Derivations of Marcus's formula

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Abstract

Two derivations of Marcus's formula for transition rates are presented. The first derivation is based on the Landau-Zener transition rate formula. The second makes use analytic expressions for the Franck-Condon factors, derived by applying the stationary phase approximation to the WKB wave functions of the oscillator Hamiltonians.

I. MARCUS'S FORMULA

The rate of an electronic transition in a molecular system, treated in the Born-Oppenheimer approximation, depends on the vibronic coordinates as well as the electronic wave functions. Marcus derived a compact formula for the vibronic effects by making three additional assumptions:

1. The transition is perturbative in the electronic degrees of freedom, and thus can be treated by Fermi's Golden Rule;

2. The vibronic dynamics is governed by the Displaced Harmonic Oscillator Hamiltonian (DHOH);

3. The transition is semiclassical in the sense that the vibronic energy scale $\hbar\omega$ is smaller than other vibronic energy scales, i.e. the barrier height and the energy difference of the two states.

The perturbation starting point for the derivation is the formula for the transition rate,

$$W_{n_a} = \frac{2\pi}{\hbar}|H_{ab}|^2 \sum_{n_b} |\langle n_a|n_b\rangle|^2 \delta(E_{ab} + E_{n_a} - E_{n_b}). \tag{1}$$

Here H_{ab} is matrix element between the electronic states a and b. It is assumed to be independent of the vibronic coordinate. The index n labels the vibronic wave functions of the initial state a and m labels the vibronic wave functions of the final state b. The argument of the δ-function is the difference in energies of the initial and final states, taking into account both electronic and vibronic contributions.

The DHOH for the a state is the simple harmonic oscillator,

$$\hat{H}_a = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega^2 x^2. \tag{2}$$

In the state b, the origin of the harmonic oscillator is shifted by an amount x_{ab},

$$\hat{H}_b = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \frac{1}{2}M\omega^2(x - x_{ab})^2. \tag{3}$$

Fig. 1 depicts the Born-Oppenheimer potential energy surfaces. The transition goes from the level n at E_n on the left to the level m on the right, at energy E_m over its Born-Oppenheimer minimum. Other relevant energies are E_{ab}, the electronic energy difference of the two configurations and E_*, the activation energy to overcome the potential barrier between the two vibronic wells.
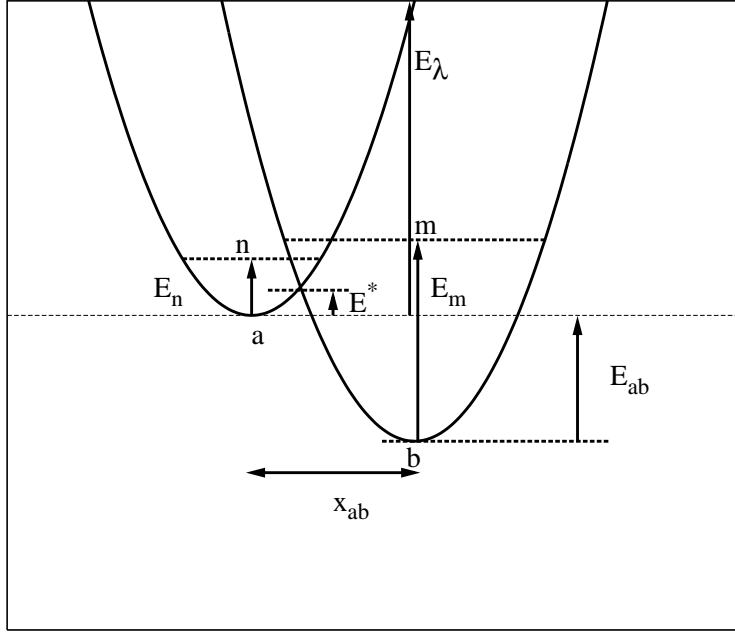
FIG. 1: Born-Oppenheimer potential energy surfaces V_a, V_b and energy levels n,m.

Besides W_n we also want to determine the transition rate at finite temperature T. The expression to be evaluated is

$$W_T = \frac{\sum_n e^{-E_n/T} W_n}{\sum_n e^{-E_n/T}}. \tag{4}$$

We shall derive the semiclassical limit of Eqs. (4) and (1) as

$$W_T \approx \frac{(2\pi)^{1/2} |H_{ab}|^2}{\omega x_{ab} (MT)^{1/2}} e^{-E_*/T}. \tag{5}$$

It may be convenient to use the energy variable $E_\lambda = \frac{1}{2} M \omega^2 x_{ab}^2$ instead of the variables x_{ab} and $E_* = (E_{ab} - E_\lambda)^2 / 4E_\lambda$ in presenting the equation. Then it becomes

$$W_T = \frac{|H_{ab}|^2}{\hbar} \sqrt{\frac{\pi}{E_\lambda T}} \exp(-\frac{(E_{ab} + E_\lambda)^2}{4E_\lambda T}), \tag{6}$$

as in Ref. [3].

II. DERIVATION FROM THE LANDAU-ZENER FORMULA

The general Landau-Zener formula for the probability that a system will cross from a to b is

$$P_{ab} = 1 - e^{-p}, \quad p = \frac{2\pi}{\hbar} \frac{|H_{ab}|^2}{\frac{d(V_a - V_b)}{dx} \frac{dx}{dt}}. \tag{7}$$

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where $V_a(x), V_b(x)$ are the Born-Oppenheimer potential energy surfaces and $\frac{dx}{dt}$ is the velocity of the system moving to the right in state a. The formula is valid assuming that V_a, V_b are slowly varying compared to the wavelength of the wave function of the moving system. See Ref. [2] for a derivation.

To get to Marcus's formula, we first need to assume that the interaction H_{ab} is weak in the sense that we can make the further approximation

$$P_{ab} \approx p \tag{8}$$

To apply the formula to the DHOH, first note that the transition rate W will be the product of the frequency the system hitting the barrier times the probability to make the transition. The frequency of oscillation is $f_a = \omega/2\pi$ but one must remember that it passes the barrier point twice in each cycle, once from the left and once from the rate. The rate is therefor

$$W = 2f_a P_{ab} = \frac{\omega}{\pi} P_{ab}. \tag{9}$$

In terms of the variables of Fig. 1, the velocity of the system at the barrier is

$$\frac{dx}{dt} = \sqrt{\frac{2}{M}(E_n - E_*)} \tag{10}$$

We also need the derivatives of the potential energy surfaces. Their difference turns out to be independent of the position of the barrier in the DHOH and is given by

$$\frac{d(V_a - V_b)}{dx} = M\omega^2 x_{ab}. \tag{11}$$

From Eq. (7,8,9,10,11) we find for the rate W_n

$$W_n = \frac{2|H_{ab}|^2}{\hbar\omega x_{ab}(2M(E_n - E_*))^{1/2}}. \tag{12}$$

We now insert this into the equation for the thermal rate, Eq. (4). We make a change of variable $z = \sqrt{E_n - E_*}$ in the numerator and approximate the sums by integrals $\sum_n \rightarrow \frac{1}{\hbar\omega} \int dE_n$. The expression for the thermal rate then becomes

$$W_T = \frac{|H_{ab}|^2}{\hbar\omega x_{ab}(2M)^{1/2}} \frac{e^{-E_*/T} \int 2z dz e^{-z^2/T}/z}{\int dE_n e^{-E_n/T}} = \sqrt{2\pi} \frac{|H_{ab}|^2}{\hbar\omega x_{ab}(MT)^{1/2}} e^{-E_*/T}. \tag{13}$$

This is the desired result.

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III. WKB DERIVATION

Our first goal is an analytic expression for the vibronic overlap $|\langle n|m\rangle|^2$, needed in Eq. (1). We start with the WKB expression [1] for the vibronic wave function $\phi_n(x)$,

$$\phi_n(x) \approx \frac{K}{(k_n(x))^{1/2}} \cos(\int_{-x_n}^{x} k_n(x')dx' - \pi/4).$$ (14)

Here $k_n(x)$ is the local reduced wave number. In the DHOH, it is

$$k_n(x) = \frac{1}{\hbar}\sqrt{2M(E_n - \frac{1}{2}M\omega^2 x^2)}.$$ (15)

The normalization constant K will be evaluated below. The lower limit of the integral is the semiclassical turning point,

$$x_n = \sqrt{\frac{2E_n}{M\omega^2}}$$ (16)

To find the normalization factor K, we separate the cosine function into exponentials, $\cos(i\int^x kdx') = (e^{+i\int^x kdx'} + e^{-i\int^x kdx'})/2$. The two terms represent waves traveling to the right and to the left, respectively. The exponents cancel in the integrand for the right-right and the left-left terms in the normalization integrals, and they are easily reduced to the textbook integral $\int_{-1}^{1}(1-z^2)^{-1/2}dz = \pi$. The right-left and left-right integrals do not reduce trivially, but their sum vanishes if x_n is determined with the quantum energy $E_n = \hbar\omega(n+\frac{1}{2})$ in Eq. (16). Under those conditions the normalization factor is

$$K = \sqrt{\frac{2M\omega}{\pi\hbar}}.$$ (17)

The WKB wave functions are remarkably accurate. This may be seen in Fig. 2, comparing $n = 10$ harmonic oscillator wave function compared with its WKB approximation. Of course, in the vicinity of the turnings the WKB approximation breaks down.

The next task is to evaluate the overlap of $\phi_n(x)$ and $\phi_m(x - x_{ab})$. We shall neglect the overlap of a right-moving wave with a left-moving wave, and use the stationary phase approximation to evaluation the overlap of waves moving in the same direction. The right-right integral is

$$I_{nm} = \frac{M\omega}{\pi\hbar} \int_{x_m}^{x_n} \frac{1}{(k_n(x)k_m(x - x_{ab}))^{1/2}} e^{i\Phi(x)}dx$$ (18)

with

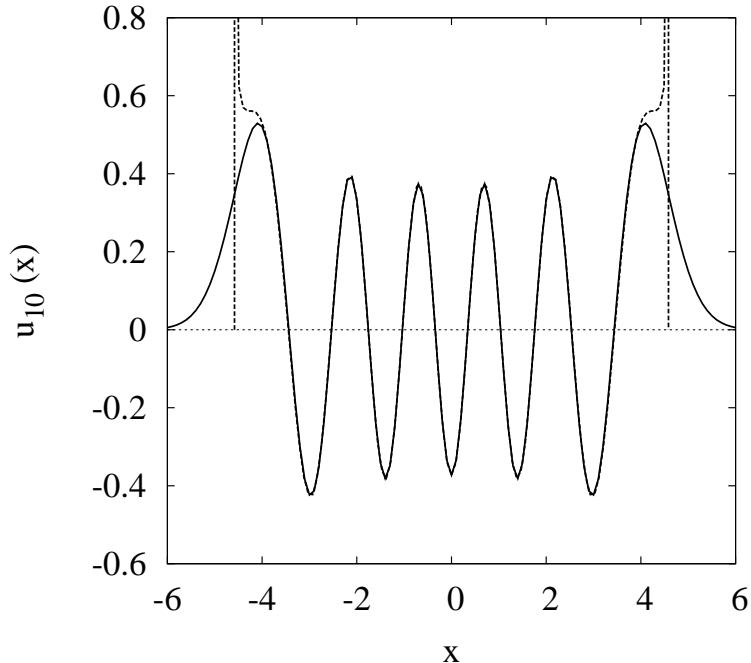$$\Phi(x) = \int^x dx' \left(k_n(x') - k_m(x' - x_{ab})\right).$$

FIG. 2: Comparison of the $n = 10$ harmonic oscillator wave function with its WKB approximation. The turning points $\pm x_n$ include a quantum correction, $\frac{1}{2}m\omega^2 x_n^2 = \omega(n + \frac{1}{2})$.

The left-left integral is the complex conjugate, I_{nm}^*. In the stationary phase approximation, one finds a point x_* at which the phase satisfies $d\Phi/dx|_{x_*} = 0$. This is within the integration range for the left-left and right-right integral if E_n and E_m are both larger than E_*. We note also that local wave numbers at the stationary phase point are equal, $k_n(x_*) = k_m(x_{ab} - x_*) = k_*$. We carry out a Taylor expansion of Φ as

$$\Phi(x) \approx \Phi(x_*) + \frac{1}{2} \left. \frac{d^2\Phi}{dx^2} \right|_{x_*} (x - x_*)^2. \tag{19}$$

We assume that the phase variation is rapid compared to the variation in the reduced wave numbers and that the integral can be extending to $\pm\infty$ to obtain a Gaussian integral on a deformed contour in the complex plane. The coefficient of the quadratic term is

$$\left. \frac{d^2\Phi}{dx^2} \right|_{x_*} = -\frac{M^2\omega^2 x_{ab}}{\hbar^2 k_*} \tag{20}$$

and the result for the modulus of the integral is

$$|I_{nm}| \approx (2\pi x_{ab} k_*)^{-1/2} \tag{21}$$

We now sum the moduli squared of the left-left and the right-right integrals assuming that the cross term depending on the phase between them vanishes on average. This gives for

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the squared overlap

$$|\langle n|m\rangle|^2 = \frac{1}{\pi x_{ab} k_*}, \quad E_n, E_m > E_* \tag{22}$$

and zero if the energy conditions are not met. Going back to our oscillator quanta labeling n_a, n_b, the formula can be conveniently expressed as

$$|\langle n_a|n_b\rangle|^2 = \frac{1}{\pi}\left((n_{max} - n_a)(n_a - n_{min})\right)^{-1/2} \tag{23}$$

where

$$n_{min}, n_{max} = n_b + n_\lambda \pm \sqrt{4n_b n_\lambda} \tag{24}$$

and $n_\lambda = E_\lambda/\hbar\omega$. Eq. (23) is compared with the exact overlap probabilities Fig. 3. For the given parameters, the allowed region of n_b is $n_{min} = 49 < n < n_{max} = 169$. One sees that the squared overlaps (shown as circles) scatter between zero and a maximum that varies smoothly with n. The WKB approximation (shown as the line) is lower than the maximum envelope. In fact it follows the average squared overlap quite well. This may be seen in Fig. 4, showing a running sum of the squared overlaps.

The transition rate formula Eq. (1) also requires the level density, which is smoothed in the approximate expression

$$\sum_{n_b} |\langle n_a|n_b\rangle|^2 \delta(E_{ab} + E_{n_a} - E_{n_b}) \approx |\langle n_a|n_b\rangle|^2 \frac{1}{\hbar\omega} \tag{25}$$

where n_b in the left-hand expression satisfies $E_{n_b} = E_{ab} + E_{n_a}$ and is not necessarily an integer. and in the DHOH. The final expression for W_n becomes

$$W_{n_a} = \frac{2|H_{ab}|^2}{\hbar^2 \omega x_{ab} k_*} = \frac{2\pi|H_{ab}|^2}{\hbar^2 \omega \sqrt{2n_\lambda(n_a + n_b) - (n_a - n_b)^2 - n_\lambda^2}}, \tag{26}$$

the same as we found via the Landau-Zener formula. The thermal rate calculation derives form this formula and will be the same as well.

IV. LIMITS OF VALIDITY

A number of steps in the derivation require $\hbar\omega$ to be small compared to other energies present in the rate equations (26) and (6). That condition is assumed for level density Eq. (25), the WKB overlap expression, Eq. (22), and for the statistical summation over the thermal ensemble, Eq. (4). The other approximation that H_{ab} is small in some sense to
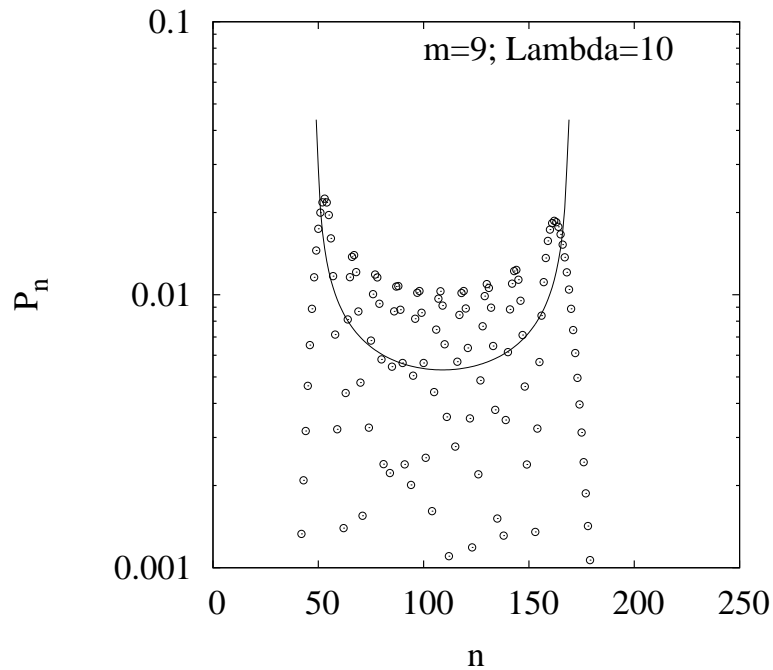
FIG. 3: Circles: squared overlaps $|\langle n'|m = 9\rangle|^2$ as a function of m. Line: WKB approximation, Eq. (22).
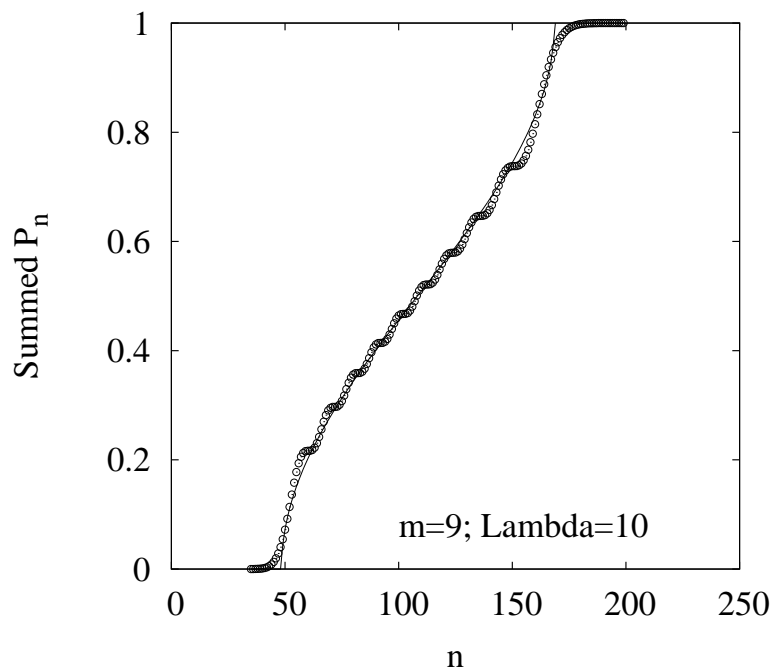

FIG. 4: Summed square overlaps $\sum_{n'<n} |\langle n'|m = 9\rangle|^2$ compared with the corresponding integrated WKB approximation.

apply perturbative rate equation Eq. (1). This limit is clearly exposed through the Landau-Zener derivation. Namely, the requirement is that $p << 1$ in Eq. (7) It may be expressed in terms of the DHOH variables as

$$\frac{\pi |H_{ab}|^2}{\hbar \omega \sqrt{E_\lambda (E_n - E_*)}} << 1. \tag{27}$$

Note that the condition Eq. (27) always breaks down for E_n close to the barrier E_*. However, above-barrier energies become dominant if the temperature is high enough. Thus the condition becomes

$$\frac{\pi |H_{ab}|^2}{\hbar \omega \sqrt{E_\lambda T}} << 1 \tag{28}$$

for the thermal rate equation. In the opposite limit,

$$\frac{\pi |H_{ab}|^2}{\hbar \omega \sqrt{E_\lambda T}} >> 1 \tag{29}$$

the theory becomes simple again. Then the states a and b are strongly coupled and the motion is adiabatic on the lowest energy surface. This regime should be described by transition-state theory. For the DHOH, the rate would be given by

$$W_T = \frac{\omega}{2\pi} e^{-(E_* - |H_{ab}|)/T} \tag{30}$$

A more quantitative assessment of the regimes of validity can be obtained by numerically solving the time-dependent Schrödinger equation for the DHOH Hamiltonian. A computer code for this purpose is provided in the Appendix. The initial state of the system is the thermal ensemble for the vibrational excitations in the electronic state a. For each vibrational state n_a in the ensemble, the code solves the time-dependent Hamiltonian equation to obtain the probability P_b of the electronic state b in the wave function at time $t = \pi/\omega$. The rate is then estimated as $W_{n_a} = P_b(t)/t$. Fig. 5 shows the computed rates in the DHOH; see the figure caption for the DHOH parameters. Circles are the calculated rates from the code; the line connecting them is to guide the eye. The solid line is obtained from the WKB formula for the rate, Eq. (26), taking n_a as a continuous variable. Fig. (6) compares the derived thermal rates. One can see from this figure that the classical formula works very well except at the lowest temperatures. But that is to be expected, based on the limits of validity discussed above.
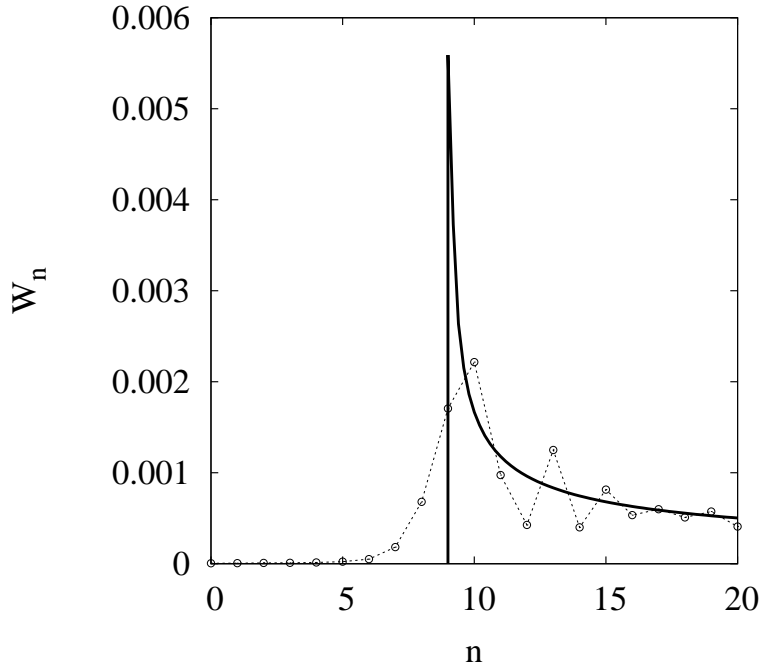
FIG. 5: Transition rates W_n in the DHOH model. Parameters are $E_* = 9, E_{ab} = 0$ and $H_{ab} = 0.1$ in units of $\hbar\omega$.

With the numerical code we can also investigate the breakdown of perturbation theory as the adiabaticity parameter in Eq. (27) becomes large. To see the effect, we take $H_{ab} = 1.5$ and otherwise the same DHOH as in Figs. 6,7. This gives adiabaticity parameter

$$\frac{\pi |H_{ab}|^2}{\hbar\omega\sqrt{E_\lambda(E_n - E_*)}} \approx \sqrt{\frac{5.5}{T}}, \tag{31}$$

which rather far from the perturbative region. The calculated rates are shown in Fig. 7. Now there are significant differences at both high and low temperatures. At the higher temperature, the perturbative formula overpredicts the rate, which is what one expects to happen if the perturbation is too large.

V.   EXERCISES FOR THE READER

For further study, the reader might try the following exercises. I have not tried them myself.

1. Effect of interference on $\langle n_a | n_b \rangle$. In approximating this quantity, we neglect interference between the left-left and the right-right contributions. Can one include the interference
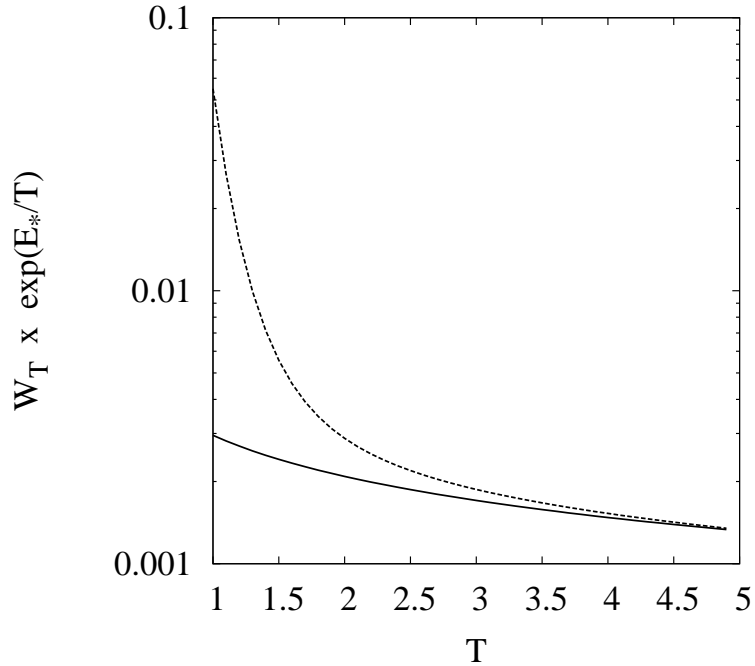
FIG. 6: Transition rates W_T as a function of temperature, for the same DHOH as in the previous figure. Solid line: WKB approximation, Eq. (6); Dashed line: using the W_n computed from the time-dependent Hamiltonian equation.

analytically in the WKB treatment, and if so, how does it compare with the numerically exact overlaps?

2. In Fig. 7, we considered an interaction strength higher than justified by the perturbative treatment. Does one gets better agreement with the transition state treatment, Eq. (30)?

VI. APPENDIX

```
#calculate the rate W_n for a range of n
# input data: v12,Ex,Eab,Nmax
# output   n   W_n    n in [:nmax]

import sys,os
from math import sqrt,pi
from numpy import *
```
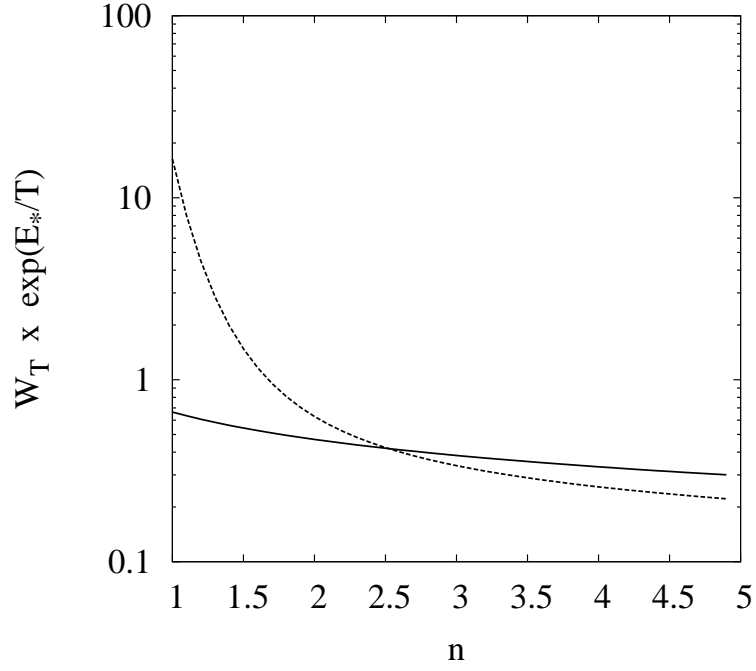
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FIG. 7: Transition rates W_T as a function of temperature, for the same DHOH except for $H_{ab} = 1.5$. Solid line: WKB approximation, Eq. (6); Dashed line: using the W_n computed from the time-dependent Hamiltonian equation.

```
from numpy.linalg import eigh
import numpy as np


def ho_h1v(H1,V,v12,Nmax):
  for i in range(Nmax):
    V[i,i] = v12
    H1[i,i] = i+0.5
  return H1,V


def h2(Lam,v12,Eab,Nmax,flag):
  H1=array([[0.0]*Nmax]*Nmax)
  H2=H1*0.0; V = H1*0.0
  Hbig = array([[0.0]*2*Nmax]*2*Nmax)
  H1,V = ho_h1v(H1,V,v12,Nmax)
```

```python
    for i in range(Nmax):
      H2[i,i] = i+0.5-Eab+Lam**2
      if i < Nmax-1:
        hij = sqrt(i+1.0)*Lam
        H2[i,i+1]=H2[i+1,i]=hij
    Hbig[:Nmax,:Nmax] = H1
    Hbig[Nmax:2*Nmax,Nmax:2*Nmax] = H2
    Hbig[:Nmax,Nmax:2*Nmax] = V
    Hbig[Nmax:2*Nmax,:Nmax] = transpose(V)
    evals,vecs = eigh(Hbig)
    return evals,vecs


def wns(v12,Ex,Eab,Nmax,nmax):
  wnL=[]
  t=pi
  Elam= Eab+2*Ex + sqrt(4*Ex*(Eab+Ex))
  Lam= sqrt(Elam)
  flag = 'dhoh'
  evals,vecs =   h2(Lam,v12,Eab,Nmax,flag)
  for ki in range(nmax+1):
    u0=vecs[ki,:]
    ut=u0*0.0j
    for i in range(Nmax*2):
      ut[i] = u0[i]*e**(-1.0j*evals[i]*t)
    vect = dot(vecs,ut)
    p0 = real(vect[ki]*conjugate(vect[ki]))
    wn = (1.-p0)/t
    wnL.append(wn)
  return wnL


if __name__ == "__main__":
```

```
print 'input v12,Ex,Eab,Nmax followed by ^D'
data = sys.stdin.readlines()
ss = data[0].split()
v12 = float(ss[0]); Ex = float(ss[1]);
Eab= float(ss[2]); Nmax=int(ss[3]); nmax = 20
wnL = wns(v12,Ex,Eab,Nmax,nmax)
for k in range(nmax+1):
    print k, wnL[k]
```

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[1] J. Mathews and R.L. Walker, *Mathematical Methods of Physics*, (Benjamin, 1970, second edition), Eq. (1.125).

[2] C. Wittig, J. Phys. Chem. B **109** 8428 (2005).

[3] R.A. Marcus and P. Siders, J. Phys. Chem **86** 2218 (1982).