MATHEMATICAL MODELING OF PARTICLE TUNNELING IN THE DOUBLE-WELL POTENTIAL

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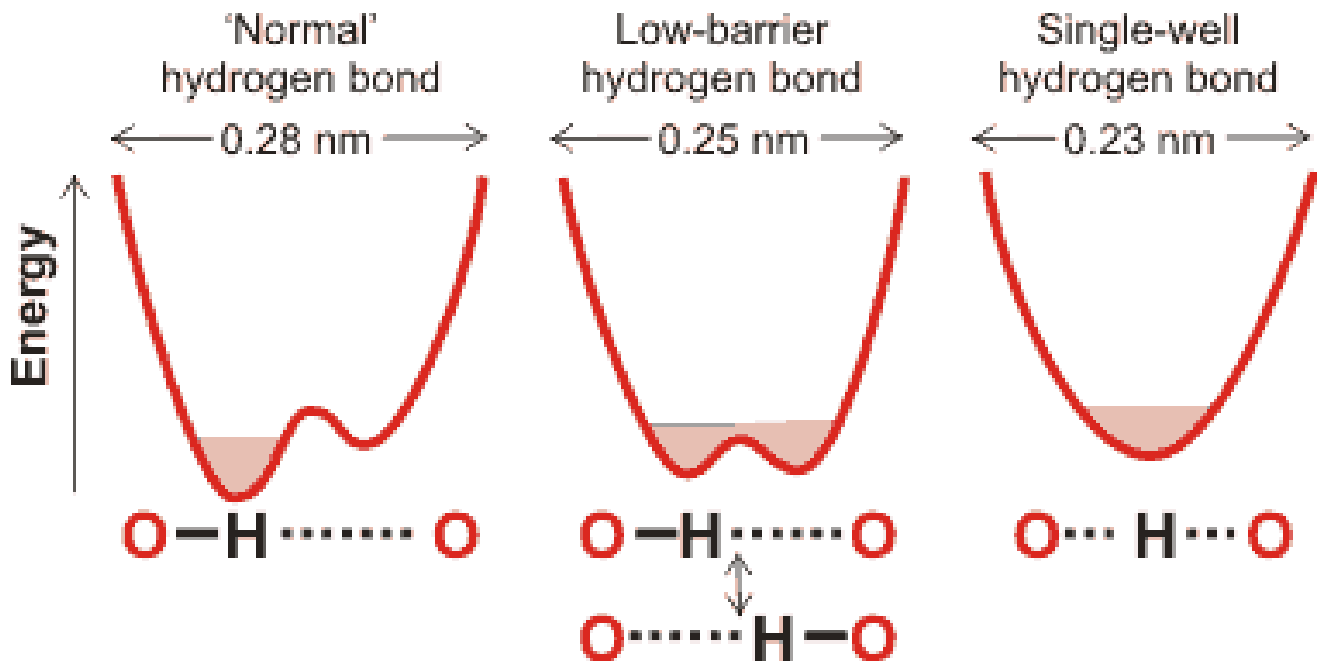
MOTIVATION

The work is devoted to the presentation of the mathematical model and the results of numerical calculations on the tunneling of the wave function in the ***double-well potential****.*

Such a model is used to describe the ***hydrogen bond*** *in physical, chemical, and biological systems, various protolytic reactions, reactions involving enzymes, chemical catalysis, and proton transfer processes.*



HYDROGEN BOND

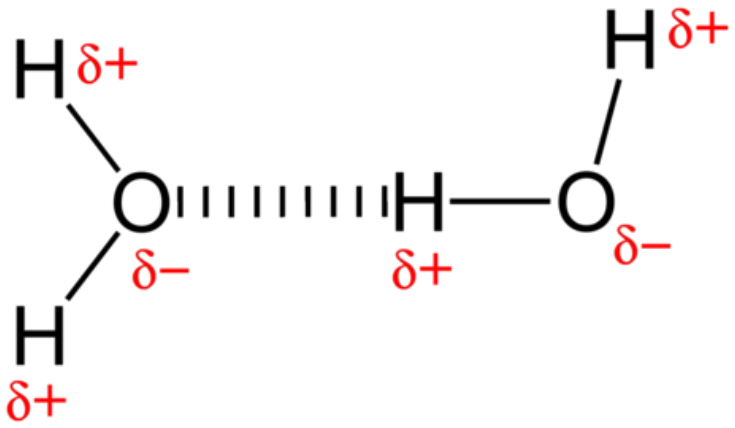
A **hydrogen bond** is a chemical bond that occurs between polar molecules in which a hydrogen atom (H) is bonded to an electronegative atom, such as fluorine (F), oxygen (O), or nitrogen (N).

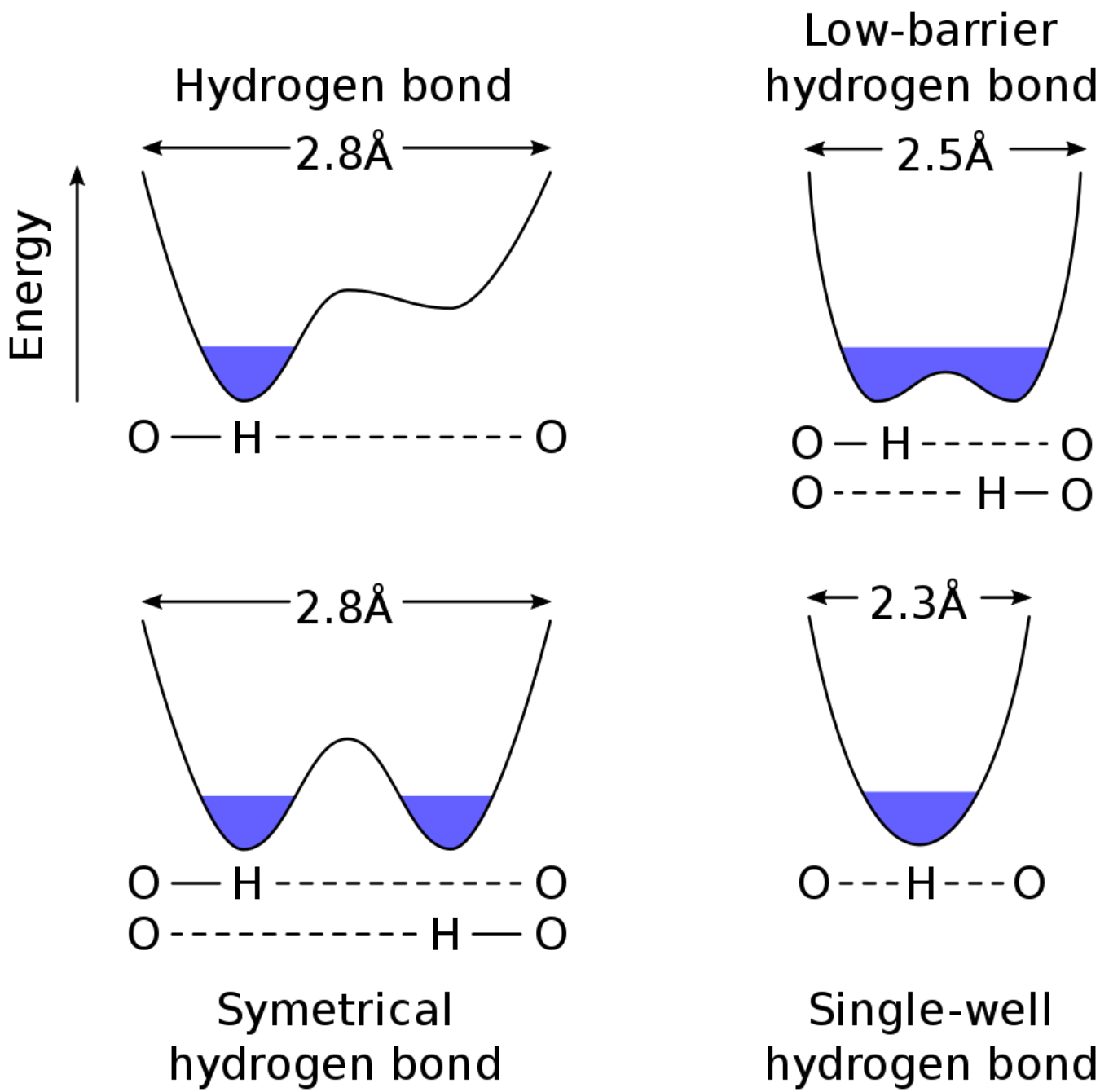
The **bond strength** H is usually in the range of 1–7 kcal / mol, which is much weaker than the covalent or ionic bond, but about 10 times greater than the van der Waals interaction.

This intermediate strength allows the creation and destruction of H-bonds in a reversible manner, which makes these bonds important in many elementary processes in chemistry and biology.

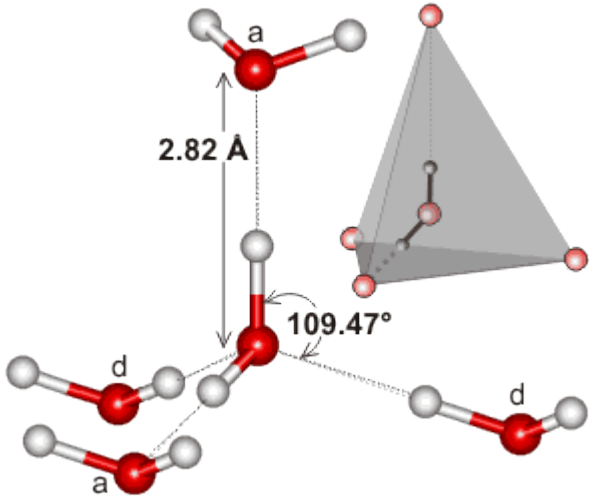
Due to the small mass of the H atom, quantum effects, for example, **tunneling** and **zero-point energy**, significantly affect the basic properties of the dynamics of the H-bond.

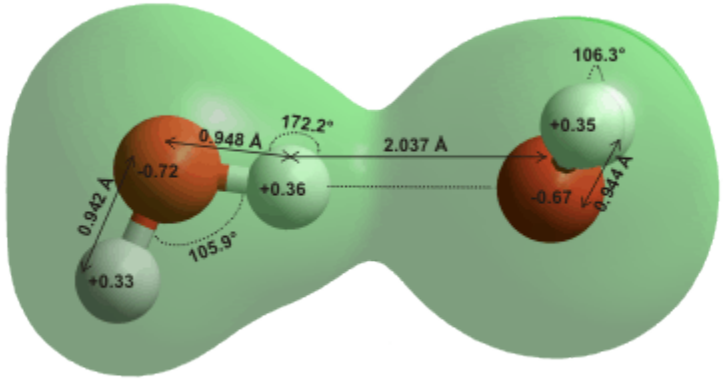
Thus, the study of hydrogen bonds in physicochemical and biological processes by modern analytical and numerical methods is an urgent task.

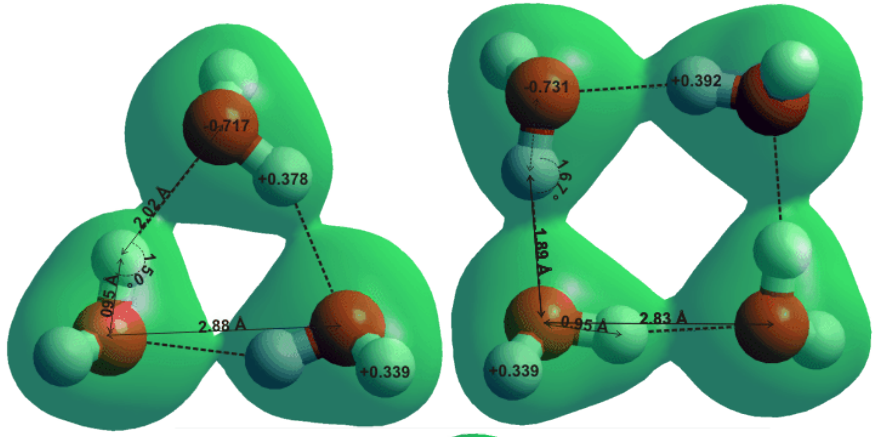


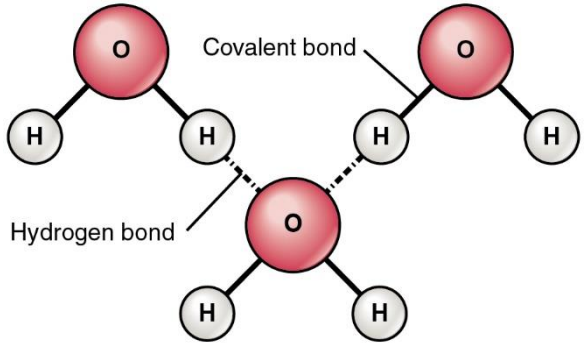

Hydrogen bond
2.8Å
Energy
O — H - - - - - - - - - - - O
Low-barrier
hydrogen bond
2.5Å
O — H - - - - - - O
O - - - - - - H — O
2.8Å
O — H - - - - - - - - - - - O
O - - - - - - - - - - - H — O
Symetrical
hydrogen bond
2.3Å
O - - - H - - - O
Single-well
hydrogen bond

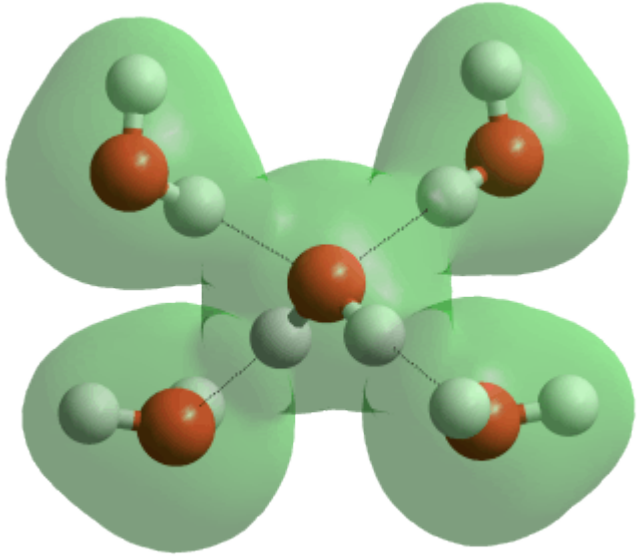
HYDROGEN BOND

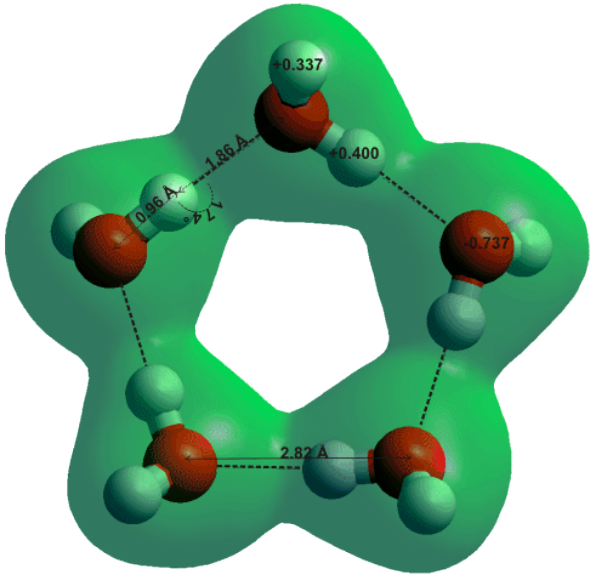












MODELING OF THE PARTICLE DYNAMICS

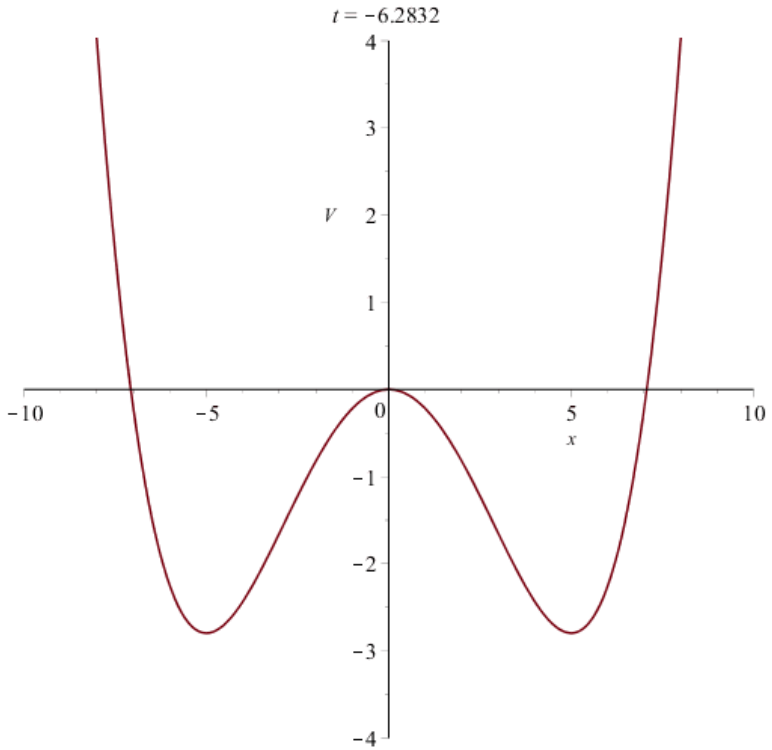
To study the effect of tunneling, the Schrödinger equation was considered :

$$\frac{1}{i}\frac{\partial}{\partial t}\psi = -\frac{1}{2}\frac{\partial^2}{\partial x^2}\psi + U(x,t)\psi$$

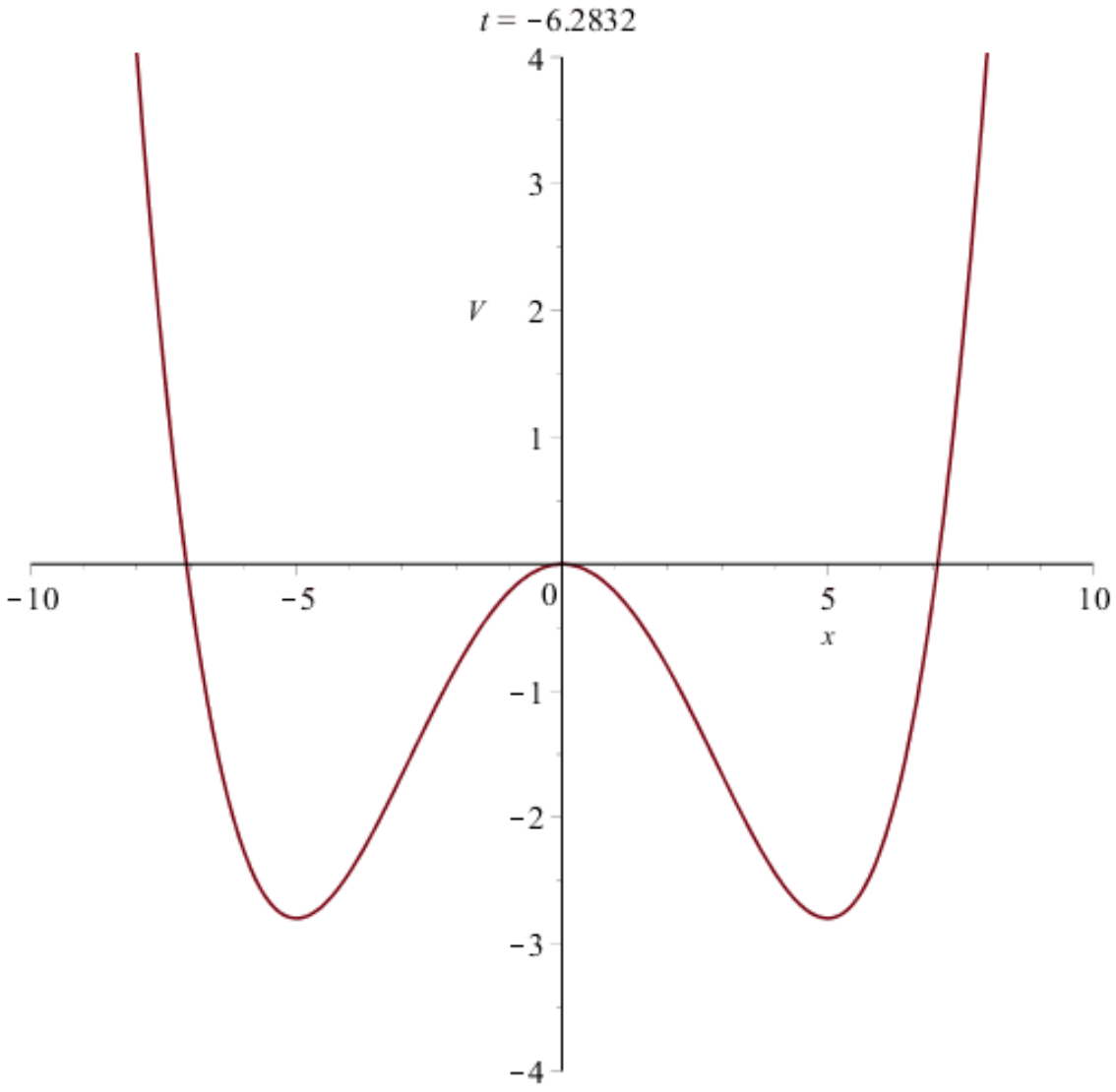
Non-stationary double-well potential:

$$U(x,t) = a(t)\left(x + x_{\min}\right)^4 - b(t)\left(x + x_{\min}\right)^2 + \frac{b^2(t)}{4a(t)}$$

$$a(t) = \frac{\alpha - \beta\cos(\varepsilon\omega t)}{2\sqrt{\alpha}} \qquad b(t) = \frac{\sqrt{\alpha - \beta\cos(\varepsilon\omega t)}}{2\sqrt{\alpha}}$$



NON-STATIONARY DOUBLE-WELL POTENTIAL



Potential barrier height:

$$\frac{\Delta U(t)}{\frac{\hbar\omega_0}{2}} = \frac{b^2(t)}{4a(t)} = \frac{1}{8\sqrt{\alpha}} = const$$

Spatial coordinates of minima:

$$\tilde{x}_{\min}^{(-)}(t) = -\tilde{x}_{\min}^{(+)}(t) = \sqrt{\frac{b(t)}{2a(t)}} = \frac{1}{\sqrt{2}}\frac{1}{\sqrt[4]{\alpha - \beta\cos(\varepsilon\omega_0 t)}}$$

Transition to dimensionless variables:

$$\tau = \frac{\omega_0 t}{2}, \qquad \tilde{x} = \frac{x}{\xi} = \frac{x}{\sqrt{\hbar / m\omega_0}}, \qquad u(\tilde{x},\tau) = \frac{U\left(\frac{x}{\xi}, \frac{\omega_0 t}{2}\right)}{\left(\frac{\hbar\omega_0}{2}\right)} = \frac{U(\tilde{x},\tau)}{\left(\frac{\hbar\omega_0}{2}\right)}$$

Schrödinger equation in dimensionless variables:

$$i\frac{\partial\psi}{\partial\tau} = -\frac{\partial^2\psi}{\partial\tilde{x}^2} + u(\tilde{x},\tau)\psi$$

$$u(\tilde{x},\tau) = a(\tau)\tilde{x}^4 - b(\tau)\tilde{x}^2$$

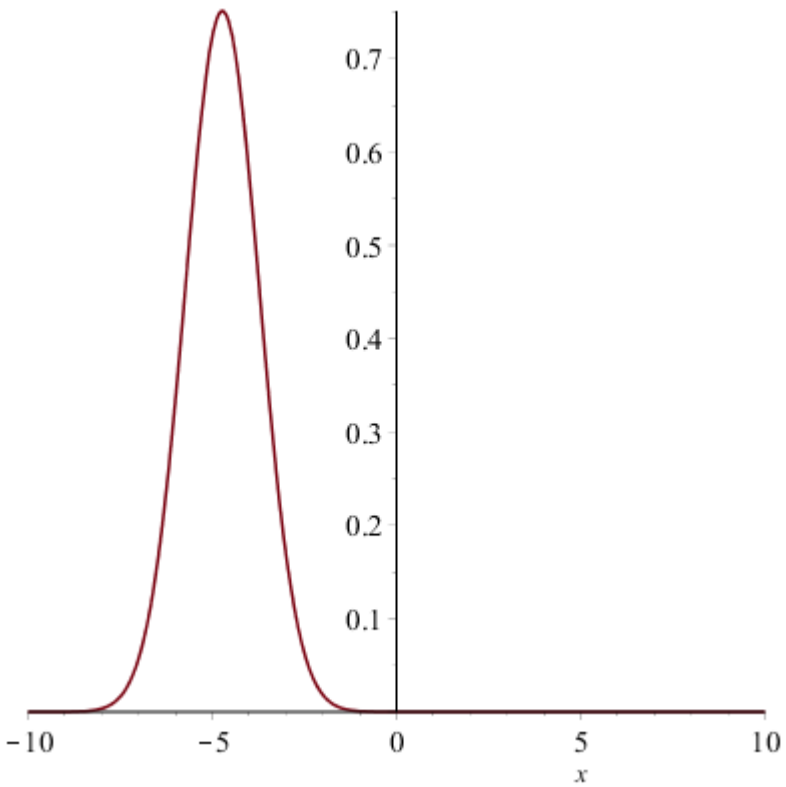
$$a(\tau) = \frac{\alpha - \beta\cos(2\varepsilon\tau)}{2\sqrt{\alpha}}, \qquad b(\tau) = \frac{\sqrt{\alpha - \beta\cos(2\varepsilon\tau)}}{2\sqrt{\alpha}}$$

To find solutions to the problem, we used the constructed step-by-step programs in the MathCad and Maple packages based on the 4th-order Runge-Kutta method.

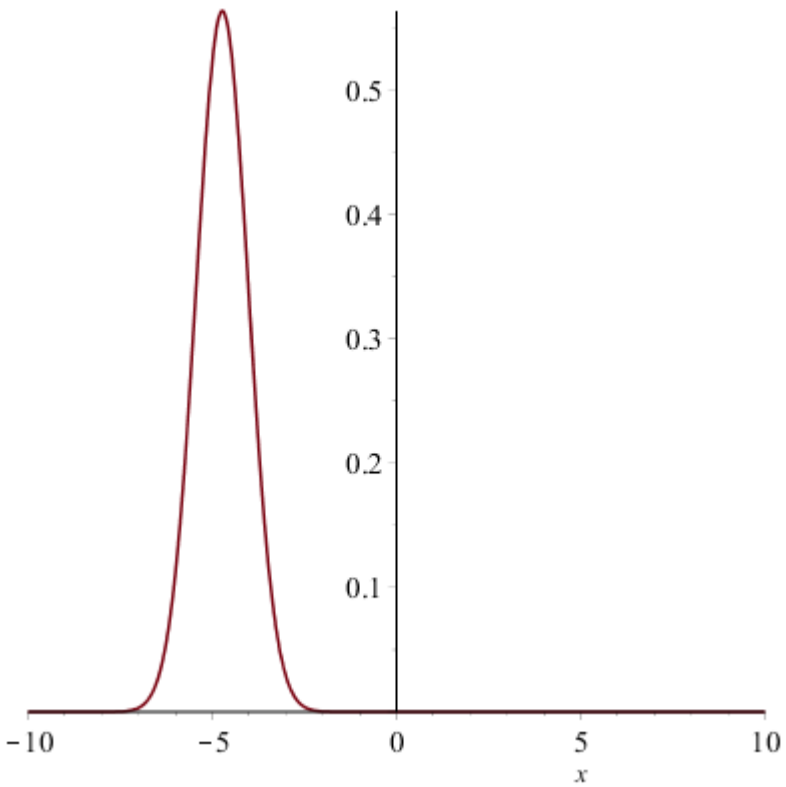
INITIAL CONDITION

$$\psi_R(\tilde{x},0)=\begin{cases}\dfrac{1}{\sqrt[4]{\pi\xi^2}}\exp\left(-\dfrac{1}{2}\left(\tilde{x}-\tilde{S}_x\right)^2\right), -N<\tilde{x}<+N \\ 0, |\tilde{x}|\geq N\end{cases}, \psi_I(\tilde{x},0)=0$$

$$\tilde{S}_x=\tilde{x}_{\min}^{(-)}=-\frac{1}{\sqrt{2}\sqrt[4]{\alpha}}$$

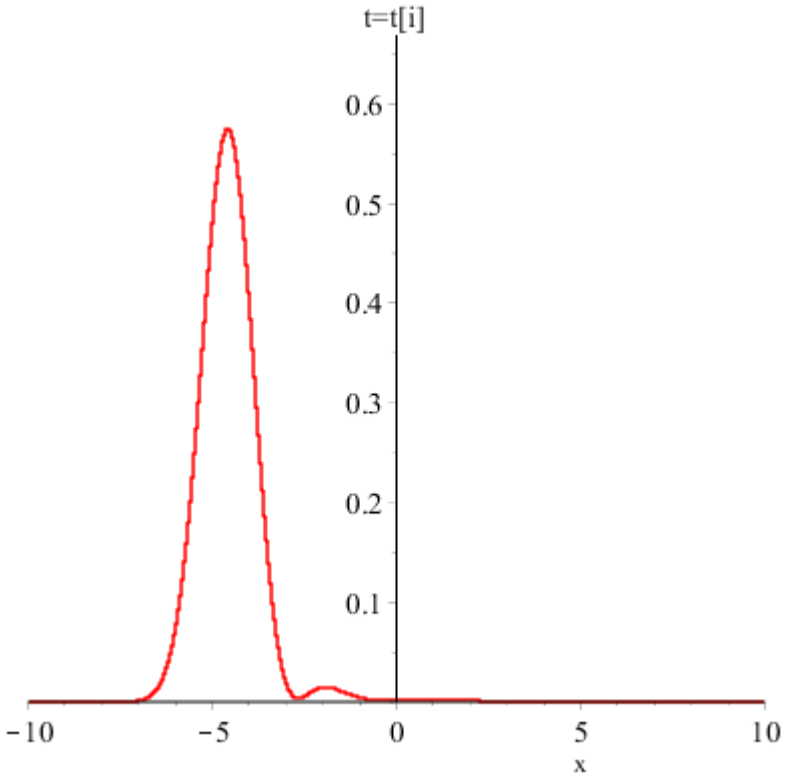


Initial wave function

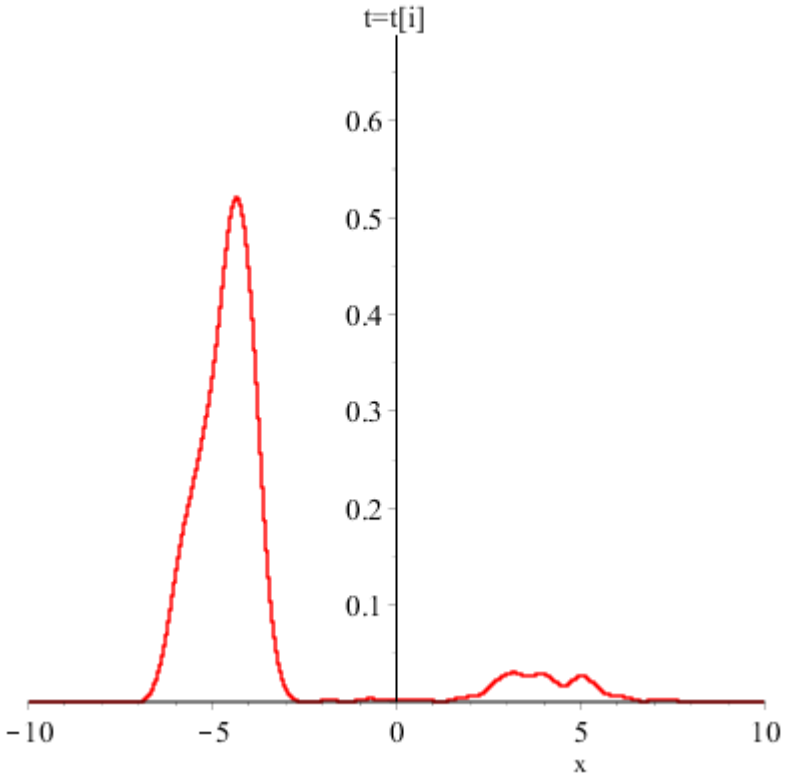


Initial probability density

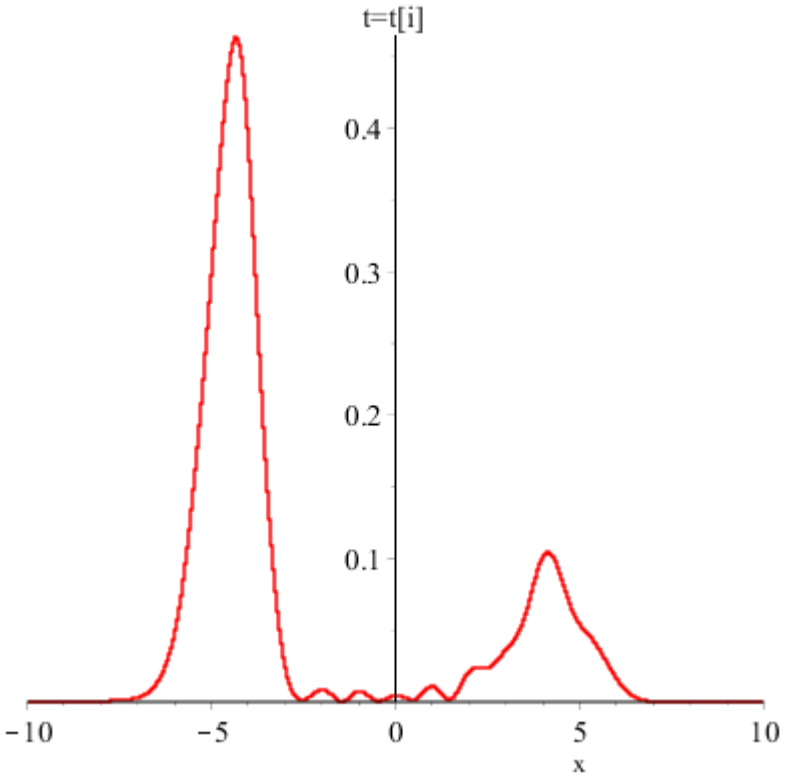
DYNAMICS OF THE WAVE PACKAGE



0-10T

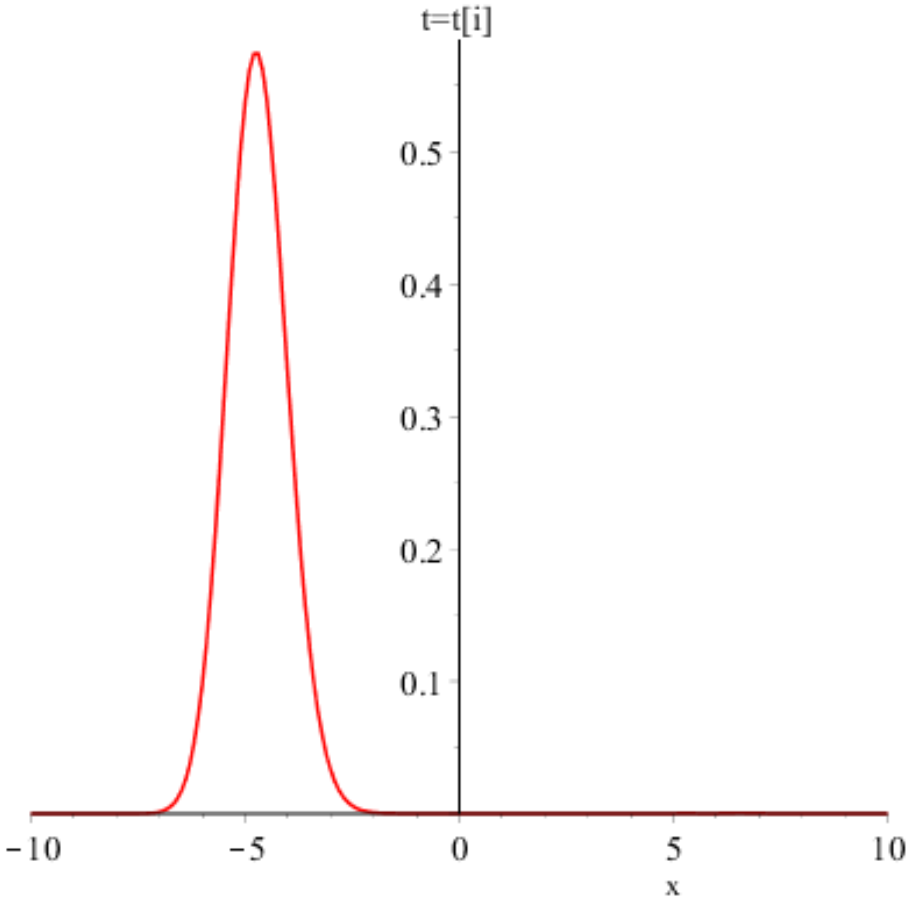


50T-60T



100T-110T

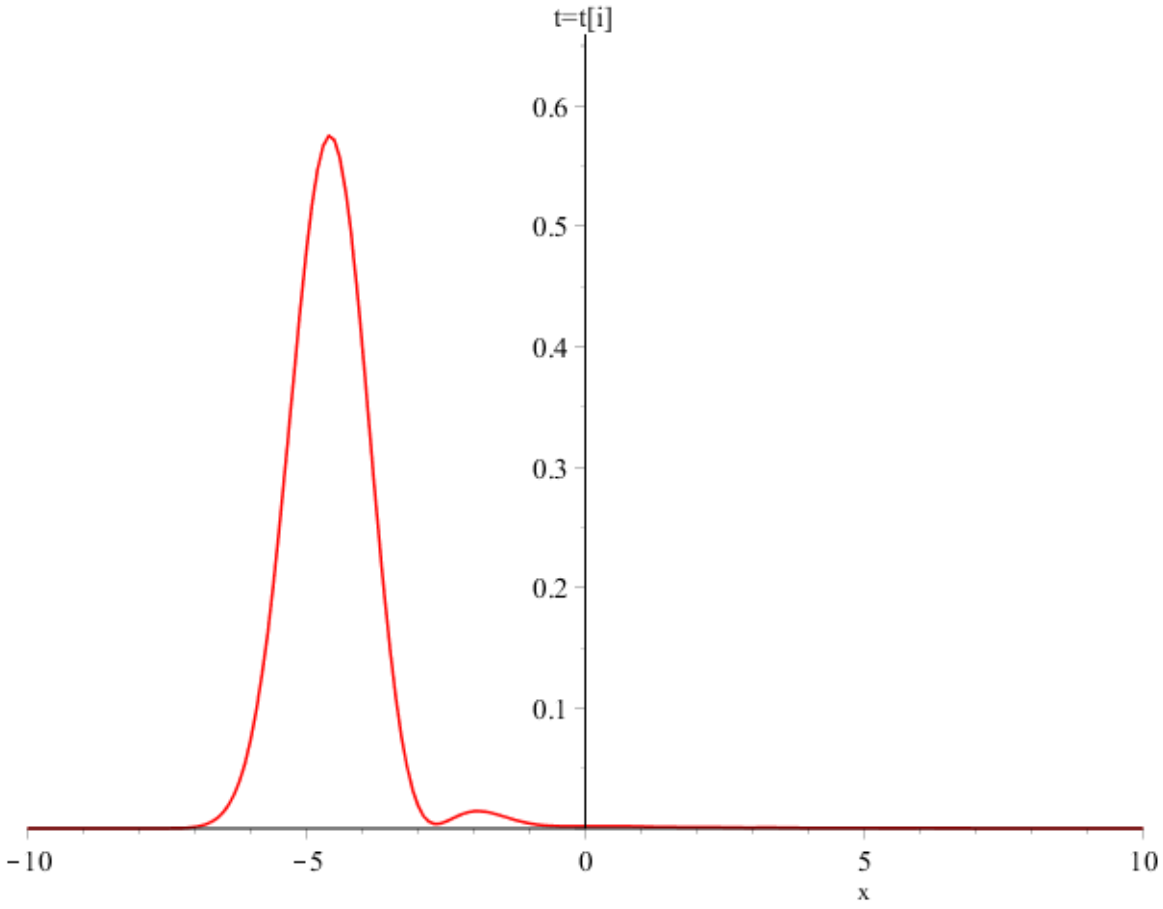
$\alpha = 0.0005 \qquad \beta = 0.0$



Stationary double-well potential

0-500T

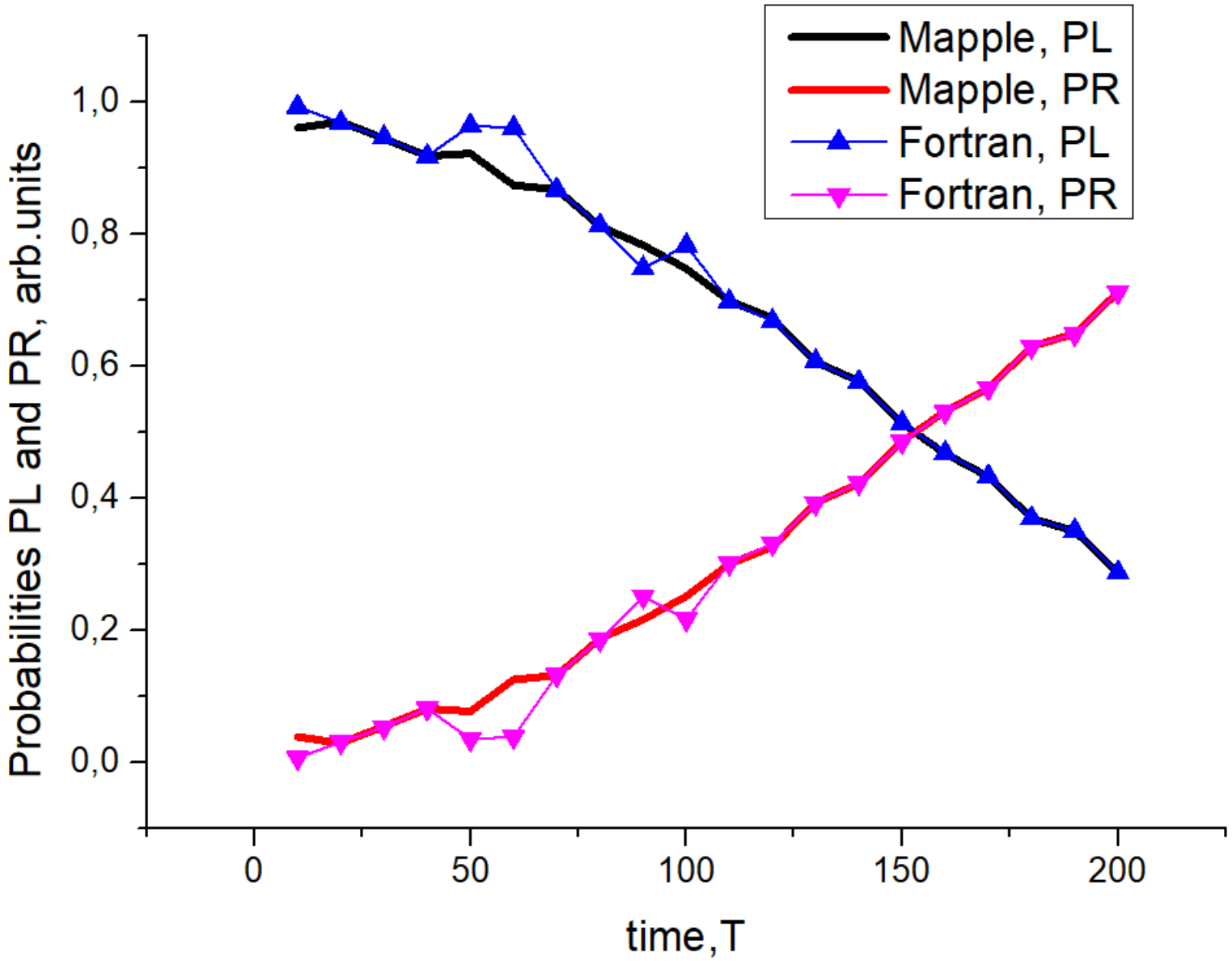
$\alpha = 0.0005 \qquad \beta = 0.0001$



Non-stationary double-well potential

0-500T

PROBABILITY TO FIND PARTICLE IN THE LEFT (PL) OR RIGHT (PR) WELL



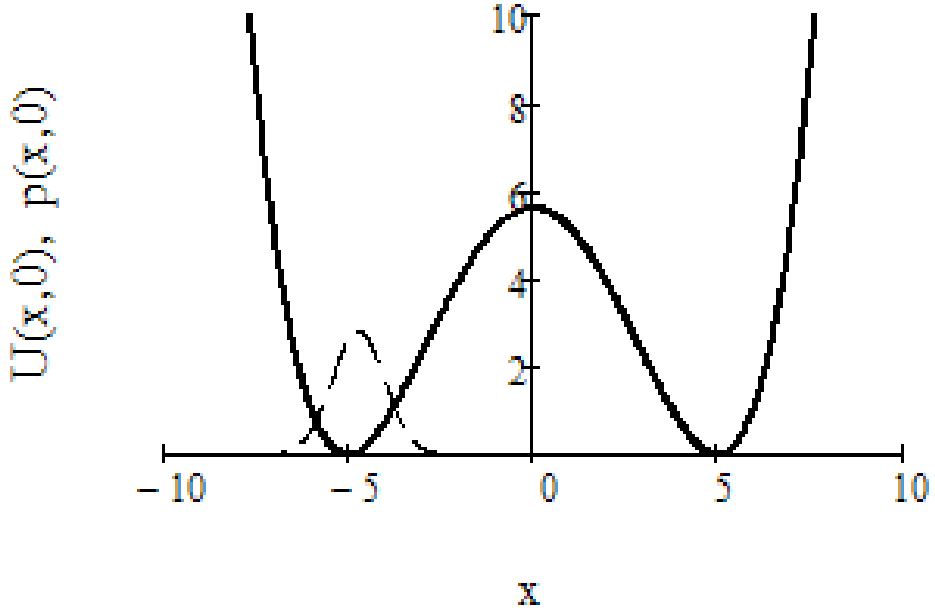
MODELING OF THE TUNNELING EFFECT

In the absence of modulation, the wave function is localized in the left well

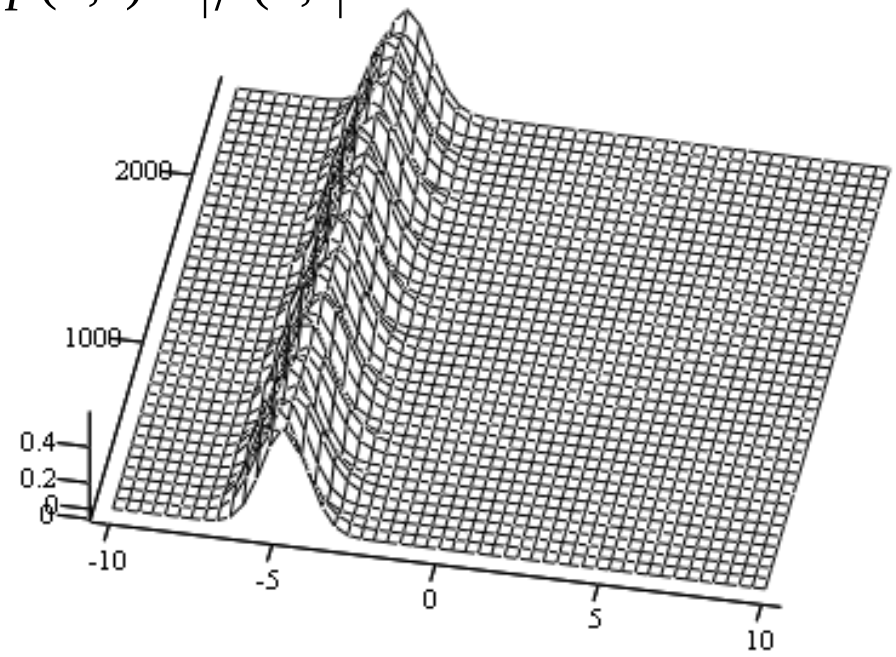
$$u(\tilde{x},\tau) = a(\tau)\tilde{x}^4 - b(\tau)\tilde{x}^2$$

$$a(\tau) = \frac{\alpha - \beta\cos(2\varepsilon\tau)}{2\sqrt{\alpha}}, \qquad b(\tau) = \frac{\sqrt{\alpha - \beta\cos(2\varepsilon\tau)}}{2\sqrt{\alpha}}$$

$\alpha = 0.0005 \qquad \beta = 0.0$



$$p(x,t) = |\psi(x,t|^2$$



Time dependence of the probability density

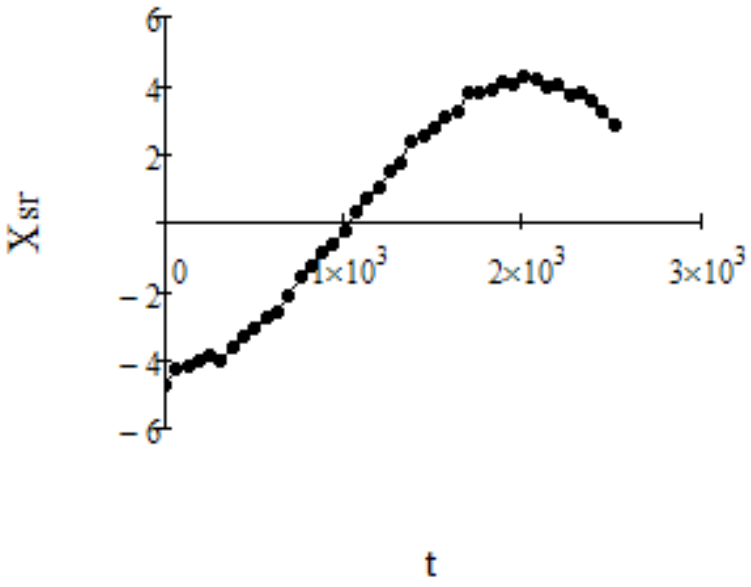
$$0 \le t \le 2500$$

MODELING OF THE TUNNELING EFFECT

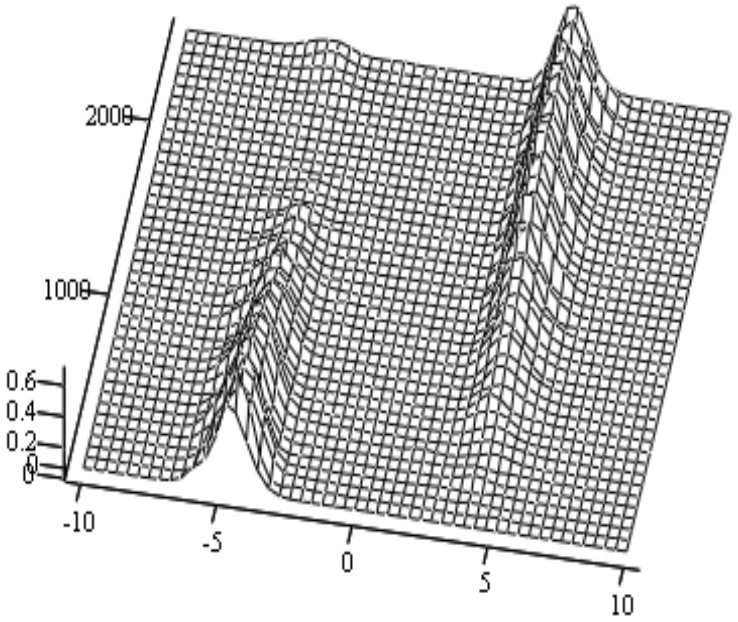
$$u(\tilde{x},\tau)=a(\tau)\tilde{x}^4-b(\tau)\tilde{x}^2$$

$$a(\tau)=\frac{\alpha-\beta\cos(2\varepsilon\tau)}{2\sqrt{\alpha}},\qquad b(\tau)=\frac{\sqrt{\alpha-\beta\cos(2\varepsilon\tau)}}{2\sqrt{\alpha}}$$

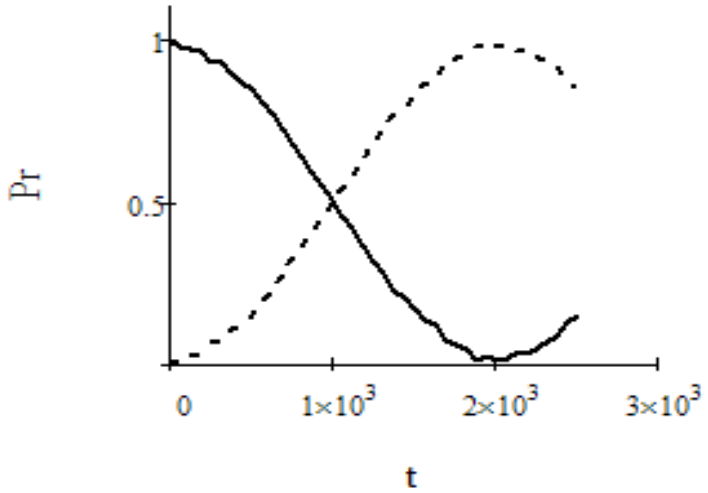
$$\varepsilon=2.0$$



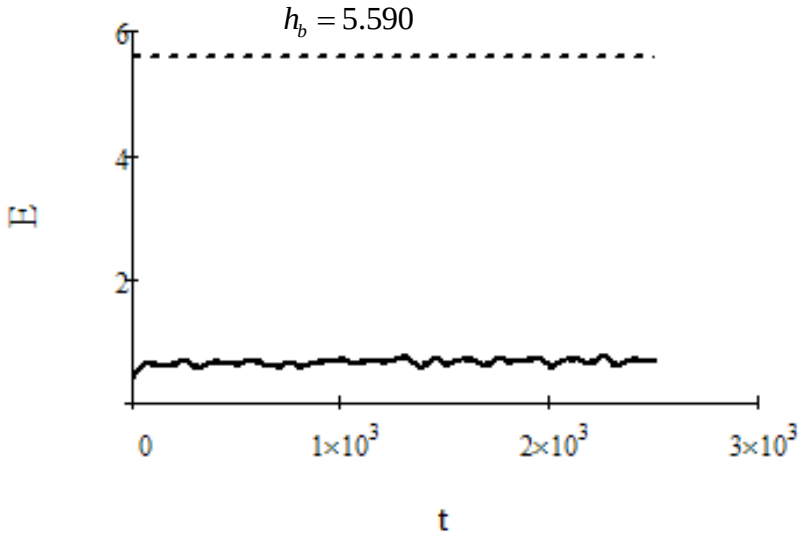
Dynamics of the particle average coordinate



Dynamics of the probability density



Dynamics of the probability to find particle in the left/right well



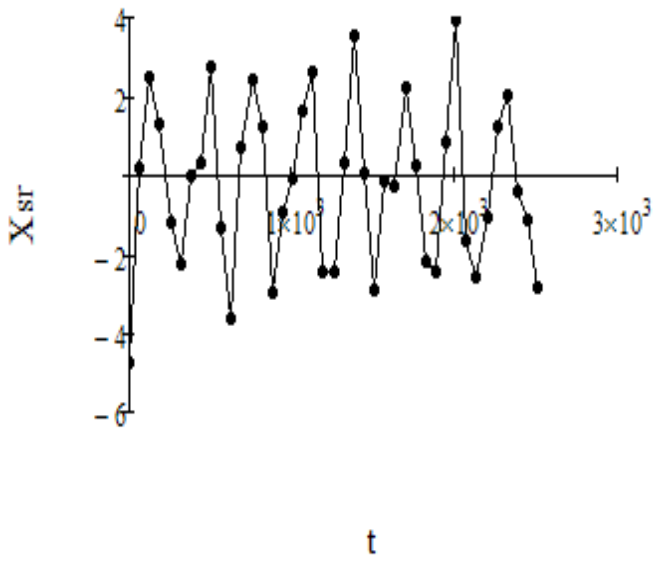
Dynamics of the particle energy;
the dotted line shows the height of the energy barrier

MODELING OF THE TUNNELING EFFECT

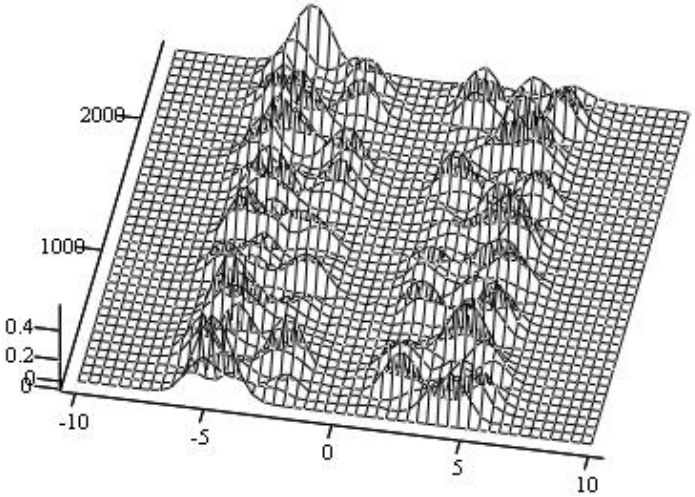
$$u(\tilde{x},\tau)=a(\tau)\tilde{x}^4-b(\tau)\tilde{x}^2$$

$$a(\tau)=\frac{\alpha-\beta\cos(2\varepsilon\tau)}{2\sqrt{\alpha}},\qquad b(\tau)=\frac{\sqrt{\alpha-\beta\cos(2\varepsilon\tau)}}{2\sqrt{\alpha}}$$

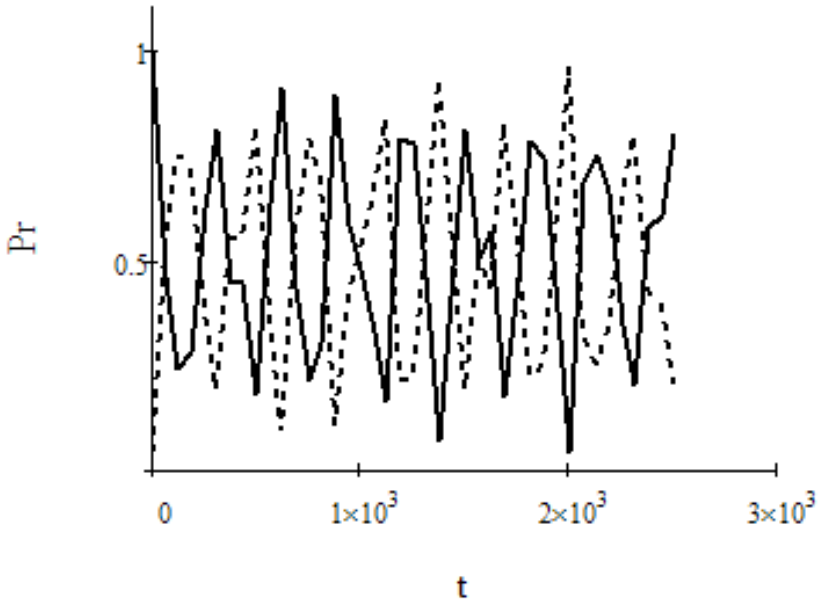
$\varepsilon=1.7$



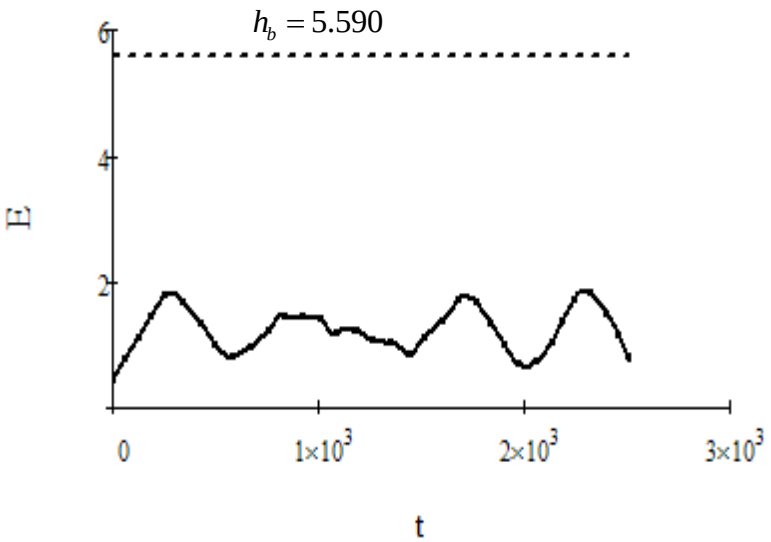
Dynamics of the particle average coordinate



Dynamics of the probability density



Dynamics of the probability to find particle in the left/right well



Dynamics of the particle energy;
the dotted line shows the height of the energy barrier

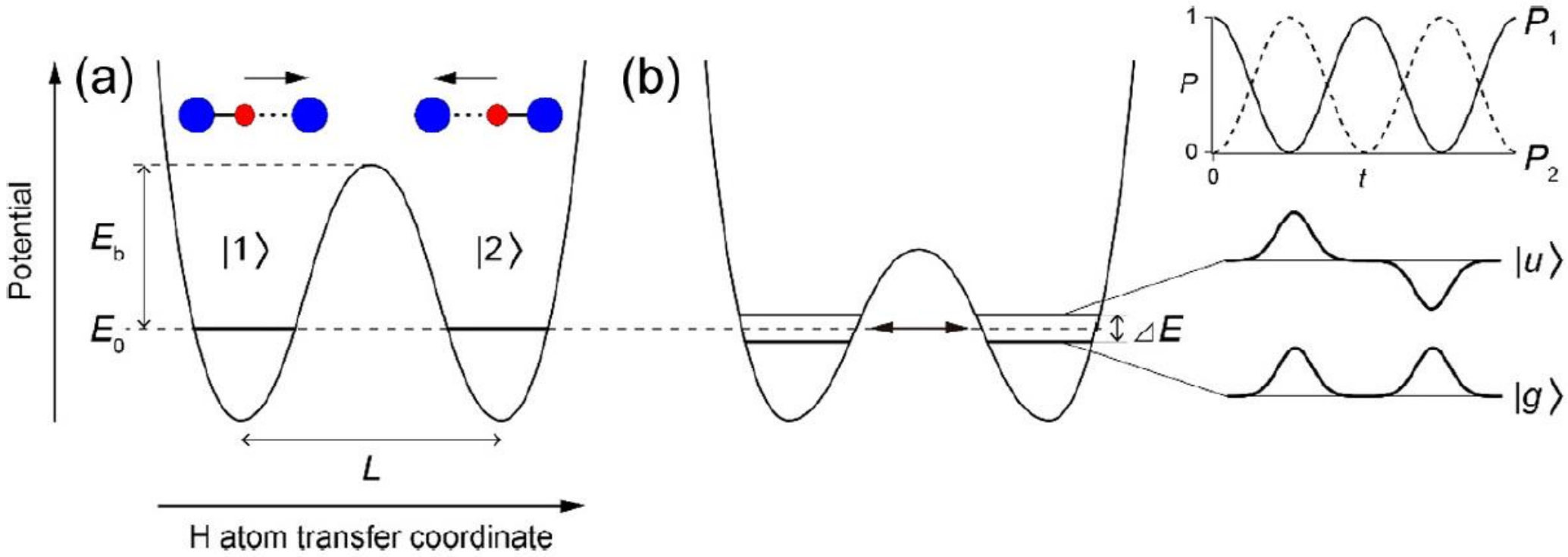
The process of H atom transfer between two identical electronegative atoms in a vacuum can be described by a symmetric double-well potential in which the energy level corresponds to the vibrational state of the H atom (harmonic oscillator). If the potential barrier (Eb) and width (L) between two wells are large, the left |1> and right |2> states are degenerate eigenstates of the system with the same energy E0. On the other hand, if the barrier and width are sufficiently small, the H atom can be transferred between two states via tunneling, and |1> and |2> are no longer eigenstates. In this situation, the eigenfunction of the system becomes their symmetric (gerade) and anti-symmetric (ungerade) linear superposition, which is expressed by

$$|g>=\frac{1}{\sqrt{2}}(|1>+|2>), |u>=\frac{1}{\sqrt{2}}(|1>-|2>)$$

The energy level splits into a doublet separated by dE with the lower and higher levels corresponding to the positive (symmetric) and negative (anti-symmetric) combination, respectively. Assuming that the system is completely isolated from the external environments (perturbations) and a wave packet is created in |1> at t = 0, the probability amplitude (P1 and P2) shows a periodic motion from |1> to |2> and vice versa with frequency of coherent tunneling. Such coherent tunneling has been observed for small water clusters and organic molecular clusters.
A tunneling frequency ranges from a few Hz to 1012 Hz,

$$\Delta E = h\nu_{tunneling}$$ The tunneling splitting

$$\nu_{tunneling}$$ frequency of coherent tunneling.



$$|g>=\frac{1}{\sqrt{2}}(|1>+|2>),\ |u>=\frac{1}{\sqrt{2}}(|1>-|2>)$$

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CONCLUSIONS

The paper presents the results of numerical calculations on the tunneling of the wave function in a double-well potential.

The biquadratic double-well potential was proposed and used. Based on a mathematical model of the time evolution of the wave function, a numerical algorithm and a program for solving the Schrödinger equation were constructed.

The potential containing the time dependence of the sinusoidal form with the frequency and modulation index was used.

The absence of tunneling was verified in the mode when sinusoidal modulation is disabled.

Modulation modes with different tunneling rate were obtained.

The possibility of adjusting the tunneling efficiency by choosing the modulation frequency is shown.

Progress in Surface Science 90 (2015) 239–291

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Review

Direct observation and control of hydrogen-bond dynamics using low-temperature scanning tunneling microscopy

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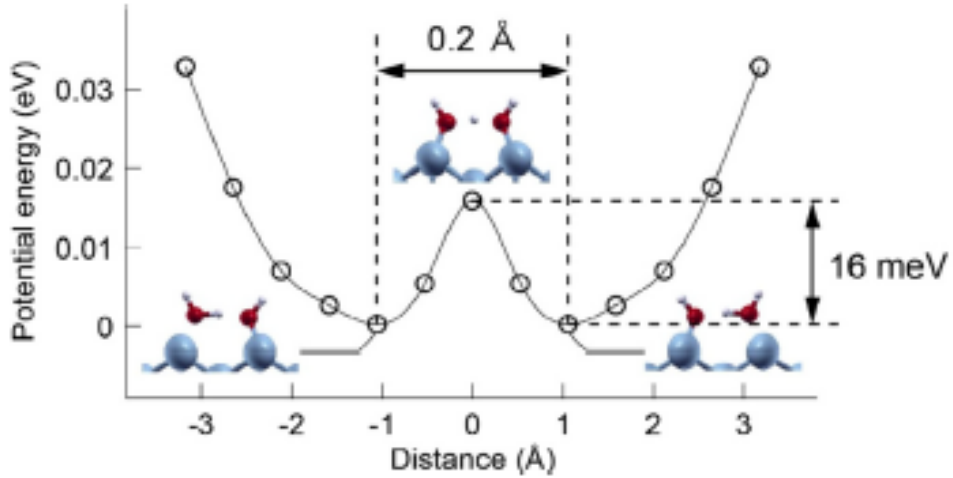

Fig. 4.6. Adiabatic potential energy along the minimum-energy path of H-atom transfer between two O atoms for a [001]-complex [44]. The two minima and the transition state correspond to the asymmetric and symmetric configurations, respectively.

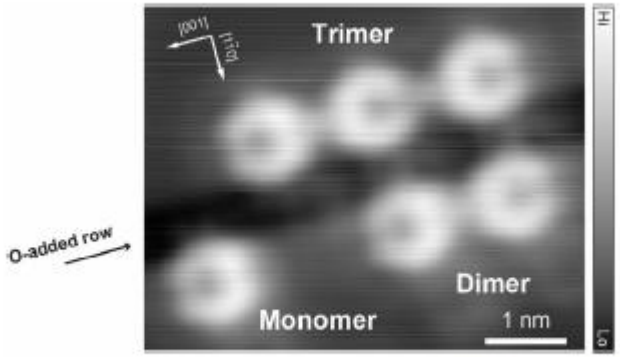

Fig. 6.15. STM image of one-dimensional oligomers of porphycene molecule formed along the O-added row structure on Cu(110) surface. The image was acquired at $V_t = 100$ mV and $I_t = 2$ nA (4.2×5.4 nm^2).