EVALUATION OF THE NUCLEAR FACTOR OF THE PROBABILITY OF A RADIATIONLESS TRANSITION BY INTEGRATION OVER THE DOMINANT REGIONS IN PHASE SPACE

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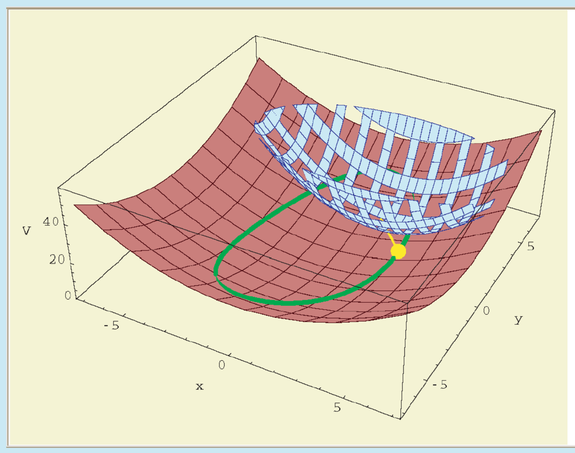
Introduction

We study a radiationless transition in a polyatomic molecule. The molecule originally vibrates around the minimum of Born – Oppenheimer surface corresponding to some excited electronic state. During the transition the electronic energy transfers to vibrational degrees of freedom of nuclei moving on the lower surface corresponding to the ground electronic state.

The subject of this study is the Franck – Condon integral, or an overlap integral between nuclear components of the molecular wavevefunctions in the initial (I) and final (F) states. It is the dominant factor of the transition rate, and it could vary by many orders of magnitude because of the tunneling nature of the transition.



Plots of the donor potential (blue porous surface) and the acceptor potential (brown solid surface) as functions of two coordinates, *x* and *y*. Yellow line (sometimes short or hidden) marks the jumping path. Green line on the acceptor surface is the classical trajectory starting from the leakage point.

Franck – Condon factor

$$f_n^2 = \left| \int d\vec{q}\, \psi^{(\mathrm{I})*}(\vec{q}) \psi_n^{(\mathrm{F})}(\vec{q}) \right|^2 = (\pi\hbar)^N \int d\vec{q} \int d\vec{p}\, \rho^{(\mathrm{I})}(\vec{q},\vec{p}) \rho^{(\mathrm{F})}(\vec{q},\vec{p})$$

Wigner function

$$\rho(\vec{q},\vec{p}) = (\pi\hbar)^{-N} \int d\vec{\eta}\, e^{-2i\vec{p}\cdot\vec{\eta}} \psi^*(\vec{q}+\vec{\eta}) \psi(\vec{q}-\vec{\eta})$$

Transition rate

$$I(E) = \frac{1}{2\delta} \sum_{E-\delta<E_n<E+\delta} f_n^2$$

Initial distribution

$$\rho^{(\mathrm{I})}(\vec{q},\vec{p}) = \frac{1}{(\pi\hbar)^N} f_0(\vec{q},\vec{p}) e^{-\frac{2}{\hbar}W(\vec{q},\vec{p})}$$

Harmonic approximation:

$$V^{(\mathrm{I})}(\vec{q}) = \frac{1}{2}\sum_{i=1}^{N} \omega_i^2 q_i^2,$$

$$W_0(\vec{q},\vec{p}) = \frac{1}{2}\sum_{i=1}^{N}\left(\frac{1}{\omega_i} p_i^2 + \omega_i q_i^2\right), \quad C(\vec{q},\vec{p}) = 1.$$

Final distribution

Leading order:

$$\rho_E^{(\mathrm{F})}(\vec{q},\vec{p}) = \delta\left(E - H^{(\mathrm{F})}(\vec{q},\vec{p})\right)$$

First order correction:

$$\hbar^2\left[\tfrac{1}{8} f_1(\vec{q},\vec{p})\delta''\left(E-H^{(\mathrm{F})}(\vec{q},\vec{p})\right) + \tfrac{1}{24} f_2(\vec{q},\vec{p})\delta'''\left(E-H^{(\mathrm{F})}(\vec{q},\vec{p})\right)\right],$$

$$f_1 = \sum_i V_{ii}^{(\mathrm{F})''}, \quad f_2 = \sum_i \left(V_i^{(\mathrm{F})}\right)^2 + \sum_{i,j} V_{ij}^{(\mathrm{F})''} p_i p_j$$

Jumping point (q*, p*)

$W(\vec{q},\vec{p})$ minimal under constraint $H^{(\mathrm{F})}(\vec{q},\vec{p}) = E$.

$$\vec{\nabla} W(\vec{q}^*,\vec{p}^*) = \lambda \vec{\nabla} H^{(\mathrm{F})}(\vec{q}^*,\vec{p}^*)$$

Results

Leading order:

$$I_0 = \frac{f_0^*}{H_1} (\pi\hbar \,\mathrm{Det}\,\mathbf{F})^{-1/2} \exp\left(-\tfrac{2}{\hbar} W^*\right),$$

$$f_0^* = f_0(\vec{q}^*,\vec{p}^*), \quad W^* = W_0(\vec{q}^*,\vec{p}^*),$$

$$H_1 = \left|\vec{\nabla} H(\vec{q}^*,\vec{p}^*)\right|, \quad F_{ij} = \frac{\partial^2}{\partial\xi_{i+1}\partial\xi_{j+1}}(W - \lambda H)$$

First order correction:

$$I_1 = \exp\left(-\frac{\lambda^3}{3\hbar^3} f_2^*\right) I_0$$

Logarithm of the rate

$$I = \exp\left(-\tfrac{2}{\hbar} w\right), \quad w = w_0 + \hbar^2 w_1,$$

$$w_0 = W^* - \tfrac{\hbar}{2}\ln\left((\pi\hbar H_1^2 \,\mathrm{Det}\,\mathbf{F})^{-1/2} f_0^*\right),$$

$$w_1 = \tfrac{1}{6}\hbar^{-2}\lambda^3 f_2^*$$

Condition of convergence

$$\tfrac{1}{6}\lambda^3 f_2^* \ll W^*$$

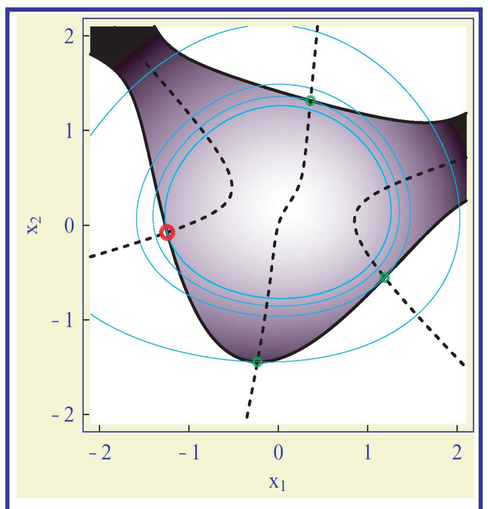


Figure 1. Finding the minimum of the function W under the energy constraint $H = E$. For this example, $W(x_1,x_2) = 0.4(x_1-0.1)^2 + 0.6(x_2-0.2)^2 + 0.05[(x_1-0.1)^3 + (x_1-0.1)^2(x_2-0.2) + (x_1-0.1)(x_2-0.2)^2 - (x_2-0.2)^3]$, $H(x_1,x_2) = \frac{1}{2}x_1^2 + \frac{1}{2}x_2^2 + 0.1[-x_1^3 - 3x_1^2x_2 + 2x_1x_2^2]$, and $E = 1$. Dashed lines represent stationary points of the function $F = W - \lambda H$. Energy-constraint points satisfying equation $H = E$ lie on the border of the dark area, $H < E$ (the darker is the color, the greater is the function W). Ellipses represent curves of constant W. Stationary points of the function W under the energy constraint are marked by circles. A point with the smallest W marked by a large circle is the solution of the problem: $x_1^* = -1.24$, $x_2^* = -0.08$, $W^* = 0.62$.

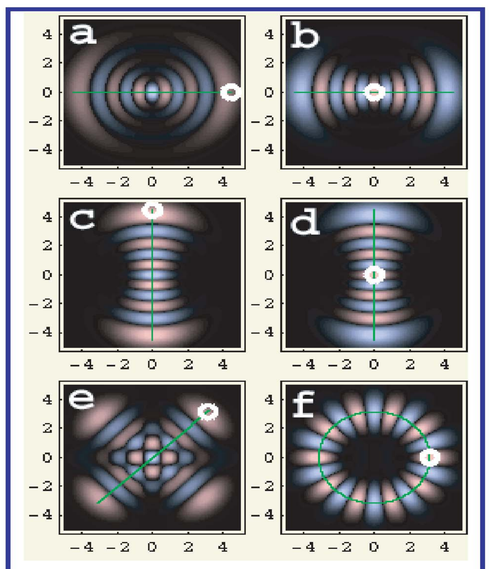


Figure 2. Pattern of the final wave function for different phase space jumps for the model of two coupled harmonic oscillators, $H_1 = \frac{1}{2}(\omega_1'^2 p_1^2 + \omega_2'^2 p_2^2 + (q_1 - Q)^2 + q_2^2)$, $H_F = \frac{1}{2}(p_1^2 + p_2^2 + q_1^2 + q_2^2)$. The white dot marks the jumping point (q_1^*, q_2^*) that with (p_1^*, p_2^*) defines the initial conditions for the classical trajectory shown by green line or ellipse. Here, $n = 10$. The parameters ω_1', ω_2' and Q are the same as in the paper of Segev and Heller (2000). For the example (e), we show only one of two symmetric jumping points of equal significance.

References

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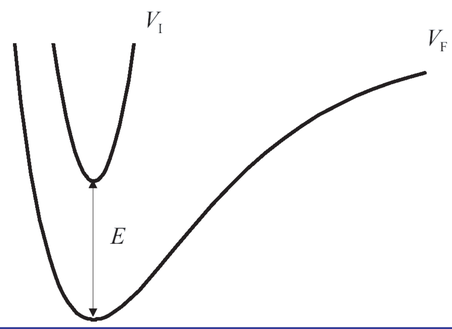
Examples

Harmonic → Morse

$$H_1(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\omega^2 q^2$$

$$H_F(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\left(J+\tfrac{1}{2}\right)\left(1-e^{-\beta q}\right)^2, \quad \beta = \left(J+\tfrac{1}{2}\right)^{-1/2}$$

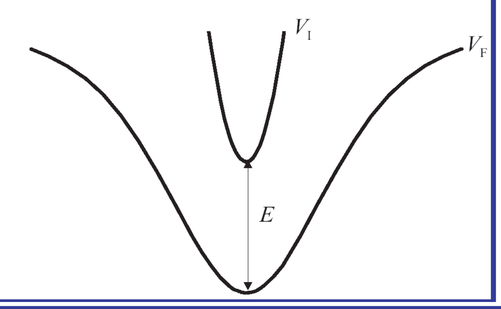


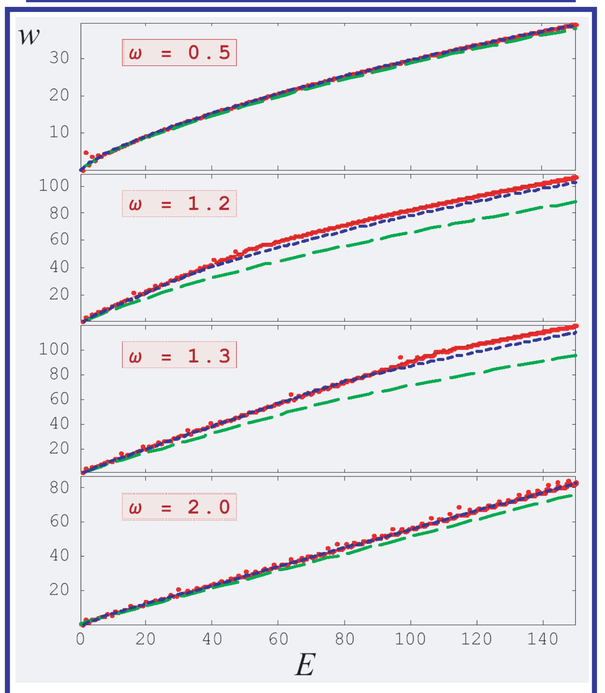
Harmonic → Poeschl – Teller

$$H_1(q,p) = \tfrac{1}{2}p^2 + \tfrac{1}{2}\omega^2 q^2$$

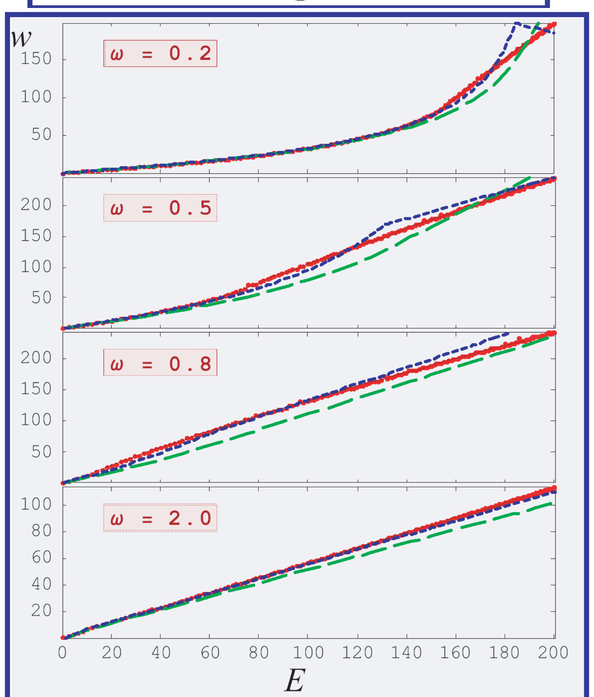
$$H_F(q,p) = \tfrac{1}{2}p^2 - \tfrac{1}{2}\alpha^{-2}\left(\cosh^{-2}\alpha q - 1\right)^2$$

$$\alpha = \left[J(J+1)\right]^{-1/4}$$





The function $w(E)$ = -1/2 Log $I(E)$ found by numerical integration with exact quantum wavefunctions at points of the discrete spectrum, $E = E_n$, n = 0, 1, ..., J-1 (dots) and results of estimation of the phase space integral (dashed and dotted lines). The acceptor is Morse oscillator.



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. POTENTIALS IN TWO VARIABLES

$$V^{(\mathrm{I})}(\boldsymbol{q}) = \tfrac{1}{2}\omega_1'^2(\cos\phi\, q_1 + \sin\phi\, q_2)^2 + \tfrac{1}{2}\omega_2'^2(-\sin\phi\, q_1 + \cos\phi\, q_2)^2$$

$$V^{(\mathrm{F})}(\boldsymbol{q}) = \tfrac{1}{2}\left(J+\tfrac{1}{2}\right)\left[1 - \exp\left(-(J+\tfrac{1}{2})^{-1/2} q_1\right)\right]^2 + \tfrac{1}{2}\omega_2^2 q_2^2$$

No.	ω_1'	ω_2'	ϕ	ω_2	$w_0(E)$	$w_0 + w_1$	$w(E)$
1	0.2	1	$\pi/3$	1	19.344	19.553	19.572
2	0.2	1	$\pi/6$	1	14.486	14.572	14.578
3	1	2	$\pi/4$	2	33.21	37.37	38.64
4	3	7	$\pi/4$	1	15.879	15.976	15.979
5	3	7	$\pi/4$	5	15.40	16.67	16.84

TABLE : Comparison of exact quantum calculation of the rate with the quasiclassical approximation for two-dimensional potentials. For all examples, $J = 300$ and $E = 100$.

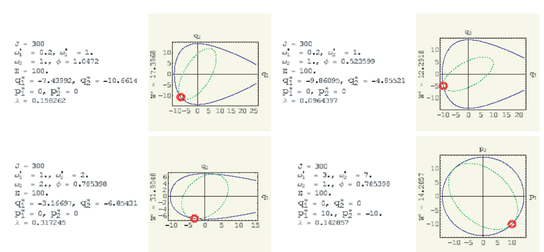

FIG. 0: The surface $H^{(\mathrm{F})}(\boldsymbol{q},\boldsymbol{p}) = E$ (solid line) and the tangent surface of equal $W(\boldsymbol{q},\boldsymbol{p})$, dotted line. The point of contact, which is $(\boldsymbol{q}^*,\boldsymbol{p}^*)$, gives the dominant contribution to the phase space integral.

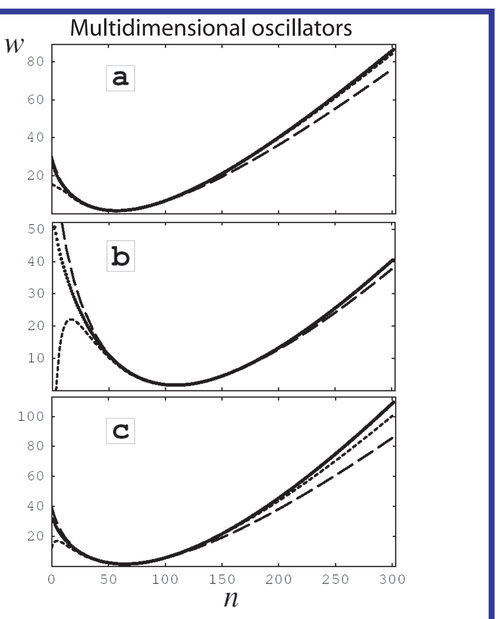

FIG. 0: The logarithm of the transition rate $w(E_n) = -\frac{1}{2}\ln I(E_n)$ as a function of the quantum number n for the generalized 10-dimensional model of harmonic oscillators described in the paper [5] . All the parameters of the examples (a), (b), and (c) are listed in [5]. Dots (often overlapping) are exact quantum calculations, dashed and dotted lines are results of estimation of the phase space integral using the leading order and a more accurate first order approximations respectively.