Tunneling dynamics of amino-acid: model for chiral evolution?

Kyunghhee Lee\textsuperscript{b}, Seokmin Shin\textsuperscript{c}, Jaejin Ka\textsuperscript{a,\*}

\textsuperscript{a}Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055, USA
\textsuperscript{b}Department of Chemistry, Sejong University, Seoul 143-747, South Korea
\textsuperscript{c}School of Chemistry and Molecular Engineering, Seoul National University, Shillim-dong San 56-1, Seoul 151747, South Korea

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Abstract

We present detailed studies on the quantum tunneling dynamics in model double-well potentials for the inversion of an amino acid. We introduce an asymmetric double-well potential with a very small difference in the depths of the two potential wells, which represents the presence of the parity-violating energy difference (PVED) between two optical isomers. From a simple extrapolation from the energy levels calculated by the time-independent method, the inversion time of model alanine molecule is estimated to be about $10^{29}$ years. The results of the model calculations on the relative probabilities of the two optical isomers showed that the presence of PVED can lead to the enrichment of one of the enantiomers such as the $L$-form of an amino acid. It is suggested that tunneling dynamics of amino acids with PVED provides a plausible mechanism for much faster development of homo-chirality.

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1. Introduction

Double-well models have been used in wide spectrum of applications. Many physical and chemical systems can be described by an effective double-well potential which has almost degenerate minima. There has been a great amount of interest in the effect of a dissipative environment on the dynamics of such systems in the classical and quantum regimes [1]. Quantum mechanical aspects of the barrier-crossing and tunneling dynamics can be studied by a wide variety of numerical methods [2]. Recently, we have investigated the quantum tunneling dynamics through high potential barrier between double-well potential models describing the inversion of molecules such as NH$_3$ and CH$_4$ [3]. Various theoretical and computational methods were compared and the feasibility of various methodologies were examined.

The other interests in double-well potential models are concerned with possible implications for the origin of homo-chirality of $L$-amino acids. The essential building blocks for life (for example, amino acids, nucleic acids, sugars) are chiral and usually in nature exist in only one of the two enantiomeric forms. Several controversial theories have been proposed to explain the development of such biomolecular homo-chirality [4–9]. R. Janoschek suggested kinetic models with intrinsic asymmetry to explain the origin of $L$-amino acids [5]. The kinetic model is based on the hypothesis that the intrinsic energies for two enantiomers $L$ and $D$ are different. The origin for the inequality in energy is associated with the parity-violating weak interaction. It is possible to evaluate theoretically the parity-violating energy difference (PVED) between two enantiomers by quantum calculations [4,10]. Earlier quantum calculations of PVEPs for simple biomolecules indicated that the naturally occurring enantiomers are stabilized by about $10^{-14} - 10^{-17} k_B T$. However, whether the definitive magnitudes for PVED can be obtained form such calculations are arguable [11]. More recent publications suggested that the relative thermodynamic stability of the $L$- or $D$- forms of an amino acid cannot be determined conclusively [12,13]. The validity of PVED model, which is still an open question, is not of our concern in the present study. Our main focus is to examine how PVED affect tunneling dynamics through high barrier between enantiomers.

The paper is organized as follows. The definition of the theoretical model and a brief description of
the computational scheme for the dynamics of the system are given in Section 2. The results presented in Sections 3 and 4 summarize the conclusions together with some discussion.

2. Theory and model

In this Section, we briefly describe theoretical backgrounds and computational methods involved in the present study. More detailed accounts can be found in the previous publication [3].

In a time-independent approach, quantum eigenstates can be obtained by solving algebraic equations with wavefunctions expanded in an orthonormal basis set such as particle-in-a-box (PIB) basis. For time-dependent methods, eigenstates of the system can be obtained by a spectral analysis on the time-correlation function. In the usual fast Fourier transform (FFT) method, eigenenergies are extracted from the peaks of the power spectrum. Filter-Diagonalization (FD) method can provide efficient technique for extracting eigenstates, while avoiding long propagation times [14–16].

For a system in thermal equilibrium at temperature \( T \), ‘thermal Gaussian wave packet’ (TGWP) can be used as an initial wavefunction, which is a statistical mixture of stationary states with weights proportional to Boltzmann factor. Instead of including all the unknown eigenfunctions of the system, the TGWP is designed to have the same total energy as that of a harmonic oscillator at \( T \), while maintaining the characteristics of Gaussian wavepacket. The TGWP is expected to be useful in ‘temperature-dependent’ quantum dynamics [3]. Once the initial wavepacket is chosen, time-evolution of the wavefunction can be done by several propagation schemes such as split-operator (SPO) and Chebyshev methods [17,18].

Ammonia inversion provides a typical example of double-well with a potential barrier. The functional form of a double-well potential is usually taken to be the 4th order polynomial,

\[ V(x) = \sum_{j=0}^{4} c_j x^j, \]

where \( x \) represents the height of the pyramidal structure or deviation from the symmetry center. In the present study, we use the following form for the potential model.

\[ V(x) = \frac{d}{\delta} \left[ \left( \frac{x}{\delta} \right)^4 - 2 \left( \frac{x}{\delta} \right)^2 + 1 \right]. \]

The values of the parameters (\( \varepsilon \): well depth; \( \delta \): half-distance between two minimum) can be estimated from ab initio calculations. We also require that the probability density outside the region determined by the molecular size to be negligible:

\[ \lim_{x \to \pm \alpha} V(x) = \infty. \]

Here the parameter \( \alpha \) may represent the bond length of NH in ammonia.

Contrary to the ammonia case, the inversion of methane or amino acids to its mirror images involves extremely high potential barrier and it may be termed as ‘nonfeasible-tunneling’. Although alanine is one of the simplest amino acids, its molecular structure is quite more complicated than ammonia or methane. We introduce a simple model-amino-acid (MAA) of alanine. In MAA, alanine is assumed to have following reduced mass:

\[ \frac{m_C \sum_{i=1}^{12} m_i}{m_C + \sum_{i=1}^{12} m_i} = 10.38 \text{ amu}. \]

Here \( m_C \) is the mass of the \( \alpha \)-carbon and \( m_i \)'s are the masses of the remaining atoms of the alanine. The inversion of the alanine is modeled by the same double-well potential with the potential parameters (\( \varepsilon \), \( \alpha \), \( \delta \)) calculated from the difference of energies of the two optical isomers and the following relations:

\[ \alpha = \frac{\sum_{i=1}^{12} m_i l_i}{\sum_{i=1}^{12} l_i}, \quad \delta = \alpha \cos \left( \frac{\theta}{2} \right), \]

where \( l_i \) denotes distances of each atom from \( \alpha \)-carbon and \( \theta = 109.5^\circ \). The well-depth (\( \varepsilon \)) of the double-well for alanine is estimated to be 45443 cm\(^{-1}\) from ab initio calculations using 6-31G** basis set. We also use the value of \( \alpha = 1.877 \) Å.

In order to examine the effect of PVED on the tunneling dynamics, we introduce an asymmetric (biased) double-well potential with a very small difference in the depths of the two potential wells. We use the following potential model:

\[ V(x) = \varepsilon \left[ 1 + \frac{5}{4} \left( \frac{\gamma - 2}{\delta} \right)^2 - \frac{3}{2} \left( \frac{\gamma - 2}{\delta} \right) \right] \left( \frac{x}{\delta} \right)^4 \]

\[ - \frac{3}{4} \left( \frac{\gamma - 2}{\delta} \right) \left( \frac{x}{\delta} \right)^5 \left( \frac{\gamma - 2}{\delta} \right) \left( \frac{x}{\delta} \right)^6, \]

where \( \gamma = \Delta/\varepsilon \) and \( \Delta \) denotes the parity-violation energy difference. According to R. Janoschek [5], PVED of alanine was estimated to be \( 1.81 \times 10^{-13} \) cm\(^{-1}\), which amounts to \( \gamma = 1.7 \times 10^{-17} \). It is noted that the L-form (\( x = -\delta \)) has lower energy than the D-form (\( x = \delta \)) by the amount of PVED: \( V(-\delta) = 0 \) and \( V(\delta) = \Delta \).

3. Results

One can calculate the energies of eigenstates for the double-well potential using time-independent methods. For states below the barrier, tunneling splitting between almost
degenerate eigenstates would be observed. Once eigenvalues of double-well potential are determined, the inversion time is obtained with the following Hund’s formula,

\[ t_{\text{inv}} = \frac{\hbar}{\Delta E_{z}}, \quad \Delta E_{z} = E_2 - E_1. \]  

(5)

We have calculated the energies of eigenstates for the double-well potential using 400 grid points in the range of [−1, 1] by the time-independent method. The tunneling splitting is not resolved up to the level of \( n = 92 \) with the energy resolution of \( 10^{-8} \text{cm}^{-1} \). Fig. 1 shows the level-spacing (tunneling splitting) in \( \log \) scale from the time-independent calculations as a function of peak number. It is noted that the energy splittings for the higher levels show monotonic increase. A simple extrapolation to the lower energy region gives the estimation of \( \Delta E_{z} = E_2 - E_1 \). The predicted inversion time would be about \( 2.9 \times 10^{29} \) years. This inversion time is much longer than that for methane [3]. This is because the reduced mass of alanine is heavier than that of methane although potential barrier of the former is lower than that of the latter. Our calculations illustrate characteristics of nonfeasible-tunneling with very high barrier for the inversion of alanine.

In the case of nonfeasible tunneling dynamics with PVED, one can not use Hund’s formula to obtain information about the inversion time. However, there is no intrinsic difficulty in performing time-dependent wavepacket propagation. It is noted that the width of the initial thermal Gaussian wave packet (TGWP) [3] is given by the following form for the asymmetric double-well potential.

\[ \omega = \sqrt{\frac{e^{48 - 39}}{m 2^{9} \Delta E_{z}^{2}}} \quad \text{at } x = \delta, \]  

\[ = \sqrt{\frac{e^{48 - 9}}{m 2^{9} \Delta E_{z}^{2}}} \quad \text{at } x = -\delta. \]  

(6)

We define D-form-probability \( \langle P_D^0 \rangle_T \), as a probability that molecules exist in D-form within time-duration, \( \tau \):

\[ \langle P_D^0 \rangle_T = \frac{1}{\tau} \int_0^\tau \frac{P_D^0(t) + P_D^0(\tau - t)}{2} \, dt. \]  

(7)

\[ P_D^0(t) = \int_0^{\tau_{\text{max}}} \Psi_{\pm, \delta}(x, t; T) \Psi_{\pm, \delta}(x, t; T) \, dx. \]  

(8)

where \( \Psi_{\pm, \delta}(x, t; T) \) is a time-dependent wavefunction launched from \( x = \pm \delta \) at time \( t = 0 \) with the system temperature of \( T \). If exactly the same amounts of optical isomers (L- and D-forms of amino acids) exist at the initial stage and if they stay at the same ratio after time \( \tau \), the D-form-probability should be 0.5. If L-form is favored somehow, it will be lower than 0.5.

There are major difficulties in examining tunneling dynamics for inversion of real amino acids by time-dependent methods. Since the PVED for an amino acid is too small and the potential barrier is extremely high, it is very difficult to produce discernable results from time-dependent propagations within reasonable computational time. In order to examine the effects of temperature or magnitude of PVED on the development of homo-chirality, we introduce an imaginary molecule of mass 2.49 amu with moderate potential barrier (2020 cm\(^{-1}\)) and PVED (\( \gamma = 2 \times 10^{-6} \sim 2 \times 10^{-2} \)). The potential barrier is similar to ammonia molecule whose inversion time is 12 ps [3] We have calculated the D-form-probability for this imaginary chiral molecule (Table 1). We choose \( \tau \) of 15.9 ps for calculating \( \langle P_D^0 \rangle_T \). It is assumed that equal amounts of optical isomers (L-form and D-form) exist at the beginning. Without PVED, the amounts of both optical isomers remain equal at all times. It is found that the L-amino acid is favored in the presence of PVED. The enrichment of L-form is

![Fig. 1. Tunneling splitting between pair of energy levels for the inversion of model alanine molecule. The unit of energy is cm\(^{-1}\). The peak number \( N \) is corresponding to the splitting between energy levels of \( E_{2N+1} \) and \( E_{2N+2} \). (a) Level-spacing for all of the states. (b) Level-spacing for the states with the tunneling splitting larger than \( 10^{-3} \) cm\(^{-1}\). The dotted line represents a simple extrapolation of the splitting data to the lower energy region.](image-url)
increasing with PVED. Higher temperature seems to enhance the disproportion of optical isomers.

4. Concluding remarks

We have presented detailed studies on the quantum tunneling dynamics in model double-well potentials for the inversion of an amino acid. We introduced an asymmetric double-well potential model with a very small difference in the depths of the two potential wells, which represents the presence of the parity-violating energy difference (PVED) between two optical isomers. From a simple extrapolation from the energy levels calculated by the time-independent method, the inversion time of model alanine molecule is estimated to be about $10^{29}$ years. This result illustrates that the tunneling dynamics of an amino acid is quite ‘non-feasible’ with extremely high barriers. In order to study the development of homo-chirality, we have examined the relative probabilities of the two optical isomers, calculated from the time-dependent wavepacket propagations. The results of the model calculations showed that the presence of PVED, albeit small, can lead to the enrichment of one of the enantiomers, e.g. L-form of an amino acid.

A kinetic model such as Janoschek’s has been introduced to explain the origin of homo-chirality of amino acids [5]. Originally, only achiral species exist at the beginning, which turn to L- and D-forms at the same time. The two optical isomers are accumulated with the same ratio until some critical point of stereoselection is reached. After this bifurcation, the system can reach new equilibrium with homo-chirality of L-amino acids. Such kinetic models assume that the intrinsic energies of the two enantiomers are different by the amount of PVED. A frequently raised questions are concerned with the observation, based on experiences in everyday chemistry, that extremely small magnitudes of PVED are not expected to be sufficient for the amplification needed to make homo-chirality possible. However, it was argued that a very large reaction volume and a very long reaction time, involved in evolution, could make PVED effective for chiral-selection. The model introduced in the present paper is basically consistent with such kinetic model. However, the detailed mechanism of chiral evolution can be somewhat different. In the kinetic model, there exists a ‘induction’ period before bifurcation point, where the amounts of the two enantiomers are equal. Tunneling dynamics through asymmetric double-well with PVED results in disproportion of optical isomers even at short-time scales. Such initial disproportion can be quickly amplified by competitive autocatalysis reactions. As a result, the development of homo-chirality is expected to occur much faster than the estimation by the original kinetic model as illustrated schematically in Fig. 2. It can be argued that tunneling dynamics of amino acids with PVED provide a plausible mechanism for accelerated chiral evolution.

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