

The classical vibrationally adiabatic potential curve is defined as:

$$V_a(s) = V_{MEP}(s) + \frac{h}{2} \sum_{i=1}^{3N-7} \omega_i(s) \quad (1)$$

being  $\omega_i$  the corresponding vibrational frequencies of the geometry  $s$ . The corresponding vibrationally adiabatic transmission coefficient can be calculated, under the Wentzel–Kramers–Brillouin (WKB) approximation, as:

$$\kappa = \frac{\int_0^\infty P(V_a) e^{-\frac{V_a}{k_B T}} dV_a}{\int_{V_a^{max}}^\infty e^{-\frac{V_a}{k_B T}} dV_a} \approx e^{\frac{V_a^{max}}{k_B T}} \frac{1}{k_B T} \int_0^\infty P(V_a) e^{-\frac{V_a}{k_B T}} dV_a \quad (2)$$

where the approximation is valid at low temperatures<sup>1</sup>. Additionally, the recrossing factor can be also estimated:

$$\gamma = e^{-\frac{|\Delta V_a^{max} - \Delta V_a^{s=0}|}{k_B T}} \quad (3)$$

being  $\Delta V_a^{s=0}$  the barrier from the reactant to the transition state, and  $\Delta V_a^{max}$  to the maximum of the adiabatic potential (the transition state may not be a maximum on the adiabatic potential...). The value of the tunneling probability for a given potential  $E$  is defined by<sup>2</sup>:

$$P(E) = (1 + e^{2 \cdot \theta(E)})^{-1} \quad E \leq V_a^{s=0} \quad \theta(E) = \frac{2\pi}{h} \int_{s<}^{s>} (2 \mu_{eff}(s) [V_a(s) - E])^{\frac{1}{2}} ds \quad (4)$$

where  $s_<$  and  $s_>$  are the values of the path coordinate at the left and right turning points, and  $\mu_{eff}(s)$  is the effective reduced mass along  $s$ . If  $\mu_{eff}$  is taken constant along the reaction path, we obtain the Zero-curvature theory (ZCT). On the other hand, the centrifugal-dominant small-curvature tunneling approximation<sup>3</sup> allows to express the dependence of  $\mu_{eff}(s)$ :

$$\mu_{eff}(s) = \mu \cdot \min \left\{ e^{-2a(s) - [a(s)]^2 + \left(\frac{dt}{ds}\right)^2}, 1 \right\} \quad \mu = \frac{1}{N_A m_e 10^3} \quad (5)$$

where  $a(s)$  and  $t(s)$  (the maximum concave-side vibrational displacement along the curvature direction) are:

$$a(s) = t(s) \eta(s) \quad t(s) = \eta^{\frac{1}{2}}(s) \left( \frac{h}{2\pi\mu} \right)^{\frac{1}{2}} \left[ \sum_i^{3N-7} B_i^2(s) \omega_i^2(s) \right]^{-\frac{1}{4}} \quad \eta(s) = \left( \sum_i^{3N-7} B_i^2(s) \right)^{\frac{1}{2}} \quad (6)$$

being  $\eta(s)$  the magnitude of the curvature, and  $B_i(s)$  the reaction path curvature components:

$$B_i(s) = \frac{1}{|g(s)|} L_i^T(s) \cdot \left[ H(s) \cdot \frac{-g(s)}{|g(s)|} \right] \quad \eta(s) = \left( \sum_i^{3N-7} B_i^2(s) \right)^{\frac{1}{2}} \quad (7)$$

In this expression,  $L_i(s)$  corresponds to the  $i$ th eigenvector of the hessian  $H$ , and  $g$  is the gradient vector (all in mass-weight coordinates:  $x_i = \sqrt{m_i} x_i^{cart}$ ;  $g_i = g_i^{cart} / \sqrt{m_i}$ ;  $h_{i,j} = h_{i,j}^{cart} / \sqrt{m_i \cdot m_j}$ ). Thus, the  $B_i(s)$  values represent the change in the direction of the  $i$ th eigenvector induced by the variation of the reaction coordinate.

1 Equations **49**, **50** from J.Phys.Chem. 1980 (84) 1730-1748

2 Equations **44**, **45** from J.Phys.Chem. 1992 (96) 5758-5772; or **1a** from J.Am.Chem.Soc. 2002 (124) 3093-3124

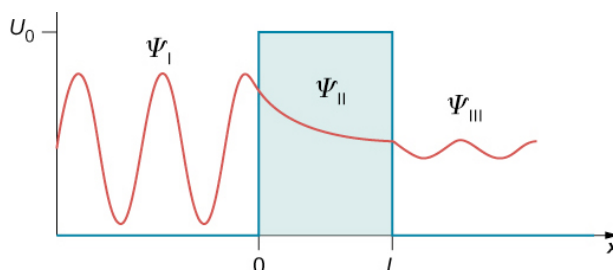
3 Equations **52**, **51**, **50**, **44** from Comput. Phys. Commun. 1992 (71) 235-262; and **3** from J.Am.Chem.Soc. 2002 (124) 3093-3124

For the particle in a box, the tunneling effect arises from the presence of a finite potential of the shape:

$$V(x) \begin{cases} 0 & x < 0 & \text{region I} \\ U_0 & 0 \leq x \leq L & \text{region II} \\ 0 & x > L & \text{region III} \end{cases}$$

The Schrödinger time-independent equation is solved for each region, thus obtaining three wave-functions, satisfying the continuity at each region, as well as in the first derivatives:

$$\psi_I(0) = \psi_{II}(0) \quad \psi_{II}(L) = \psi_{III}(L) \quad \left. \frac{d\psi_I(x)}{dx} \right|_{x=0} = \left. \frac{d\psi_{II}(x)}{dx} \right|_{x=0} \quad \left. \frac{d\psi_{II}(x)}{dx} \right|_{x=L} = \left. \frac{d\psi_{III}(x)}{dx} \right|_{x=L}$$



The transmission coefficient represents the probability flux of the transmitted wave relative to that of the incident wave. Using the WKB approximation<sup>4</sup>, one can obtain a tunneling coefficient that looks like (which depends on the particular system):

$$T = \frac{e^{-2 \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2} (V(x) - E)} dx}}{\left( 1 + \frac{1}{4} e^{-2 \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2} (V(x) - E)} dx} \right)^2}$$

where  $x_1, x_2$  are the two classical turning points for the potential barrier.

A description of the Variational Transition-State theory can be found at J.Phys.Chem. 1980 (84) 1730-1748

$$\theta(x) = \frac{s}{kg m^2} \int_{s<}^{s>} (\mu)^{\frac{1}{2}} \sqrt{2kg \frac{m^2}{s^2}} \text{Å} \sqrt{\frac{g}{mol}}$$

$$\theta(x) = \left( \frac{s}{kg m^2} \int_{s<}^{s>} (\mu)^{\frac{1}{2}} \sqrt{kg} \frac{m^2}{s} \sqrt{kg} \right) \sqrt{2} \frac{10^{-10}}{\sqrt{10^3 \cdot N_A}} \frac{2 \cdot \pi}{h}$$

$$a(s): \text{dimensionless} \quad ; \quad t(s): s^{-1} \quad ; \quad \eta(s): s \quad ; \quad B_m(s): s$$