## Solution to the Last Homework Set

### Problem 1: Finite Difference Approximation

*Derive a finite difference approximation to the Schrödinger equation for a particle moving in a potential $V(x)$*

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x)$$

*that can be used to calculate iteratively the wavefunction over all space if the value of the energy is known as well as the value of the wave function at two adjacent discretization points on the x-axis.*

*Answer:*

It is convenient to first rewrite the Schrödinger equation to reduce the number of known constants. Let $\epsilon = 2mE/\hbar^2$ and $v(x) = 2mV(x)/\hbar^2$. After moving the potential energy term to the right hand side, the equation becomes

$$\psi''(x) = (v(x) - \epsilon)\psi(x)$$

Now discretize the x-axis, i.e. divide it up into segments of length $h$ and use the standard, central finite difference to express the second derivative of $\psi$ in terms of values of $\psi$ at adjacent grid points

$$\psi''(x) = \frac{\psi(x+h) + \psi(x-h) - 2\psi(x)}{h^2}$$

Rearrange to leave only $\psi(x+h)$ on the left hand side of the equation

$$\psi(x+h) = \left[2 + h^2(v(x) - \epsilon)\right]\psi(x) - \psi(x-h)$$

Each time this equation is iterated, the value of the wave function is found one step further along the x-axis.

### Problem 2: Vibrational (normal) modes

*Find the vibrational frequency and atomic displacement vectors for the stretching modes of the $CO_2$ molecule by doing an eigenvalue calculation of the motion of the*

*atoms along the molecular axis (i.e. a 1-dimensional approximation which does not include the bends). The interaction between each of the O-atoms and the central C-atom can be approximated by a Morse potential function*

$$V(r) = D\left(e^{-2\beta(r-r_b)} - 2e^{-\beta(r-r_b)}\right)$$

*with parameters taken to represent a C-O bond. A rough approximation for the well depth and bond length can be obtained from the properties of the CO molecule, which is found to have a bond energy of 11 eV and bond length of 1.1 Ångstrøm. Adjust the value of the parameter $\beta$ to get a best fit of the measured vibrational excitations of $CO_2$ which correspond to: 2349 $cm^{-1}$, 1333 $cm^{-1}$ and 667 $cm^{-1}$. Note that one of these values refers to the two bending modes (which one?) and is not relevant for this discussion.*

*Answer:*

The effect of varying the parameter $\beta$ can be seen in fig. 1. The two values used there are $\beta = 2.0\text{Å}^{-1}$ and $\beta = 2.5\text{Å}^{-1}$. Note that the curvature and, thereby, the vibrational
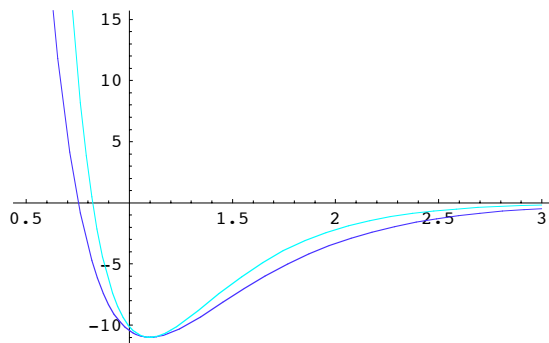


Figure 1: *Morse potential energy curves for $C - O$ stretch where $D = -11$ eV and $r_b = 1.1\text{Å}$. The dark blue curve corresponds to $\beta = 2.0\text{Å}^{-1}$ and the light blue curve corresponds to $\beta = 2.5\text{Å}^{-1}$. The larger $\beta$ is, the larger the curvature and higher the vibrational frequency.*

frequency increases as $\beta$ increases. A normal mode analysis needs to be done to calculate the frequency of the symmetric and asymmetric stretches. The two higher wave numbers, 2349 $cm^{-1}$ and 1333 $cm^{-1}$, correspond to excitation of the stretches, the lowest wave number corresponds to the two bends. In analogy with the example discussed in the lecture notes (where all three masses were the same) we can expect the asymmetric stretch to have higher frequency than the symmetric stretch. By multiplying with the speed of light, we get the vibrational frequencies: $\nu_a = 3.0 \cdot 10^{10}$ $cm/s \cdot 2349$ $cm^{-1} = 7.405 \cdot 10^{13}$ $s^{-1}$ and $\nu_s = 3.0 \cdot 10^{10}$ $cm/s \cdot 1333$ $cm^{-1} = 4.00 \cdot 10^{13}$ $s^{-1}$.

The matrix consisting of the three equations of motion for a linear triatomic molecule is (see lecture notes)

$$
\begin{bmatrix}
-\frac{k_{AB}}{m_A} & \frac{k_{AB}}{m_A} & 0 \\
\frac{k_{AB}}{m_B} & -\frac{k_{AB}}{m_B} - \frac{k_{BC}}{m_B} & \frac{k_{BC}}{m_B} \\
0 & \frac{k_{BC}}{m_C} & -\frac{k_{BC}}{m_C}
\end{bmatrix}
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
= -\omega^2
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
\tag{1}
$$

Here, for the $CO_2$ molecule, this simplifies because $k_{AB} = k_{BC} = k$ and for a the Morse potential $k = \frac{d^2 V}{dr^2}\big|_{r=r_b} = 2\beta^2 D$. Also, $m_A = m_C = 16 \ amu$ and $m_B = 12 \ amu = \frac{3}{4} m_A$. After dividing through by $\frac{k}{m_A}$ and defining $\lambda \equiv -m_A \omega^2 / k$ this becomes

$$
\begin{bmatrix}
-1 & 1 & 0 \\
4/3 & -8/3 & 4/3 \\
0 & 1 & -1
\end{bmatrix}
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
= \lambda
\begin{bmatrix} x_A \\ x_B \\ x_C \end{bmatrix}
\tag{2}
$$

A non-trivial solution to this eigenvalue problem can only be found when the determinant of the matrix

$$
\begin{bmatrix}
-(1+\lambda) & 1 & 0 \\
4/3 & -(8/3+\lambda) & 4/3 \\
0 & 1 & -(1+\lambda)
\end{bmatrix}
\tag{3}
$$

vanishes. Expanding the determinant gives the quation for the roots of the cubic polynomial for $\lambda$

$$
-(1+\lambda)\left[(\frac{8}{3}+\lambda)(1+\lambda) - \frac{4}{3}\right] + (1+\lambda)(\frac{4}{3}) = 0
$$

which has the solutions: $\lambda = 0$ for translation, $\lambda = -1$ for symmetric stretch, and $\lambda = -11/3$ for asymmetric stretch.

The ratio of the frequency for the symmetric and asymmetric stretches is fixed in this model and is independent of the free parameter $\beta$. The ratio is $\sqrt{11/3} = 1.91$ while the ratio of the measured frequencies is $2349/1333 = 1.76$ which is quite acceptable agreement for such a simple potential form for the atomic interactions.

The calculated frequency of the symmetric stretch is $\nu_s = -\omega/2\pi = (1/2\pi)\sqrt{k/m_A} = (1/2\pi)\sqrt{2\beta^2 D/m_A}$. One way to determine $\beta$ is to set this calculated expression, which depends on $\beta$, equal to the measured frequency of the symmetric stretch

$$
\beta = 2\pi\nu_s\sqrt{m_A/2D} = 2\pi 4.00 \cdot 10^{13} \cdot \sqrt{16/2 \cdot 11} \ sec^{-1}\sqrt{amu/eV} = 2.14 \ A^{-1}
$$

In the last unit conversion, the approximate relationship $\sqrt{eV/(amu \ A^2)} = 1.0 \times 10^{14} \ sec^{-1}$ was used. A better choice for $\beta$ would be one that gives roughly the same error in both the stretch frequencies, rather than reproducing one accurately (the symmetric stretch) and leaving a significant error in the other (8% too large frequency for the asymmetric stretch). This can be done by reducing beta by 4%, to $\beta = 2.14 \ A^{-1}/1.04 = 2.06 \ A^{-1}$. Then, the calculated frequency for the symmetric

stretch is 4% too small and the calculated frequency for the asymmetric stretch is 4% too large.

## Problem 3:  Classical trajectories on a 2-dimensional PES

*Use the contour plot of the LEPS potential energy surface for a tri-atomic molecule in one-dimension shown below. Assume $r_{AB}$ is on the y-axis and $r_{BC}$ on the x-axis, and the unit length of the axes is one Ångstrøm. (Compare with figure 9.25 in the text book by Laidler et al. and the relevant text in section 9.11).*
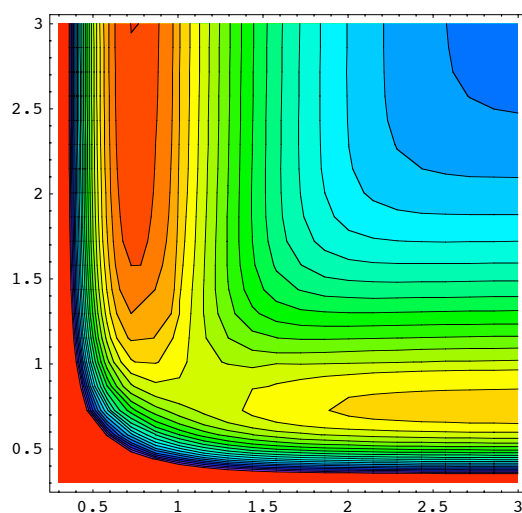


Figure 2: *Contour plot of a LEPS potential surface for three atoms placed along a line where each atom can only form one bond.*

*Sketch classical trajectories for the following situations (assuming the total energy of the molecule is constant, i.e. no connection with a heat bath):*

*(a)   Atom A is initially 3 Å away from the center of a BC molecule and is moving towards the molecule, collides with it, and an exchange reaction occurs. The BC molecule is initially vibrating with an amplitude of 0.1 A.*

*(b)   Same as part (a) except that an exchange reaction does NOT occur.*

*(c)   Which degree of freedom is more efficient in promoting an exchange reaction, the translational energy of the A-atom or the vibrational energy of the BC-molecule?*

*Answer:*

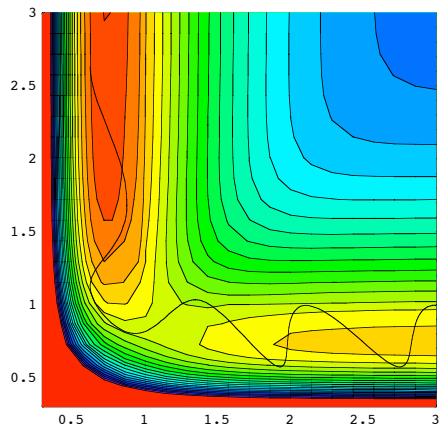For the answer to part (a) see Fig. 3. For the answer to part (b) see Fig. 4.



Figure 3: *Trajectory where the B-C distance has been reduced by 0.1Å from the optimal distance and atom A is 2.63 Å from the center of the B-C molecule (3 Å from the B atom). The initial velocity of the A atom is 0.21 Å/fs. An exchange reaction occurs.*



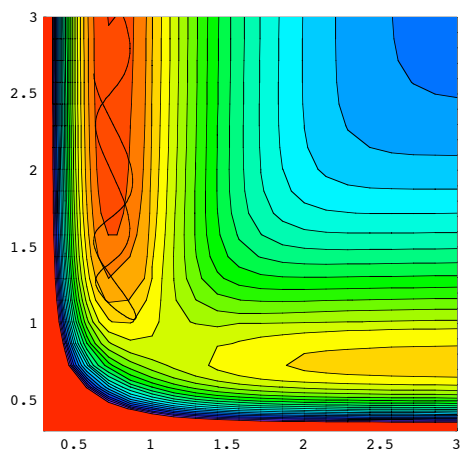Figure 4: *Trajectory where the B-C distance has been reduced by 0.1Å from the optimal distance and atom A is 2.63 Å from the center of the B-C molecule (3 Å from the B atom). The initial velocity of the A atom is 0.15 Å/fs. An exchange reaction does not occur and atom A gets reflected back from the B-C molecule.*

*Answer to (c):*

The vibration of the B-C molecule gives the trajectory the right direction to get over the barrier, while the translation of the A-atom simply sends the trajectory up the repulsive wall of the A-BC interaction. Note that the importance vibration vs. translation is reversed for the reverse direction, that is translational energy of a C atom is more efficient in inducing exchange reaction than vibration of a A-B molecule.

## Problem 4: Transition state theory (TST)

*(a) What are the four basic assumptions of TST? What should the shape of the potential energy surface be like in order for TST to give a good approximation to the rate constant of a transition?*

*Answer to part (a):*

The four basic assumptions are: (1) The Born-Oppenheimer approximation is valid, i.e. the time scale of the motion of electrons is so much shorter than the time scale of the motion of atoms that we can solve for the electronic degrees of freedom for fixed position of the nuclei. This gives a potential energy surface (PES) for the motion of the nuclei. (2) The dynamics of the nuclei can be described by Newton's equations of motion, i.e. classical dynamics. (3) The transitions are slow enough that a Boltzmann distribution of energy is established and maintained for each degree of freedom of the reactant(s). (4) If the system makes it to the transition state dividing surface and the velocity is pointing towards the region of configuration space associated with the products, then the system will continue to go towards the energy well associated with the products and will stay there for an extended time - long compared with vibrational periods. A reactive trajectory must cross the transition state dividing surface that separates reactants and products, but the trajectory should only cross the transition state once. If a trajectory crosses the tranistion state twice, it will end up in the reactant region i.e. is non-reactive, but gets counted as being reactive in the TST estimate of the rate constant. Also, if a trajectory crosses the transition state three times, it gets counted as two reactive events by the fourth assumption of TST. Any recrossing of the transition state leads to an overestimate of the rate constant in the TST approximation. In order to reduce the probability of recrossings, the potential surface should have a narrow and simple barrier in between the initial and final state (without dips and without significant curvature of the minimum energy path). Then TST can be expected to give a good approximation for the rate constant.

*(b) A hydrogen atom adsorbed on the surface of a metal crystal can diffuse by hopping from one binding site to another. The atom can be considered to be a particle moving on*

a periodic potential surface (PES) while the metal atoms can be taken to be stationary. This is a good first approximation because the metal atoms are so much heavier than the hydrogen atom. For a hydrogen atom on the (001) surface of an FCC metal, the potential energy of the hydrogen atom can be approximated by the function

$$V(x, y, z) = V_s \left( e^{-\cos(2\pi x/b) - \cos(2\pi y/b) - 2\alpha z} - 2e^{-\alpha z} \right)$$

where $V_s$ is 0.2 eV, b is 3 Å and $\alpha = 2$ Å$^{-1}$. The normal to the crystal surface lies along the z-axis.

(Note on units: It is convenient to use the following, approximate relationship $\sqrt{eV/(amu\ A^2)} = 1.0 \times 10^{14}\ sec^{-1}$).

Evaluate the rate constant for diffusion hops using the harmonic approximation to TST. Here are the steps you need to take in order to do that (see lecture notes):

(1) Identify the minima and saddle points on the potential energy surface. You should do this first of all by making a contour plot of the potential surface in the plane of the surface (x,y), using for example Matlab. By inspecting the plot, you can get the x and y coordinates of the minima and the saddle points. Then, you need to minimize the energy with respect to z given these values of x and y.

(2) Differentiate the potential function with respect to x, y and z and show that each one of the derivatives is zero at a minimum and at a saddle point. This verifies that you have found the right coordinates. The activation energy is obtained from the difference in the potential energy at the saddle point and at the minimum.

(3) In order to evaluate the prefactor of the rate constant, do a Taylor expansion of the potential energy function up to second order at a minimum and at a saddle point. You can use Matlab to do that. Get the frequency of each vibrational mode. Note that one of the modes at the saddle point corresponds to negative curvature (imaginary frequency). The ratio of products of the vibrational frequencies gives the prefactor (see lecture notes).


*Answer to part (b):*
A contour plot of the potential energy surface in the z=0 plane is shown in fig. 5. From the contour plot one can see that the periodically replicated minima are located at $(x, y, z) = (ib, jb, z_{min})$, where $i$ and $j$ are integers. For example, focus on the $i = j = 0$ minimum. By finding the minimum of the function $V(0, 0, z)$ with respect to $z$, it can be seen that $z_{min} = -2/\alpha = -1$Å and the value of the potential energy at the minimum is $V_{min} = -V_s e^2 = -1.48$ eV. The saddle points on the PES are of two types. One half of them is a maximum with respect to variation along the x-axis but a minimum with respect to variation in y and z. These are located at $(x, y, z) = ((i + 1/2)b, jb, z_{sp})$. The other half is a maximum with respect to variation in the $y$-direction but minimum along
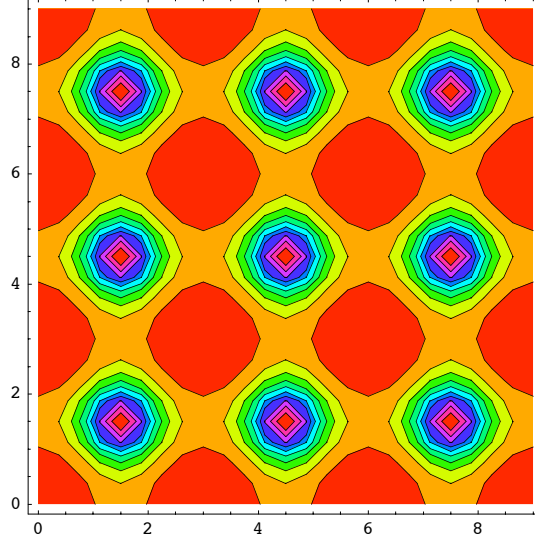
Figure 5: *Contour plot of a potential surface for an H-atom on a frozen metal surface.*

the other two directions. These saddle points are located at $(x, y, z) = (ib, (j+1/2)b, z_{sp})$. One saddle point of the former type is, for example, at $x = b/2$ and $y = 0$. Minimization of the function $V(b/2, 0, z)$ with respect to $z$, gives $z_{sp} = 0$ and the energy at the saddle point is $V_{SP} = -V_s = -0.2eV$. The activation energy for diffusion hops (ignoring quantum effects) is, therefore, $E_a = -0.2 + 1.48 = 1.28eV$. This is a rather large activation energy. The temperature dependence of the HTST approximation to the rate constant can then be obtained as $k^{HTST} \sim exp(-1.28eV/k_BT)$.

Note, that the $z$ coordinate of the minima and the saddle points is not the same. Fig. 6 shows the potential energy as a function of $z$ at a location in the $(x, y)$ plane that corresponds to a minimum in the PES, i.e. the function $V(0, 0, z)$, as well as the potential energy as a function of $z$ for a saddle point location in the $(x, y)$ plane, i.e. the function $V(b/2, 0, z)$.

The full expression for the rate constant in the HTST approximation is

$$k^{HTST} = \frac{\Pi_i^3 \nu_{R,i}}{\Pi_i^2 \nu_{\ddagger,i}} \, e^{-(V_{SP} - V_{min})/k_BT}$$

The prefactor of the rate constant (i.e. the factor in front of the exponential) can be evaluated by finding the normal modes of vibration at the minimum and at the saddle point. The prefactor is $\Pi_i^D \nu_{R,i} / \Pi_i^{D-1} \nu_{\ddagger,i}$ where the $\nu_{R,i}$ are the normal mode frequencies at the reactant state minimum on the PES, the $\nu_{\ddagger,i}$ are the frequencies of the stable normal modes at the saddle point and $D$ is the number of degrees of freedom in the system. A Taylor expansion up to second order of the PES around the minimum at
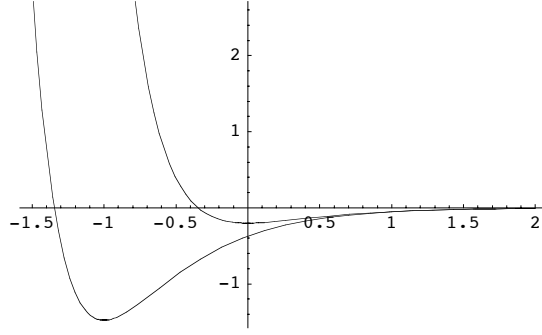
8

Figure 6: *Fig. 6: Variation of the potential energy along the z-direction for (x,y)=(0,0), a location that includes a minimum, and for (x,y)=(b/2,0), a location that includes a saddle point on the PES. The figure illustrates how different the optimal value of z is at the two locations in the (x,y) plane.*

(0,0,-1) gives (after setting $b = 3\text{Å}$ and $\alpha = 2\text{Å}^{-1}$)

$$V(x, y, z) = V_s e^2 \left( -1 + 4(z + 1)^2 + \frac{2\pi^2}{9}y^2 + \frac{2\pi^2}{9}x^2 \right)$$

and an expansion around the saddle point at (b/2,0,0) gives

$$V(x, y, z) = V_s \left( -1 + 4z^2 + \frac{2\pi^2}{9}y^2 - \frac{2\pi^2}{9}(x - 1.5)^2 \right)$$

The Taylor expansion around the minimum shows that the matrix of second derivatives is already diagonal, that is all the mixed second derivatives are zero. Only $\frac{\partial^2 V}{\partial x^2}$, $\frac{\partial^2 V}{\partial y^2}$ and $\frac{\partial^2 V}{\partial z^2}$ are non-zero. The Cartesian coordinates are, therefore, the normal mode coordinates and there is no need in this case to solve a matrix eigenvalue problem. Each of the three equations of motion for the hydrogen atom only involves one of the Cartesian coordinates. The frequency of the motion in the x-direction is $\omega_x = \sqrt{k_{xx}/m}$ where $k_{xx} = \frac{\partial^2 V}{\partial x^2}$. Plugging in the expression for the second derivative (twice the coefficient of $x^2$ in the Taylor expansion above) gives $\omega_x = \frac{\sqrt{0.8}e\pi}{3}\sqrt{\frac{eV}{amu\ A^2}}$. So, the vibrational frequency is $\omega_x = 2.5 \times 10^{14}\ sec^{-1}$. The frequency of motion in the y-direction is the same since the second derivative is the same (as it has to be by symmetry). The frequency of motion in the $z$-direction, however, is larger by a ratio of $\sqrt{k_{zz}/k_{xx}} = \sqrt{\frac{4}{2\pi^2/9}} = 1.35$, that is $\omega_z = 3.4 \times 10^{14}\ sec^{-1}$.

At the saddle point at (b/2,0,0), there are only two stable modes, the vibration in y-direction and vibration in z-direction. The motion in x-direction corresponds to going over the potential barrier and the corresponding second derivative of the potential is negative, as can be seen from the Taylor expansion above. The frequency of the two

stable modes is the same as for the minimum except for a factor of $1/e$ since the second derivatives of the potential are the same except for the missing factor of $e^2$ in front of the bracket in the Taylor expansion at the minimum, so $\omega_y = 9.3 \times 10^{13}\ sec^{-1}$ and $\omega_z = 1.3 \times 10^{14}\ sec^{-1}$.

The prefactor in the HTST estimate of the rate constant is

$$\frac{\Pi_i^3 \nu_{R,i}}{\Pi_i^2 \nu_{\ddagger,i}} = \frac{1}{2\pi}\frac{\Pi_i^3 \omega_{R,i}}{\Pi_i^2 \omega_{\ddagger,i}} = \frac{(2.5 \times 10^{14})^2\ 3.4 \times 10^{14}}{0.93 \times 10^{14} \cdot 1.3 \times 10^{14}/e} = 2.8 \times 10^{14}\ sec^{-1}$$

Finally, the HTST approximation to the rate constant is

$$k^{HTST} = 2.8 \times 10^{14}\ sec^{-1}\ e^{-1.28eV/k_B T}.$$

*(c) What is the average length of time in between diffusion hops at room temperature, at 400 K and at 500 K? Notice the dramatic change as the temperature is increased.*

*Answer to part (c):*

At room temperature, $k_B T = 0.025\ eV$ (approximately) and the rate constant then has the value of $k^{HTST} = 1.6 \times 10^{-8} sec^{-1}$. The average time between diffusion hops is then $\tau = 1/k = 6.1 \times 10^7\ sec$. That is about two years! The hydrogen atoms therefore hardly diffuse at all on our time scale at room temperature.

It the temperature is raised to 400 $K$, then $k_B T = 0.025 \times 4/3\ eV = 0.033\ eV$ and the rate constant becomes $k^{HTST} = 0.004\ sec^{-1}$ and the time in between hops is on the average 4 minutes. Note the dramatic increase in hopping rate as the temperature is raised from 300 K to 400 K.

If the temperature is further increased to 500 K, then the rate constant becomes $k^{HTST} = 16\ sec^{-1}$, that is the atoms hops on average 16 times per second.