

# Dominant channels of vibronic transitions in molecules with several identical modes

Bilha Segev\* and A.V. Sergeev

*Department of Chemistry, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, ISRAEL*

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## Abstract

Weak-coupling radiationless transitions (internal conversion or inter system crossing) are studied assuming separability and symmetry over  $N$  identical modes. Franck-Condon factors control the branching ratios between exciting just one of the equivalent modes, or equally distributing the available energy. The dominant process can be predicted by an exact quantum mechanical solution if the wavefunctions are known (Gaussian initial distributions and accepting Morse or Poeschl - Teller oscillators, for example); or more generally by a Wigner phase space *surface-jumping* analysis based on a classical limit of the Wigner function, using only the donor distribution and the acceptor potential surface.

**KEYWORDS:** degenerate oscillators, transition rate, Wigner function, radiationless transitions, local modes, branching ratios

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\*To whom correspondence should be addressed, Dr. Bilha Segev, Department of Chemistry, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, ISRAEL, Fax 972-8-6472943 (bsegev@bgumail.bgu.ac.il)

# 1 Introduction

Suppose that a multidimensional system undergoes a relaxation process. It is interesting to know what will be the preferred channel for relaxation if many possible channels exist. Here we focus on a very specific example of competing channels:  $N$  separable and identical degrees of freedom. Model examples include  $N$  identical oscillators, say  $N$  degenerate vibrations of some symmetric polyatomic molecule, or  $N$  identical electron acceptors connected symmetrically to an electron donor. For concreteness we focus on the oscillator case, and consider as an example a weak radiationless transition between two Born-Oppenheimer potential energy surfaces as in Refs. [1]-[3]. We have in mind a weak transition whose rate is given by Fermi-Golden Rule and not a fast transition, say by a conical intersection. In this transition a given energy  $E$  determined by the electronic energy gap is converted from electronic to vibrational energy, exciting the  $N$  oscillators in some specific way that we would like to determine. We further assume that the initial wave function is known and is symmetric with respect to the  $N$  identical coordinates, for simplicity we shall assume it is Gaussian in all the  $N$  coordinates.

The rate of the relaxation process as well as branching ratios between competing channels are determined by several factors [4]-[7]. An important factor that can vary by many orders of magnitude is the final density of states times the square of the Franck-Condon overlap integral between the initial and final nuclear wavefunctions [8]. This factor would determine the dominant relaxation process if, as we assume here, the electronic coupling is roughly the same for all the channels.

We show that three generic types of behavior can be recognized. In the first class of oscillators, all the energy goes to exciting one of the identical modes. In the second class

of oscillators, the energy is equally shared between the identical oscillators. In the third class the Frank-Condon factor is insensitive to how the energy is shared. Examples of Morse, Poeschl - Teller, and harmonic accepting potentials belong to the classes 1 or 3, 2 or 3, and 3 respectively.

In vibrational spectroscopy, the distribution of energy over different modes (including local modes) was studied in different contexts [9]-[12]. For example, Mills and Robiette [13] studied the pattern of excitations in a specific non-harmonic potential as a function of the anharmonicity. Their results depend on mixed anharmonic terms that couple between the normal modes. In contrast, in our problem mixing of states occurs because of the competition between transition channels, and the result depends on the *diagonal* anharmonic constants of the acceptor.

The letter is organized as follows. We first consider relaxation transitions where the donor and acceptor wave functions are known and exact quantum calculations can determine the excitation pattern. Second, we present a general method to determine the preferred partition of energy when the wave functions are not known. The method of *surface jumping* was introduced in Refs. [14]-[17]. It is based on analysis in phase space and generalizes the mechanism of surface hopping by extending it to Franck-Condon suppressed transitions [18]. Two ways of using this approach are presented. Finally, we compare the results of the surface jumping method with the exact quantum calculations.

## 2 Exact quantum calculations

Consider the initial (donor's) wave function:

$$\Psi^{(I)}(\vec{q}) = \prod_{i=1}^N \psi^{(I)}(q_i), \quad \psi^{(I)}(q) = \left(\frac{\omega}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}\omega q^2\right), \quad (1)$$

and the final (acceptor's) Hamiltonian:

$$H^{(F)}(\vec{q}, \vec{p}) \equiv \sum_{i=1}^N h^{(F)}(q_i, p_i) \equiv \sum_{i=1}^N \left( \frac{p_i^2}{2} + V^{(F)}(q_i) \right). \quad (2)$$

Suppose that we know the one dimensional eigenfunctions and eigenvalues  $h^{(F)}\psi_n^{(F)} = \epsilon_n^{(F)}\psi_n^{(F)}$ .

The competing accepting channels are  $\psi_{n_1}^{(F)}(q_1)\psi_{n_2}^{(F)}(q_2)\dots, \psi_{n_N}^{(F)}(q_N)$  where each channel has different vibrational quantum numbers  $n_1, n_2, \dots, n_N$ . Defining one dimensional overlap integrals,

$$f_n = \left| \int_{-\infty}^{\infty} \psi^{(I)*}(q)\psi_n^{(F)}(q) dq \right|^2, \quad (3)$$

the problem of finding the accepting mode for the transition reduces under the assumptions above to finding the maximum of the  $N$  dimensional overlap integral  $f_{n_1}f_{n_2}\dots f_{n_N}$  multiplied by the final density of states under the constraint:  $\epsilon_{n_1}^{(F)} + \epsilon_{n_2}^{(F)} + \dots + \epsilon_{n_N}^{(F)} = E$ .

It looks as if a huge number of possibilities should be compared in order to find the best channel. We show, however, that it is enough to calculate one function of a single oscillator's energy  $w(\epsilon)$ . In the rest of this section we define this function and prove that the partition of energy between the identical accepting oscillators is determined by the concavity or convexity of this function. We then calculate it numerically for two examples.

The function  $w(\epsilon)$  is defined by:

$$w(\epsilon) = -\frac{\hbar}{2} \log f(\epsilon), \quad (4)$$

where the discrete probabilities  $f_n$  were replaced by a probability density:

$$f(\epsilon) = \left( \frac{d\epsilon(n)}{dn} \right)^{-1} f_n, \quad (5)$$

and where  $\epsilon(n)$  is a continuous energy such that  $\epsilon(n) = \epsilon_n$  on the integers.

Generally, the function  $w$  may be a function of irregular or oscillatory behavior leading to a complicated problem of global minimization which is out of scope of the present paper, yet the

proof for the three generic cases is simple. The preferred channel corresponds to the minimum of the function

$$\sum_{i=1}^N w(\epsilon_i), \quad (6)$$

which has the same units as an action, under the constraint

$$\sum_{i=1}^N \epsilon_i = E \quad (7)$$

for all possible nonnegative energies  $\epsilon_1, \epsilon_2, \dots, \epsilon_N$ . If the function  $w$  is convex, the sum (6) can be minimized by replacing both  $\epsilon_1$  and  $\epsilon_2$  by their arithmetic mean. The sum (6) cannot be farther minimized only when  $\epsilon_1 = \epsilon_2 = \dots = \epsilon_N = E/N$ . On the contrary, if the function  $w$  is concave, the sum (6) can be minimized by replacing  $\epsilon_1$  by zero and  $\epsilon_2$  by  $\epsilon_1 + \epsilon_2$ . It cannot be farther minimized only when all  $\epsilon_1, \epsilon_2, \dots, \epsilon_N$  but one are zero. The third case is an inconclusive case when  $w$  is a linear function and the sum (6) is the same for all the allowed sets of  $(\epsilon_1, \epsilon_2, \dots, \epsilon_N)$ .

This analysis proves that only one of the equivalent modes is excited when the function  $w$  is convex. All the equivalent modes are symmetrically excited if it is concave. When  $w$  is linear, no specific pattern of excitation dominates.

Let us consider two examples. Suppose first that

$$h^{(F)}(q, p) = \frac{1}{2}p^2 + \frac{1}{2} \left( J + \frac{1}{2} \right) \left( 1 - e^{-\beta q} \right)^2, \quad (8)$$

where  $J$  is the number of bound states in the Morse potential, and  $\beta = (J + \frac{1}{2})^{-1/2}$ . The eigenfunctions are expressed in terms of the associated Laguerre polynomials [19]

$$\psi_n^{(F)}(q) = C_n^{-1/2} \exp\left(-\frac{1}{2}\xi\right) \xi^{J-n} L_n^{2(J-n)}(\xi), \quad (9)$$

$$\epsilon_n = n + \frac{1}{2} - (2J + 1)^{-1} \left( n + \frac{1}{2} \right)^2, \quad (10)$$

where  $C_n = [2\beta(J-n)n!]^{-1}(2J-n)!$  and  $\xi = (2J+1)e^{-\beta q}$ . Results of the numerical calculation of  $w(E)$  are shown in Fig. 1. When the curves are concave, one oscillator is excited.

For the second example, the accepting Hamiltonian is given by

$$h^{(F)}(q, p) = \frac{1}{2}p^2 - \frac{1}{2}\alpha^{-2} (\cosh^{-2}\alpha q - 1), \quad (11)$$

where  $J$  is the number of bound states in the Poeschl-Teller potential, and  $\alpha = [J(J+1)]^{-1/4}$ .

The eigenfunctions are expressed in terms of the hypergeometric function [20]

$$\psi_n^{(F)}(q) = C_n(1+\xi)^{(J+1)/2} {}_2F_1\left(\frac{n+1}{2}, \frac{2J-n+1}{2}, \frac{1}{2}; -\xi\right), \quad (12)$$

$$\epsilon_n = -\frac{1}{2}\alpha^2(J-n)^2 + \frac{1}{2}\alpha^{-2}, \quad (13)$$

where  $C_n$  is a normalization factor and  $\xi = \sinh^2\alpha q$ . Results of the numerical calculation of  $w(E)$  are shown in Fig. 2. If the energy gap is not too large, the resulting convex curves imply equal sharing of the energy between the identical oscillators.

Other examples can be considered in a similar way - but the final wave functions must be found first. In the next section we introduce another method which does not require knowledge of the final wave functions.

### 3 Surface jumping approach

A general method was recently developed for choosing among competing channels when the branching ratios are determined by the respective Franck Condon factors multiplied by the final density of states [14]-[18]. According to this method one should represent the initial distribution by its Wigner function  $\rho(\vec{q}, \vec{p})$ , and find the point in phase space of coordinates  $\vec{q}^m$  and momenta  $\vec{p}^m$  which gives a maximum for this initial Wigner function under the constraint that the final,

accepting, Hamiltonian  $H^{(F)}(\vec{q}, \vec{p})$  is equal to the available energy  $E$ . The transition probability is then proportional to the value of the initial Wigner function at that point.

Applying this method to the problem considered here, we are looking for a maximum of the initial symmetric distribution given by the Gaussian Wigner function:

$$\rho^{(I)}(\vec{q}, \vec{p}) = \left( \frac{1}{\pi\hbar} \right)^N \exp \left( -\frac{1}{\hbar} \sum_{i=1}^N (\omega q_i^2 + \omega^{-1} p_i^2) \right), \quad (14)$$

under the constraint:

$$\sum_{i=1}^N \left( \frac{p_i^2}{2} + V^{(F)}(q_i) \right) = E. \quad (15)$$

The solution is now straightforward. Define  $V(q) \equiv \max(V^{(F)}(q), V^{(F)}(-q))$ . If  $V(q) < \frac{1}{2}\omega^2 q^2$  for every  $q$ , then  $\vec{q}^m = 0$ ,  $|\vec{p}^m| = \sqrt{2E}$ , and the transition probability is proportional to

$$\rho^{(I)}(\vec{q}^m, \vec{p}^m) = \left( \frac{1}{\pi\hbar} \right)^N \exp \left( -\frac{2E}{\hbar\omega} \right), \quad (16)$$

regardless of the direction of  $\vec{p}^m$ . In the language of surface jumping it is a *momentum jump* [14]. The insensitivity to the direction of the jump implies that the transition probability is insensitive to how the energy is shared between the  $N$  identical accepting oscillators.

If, however,  $V(q) > \frac{1}{2}\omega^2 q^2$  everywhere, then  $\vec{p}^m = 0$ , and  $\vec{q}^m$  is the closest point to the origin on the hypersurface defined by

$$\sum_{i=1}^N V(q_i) = E. \quad (17)$$

A contour plot of  $V(q_1) + V(q_2)$  would show where equal energy surfaces for a given potential come closest to the origin. If the two dimensional contour plot comes closest to the origin for  $q_1 = q_2$ , then the solution of the  $N$  dimensional problem is:  $q_1^m = q_2^m = \dots = q_N^m \equiv Q_{\text{II}}$ , where  $Q_{\text{II}}$  is found by solving:

$$V(Q_{\text{II}}) = \frac{E}{N}, \quad (18)$$

and the transition probability is proportional to:

$$\rho^{(I)}(\vec{q}^m, \vec{p}^m) = \left(\frac{1}{\pi\hbar}\right)^N \exp\left(-\frac{2E_{II}}{\hbar\omega}\right), \quad (19)$$

$$E_{II} = \frac{N}{2}\omega^2 Q_{II}^2. \quad (20)$$

In this case all  $N$  oscillators equally share the available energy. In the same way, if the two dimensional contour plot comes closest to the origin for  $q_i = 0$ ,  $i = 1$  or  $2$ , then there are  $N$  equivalent solutions of the  $N$  dimensional problem each corresponding to the excitation of just one accepting oscillator:  $q_1^m = Q_I$ ,  $q_2^m = q_2^m = \dots = q_N^m = 0$ , where  $Q_I$  is found by solving:

$$V(Q_I) = E, \quad (21)$$

and the transition probability is proportional to:

$$\rho^{(I)}(\vec{q}^m, \vec{p}^m) = \left(\frac{1}{\pi\hbar}\right)^N \exp\left(-\frac{2E_I}{\hbar\omega}\right), \quad (22)$$

$$E_I = \frac{1}{2}\omega^2 Q_I^2. \quad (23)$$

In this case only one accepting oscillator is excited. Harmonic oscillators give inconclusive results because the respective contours are circles. Fig. 3 show some examples of contour plots.

The excitation pattern for an initial distribution (14) characterized by  $\omega$ , accepting potential of  $N$  identical oscillators  $V^{(F)}(q_i)$ , and an energy gap  $E$ , can therefore be easily found: *Solve equations (21) and (18) to obtain  $Q_I$  and  $Q_{II}$  and equations (23) and (20) to obtain  $E_I$  and  $E_{II}$ . A single oscillator is excited if  $E_I$  is smaller than  $E$  and  $E_{II}$ . All  $N$  oscillators are excited in a symmetric way if  $E_{II}$  is the smallest. Other cases are inconclusive.* Physically, the first case corresponds to a coordinate jump of one oscillator to the turning point at  $V(q) = E$ ; the second to a coordinate jump of each oscillator to the turning point at  $V(q) = E/N$ . The inconclusive case is a jump in an arbitrary direction in phase space.

Numerical examples show excellent agreement between predictions of this simple surface jumping picture and the exact quantum calculations from the previous section for most cases. Some examples and exceptions are discussed in the next section.

## 4 Numerical comparison

In this section we compare the results of the exact quantum calculations to the results obtained using two different applications of surface jumping. First we calculate an approximation to  $w(\epsilon)$  and compare it to the exact results, and second we compare results of sections 2 and 3.

In the surface-jumping approach the transition probability is proportional to the initial Wigner function at the jumping point. Using the one dimensional initial Wigner function:

$$\rho^{(I)}(q, p) = \left( \frac{1}{\pi\hbar} \right) \exp \left( -\frac{1}{\hbar} (\omega q^2 + \omega^{-1} p^2) \right), \quad (24)$$

we find the one dimensional jumping point  $(q_0, p_0)$ : the point for which  $\omega q^2 + \omega^{-1} p^2$  is minimal under the constraint  $p^2/2 + V^{(F)}(q) = \epsilon$ , and obtain an approximation for  $w(\epsilon)$  :

$$w(\epsilon) \approx \omega q_0^2 + \omega^{-1} p_0^2. \quad (25)$$

Results for Morse oscillators and Poeschl - Teller oscillators are shown in Figs. 4 and 5.

The surface jumping results, Figs. 4 and 5, follow the exact curves, Figs. 1 and 2. The exact quantum calculations for cases of nonzero momentum jump show interference effects which the phase-space curves average over [6]. There is an excellent agreement for curves with distinct concave, convex, or linear nature. Curves that change between convex or concave and linear behavior are qualitatively reproduced, but the energy for which the change occurs is shifted.

Table 1 shows the results of testing the simple criteria of section 3 for some examples from section 2. For Morse oscillators, there is an agreement between the surface-jumping predictions and the exact quantum calculations except for the case of  $\omega = 1.3$  and  $E = 100$ . For Poeschl - Teller oscillators, there is an agreement except for two cases with  $\omega = 0.8$ . The discrepancies correspond to curves of  $w(\epsilon)$  which change from concave or convex to linear as a function of  $\epsilon$ . For example, for Morse oscillator with  $\omega = 1.3$  the curve  $w(\epsilon)$  becomes concave for  $\epsilon > 60$  in the phase space approximation while the exact curve  $w(\epsilon)$  becomes concave only for  $\epsilon > 110$ . This shift in the energy in which a change occurs, indicate that the transition rate is not exactly proportional to the value of the Wigner function at the jumping point for these cases.

## 5 Conclusions

When  $N$  identical oscillators “compete” for a given energy  $E$ , one of the following processes can occur: the energy can all go to one of the oscillators, it can be equally divided between them or it can be distributed in an arbitrary manner. We found a simple way to predict which would be the dominant process. The prediction depends on the initial distribution, the shape of the accepting potential, and the energy gap as described above. Exact quantum mechanical solution, based on solving first the Schrödinger equation for the acceptor potential, was presented for some examples. An alternative analysis which does not require such a solution and suggests an intuitive physical picture of the process utilizes the concept of surface jumping introduced and studied in Refs. [14]-[18]. Numerical comparison of the two methods has shown that they give the same results except for few exceptions. The surface jumping analysis is based on a semiclassical asymptotic series expansion for the final Wigner function [14]-[17]. A

criterion for the validity of this expansion is that the acceptor Wigner function would behave in some sense more classically than the donor Wigner function. When this condition does not hold, for example when the energy gap between the two surfaces is too small, discrepancies between the surface jumping method and the exact analysis are observed.

The method of surface jumping analysis for recognizing the dominant accepting mode among several competing channels is not restricted to identical or even separable oscillators, and can in fact be applied just as easily to any initial distribution and final energy surface. For example, an extension to the more practical situation of  $N$  similar yet not exactly identical oscillators such as OH stretches of the first solvation shell water molecules, can be made in a straightforward way using the surface jumping approach.

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Figure 1: The function  $w(\epsilon)$ , found by numerical integration with exact wavefunctions at the points of the discrete spectrum,  $\epsilon = \epsilon_n$ ,  $n = 0, 1, \dots, J - 1$ . The donor wave function and the acceptor Hamiltonian are given by equations (1) and (8) respectively. The number of bound states is  $J = 300$ . Curves are labelled by the values of the initial oscillator's frequency  $\omega$ .  $\hbar = 1$ .

Figure 2: The same as Fig. 1, but for accepting Poeschl - Teller oscillators.  $w(\epsilon)$  is defined at  $\epsilon = \epsilon_n$ ,  $n = 0, 2, 4, \dots$  (the overlap vanishes for odd parity states). The donor wave function and the acceptor Hamiltonian are given by equations (1) and (11) respectively,  $J = 400$ .

Figure 3: Contour plots of  $V^{(F)}(q_1) + V^{(F)}(q_2)$  for (a) Morse, (b) Poeschl - Teller, and (c) harmonic oscillators. The harmonic contours are circles, the Morse contours are closest to the origin at  $q_i = 0$ , and the Poeschl - Teller contours at  $q_1 = q_2$ .

Figure 4: An approximation of  $w(\epsilon)$  obtained by finding the one dimensional jumping point  $(q_0, p_0)$  as explained in section 4. Dashed lines indicate that  $p_0 \neq 0$ . The donor wave function and the acceptor Hamiltonian are given by equations (1) and (8) respectively. Compare these curves with the exact quantum results for the Morse oscillator shown in Fig. 1.

Figure 5: The same as Fig. 4, but for Poeschl - Teller oscillators. The donor wave function and the acceptor Hamiltonian are given by equations (1) and (11) respectively,  $J = 400$ . Compare these curves with the exact quantum results for Poeschl - Teller oscillators shown in Fig. 2.

Table 1: Comparison between surface-jumping predictions and exact quantum results. The minimal energy among  $E$ ,  $E_I$ , and  $E_{II}$  (defined in section 3) is highlighted in bold. Case (a):  $E_I$  is the smallest and a single oscillator is excited. Case (b):  $E_{II}$  is the smallest and all  $N$  oscillators are equally excited. Case (c):  $E$  is the smallest and the excitation is arbitrary.

Potential	$\omega$	$E$	$E_I$	$E_{II}^{(N=2)}$	$E_{II}^{(N=5)}$	$E_{II}^{(N=10)}$	Case
Morse	0.5	100.0	<b>13.4</b>	15.6	18.2	19.8	a
	1.0	100.0	<b>53.5</b>	62.3	72.7	79.1	a
	1.3	<b>50.0</b>	52.7	59.4	66.9	71.3	c
	1.3	100.0	<b>90.4</b>	105.3	122.8	133.8	a
	2.0	<b>100.0</b>	213.9	249.3	290.7	316.6	c
	5.0	<b>100.0</b>	1336.7	1558.3	1817.0	1978.6	c
Poeschl - Teller	0.2	100.0	6.2	<b>4.8</b>	<b>4.3</b>	<b>4.1</b>	b
	0.5	100.0	38.8	<b>30.2</b>	<b>26.8</b>	<b>25.9</b>	b
	0.8	50.0	38.6	<b>34.9</b>	<b>33.1</b>	<b>32.5</b>	b
	0.8	100.0	99.4	<b>77.2</b>	<b>68.6</b>	<b>66.2</b>	b
	1.0	<b>100.0</b>	155.2	120.7	107.2	103.5	c
	2.0	<b>100.0</b>	621.0	482.7	428.9	413.8	c