ ($v_n = 3, 6, 9, 12, 15$), respectively. The evolutions of the entropies are both regular and periodic in HCN and DCN molecule. With the increase of the vibrational quantum number $v_n$, the values of entropy become larger and the period of the entropy become shorter. Furthermore, the oscillation frequencies of HCN are larger than those of DCN. It should be mentioned that the initial states are difficult to be obtained because the excitation of C-H (or C-D) bond is much easier than that of C-N bond.

For initial states $|\frac{v_n}{2}, \frac{v_n}{2}\rangle$ (or $|\frac{(v_n-1)}{2}, \frac{(v_n+1)}{2}\rangle$) ($v_n = 3, 6, 9, 12, 15$), the entanglement behaviors in HCN and DCN are given in Figs. 3 and 4. The oscillations of the entropy become irregular as $v_n$ increases. However, in Fig. 7 it is interesting that the “classical”-like beat phenomena of the entropy happen in longer time evolution when $v_n = 2, 3, 4$. From Fig. 7, we can also see the beat has the longer period in entanglement for DCN which means the entanglement can last for a long time. In addition, we find that the behaviors of entanglement are similar for the initial states $|\frac{(v_n-1)}{2}, \frac{(v_n+1)}{2}\rangle$ and $|\frac{(v_n+1)}{2}, \frac{(v_n-1)}{2}\rangle$. Thus we only give the results of the former.

Figures 5 and 6 give the entanglement dynamics of vibrations in HCN and DCN for initial states $|v_n, 0\rangle$ ($v_n = 3, 6, 9, 12, 15$), respectively. The period of entropy becomes longer as $v_n$ increases which is different from the entanglement behavior.
Fig. 3. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n - v_0\rangle$ in HCN with $v_0 = \text{Fix}\{v_n/2\}$ and $v_n = 3, 6, 9, 12, 15$.

Fig. 4. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n - v_0\rangle$ in DCN with $v_0 = \text{Fix}\{v_n/2\}$ and $v_n = 3, 6, 9, 12, 15$.

with initial states $|0, v_n\rangle$. The evolution of the entropy in DCN molecule has better quasiperiodic behavior than in HCN molecule. For HCN molecule, the oscillation becomes irregular as $v_n$ increases. But we find that there is a valuable phenomenon in the behavior of the entropy for HCN when we take the high-excited states $v_n = 15, 20, 25$ as the initial states. The period of the entropy becomes regular and smaller, at the same time, the amplitude of the entropy decreases as $v_n$ increases (see Fig. 8(a)). This result would be usable for quantum computation and quantum information because the state which is in entanglement has the tendency of disentanglement.\textsuperscript{1) Virtually, it is the strong local-mode vibration of C-H bond which causes to the interesting property in HCN.\textsuperscript{13) That is to say, the vibration of C-H bond has a strong local character in high-excited states. In addition, the phenomenon can also be observed in Fig. 8(b) in which $v_n$ is taken to be 35, 40, 45. The initial states are taken to be the higher excited state for DCN because the anharmonic parameter of DCN is much smaller than that of HCN molecule. Generally, the entropy has better quasiperiodic character for the local-mode initial states than that for normal-mode states, this character has been mentioned in other researches.\textsuperscript{13, 14) Additionally, the amplitude of the entropy is larger for the normal-mode initial states.}

The corresponding Lyapunov functions in evolution are given in Figs. 9 and 10. The Lyapunov functions have the similar behaviors with the linear entropy. It is shown that the “distance” between the initial state and the state in evolution is also related to the initial state. The state in evolution may still stay at the initial state ($L_y(t) = 0$) or transit to other states completely ($L_y(t) = 1$). From those figures, we can see that there is more probability to transit from the initial state to other states for the normal-mode initial state (see Figs. 9(b) and 10(b)) than the local mode initial state (see Figs. 9(a)(c) and 10(a)(c)) in evolution. Furthermore, we also
Fig. 5. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n - v_0 \rangle$ in HCN with $v_0 = v_n$ and $v_n = 3, 6, 9, 12, 15$.

Fig. 6. The linear entropy $S_l(t)$ (a) and the von Neumann entropy $S_n(t)$ (b) for the initial states $|v_0, v_n - v_0 \rangle$ in DCN with $v_0 = v_n$ and $v_n = 3, 6, 9, 12, 15$.

Fig. 7. The linear entropy $S_l(t)$ for the initial states $|v_0, v_n - v_0 \rangle$ in HCN (a) and DCN (b) with $v_0 = \text{Fix}\{v_n/2\}$ and $v_n = 2, 3, 4$.

Fig. 8. The linear entropy $S_l(t)$ for the initial states $|v_0, v_n - v_0 \rangle$ in HCN (a) and DCN (b). (a) $v_0 = v_n$ and $v_n = 15, 20, 25$; (b) $v_0 = v_n$ and $v_n = 35, 40, 45$.

notice that the value of the “distance” is close to 1 more quickly for $|v_n, 0 \rangle$ states than $|0, v_n \rangle$ states as $v_n$ increases. This means the excitation of C-H (or C-D) bond is the main factor which promotes the chaotic motion. The result also coincides with the other research.31)

At last, Figs. 11 and 12 give the mean entanglement and the mean Lyapunov function, respectively. They display the similar behavior for the total vibrational
Lie Algebraic Approach to Dynamical Entanglement

quantum number $v_n = 15$ and $v_n = 20$. The mean entropies and Lyapunov functions increase as $v_0$ increases at first, and the values for DCN are larger than for HCN. Then the mean entropy and Lyapunov function go to fixed values with small fluctuations. However, in Figs. 11 (b) and 12 (b), we can see an obvious turn for HCN when the vibrational quantum number $v_0$ is near the total vibrational quantum number $v_n = 20$. The phenomenon has the same reason as we explained in Fig. 8(a). The turns of the mean entropies show the normal-to-local transition. It should be pointed out that the turn of the mean entropy can also be observed in DCN as long as the vibrational quantum number $v_0$ is high enough. From these figures, we can see that the choice of the initial state has a crucial impact on the dynamical entanglement of anharmonic stretching vibrations in realistic molecules.

§4. Conclusions and discussion

In summary, we have studied the entanglement dynamics of anharmonic stretching vibrations in triatomic molecules for different initial states by the Lie algebraic approach successfully. We take HCN and DCN molecules as examples. Both the linear entropy and von Neumann entropy are used to measure the dynamical entanglement, and the two measurements are found to have the similar behavior. For all initial states, the entropy has a better periodic behavior for the local-mode initial state $|0, v_n \rangle$ and $|v_n, 0 \rangle$ than for the normal-mode initial state $|v_0, v_n - v_0 \rangle$ ($v_0 = \text{Fix}\{v_n/2\}$). Furthermore, the entropy in DCN displays a longer period and a larger amplitude than in HCN. We also find the dynamical entanglement is related to the vibrational transition of the local-mode and normal-mode. The interesting changes in Fig. 8 and the turns of the mean entropy in Fig. 11 can exhibit the char-
The other significant phenomenon is the longer-period of the “classical”-like beat in the entanglement as we have seen in Fig. 7. That behavior means the entanglement can last for a long time which may be a valuable character for quantum computing based on vibrational states. With the aid of long-time entanglement, otherwise impossible tasks may be achieved in quantum computing. As a whole, the dynamical entanglement of anharmonic stretching vibrations in triatomic molecules heavily depends on the initial states. We can obtain the required entanglement by choosing the different initial state. It is worth to investigate the impact of different initial states on the entanglement in realistic molecular systems. The results may be helpful in quantum computing based on vibrational states.

The method can also be used to study the dynamical entanglement in other polyatomic molecules. Further theoretical studies about the influence of chaos on the dynamical entanglement in the high-excited molecular system are in progress.

Acknowledgements

This work is supported by the National Natural Science Foundation of China under Grant Nos. 10874102 and 10947103. Partial financial supports from the Science Foundation of Shandong Province, China.
References

28) S. Ceng, *Introduction to Quantum Mechanical System Control* (Scientic Press, Beijing, 2006).